

1-Chloro-3,3,5,5-tetraphenyl- λ^4 -thia-2,4,6-triaza-3 λ^5 ,5 λ^5 -diphosphorine; Preparation, X-Ray Crystal Structure, and Conversion into a Tricyclic PSN Ring

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The reaction of chlorodiphenylphosphine with S_4N_4 in acetonitrile produces the six-membered heterocycle $(Ph_2PN)_2NSCl$, which is converted into a tricyclic ring on treatment with $Me_3SiNSNSiMe_3$; the structures of these new PSN ring systems have been determined by X-ray crystallography.

Our investigations of the reactions of R_2PPR_2 ($R = Me, Ph$)¹⁻³ and Ph_2PH^3 with S_4N_4 have led to the structural characterization of both six- and eight-membered PSN heterocycles (1)–(3) containing two-co-ordinate sulphur atoms.† We now report that S_4N_4 reacts with Ph_2PCl in acetonitrile to give the compound $(Ph_2PN)_2NSCl$ (4) shown by X-ray crystallography to be a six-membered ring with a three-co-ordinate sulphur atom. Treatment of (4) with $Me_3SiNSNSiMe_3$ unexpectedly produces a tricyclic compound, (5), the structure of which has also been elucidated by X-ray crystallography.

The treatment of S_4N_4 (5.43 mmol) with chlorodiphenylphosphine (16.3 mmol) in acetonitrile (25 ml) at 23 °C under nitrogen for 24 h produced (4) in ca. 80% yield after filtration (to remove small amounts of $S_4N_3^+Cl^-$) and cooling to –20 °C.

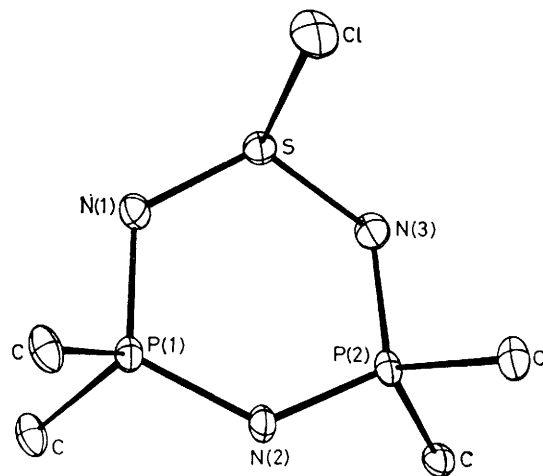
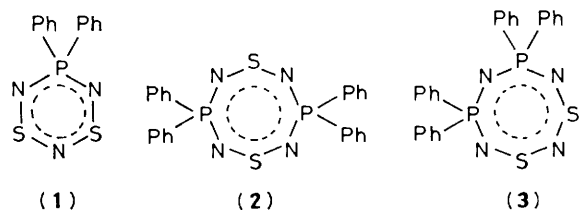


Figure 1. ORTEP plot (50% probability ellipsoids) for $(Ph_2PN)_2NSCl$, (4), showing the atomic numbering scheme. For clarity only the α -C atoms of the phenyl rings are shown. Principal bond distances (e.s.d.s in parentheses) are: S–N(1), 1.560(5); S–N(3), 1.557(5); N(1)–P(1), 1.660(6); N(3)–P(2), 1.671(6); N(2)–P(1), 1.589(5); N(2)–P(2), 1.582(5) Å. Principal bond angles are: N(1)–S–N(3), 117.7(3); S–N(1)–P(1), 121.0(3); S–N(3)–P(2), 121.1(3); N(1)–P(1)–N(2), 115.7(2); N(3)–P(2)–N(2), 114.4(3); P(1)–N(2)–P(2), 124.8(3)°.

† Delocalized bonds have been used to represent these structures since they provide a better representation of the electron distribution in these inorganic heterocycles than the alternative valence bond model.

Compound (4) is a pale yellow, crystalline solid, m.p. 174–175 °C, which is readily hydrolysed to give $[H_2NPh_2PNPPh_2NH_2]^+ Cl^-$.⁴ The $\{^1H\}^{31}P$ n.m.r. spectrum (in $CDCl_3$) shows a singlet at +7.8 p.p.m. (ref. external 85% H_3PO_4). Needles of (4) suitable for an X-ray structural determination were obtained from acetonitrile.

Crystal data: (4) $C_{24}H_{20}ClN_3P_2S$, $M = 520.5$, monoclinic, space group $P2_1$, $a = 11.376(4)$, $b = 7.512(1)$, $c = 14.808(6)$ Å, $\beta = 95.99(1)^\circ$, $U = 1259(1)$ Å³, $Z = 2$, and $D_e = 1.37$ g cm⁻³. A total of 2932 reflections were measured at –100(5) °C of which 2749 had $I > 3\sigma(I)$. The data were collected on a CAD4F diffractometer operating in the ω - 2θ mode and using Cu- K_α radiation ($\lambda = 1.5418$ Å, Ni pre-filter). The structure was solved by direct methods (MULTAN 78) and refined by full matrix least-squares techniques on F to give a final, unweighted R -value of 0.047.

The structure of (4) is shown in Figure 1. The five atom NPNPN unit is planar to within 0.05 Å, while the sulphur atom lies ca. 0.31 Å out of this plane.⁵ This six-membered heterocycle can be considered as a hybrid of the well known inorganic ring systems $(Ph_2PN)_3$ ⁶ and $(NSCl)_3$.⁷ The S–N bond distances [mean value 1.558(5) Å] in (4) are somewhat

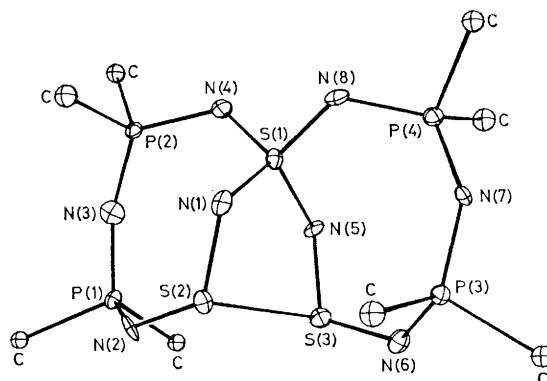


Figure 2. ORTEP plot (50% probability ellipsoids) for $(Ph_2PNPPh_2)_2S_3N_6$, (5), showing the atomic numbering scheme. For clarity only the α -C atoms of the phenyl rings are shown. Principal bond distances are: S(1)–N(1), 1.616(8); S(1)–N(4), 1.562(8); S(1)–N(5), 1.608(8); S(1)–N(8), 1.554(8); N(1)–S(2), 1.611(9); S(2)–N(2), 1.582(8); N(2)–P(1), 1.623(8); P(1)–N(3), 1.585(9); N(3)–P(2), 1.569(9); P(2)–N(4), 1.610(8); N(5)–S(3), 1.612(8); S(3)–N(6), 1.601(8); N(6)–P(3), 1.618(8); P(3)–N(7), 1.587(8); N(7)–P(4), 1.570(8); P(4)–N(8), 1.608(8) Å. Principal bond angles are: N(1)–S(1)–N(4), 113.5(4); N(1)–S(1)–N(5), 105.6(4); N(1)–S(1)–N(8), 108.8(4); N(4)–S(1)–N(5), 110.1(4); N(4)–S(1)–N(8), 105.0(4); N(5)–S(1)–N(8), 114.0(4); S(1)–N(1)–S(2), 120.7(5); N(1)–S(2)–N(2), 117.8(4); S(2)–N(2)–P(1), 130.8(5); N(2)–P(1)–N(3), 119.4(4); P(1)–N(3)–P(2), 141.5(6); N(3)–P(2)–N(4), 121.0(5); P(2)–N(4)–S(1), 122.5(5); S(1)–N(5)–S(3), 120.6(5); N(5)–S(3)–N(6), 117.0(4); S(3)–N(6)–P(3), 129.5(5); N(6)–P(3)–N(7), 120.0(4); P(3)–N(7)–P(4), 140.7(5); N(7)–P(4)–N(8), 121.4(4); P(4)–N(8)–S(1), 125.7(5)°.

shorter than the corresponding distance in $(\text{NSCl})_3$ [1.605(5) Å],⁷ but the mean P–N distance of 1.585(5) Å in the $\text{Ph}_2\text{PNPPPh}_2$ unit is not significantly different from the mean P–N bond length of 1.597(6) Å found for $(\text{Ph}_2\text{PN})_3$.⁶ However, the P–N bonds linking this unit to the S atom are considerably longer [1.665(6) Å] suggesting a tendency towards localization of π -bonding at opposite ends of the molecule.

The S–Cl distance of 2.357(2) Å is significantly longer than the corresponding bond lengths in $(\text{NSCl})_3$ [2.084(4) and 2.150(4) Å] or $\text{S}_3\text{N}_2\text{Cl}^+$ (2.168 Å)⁸ but shorter than the bridging S–Cl distances in polymeric $\text{S}_4\text{N}_5\text{Cl}$ [2.811(2) Å].⁹ There is no evidence for bonding interactions between MeCN of crystallization and any atoms of the heterocyclic ring.

The monofunctionality of (4) provides a unique opportunity to investigate reactions at the sulphur centre of the P_2SN_3 heterocycle and preliminary results indicate that such studies will reveal unexpected results. For example, the reaction of (4) with $\text{Me}_3\text{SiNSNSiMe}_3$ (2:1 molar ratio) in methylene chloride at 23 °C produced (5) in ca. 20% yield. The $\{^1\text{H}\}^{31}\text{P}$ n.m.r. spectrum of (5) (in CDCl_3) shows two sharp singlets of equal intensity at +5.4 and +1.8 p.p.m.

Crystal data: (5), $\text{C}_{48}\text{H}_{40}\text{N}_8\text{P}_4\text{S}_3\cdot\text{CH}_2\text{Cl}_2$, $M = 1033.0$, orthorhombic, space group $Pna2_1$, $a = 24.927(5)$, $b = 9.249(1)$, $c = 20.263(5)$ Å, $U = 4672(2)$ Å³, $Z = 4$, and $D_c = 1.47$ g cm⁻³. A total of 6359 reflections, of which 3982 had $I > 3\sigma(I)$, were measured at -100(5) °C using Mo- K_α radiation ($\lambda = 0.70926$ Å, graphite monochromator). The final unweighted R -value is 0.066.

The structure of (5) is shown in Figure 2. It consists of two eight-membered 1,3- $(\text{Ph}_2\text{PNPPPh}_2)\text{S}_2\text{N}_3$ rings, (3), fused at a common (spirocyclic) sulphur atom and linked by a weak interaction between S(2) and S(3) [2.368(3) Å] to give a tricyclic structure. The geometry at S(1) is approximately tetrahedral with bond angles in the range 105–114°. For each eight-membered ring, one of the S(1)–N bond lengths is ca. 1.56 Å and the other is ca. 1.61 Å. The average P–N bond length (1.60 Å) and bond angle at phosphorus (120.5°) are typical for tetrameric cyclophosphazenes,¹⁰ while the angles at nitrogen are in the range 121–141°.

The heterocycle (4) is one example of a potentially larger class of inorganic ring systems represented by the general formula $(\text{Ph}_2\text{PN})_x(\text{NSCl})_y$ (where $x + y = 3, 4, 5$ etc.). Other members of this series should be readily accessible by reaction of (1), (2), or (3) with suitable halogenating agents.

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