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

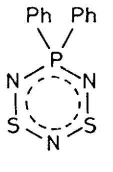
Tristram Chivers,* M. N. Sudheendra Rao, and John F. Richardson

Department of Chemistry, The University of Calgary, Calgary, T2N 1N4, Alberta, Canada

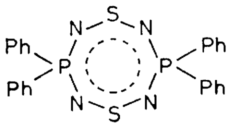
The reaction of chlorodiphenylphosphine with S_4N_4 in acetonitrile produces the six-membered heterocycle $(Ph_2PN)_2NSCl$, which is converted into a tricyclic ring on treatment with $Me_3SiNSNSiMe_3$; the structures of these new PSN ring systems have been determined by *X*-ray crystallography.

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.

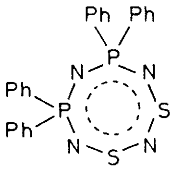
The treatment of S_4N_4 (5.43 mmol) with chlorodiphenylphosphine (16.3 mmol) in acetonitrile (25 ml) at 23 °C under nitrogen for 24 h produced (**4**) in *ca.* 80% yield after filtration (to remove small amounts of $S_4N_3{}^+Cl^-$) and cooling to −20 °C.



(**1**)



(**2**)



(**3**)

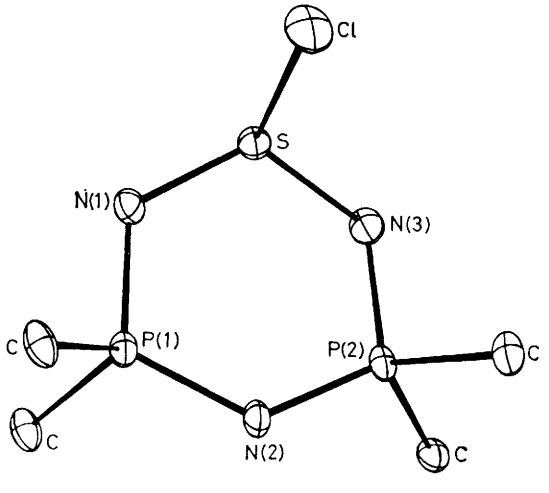


Figure 1. ORTEP plot (50% probability ellipsoids) for $(Ph_2PN)_2$-NSCl, (**4**), showing the atomic numbering scheme. For clarity only the α-C atoms of the phenyl rings are shown. Principal bond distances (e.s.d.s in parentheses) are: S–N(1), 1.560(5); S–N(3), 1.557(5); N(1)–P(1), 1.660(6); N(3)–P(2), 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)–(2), 114.4(3); P(1)–N(2)–P(2), 124.8(3)°.

Compound (**4**) is a pale yellow, crystalline solid, m.p. 174—175 °C, which is readily hydrolysed to give $[H_2NPh_2PNPPh_2$-$NH_2]^+$ 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**) $C_{24}H_{20}ClN_3P_2S.CH_3CN$, $M = 520.5$, monoclinic, space group $P2_1$, a = 11.376(4), b = 7.512(1), c = 14.808(6) Å, β = 95.99(1)°, U = 1259(1) Å^3, Z = 2, and D_c = 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 (λ = 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

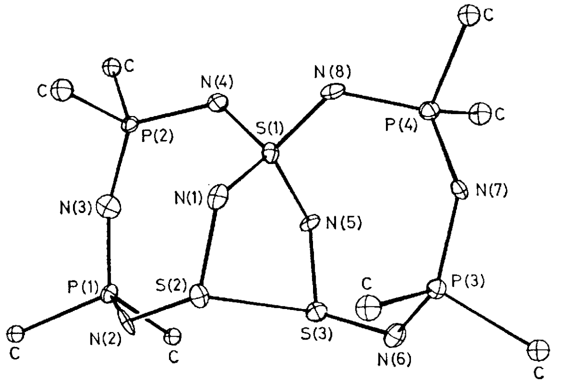


Figure 2. ORTEP plot (50% probability ellipsoids) for $(Ph_2$-$PNPPh_2)_2S_3N_6$, (**5**), showing the atomic numbering scheme. For clarity only the α-C atoms of the phenyl rings are shown. Principal bond distances are: S(1)–N(1), 1.616(8); S(1)–N(4), 1.562(8); S(1)–N(5), 1.608(8); S(1)–N(8), 1.554(8); 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)°.

---

† 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.

shorter than the corresponding distance in $(NSCl)_3$ [1.605(5) Å],[7] but the mean P–N distance of 1.585(5) Å in the Ph_2PNPPh_2 unit is not significantly different from the mean P–N bond length of 1.597(6) Å found for $(Ph_2PN)_3$.[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 $(NSCl)_3$ [2.084(4) and 2.150(4) Å][7] or $S_3N_2Cl^+$ (2.168 Å)[8] but shorter than the bridging S–Cl distances in polymeric S_4N_5Cl [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 $Me_3SiNSNSiMe_3$ (2:1 molar ratio) in methylene chloride at 23 °C produced (**5**) in *ca.* 20% yield. The $\{^1H\}^{31}P$ 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**), $C_{48}H_{40}N_8P_4S_3.CH_2Cl_2$, $M = 1033.0$, orthorhombic, space group $Pna2_1$, $a = 24.927(5)$, $b = 9.249(1)$, $c = 20.263(5)$ Å, $U = 4672(2)$ Å^3, $Z = 4$, 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-$(Ph_2PNPPh_2)S_2N_3$ 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 $(Ph_2PN)_x(NSCl)_y$ (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.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Received, 3rd June 1982; Com. 622

References

1 N. Burford, T. Chivers, R. T. Oakley, A. W. Cordes, and P. N. Swepston, *J. Chem. Soc., Chem. Commun.*, 1980, 1204; N. Burford, T. Chivers, A. W. Cordes, W. G. Laidlaw, M. Noble, R. T. Oakley, and P. N. Swepston, *J. Am. Chem. Soc.*, 1982, **104**, 2182.

2 N. Burford, T. Chivers, P. W. Codding, and R. T. Oakley, *Inorg. Chem.*, 1982, **21**, 982.

3 N. Burford, T. Chivers, and J. F. Richardson, *Inorg. Chem*, submitted for publication.

4 I. I. Bezman and J. H. Smalley, *Chem. Ind. (London)*, 1960, 839.

5 S. Pohl, O. Petersen, and H. W. Roesky, *Chem. Ber.*, 1979, **112**, 1545; H. W. Roesky, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 642. These papers report the preparation of a similar compound $(Cl_2PN)_2NSCl$, an oil whose crystal structure was not determined. However, the cation $(Cl_2PN)_2NS^+$, formed by reaction of the oil with $SbCl_5$, was shown to consist of an essentially planar six-membered ring by *X*-ray crystallography.

6 F. R. Ahmed, P. Singh, and W. H. Barnes, *Acta Crystallogr., Sect. B*, 1969, **25**, 316.

7 G. A. Wiegers and A. Vos, *Acta Crystallogr.*, 1966, **20**, 192.

8 E. Zalkin, T. E. Hopkins, and D. M. Templeton, *Inorg. Chem.*, 1966, **5**, 1767.

9 T. Chivers and L. Fielding, *J. Chem. Soc., Chem. Commun.*, 1978, 212; T. Chivers, L. Fielding, W. G. Laidlaw, and M. Trsic, *Inorg. Chem.*, 1979, **18**, 3379.

10 S. S. Krishnamurthy, A. C. Sau, and M. Woods, *Adv. Inorg. Chem. Radiochem.*, 1978, **21**, 41.