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The first structurally characterised cyclotriphosphazene substituted with a sulfonamide nitrogen

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Abstract

The reaction between two equivalents of *N*-(2-hydroxyphenyl)-*p*-toluenesulfonamide (H_2sulf) and [N_3P_3(biph)$_2Cl_2$] (H_2biph = 2,2′-biphenol) produces the compound *bis*(2,2′-biphenylato)*bis*(2-oxyphenyl)-*p*-toluenesulfonamide cyclotriphosphazene (H_2L) containing two geminal Hsulf moieties. Further reaction of H_2L in basic conditions results in the removal of the sulfonamide arm and the slow formation of a novel phosphazene containing the spirocyclic sulf moiety. When this occurs in the presence of [Pd(bpy)Cl_2] the reaction is facile and the new complex [Pd(bpy)(sulf)] (**2**) is also formed. Compounds H_2L, **1** and **2** have all been characterised by single crystal X-ray crystallography.

Keywords: Cyclotriphosphazene; *N*-(2-hydroxyphenyl)-*p*-toluenesulfonamide; Palladium; 2,2′-Bipyridine; X-ray structure

As part of our program to investigate the coordination chemistry of ligands bound to the cyclotriphosphazene core [1–6], we have examined the reactivity of a potentially dianionic ligand, H_2L, which contains a *bis*-sulfonamide donor set (see Scheme 1). In this communication, we report that when H_2L reacts with [Pd(bpy)Cl_2] in the presence of triethylamine (NEt_3) in an attempt to prepare the complex [Pd(bpy)L], an unexpected reaction occurs in which a sulfonamide moiety is lost from H_2L to afford a new spirocyclic phosphazene, [N_3P_3(biph)$_2$(sulf)] (**1**). Although substitution on the phosphorus atoms of cyclotriphosphazenes has been performed using numerous different nucleophiles, compound **1** represents the first structurally characterised example in which a ring phosphorus atom has been substituted by the nitrogen atom of a sulfonamide moiety.

Two equivalents of H_2sulf and [N_3P_3(biph)$_2Cl_2$] react at room temperature in acetone in the presence of Cs_2CO_3 as base, to produce the new phosphazene, H_2L [7]. The subsequent reaction of H_2L with [Pd(bpy)Cl_2] using NEt_3 as base, results in the removal of a sulfonamide arm from H_2L, forming the new spirocyclic phosphazene **1** and compound **2** (Scheme 1). Compound **2** was also prepared from the reaction between [Pd(bpy)Cl_2] and H_2sulf and characterised by X-ray crystallography.

The IR spectrum (KBr disk) of H_2L shows bands at 1123 and 1175 cm^{-1} assigned to the PN ring stretching modes. Similar strong bands are observed in the spectrum of **1** at 1232, 1224, 1201 and 1192 cm^{-1} for PN stretches. The SO_2 stretches are tentatively assigned to bands at 1158 and 1160 cm^{-1} for H_2L and **1**, respectively. The SO_2 stretch in H_2sulf occurs at 1155 cm^{-1} and this moves to 1139 cm^{-1} in the complex **2**, which is consistent with deprotonated sulfonamide nitrogen binding and has been observed in other complexes containing sulfonamide ligands [8].

The X-ray structural data [9] obtained for H_2L confirm the double substitution of the chloride ions in [N_3P_3(biph)$_2Cl_2$] with sulfonamide moieties (Fig. 1). The compound shows standard length P–N bonds in the phosphazene ring, ranging between 1.557(7) and 1.591(7) Å. The N–P–N angles [between 118.4(4) and 119.0(4)°] and P–N–P angles

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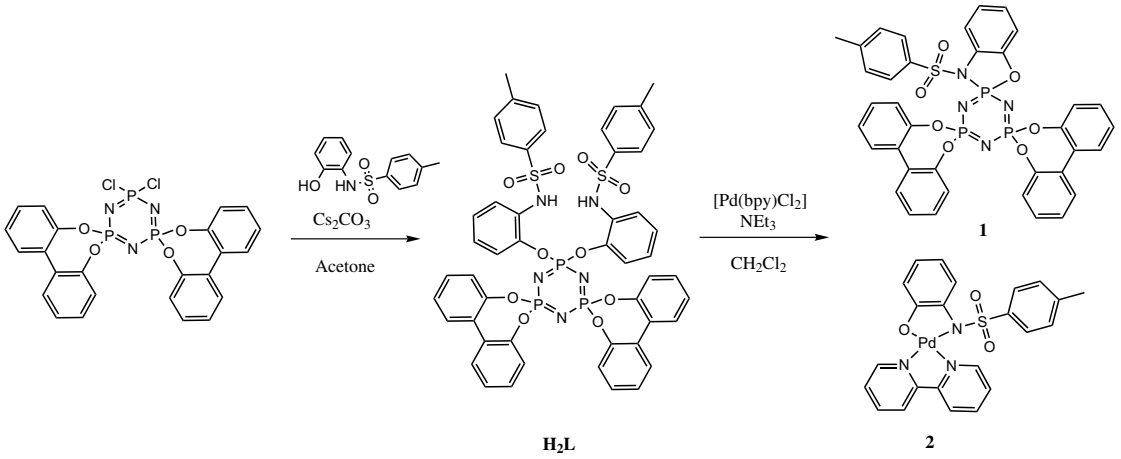


Scheme 1.

[between 122.2(5) and 120.4(4)°] are also in the normal range and the rms standard deviation of the phosphazene ring atoms from their mean plane is 0.0403 Å.

The sulfonamide arms are orientated such that they fold back above and below the plane of the phosphazene ring. There are weak intramolecular H–π interactions between H40 and H37 of different spirocyclic biphenyl rings and toluene rings C7–C12 and C20–C25, respectively. This arrangement of the arms exposes the NH sulfonamide protons which engage in intermolecular hydrogen bonding interactions with sulfonamide oxygen atoms on different adjacent molecules. Specifically, the donor–acceptor distances for the arrays N5–H5N···O9# (symmetry operation: $x+1$, y, z) and N4–H4N···O12# (symmetry operation: $x-1$, y, z) are 3.044(9) and 2.884(9) Å, respectively.

The X-ray structure [10] of the phosphazene **1** is shown in Fig. 2 and this compound represents the first structurally characterised cyclotriphosphazene in which a ring phosphorus atom has been substituted with a sulfonamide nitrogen. The geometries around the phosphazene ring

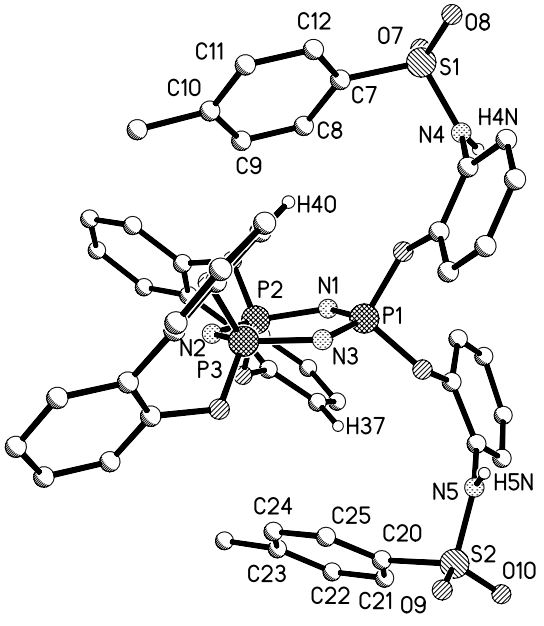


Fig. 1. Crystal structure of H_2L with most of the hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): P1–N1, 1.571(7); P1–N2, 1.557(7); P2–N2, 1.578(7); P2–N3, 1.591(7); P3–N1, 1.579(7); P3–N3, 1.572(7); N4–S1, 1.642(7); N5–S2, 1.631(6); S1–O7, 1.426(6); S1–O8, 1.429(6); S2–O10, 1.426(6); S2–O9, 1.437(6); P1–N1–P2, 122.2(5); P1–N3–P3, 120.5(4); P2–N2–P3, 120.4(4); N1–P1–N3, 118.4(4); N1–P2–N2, 118.5(4); N2–P3–N3, 119.0(4); N4–S1–O7, 104.6(4); N4–S1–O8, 108.5(4); O7–S1–O8, 118.7(4); N5–S2–O10, 109.6(4); N5–S2–O9, 104.5(4); O9–S2–O10, 119.4(4).

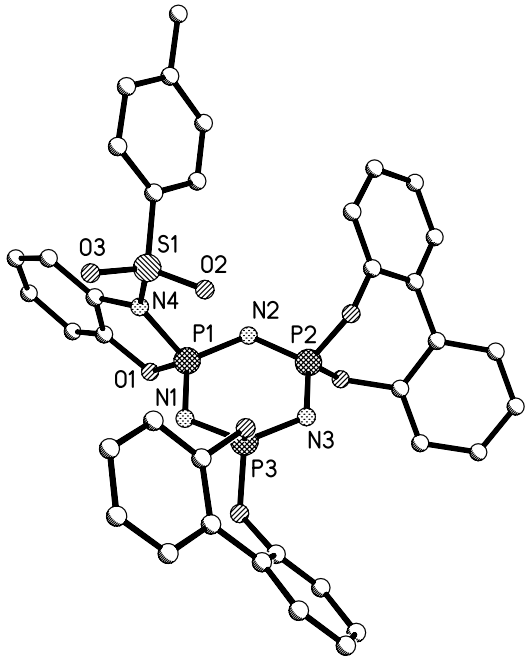


Fig. 2. Crystal structure of **1** with hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): P1–N1, 1.585(4); P1–N2, 1.577(4); P2–N3, 1.578(4); P2–N2, 1.580(4); P3–N1, 1.581(4); P3–N3, 1.574(4); P1–N4, 1.708(4); P1–O1, 1.614(3); N4–S1, 1.641(4); S1–O2, 1.434(3); S1–O3, 1.434(3); P1–N2–P2, 121.8(2); P2–N3–P3, 121.8(2); P1–N1–P3, 120.3(2); N1–P1–N2, 118.32(19); N2–P2–N3, 117.75(19); N1–P3–N3, 117.85(19); O1–P1–N4, 93.18(17); N4–S1–O3, 108.8(2); N4–S1–O2, 104.06(19); O2–S1–O3, 119.3(2).

are normal for cyclotriphosphazenes with P–N–P angles between 120.3(2) and 121.9(2)° and N–P–N angles between 117.75(19) and 118.32(19)°. The phosphazene ring is essentially planar with the mean deviation of the atoms from the plane of the ring being 0.0508 Å and the largest deviations are for P3 and N1, which lie 0.0929 Å above and below the plane. The P–N bond lengths in the ring range between 1.574(4) and 1.585(4) Å. The P–O1 bond length is 1.614(3) Å and similar to the P–O bond lengths reported in $[N_3P_3(cat)_3]$ (H_2cat = catechol) [11]. The P–N4 bond length of 1.708(4) is typical for a P–N single bond and similar to other $P–N_{sulfonamide}$ bonds [12]. Where the O–P–O angles for the spirocyclic 2,2′-biphenylato moieties are 103.38(16) and 103.76(16)°, the O1–P–N4 angle formed by the five membered ring of the spirocyclic sulf group is expectedly smaller at 93.18(17)° and more closely resembles the O–P–O angles in $[N_3P_3(cat)_3]$ which are 97.4(8)° [11].

The X-ray structure [13] of the palladium complex is shown in Fig. 3. Some disorder exists in the crystals of the molecule and the tosyl ring was modelled in two slightly different orientations with approximately 0.81:0.19 occupancy. The Pd(II) centre has a distorted square planar geometry comprised of a 'N_3O' donor set. The Pd–N bonds are of similar length [between 2.006(3) and 2.022(3) Å] with the Pd–O bond being slightly shorter at 1.984(3) Å. The Pd–N bond lengths are similar to those observed in a related palladium complex containing a sulfonamide ligand [8] and the Pd–N and Pd–O bond lengths are similar to those in [Pd(bpy)(cat)] [14]. The bond angles between donor atoms within the complex deviate somewhat from a regular square planar geometry, lying between 80.38(13) and 102.00(13)°. The largest deviation is for the angle N3–Pd–N1 between pyridyl and sulfonamide donors and may be due to the steric impediment provided by the bulky sulfonamide moiety. The bite angle of 83.97(12)° for the sulf ligand is similar to that observed [14] for catecholate dianion [85.6(1)°] in the complex [Pd(bpy)(cat)].

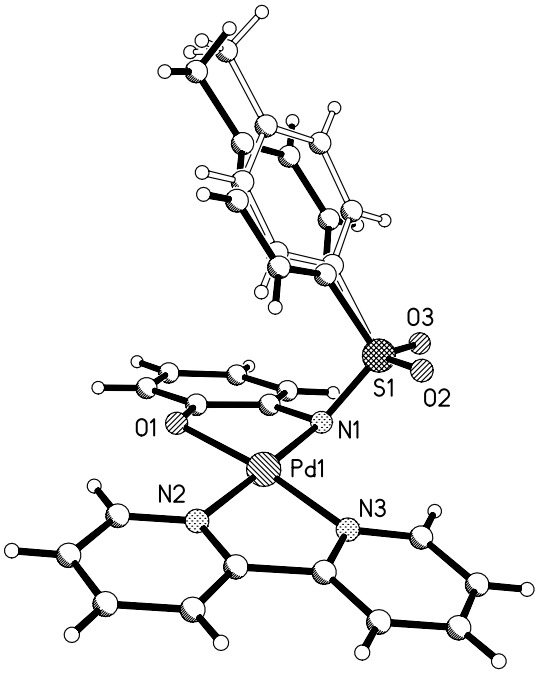
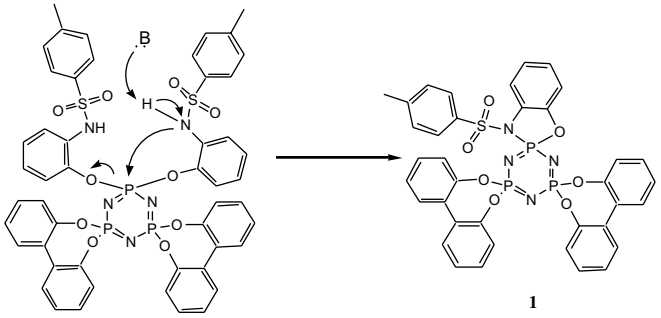


Fig. 3. Crystal structure of **2**. Selected bond lengths (Å) and angles (°): Pd1–O1, 1.984(3); Pd1–N1, 2.022(3); Pd1–N2, 2.006(3); Pd1–N3, 2.018(3); N1–S1, 1.615(3); S1–O2, 1.444(3); S1–O3, 1.439(3); O1–Pd1–N1, 83.97(12); O1–Pd1–N2, 93.53(12); N2–Pd1–N3,80.38(13); N1–Pd1–N3, 102.00(13); O1–Pd1–N3, 172.88(11); N1–Pd1–N2, 176.93(13), O2–S1–N1, 107.89(16); O3–S1–N1, 110.68(17); O2–S1–O3, 116.90(17).

Since we had not observed **1** during the preparation of H_2L in acetone with Cs_2CO_3 as base, we conducted a series of reactions to determine whether the compound was accessible under other conditions. The reactions were monitored by ^{31}P NMR and a table of results is given in the supplementary information. When Cs_2CO_3 is used with only one equivalent of H_2sulf (rather than two) over the same period, the major product observed is still H_2L and this is present in a near 1:1 mixture with the unreacted starting material and a trace amount of the spirocyclic product **1**. At room temperature in THF, the reactions between one equivalent of H_2sulf and $[N_3P_3(biph)_2Cl_2]$ proceed slowly, there being little reaction after several days at room temperature with the base, NaH, and none with NEt_3. Similar results are obtained at room temperature when two equivalents of H_2sulf are used in the reaction.

When the reactions are performed in THF at reflux using NEt_3 or NaH as a base H_2L does form, however, as the reactions are driven to completion, **1** also begins to form and hence the reactions give a mixture of products. If a solution containing H_2L and NEt_3 is allowed to stir at room temperature then decomposition of H_2L into **1** is also observed. It seems likely that when the stronger bases, NEt_3 or NaH, are present, geminal substitution to form H_2L occurs initially followed by decomposition into the spirocyclic **1** possibly according to Scheme 2. Hence $[Pd(bpy)Cl_2]$ is not required for the decomposition of H_2L but appears to facilitate the process, presumably by either forming an intermediate with a deprotonated form of H_2L or by removing the ejected sulf ligand from the reaction mixture *via* complexation.

In conclusion, the sulfonamide H_2sulf can react with $[N_3P_3(biph)_2Cl_2]$ in the presence of base to form either the spirocyclic product **1** or the doubly substituted product H_2L. A preference for the doubly substituted product is found when Cs_2CO_3 is used as a base in acetone or THF but mixtures of both species are obtained when NaH or



Scheme 2.

NEt_3 are used in THF. This observation would be consistent with the weaker carbonate base being unlikely to deprotonate the sulfonamide nitrogen. When H_2L is treated with NEt_3, the spirocyclic compound **1** may be formed slowly. This process is accelerated in the presence of $[Pd(bpy)Cl_2]$ in which case the new complex **2** is also formed.

Acknowledgements

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Appendix A. Supplementary material

CCDC 635419, 635420, and 635421 contain the supplementary crystallographic data for H_2L, **1**, and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this paper can be found, in the online version, at doi:10.1016/j.inoche.2007.05.014.

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[9] *Crystal refinement data for* H_2L: $C_{50}H_{40}N_5O_{10}P_3S_2$, $M_r = 1027.90$, Monoclinic, $P2(1)/n$, $a = 8.9340(6)$, $b = 26.9133(19)$, $c = 19.4925(14)$, $\beta = 92.667(2)$, $V = 4681.8(6)$ Å^3, $Z = 4$, $\rho_{calc} = 1.458$, $T = 84(2)$, $\mu = 0.283$, independent reflections 6688, final R indices $[I > 2\sigma(I)]$ are $R_1 = 0.0898$, $wR_2 = 0.1508$; R indices (all data), $R_1 = 0.2044$, $wR_2 = 0.1878$ and the goodness of fit on F^2 is 1.059.
[10] *Crystal refinement data for* **1**$.0.5C_5H_{12}$: $C_{39.5}H_{33}N_4O_7P_3S$, $M_r = 800.70$, triclinic, $P\bar{1}$, $a = 10.9621(3)$ Å, $b = 11.2188(3)$ Å, $c = 16.5503(4)$ Å, $\alpha = 10.9621(3)°$, β=11.2188(3) °, γ=16.5503(4)°, $V = 1775.32(8)$ Å^3, $Z = 2$, $\rho_{calc} = 1.497$, $T = 84(2)$, $\mu = 0.261$, independent reflections 6706, final R indices $[I > 2\sigma(I)]$ are $R_1 = 0.0714$, $wR_2 = 0.1365$; R indices (all data), $R_1 = 0.1197$, $wR_2 = 0.1549$ and the goodness of fit on F^2 is 1.058.
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[13] *Crystal refinement data for* **2**: $CHCl_3 \cdot 0.5C_5H_{12}$:$C_{26.5}H_{26}Cl_3N_3O_3PdS$, $M_r = 679.36$, Monoclinic, $C2/c$, $a = 20.6821(8)$ Å, $b = 8.4112(3)$ Å, $c = 31.9672$ Å, β=103.223(1)°, $V = 5413.6(4)$ Å^3, $Z = 8$, $\rho_{calc} = 1.667$, $T = 89(2)$, $\mu = 1.094$, independent reflections 4946, final R indices $[I > 2\sigma(I)]$ are $R_1 = 0.0413$, $wR_2 = 0.1016$; R indices (all data), $R_1 = 0.0483$, $wR_2 = 0.1052$ and the goodness of fit on F^2 is 0.903.
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