Cavity-Containing Cyclophosphazanes: $[C_6H_4N_2(\mu\text{-PhP})(PPh)]_2$ and $[C_6H_4N_2(\mu\text{-PhP})(PhPS)]_2$

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Molecules containing donor atom functionality within a cavity, cleft, or otherwise sterically restricted region are of considerable interest[1–6] and such molecules containing phosphorus(III) donor sites are rare. We now report the first example of a novel class of phosph(III)azane donor cavity molecules $[C_6H_4N_2(\mu\text{-PhP})(PhPX)]_2$ (X = lone pair, S), a system incorporating PhP units into a heteroatom-bridged [3.3]orthocyclophane[7] structure.

Reaction of $PhPCl_2$ with $1,2\text{-}(NH_2)_2C_6H_4$ (1:1 mol/mol) and excess Et_3N in refluxing toluene under N_2 yields Et_3NHCl precipitate, $[C_6H_4N_2(\mu\text{-PhP})(PhP)]_2$ (**1**; ^{31}P NMR triplets, δ 111.3 and 85.4; 15%), and uncharacterized high molecular weight oligomers/polymers (^{31}P NMR, broad singlets, δ 95–102 and 114–120; 85%) in solution. Passage of the mixture through a 5-cm silica column followed by repeated crystallization from toluene yields pure **1**.[8] **1** reacts with S_8 (1:4 ratio, mol/mol) during 24 h at 100 °C in toluene to quantitatively form a disulfide $[C_6H_4N_2(\mu\text{-PPh})(PhPS)]_2$ (**2**). Recrystallization from toluene yields pure **2** (60% yield).[8]

Characterization of **1** and **2** is based on spectral (MS and ^{31}P and ^1H NMR) data and is confirmed by a single-crystal X-ray analysis of **2**. **1** exhibits a mass spectral M^+ ion at *m/e* 640 and **2** gives a $M^+ - S$ ion at *m/e* 672. The ^{31}P NMR spectra of **1** and **2** consist of pairs of equal-area triplets in characteristic A_2X_2 patterns[9] consistent with that expected for a C_2-symmetry P_4N_4 ring. Resonances for **1** (δ 111.3 and 85.4) are in the region characteristic for P(III) phosphazanes.[6a,10,11] In **2**, one triplet occurs at markedly higher field (δ 61.0) as expected for a P(V) sulfide center.[12] ^{31}P NMR spectra of **1** and **2** are temperature independent between −80 and 100 °C, indicating that isomer equilibration or interconversion does not occur.

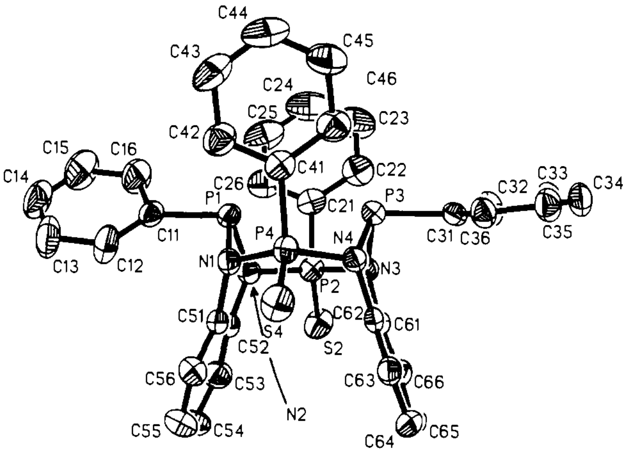

Figure 1. Structure and atom-numbering system for $[C_6H_4N_2(\mu\text{-PPh})(PhPS)]_2$ (**2**). Thermal ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): P(1)–N(1), 1.747 (2); P(1)–N(2), 1.759 (2); P(3)–N(3), 1.752 (2); P(3)–P(4), 1.749 (2); P(2)–N(2), 1.697 (2); P(2)–P(3), 1.706 (2); P(4)–N(1), 1.701 (2); P(4)–N(4), 1.700 (2); P(1)–N(2)–P(2), 119.3 (1); N(2)–P(2)–N(3), 109.0 (1); P(2)–N(3)–P(3), 119.4 (1); N(3)–P-(3)–N(4), 93.0 (1); P(3)–N(4)–P(4), 121.4 (1); N(1)–P(4)–N(4), 108.4 (1); P(1)–N(1)–P(4), 117.5 (1); N(1)–P(1)–N(2), 92.3 (1).

X-ray analysis of **2** confirms the ring structure of **2**[13] and indirectly that of **1**. **2** contains a P_4N_4 ring of alternating P and N atoms (Figure 1) in a boat conformation. Atoms P(2) and P(4) and the four N atoms are close to coplanar; the dihedral angle between the N(1),N(2),P(2),P(4) and N(3),N(4),P(2),P(4) planes is 10.7°. The two $o\text{-}C_6H_4$ (*o*-phenylene) units are situated cis relative to the P_2N_4 plane, in a [3.3] bridge heteroatom-substituted orthocyclophane system.[7] The P–N bond distances in the 1,3,2-diazaphosphole rings are longer (mean 1.751 Å) than the others in the P_4N_4 ring (mean 1.701 Å), consistent with data reported previously for N-substituted diazaphospholes.[14,15] The $o\text{-}C_6H_4$ bridges maintain the rigidity of the P_4N_4 ring. The $o\text{-}C_6H_4$ rings are nearly planar with a C(51)–C(56)/C(61)–C(66) interplane dihedral angle of 36°. The $o\text{-}C_6H_4$ rings are 3.48 Å apart at closest approach [C(51)...C(62) and C(52)...C(61)], distances not atypical for orthocyclophanes.[7] The P(2) and P(4) electron pairs are oriented outward (exo) and the atoms P(1) and P(3) pairs are pointed inward over (endo) the P_4N_4 ring. P(1) and P(3) are 3.30 Å apart, more than a P–P bonding distance but less than typical P...P van der Waals distances (3.8 Å).[16] The phenyl groups on

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(7) *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; Vol. 1. Systematic nomenclature of **1**: 1,3,6,9-tetraaza-2,7-diphospha-2,7-diphenyl-3,6-(phenylphosphido)-1,8-(phenylphosphido)-*syn*-[3.3]orthocyclophane.

(8) **1**: mp 290 °C (dec); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 111.3 (t, a 2, $^2J_{PNP} = 18.0$ Hz), 85.4 (t, a 2); ^1H NMR (C_6D_6) δ 7.37–6.60 (m; C_6H_5, C_6H_4); MS, M^+ ($^{12}C_{36}H_{28}N_4P_4^+$), *m/e* 640. **2**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 103.2 [t, a 2, $^2J_{PNP} = 46.4$ Hz; P(1), P(3)], 61.0 [t, a 2; P(2), P(4)]; ^1H NMR (C_6D_6) δ 7.33–6.40 (m; C_6H_5, C_6H_4); MS, $M^+ - S$ ($^{12}C_{36}H_{28}N_4P_4S^+$), *m/e* 672; IR (KBr) 640 (P=S) cm^{-1}. Satisfactory elemental analyses were obtained.

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(13) X-ray analysis of **2**: $C_{36}H_{28}N_4P_4S_2$, fw 704.6 amu, triclinic, $P\bar{1}$, $a = 10.8724\ (12)$ Å, $b = 11.1319\ (16)$ Å, $c = 14.219\ (2)$ Å, $\alpha = 99.812\ (11)°$, $\beta = 93.707\ (10)°$, $\gamma = 91.460\ (10)°$, $V = 1691.1\ (4)$ Å³, $Z = 2$, $d_{calc} = 1.384$ g cm^{-3}; Nicolet P3/F autodiffractometer, 25 °C, Mo Kα ($\lambda = 0.71069$ Å); Wycoff ω scan, $3.0 < 2\theta < 45.0$, 3192 observed reflections [$F_o > 6\sigma(F_o)$]; solved with SHELXTL-PLUS; $R = 0.031$, $R_w = 0.042$. Positional and thermal parameters are available as Supplementary Material.

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P(2) and P(4) are oriented approximately parallel and are 6.46 Å apart at their midpoints. These rings and atoms P(1) and P(3) form a well-defined donor molecular cavity.

That **1** and **2** are obtained in only the cis isomeric form and in a boat conformation is surprising when compared to the fourfold-symmetric $(RNPR)_4$ (R = Me, Et)[10] and $[(n\text{-Pr})(NCH_2CH_2NP)]_4$[14] reported earlier which each contain only one type of phosphorus environment. Also, the integrity of the P_4N_4 ring in **1** and **2** appears to be maintained in solution and in the gas phase. No evidence for dissociation[14] of **1** or **2** to monomer, e.g., $[C_6H_4N_2(PhP)_2]$ or acyclic dimers, or for cis–trans isomerism is seen. After thermolysis at 100 °C for 10 days, no conversion of **1** or **2** to higher oligomers occurs. The exceptional thermal stability and advantageous P(1)–P(3) and Ph(2)–Ph(4) separations in **2** and **1** make them cavity-containing molecules into which selective coordination of other atoms or metal moieties is expected. **2**, with its exo phosphorus atoms oxidized, should show especially selective P(III) donor coordination. Elemental sulfur with **2** after 100 h at 100 °C yields only traces of trisulfide $[(C_6H_4N_2)_2(PhPS)_3(PhP)]$. **2** reacts with $(Ph_3P)_2Ni(CO)_2$ to form a $\mathbf{2}\cdot Ni(CO)_2$ complex, but not with $(CO)_5Mo(CH_3CN)$ or norbornadiene$\cdot Mo(CO)_4$ possibly because the $Mo(CO)_5$ and $Mo(CO)_4$ units are too large for the cavity. This coordination selectivity, the differential reactivity of phosphorus atom pairs in the structure, and the possibility that higher order cyclooligomers of type $[C_6H_4N_2(PhP)_2]_n$ (e.g., n = 3) might form are under investigation currently.

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Supplementary Material Available: Tables of crystal data, positional and isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters for **2** (9 pages). Ordering information is given on any current masthead page.

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Synthesis and X-ray Analysis of 1,2,4,5-Trioxazinane

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As a strategy for the synthesis of six-membered heterocyclic compounds, [3 + 3] cycloadditions between two different 1,3-dipoles would be attractive. The few examples of this type of reaction reported to date show some potential synthetic utility.[2] Although the dimerization of carbonyl oxides to give 1,2,4,5-tetroxanes is well-known,[3] we report, herein, the first example of [3 + 3] cycloadditions involving carbonyl oxides and nitrones which gave rise to 1,2,4,5-trioxazinanes, derivatives of a novel class of cyclic peroxides.

Table I. Synthesis of 1,2,4,5-Trioxazinane

vinyl ether	nitrone	trioxazinane (% yield)
1a; R^1 = H, R^2 = $CH_2CH(CH_3)_2$	**2a**; R^3 = R^5 = Ph, R^4 = H	**3a** (84)
1a	**2b**; R^3 = Ph, R^4 = H, R^5 = CH_2Ph	**3b** (71)
1a	**2c**; R^3 = $(CH_2)_6CH_3$, R^4 = H, R^5 = CH_2Ph	**3c** (52)[a]
1a	**2d**; R^3 = R^4 = R^5 = Ph	**3d** (80)
1a	**2e**; R^3 = R^4 = Ph, R^5 = CH_3	**3e** (91)
1b; R^1 = Ph, R^2 = CH_3	**2a**	**3f** (38)[b]
1b	**2b**	**3g** (41)[b]
1b	**2c**	**3h** (42)[a]
1b	**2d**	**3i** (96)
1c; R^1 = $(CH_2)_6CH_3$, R^2 = CH_3	**2a**	**3j** (86)[c]
1c	**2c**	**3k** (70)[d]
1c	**2d**	**3l** (90)
1c	**2e**	**3m** (81)

[a] **3k** was also produced in around 8% yield. [b] Benzaldehyde (around 30% yield) and 3,6-diphenyl-1,2,4,5-tetroxane (around 15% yield) were also isolated. [d] The cis/trans ratio = 51:49. [e] The cis/trans ratio = 66:34.

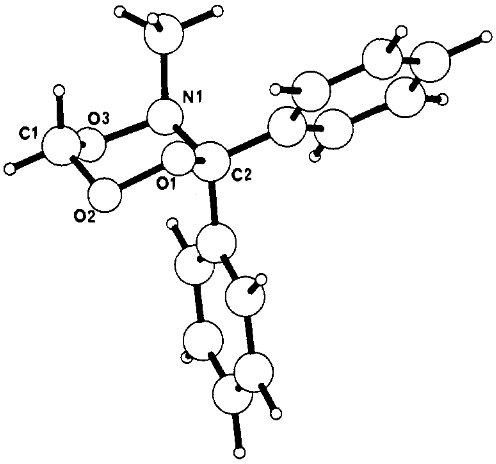

Figure 1. The X-ray crystal structure of the 1,2,4,5-trioxazinane **3e**. Some important geometrical parameters are as follows: O(1)–O(2) 1.474 (3), O(2)–C(1) 1.402 (5), C(1)–O(3) 1.414 (5), O(3)–N(1) 1.453 (4), N(1)–C(2) 1.458 (4), C(2)–O(1) 1.455 (4) Å; O(2)–C(1)–O(3) 110.8 (3), O(2)–O(1)–C(2) 105.7 (2), C(1)–O(2)–O(1) 105.0 (2), O(1)–C(2)–N(1) 110.7 (2), C(2)–N(1)–O(3) 107.9 (2), C(1)–O(3)–N(1) 111.4 (3)°.

After ozonation (2 mmol of ozone) of a mixture of the appropriate vinyl ether **1** (2 mmol) and nitrone **2** (1 mmol) in methylene chloride at 0 °C, the products, including the 1,2,4,5-trioxazinanes **3a–m**, were isolated by rapid column chromatography on silica gel (Table I). Since the new products could not be fully characterized by conventional analytical and spectroscopic techniques (Supplementary Material), an X-ray crystallographic study was undertaken of adduct **3e** to establish unambiguously the structure of the new ring system. The crystal structure (Figure 1) shows that the central 1,2,4,5-trioxazinane ring system adopts a chair conformation with the *N*-methyl being accommodated in an axial position. The bond distances around the heterocyclic ring are generally within expected ranges.

Cycloadditions involving unsymmetrically substituted dipolar components would be expected to give rise to the trioxazinanes

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