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Hexacoordination via Sulfur Donor Action in Bicyclic Pentaoxyphosphoranes[1]

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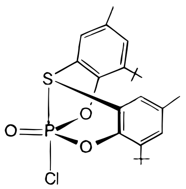
New bicyclic oxyphosphoranes, $S[(t\text{-Bu})MeC_6H_2O]_2P(OC_6H_5)(O_2C_6H_3F)$ (**1**) and $S[(t\text{-Bu})MeC_6H_2O]_2P(OC_6H_5)(O_2C_6H_4)$ (**3**), were synthesized by displacement reactions of a monocyclic pentaoxyphosphorane by a diol, and $S[(t\text{-Bu})_2C_6H_2O]_2P(OCH_2CF_3)(O_2C_6Cl_4)$ (**2**) and $S[(t\text{-Bu})_2C_6H_2O]_2P(C_6H_5)(O_2C_6Cl_4)$ (**4**), by oxidative addition reactions of a phosphite or phosphine with tetrachlorobenzoquinone. X-ray studies revealed hexacoordinated structures formed by the presence of a sulfur donor atom incorporated in a flexible eight-membered ring. The structures were displaced along a coordinate from a square pyramid toward an octahedron. ^{31}P and ^{1}H NMR data are also reported. Comparisons are made between bicyclic tetraoxyphosphoranes and monocyclic and bicyclic pentaoxyphosphoranes which show the importance of ligand electronegativity in increasing the degree of hexacoordination. Of the various series now studied, the extent of sulfur donor atom coordination increases in the following order: phosphates < phosphites < oxyphosphoranes. It is concluded that, in general, sulfur donor atom coordination will take place with phosphorus in any of the common coordination geometries in the presence of sufficiently electronegative ligands.

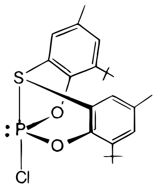
Introduction

The ease with which phosphorus undergoes increased coordination via donor action has been fairly well established in recent work.[2] Using sulfur as the donor atom supplied as a component of a flexible eight-membered ring system, phosphites,[3] phosphates,[3] and oxyphosphoranes[2,4−12] have been shown by X-ray studies to undergo substantial geometrical changes. In the process of expanding their degree of coordination, phosphites and phosphates[3] traverse a reaction coordinate from pyramidal to pseudo trigonal bipyramidal and from tetrahedral to trigonal bipyramidal (TBP), respectively. In the case of oxyphosphoranes, the displacement is from square pyramidal to octahedral. Representation of these classes of phosphorus compounds that follow these displacement coordinates are **A**−**D**,[3,8,11] which involve monocyclic and bicyclic members. P−S distances and percent displacements are also listed. It is seen that a range of P−S distances are involved which induce varying degrees of geometrical changes that accompany donor action.



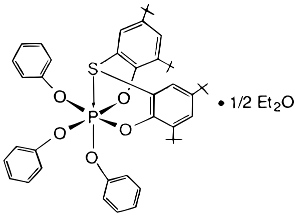
P–S = 3.114(2)Å; 35.0%

A [3]



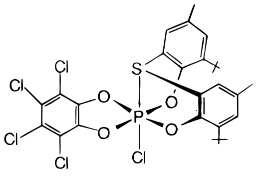
P–S = 2.816(2)Å; 54.5%

B [3]



P–S = 2.640(2)Å; 60.8%

C [8]



P–S = 2.479(2)Å; 70.8%

D [11]

What remains to be determined in a more quantitative sense is the extent to which donor action takes place with each class of phosphorus compounds. As implied by the data associated with the formulations **A**−**D**, phosphates may experience donor action to a lesser degree than phosphites. For example, back bonding from the phosphoryl oxygen atom in **A** may render the phosphorus atom less electrophilic than that in **B**. It is known from previous work[11,13] that a high electronegativity of ligands attached to phosphoranes is required to obtain substantial conversion to an octahedral geometry.

Thus far, the class that has been least investigated with regard to the ability to form hexacoordinated geometries by Lewis base donor action[7] is the bicyclic pentaoxyphosphoranes. To address this issue, the present study was undertaken and three members

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(1) (a) Pentacoordinated Molecules. 119. (b) Part 118: Sherlock, D. J.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.*, in press.

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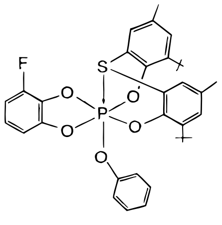
Table 1. Crystallographic Data for Compounds **1**−**4**

compd	**1**	**2**	**3**	**4**
formula	$C_{34}H_{36}FO_5PS$	$C_{36}H_{42}Cl_4F_3O_5PS\cdot{}^1/_2C_6H_{14}$	$C_{34}H_{37}O_5PS$	$C_{40}H_{45}Cl_4O_4PS$
fw	606.7	859.6	588.7	794.6
cryst system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
cryst size, mm	0.50 × 0.57 × 0.70	0.12 × 0.25 × 0.55	0.57 × 0.75 × 1.00	0.42 × 0.45 × 0.50
a (Å)	17.292(3)	10.766(1)	16.786(2)	24.218(3)
b (Å)	9.891(3)	11.228(1)	9.989(2)	13.788(4)
c (Å)	18.224(2)	18.899(2)	18.365(1)	25.753(4)
α (deg)	90	96.180(8)	90	90
β (deg)	96.59(1)	97.640(8)	97.265(8)	107.61(1)
γ (deg)	90	104.07(1)	90	90
V (Å^3)	3096(1)	2172.9(4)	3054.6(7)	8196(3)
Z	4	2	4	4
D_{calc} (g/cm^3)	1.301	1.314	1.280	1.288
μ(Mo Kα) (cm^{-1})	2.03	4.10	1.99	4.17
tot. reflns	3539	4958	3495	9339
reflns with $I > 2\sigma_I$	2056	3125	2529	5125
R^a	0.0526	0.0569	0.0390	0.0492
$R_w{}^b$	0.1136	0.1296	0.0951	0.1001

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w(F_o{}^2) = \{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^4\}^{1/2}$.

1−**3** were synthesized as well as a bicyclic tetraoxyphosphorane **4**. These were subjected to X-ray analysis of their molecular structures.



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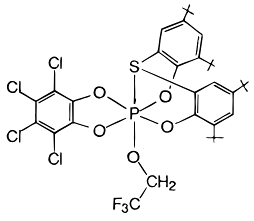

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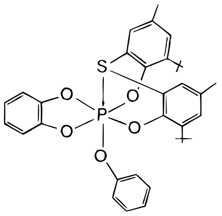

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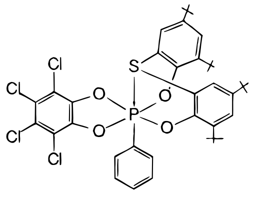

4

Experimental Section

Phosphorus trichloride, dichlorophenylphosphine, catechol, 3-fluorocatechol, and tetrachloro-1,2-benzoquinone were used as supplied from Aldrich. Triethylamine (Eastman) was distilled from potassium hydroxide. Solvents were of HPLC grade and were purified according to standard procedures.[14] 2,2′-Thiobis(4-methyl-6-*tert*-butylphenol),[8] [2,2′-thiobis(4-methyl-6-*tert*-butylphen-oxy)]triphenoxyphosphorane,[8] 2,2′-thiobis(4,6-di-*tert*-butylphenol),[15] [2,2′-thiobis(4,6-di-*tert*-butylphenyleneoxy)-*O*,*O*′](2,2,2-trifluoroethoxy)phosphine,[7] and *N*-chlorodiisopropylamine[16] were prepared by literature methods. All reactions were carried out in a dry nitrogen atmosphere using standard Schlenk-type glassware.[17] Melting points are uncorrected. Proton NMR spectra were recorded on a Bruker AC200 FT-NMR spectrometer. Phosphorus-31 NMR spectra were recorded on a Bruker MSL300 FT-NMR spectrometer. All proton spectra were recorded in $CDCl_3$ except where otherwise noted. Phosphorus-31 NMR were recorded in toluene unless stated otherwise. Chemical shifts are reported in ppm, downfield positive, relative to tetramethylsilane (^{1}H) or 85% H_3PO_4 (^{31}P). All NMR spectra were recorded at about 23 °C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. [2,2′-Thiobis(4,6-di-*tert*-butyl-*o*-phenyleneoxy)](phenyl)phosphine, S[(*t*-Bu)$_2$C$_6$H$_2$O]$_2$P(C$_6$H$_5$) (5). A solution of 16.29 g (36.85 mmol) of 2,2′-thiobis(4,6-di-*tert*-butylphenol) in 300 mL of Et_2O was cooled to 0 °C. A solution of Et_3N (10.24 mL, 73.70 mmol) and $PhPCl_2$ (5.00 mL, 36.8 mmol) in Et_2O (100 mL) was added to the cooled mixture. The system was stirred for 48 h. The mixture was filtered, removing the triethylamine hydrochloride. The resultant colorless solution was left for crystallization under a flow of nitrogen. A white solid product resulted. The ^{31}P NMR spectrum of this product showed a product peak ($\delta(^{31}P)$ 167.7) and a small phosphate peak (∼10%) at $\delta(^{31}P)$ 10.66 ppm. Its reactivity toward hydrolysis prevented further purification. It was used in the preparation of **4**. ^{1}H NMR ($CDCl_3$): 1.13 (s, 18 H, $C(CH_3)_3$), 1.30 (s, 18 H, $C(CH_3)_3$), 6.87−7.74 (m, 12 H (Ar)).

[2,2′-Thiobis(4-methyl-6-*tert*-butyl-*o*-phenyleneoxy)](phenoxy)(3-fluoro-1,2-benzenedioxy)phosphorane, S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(OC$_6$H$_5$)(O$_2$C$_6$H$_3$F) (1). [2,2′-Thiobis(4-methyl-6-*tert*-butyl-*o*-phenyleneoxy)]tris(phenoxy)phosphorane (1.00 g, 1.50 mmol) and 3-fluorocatechol (0.190 g, 1.50 mmol) were dissolved in dry toluene (15 mL) and heated under reflux for 3 h. The solvent was removed under vacuum and the residue dissolved in a mixture of dichloromethane and Skelly-C (50 mL, 1:1). The solution was left under a nitrogen flow to obtain the crystalline product, mp 190 °C (yield 0.66 g, 66%). ^{1}H NMR (toluene): 1.40 (s, 18 H, $C(CH_3)_3$), 2.24 (s, 6 H, CH_3), 6.48−7.21 (m, 12 H, H(Ar)). ^{31}P NMR (toluene): −58.81. Anal. Calcd for $C_{34}H_{36}FO_5SP$: C, 67.33; H, 5.94. Found: C, 67.93; H, 6.16.

[2,2′-Thiobis(4,6-di-*tert*-butyl-*o*-phenyleneoxy)](2,2,2-trifluoroethoxy)(tetrachloro-1,2-benzenedioxy)phosphorane, S[(*t*-Bu)$_2$C$_6$H$_2$O]$_2$P(OCH$_2$CF$_3$)(O$_2$C$_6$Cl$_4$) (2). [2,2′-Thiobis(4,6-di-*tert*-butylphenyleneoxy)-*O*,*O*′](2,2,2-trifluoroethoxy)phosphine (0.50 g, 0.88 mmol) and tetrachloro-1,2-benzoquinone (0.22 g, 0.88 mmol) were dissolved in dry toluene (15 mL) and heated under reflux for 30 min. The solvent was removed under vacuum and the residue dissolved in a mixture of dichloromethane and hexane (40 mL, 1:1). Concentration of this solution under a flow of nitrogen afforded colorless crystals of **2**, mp 227−229 °C (yield 0.32 g, 45%). ^{1}H NMR ($CDCl_3$): 1.28 (s, 18 H, $C(CH_3)_3$), 1.43 (s, 18 H, $C(CH_3)_3$), 4.53 (q, 2 H, OCH_2CF_3), 7.38 (s, 2 H, H(Ar)), 7.43 (s, 2 H, H(Ar)). ^{31}P NMR ($CDCl_3$): −61.96. Anal. Calcd for $C_{36}H_{42}Cl_4F_3O_5SP$: C, 52.90; H, 5.14. Found: C, 53.47; H, 5.57.

[2,2′-Thiobis(4-methyl-6-*tert*-butyl-*o*-phenyleneoxy)](phenoxy)(1,2-benzenedioxy)phosphorane, S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(OC$_6$H$_5$)(O$_2$C$_6$H$_4$) (3). [2,2′-Thiobis(4-methyl-6-*tert*-butyl-*o*-phenyleneoxy)]-

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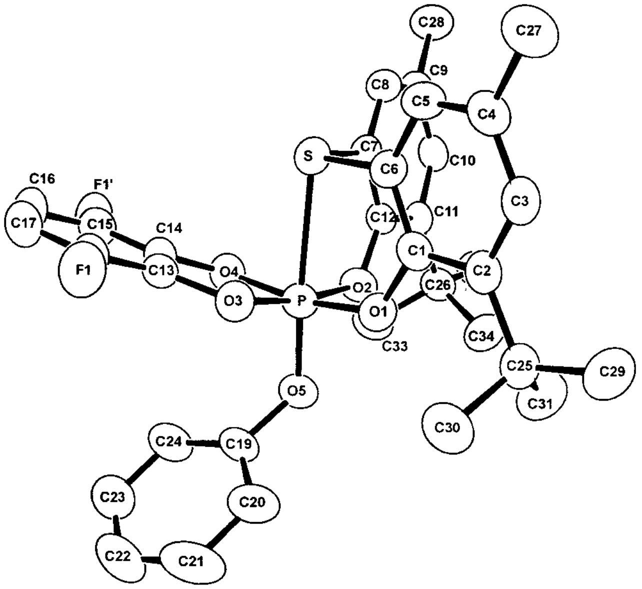


Figure 1. ORTEX diagram of **1**. Fluorine atoms F1 and F1′ each have 0.5 occupancy.

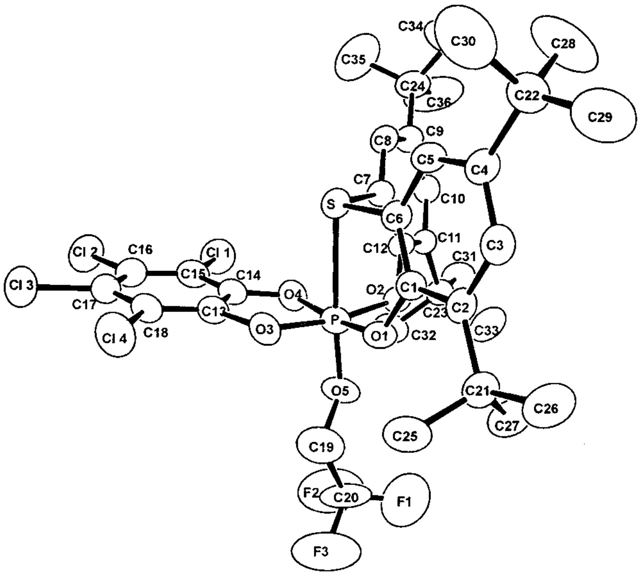


Figure 2. ORTEX diagram of **2**.

tris(phenoxy)phosphorane (0.50 g, 0.75 mmol) and catechol (0.080 g, 0.75 mmol) were dissolved in dry toluene (15 mL) and heated under reflux for 3 h. The solvent was removed under vacuum. The residue was dissolved in a mixture of dichloromethane and Skelly-C (50 mL, 1:1). The solution was left under a nitrogen flow to obtain the crystalline product, mp 213−215 °C (yield 0.21 g, 47%). ^{1}H NMR (CH$_2$CD$_2$): 1.31 (s, 18 H, C(CH$_3$)$_3$), 2.14 (s, 6 H, CH$_3$), 6.61−7.31 (m, 13 H, H(Ar)). ^{31}P NMR (toluene): −58.29. Anal. Calcd for C$_{34}$H$_{37}$O$_5$SP: C, 69.38; H, 6.29. Found: C, 69.30; H, 6.48.

[2,2′-Thiobis(4,6-di-*tert*-butyl-*o*-phenyleneoxy)](phenyl)(tetrachloro-1,2-benzenedioxy)phosphorane, S[(*t*-Bu)$_2$C$_6$H$_2$O]$_2$P(C$_6$H$_5$)(O$_2$C$_6$Cl$_4$) (4). [2,2′-Thiobis(4,6-di-*tert*-butyl-*o*-phenyleneoxy](phenyl)phosphine (**5**) (0.50 g, 0.91 mmol) and tetrachloro-1,2-benzoquinone (0.22 g, 0.91 mmol) were dissolved in 15 mL of toluene and heated under reflux for 2 h. The solvent was removed and the resultant brown solid dissolved in a mixture of Et$_2$O and hexane (30 mL, 1:1). Concentration under nitrogen yielded colorless crystals, mp 186 °C (yield 0.31 g, 41%). ^{1}H NMR (CDCl$_3$): 1.36 (s, 18 H, C(CH$_3$)$_3$), 1.47 (s, 18 H, C(CH$_3$)$_3$), 6.92−7.46 (m, 9 H, H(Ar)). ^{31}P NMR: −54.56. Anal. Calcd for C$_{40}$H$_{45}$Cl$_4$O$_4$SP: C, 60.45; H, 5.67. Found: C, 60.24; H, 5.62.

X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Details of the experimental procedures have been described previously.[18]

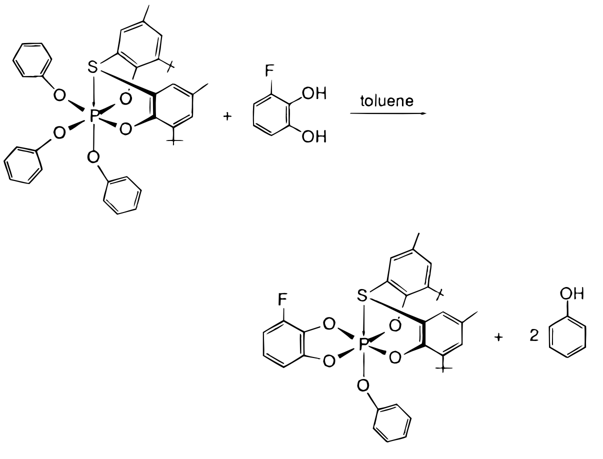
The colorless crystals were mounted in thin-walled glass capillaries which were sealed to protect the crystals from the atmosphere as a precaution. Data were collected using the $\theta-2\theta$ scan mode with $3° \leq 2\theta(\text{Mo K}\bar{\alpha}) \leq 43°$ at 23 ± 2 °C. No corrections were made for absorption. All of the data were included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least-squares. Refinements were based on F^2 and computations were performed on a 486/66 computer using SHELXS-86 for solution[19] and SHELXL-93 for refinement.[20] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded carbon atoms. The final agreement factors are based on the reflections with $I \geq 2\sigma(I)$. Crystallographic data are summarized in Table 1.

In compound **1** the fluorine atom was disordered. It was situated on either side of the catechol ring. In compound **2** there was a hexane molecule placed around an inversion center. Compound **4** had two molecules per asymmetric unit.

Results and Discussion

The atom-labeling schemes for **1**−**4** are given in the ORTEX[21] plots of Figures 1−4, respectively. Thermal ellipsoids are all shown at the 40% probability level, and all hydrogen atoms are omitted for clarity. Selected bond parameters are presented in Table 2 for **1**−**4**, respectively.

Syntheses. The syntheses of **1** and **3** take advantage of the chelation effect of forming a bicyclic system from a monocyclic one. In the case of **1**, 3-fluorocatechol is the displacing agent, whereas catechol is used in the formation of **3**. In both syntheses, phenol is displaced from the same monocyclic pentaoxyphosphorane. The process is illustrated for the formation of **1** eq 1.



1 (1)

The preparations of **2** and **4** are the result of oxidative addition reactions with the use of tetrachloroquinone acting on the respective sulfur-containing cyclic phosphite or phosphine. All reactions were carried out in toluene solution with yields varying from 41 to 66%.

Basic Structures and Structural Displacement. All of the bicyclic oxyphosphoranes **1**−**4** have geometries that are located

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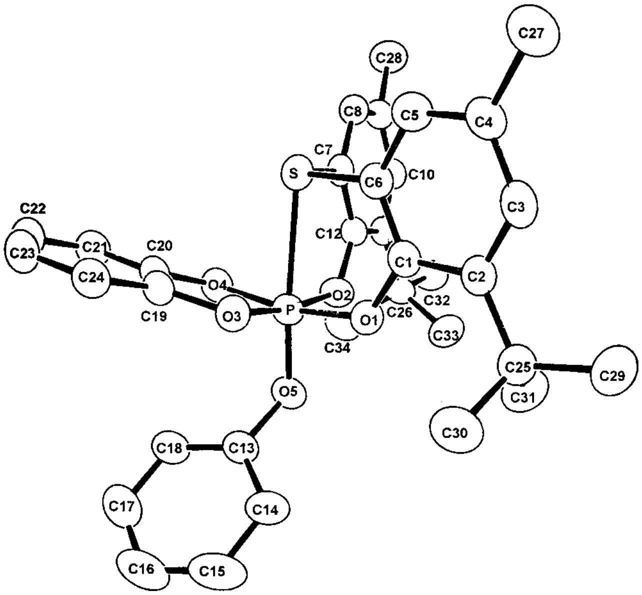


Figure 3. ORTEX diagram of **3**.

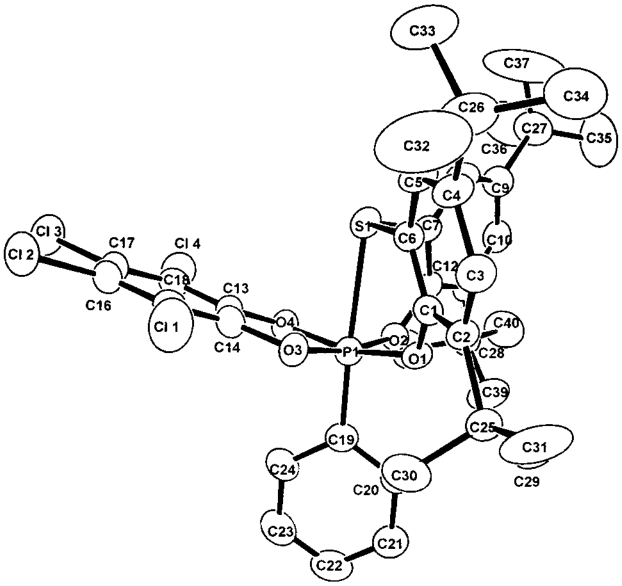
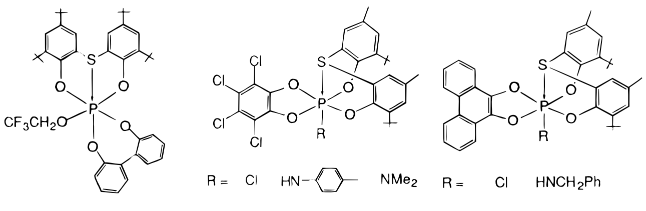


Figure 4. ORTEX diagram of **4**. Only one of the two molecules is shown. The carbon atoms of the second molecule are numbered by adding 40 to the carbon atom numbers of this molecule.



E **D** **F** **G** **H** **I**

along a coordinate between a square pyramid (SP) and an octahedron. The SP is viewed as the geometry in the absence of the sulfur atom. In this case, the *trans* basal angles are taken as 150° for an ideal SP which is the angle indicated for main group atoms that lack d orbital interactions.[22−24] With this value for the *trans* basal angles, the phosphorus atom is displaced 0.437 Å from the plane of the four basal oxygen atoms with the use of an average value of the P−O bond distance of 1.687 Å. The latter distance is an average value of the P−O basal distances for **1**−**4**. The displacement from the SP toward the octahedron is then calculated. These values are listed in Table 2 along with selected bond parameters for **1**−**4**. Similar data are listed for the bicyclic pentaoxyphosphorane **E**[7] and previously studied bicyclic tetraoxyphosphoranes **D** and **F**−**I**.[11] The combined series spans the range of P−S distances from 3.041(3) to 2.373(5) Å, nearly 0.7 Å, while the geometry is increasingly displaced from the SP toward the octahedron over the range 24−71% as the P−S distance decreases. Figure 5 gives a graphical display of P−S distances vs % octahedral character for the oxyphosphoranes listed in Table 2. There is little change in geometry for the bicyclic pentaoxyphosphoranes **1**−**3**. Independent of the ligand constitution, the octahedral character remains close to 65%. The relatively high degree of octahedral formation is most likely due to the presence of five directly attached electronegative oxygen atoms. The similar geometry for **1**−**3** is promoted by this common degree of electronegativity and no doubt by the presence in each case of a five-membered cyclic component supplied by a catechol moiety. For the pentaoxyphosphorane **E**,[7] which contains a more flexible seven-membered ring, the geometry is positioned slightly closer toward the octahedron, 71%. However, for the tetraoxyphosphorane **4**, which has a similar overall ring structure to **1**−**3**, the geometry is less octahedral, 55%. This is expected since an oxygen atom has been replaced by a less electronegative phenyl group.

Structural Comparisons. The bicyclic pentaoxyphosphoranes **1**−**3** and **E** contrast with the tetraoxyphosphoranes **4**, **D**, and **F**−**I**. As shown in Table 2, the latter series has P−S distances which span from 3.041(3) to 2.479(2) Å with the respective octahedral character going from 24 to 71%. Here, there is a greater variation possible with the fifth ligand located in each compound *trans* to the sulfur atom. Again an electronegativity effect is apparent as the chloro derivatives **D** and **H** tend more toward an octahedron than the nitrogen ligated ones **F**, **G**, and **I**. We have reasoned earlier[11] that P−N π back-bonding contributes to a lowering of the phosphorus electrophilicity as a primary cause of the lower sulfur donor action that results in less displacement toward an octahedron.

Perhaps surprising is the relatively large range in P−S distances found for six monocyclic pentaoxyphosphoranes[6,8,10,25] (of which **C**[8] is representative) in view of what we said regarding the small range for the bicyclic pentaoxyphosphoranes **1**−**3** and **E**. These distances span over 0.5 Å from 2.88 to 2.36 Å while the octahedral character goes from 44 to 76%, respectively. Two factors appear to be operating to cause this larger range for the monocyclic pentaoxyphosphoranes. First, a greater variability exists in the ligand composition. In contrast to the common catechol component for **1**−**3**, the monocyclic series contains the pentafluorophenoxy ligand which results in the member with the most octahedral geometry[25] as well as members with trifluoroethoxy[6,10] and phenoxy ligands.[8]

A second feature of importance results from ring substitution on the sulfur containing eight-membered ring system. The member having the least octahedral geometry is **J**[8] that has only methyl substituents on the aforementioned ring. It has been our observation that whenever this type of substitution is present, the P−S distance elongates so that the geometry reverts toward SP as in **J** or the ring conformation goes from a boatlike (which

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Table 2. Selected Bond Parameters for Bicyclic Oxyphosphoranes Measuring the Degree of Octahedral Coordination^a

	bond distances, Å						bond angles, deg			
compd no.	P−O4	P−O1	P−O3	P−O2	P−R	P−S	O4−P−O1^b	O3−P−O2^b	R−P−S	% octa^c
3 (R = O)	1.702(2)	1.680(2)	1.687(2)	1.657(2)	1.609(2)	2.509(1)	168.4(1)	170.2(1)	174.9(1)	64.2
1 (R = O)	1.706(4)	1.677(4)	1.698(4)	1.655(4)	1.610(4)	2.496(2)	168.8(2)	170.1(2)	175.9(2)	64.6
2 (R = O)	1.708(4)	1.661(4)	1.712(4)	1.658(4)	1.613(4)	2.499(2)	170.1(2)	169.5(2)	175.1(2)	65.7
E (R = O)	1.655(8)	1.699(8)	1.661(8)	1.711(8)	1.630(8)	2.373(5)	169.8(4)	171.9(4)	175.5(3)	70.8
I (R = N)	1.675(5)	1.651(5)	1.694(5)	1.670(5)	1.630(7)	3.041(3)	145.3(3)	169.4(3)	165.4(2)	23.8
G (R = N)	1.723(3)	1.670(3)	1.716(3)	1.659(3)	1.645(4)	2.731(2)	159.3(2)	163.8(2)	177.6(1)	37.1
F (R = N)	1.714(4)	1.656(4)	1.693(4)	1.638(4)	1.662(5)	2.665(2)	160.9(2)	168.0(2)	174.7(2)	47.4
4(1)^d (R = C)	1.736(4)	1.671(4)	1.716(4)	1.661(4)	1.811(6)	2.594(2)	163.8(2)	168.2(2)	177.1(2)	52.7
4(2)^d (R = C)	1.733(4)	1.671(4)	1.740(4)	1.671(4)	1.824(6)	2.530(2)	167.9(2)	166.8(2)	177.7(2)	57.0
H (R = Cl)	1.677(3)	1.654(3)	1.680(3)	1.667(3)	2.064(2)	2.581(2)	171.3(2)	166.7(2)	175.0(1)	62.9
D (R = Cl)	1.695(3)	1.648(3)	1.704(3)	1.645(3)	2.061(2)	2.479(2)	172.2(1)	170.6(1)	176.5(1)	70.8

^{a} Data for **E** are taken from ref 7, and data for **D** and **F**−**I** are from ref 11. ^{b} Relative to a square pyramid, these are *trans* angle values. For **F**−**J**, respectively, *cis* angle values for O1−P−O2 are 93.5(1), 91.9(2), 90.9(2), 91.2(2), and 92.0(3), and for O3−P−O4, they are 90.0(1), 89.0(2), 88.4(2), 91.1(2), and 89.6(3). ^{c} The degree of structural displacement from a square pyramid toward an octahedron based on the distance of the phosphorus atom from the basal plane of the four oxygen atoms. ^{d} Compound **4** has two independent molecules per unit cell.

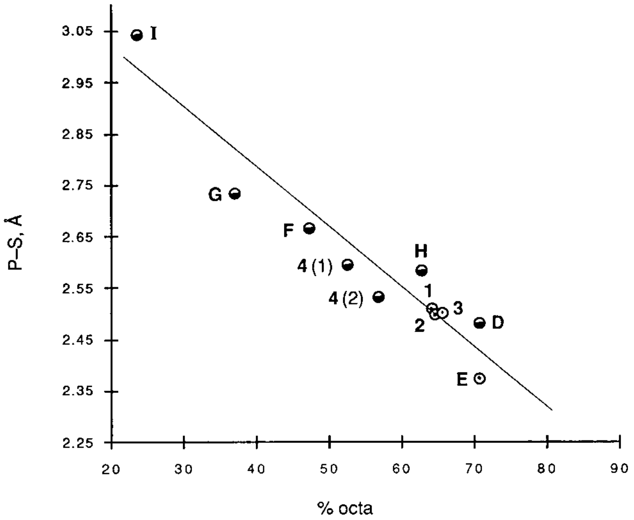
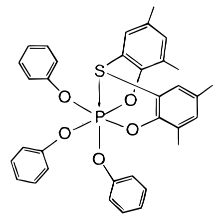


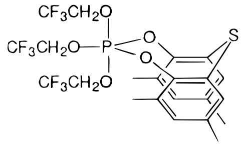
Figure 5. Variation of the P−S distance with the percent octahedral character of the bicyclic oxyphosphoranes listed in Table 2. The open circles refer to bicyclic pentaoxyphosphoranes. The half-filled circles refer to bicyclic tetraoxyphosphoranes.



P-S = 2.880(1)Å; 44.1%

J[8]

is the one present in all cases discussed so far) to a chairlike orientation, *e.g.* **K**.[10] In the latter ring conformation, the P−S



P-S = 3.504(3)Å

K[10]

distance approaches the sum of the Van der Waals radii of 3.75 Å.[26] Nevertheless, a greater sampling of ligand compositions for the bicyclic pentaoxyphosphorane series must be obtained before a more definitive answer is available.

The various phosphorane series discussed above all contrast with a recent study of monocyclic phosphites and phosphates.[3] Although these derivatives have the same type of sulfur-containing ring system, P−S donor action is considerably less, which is in line with the overall reduction in electronegative ligand attachments from five to three or four. What may be surprising is that there is any donor action at all for these lower coordinated phosphorus compounds. The displacement coordinate traversed in these derivatives takes the pyramidal or tetrahedral geometry for the phosphite or phosphate, respectively, in the presence of sulfur coordination to a pseudo-TBP or TBP.[3] Representative members are **A** and **B** shown in the Introduction. The lower displacement value for the phosphate **A** compared to the phosphite **B** has been ascribed to π back-bonding from the phosphoryl oxygen atom.[3] This is the same reasoning that was applied to the lower sulfur donor action discussed for the nitrogen-bonded oxyphosphoranes listed in Table 2.

Conclusion

When they are viewed overall, it would appear that phosphorus compounds, irrespective of common coordination geometries, will interact with nearby donor atoms and undergo an increase in coordination number provided the ligand attachments have sufficient electronegativity to allow phosphorus to possess the necessary electrophilicity. An implication in phosphoryl transfer enzymes and cAMP molecules is that a rate enhancement effect may occur as a result of a more tightly coordinated activated complex as a result of donor action relative to a lesser amount associated with the phosphorus substrate of lower coordination.

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Supporting Information Available: Tables of atomic coordinates and *U* values, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters and figures showing thermal ellipsoids for **1**−**4** (29 pages). Ordering information is given on any current masthead page.

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