

Increased Coordination via Sulfur Donor Action in Cyclic Pentaoxyphosphoranes and the Parent Cyclic Phosphite. Influence of Pentafluorophenoxy Ligands¹

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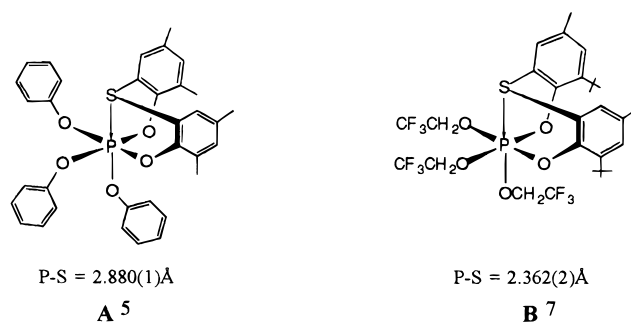
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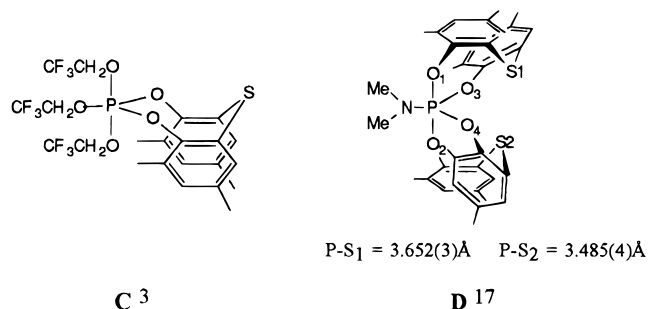
The pentafluorophenoxy ligand was introduced into the new cyclic pentaoxyphosphoranes $S[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P}(\text{OC}_6\text{F}_5)(\text{O}_2\text{C}_6\text{Cl}_4)$ (**1**), $S[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P}(\text{OC}_6\text{F}_5)(\text{O}_2\text{C}_{14}\text{H}_8)$ (**2**), and $S[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P}(\text{OC}_6\text{F}_5)_3$ (**3**). X-ray analysis revealed hexacoordinate structures formed by sulfur donor action present as a bridging atom in flexible eight-membered rings for **1–3**. X-ray analysis showed that sulfur coordination also occurred with the same type of ring system as part of the phosphite $S[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P}(\text{OC}_6\text{F}_5)$ (**4**) to give a pseudo-trigonal-bipyramidal geometry. The pentafluorophenoxy ligand present in the oxyphosphoranes **1–3** as well as in the phosphite **4** acts comparably to a chlorine atom in its ability to enhance phosphorus electrophilicity as measured by the degree of P–S coordination and geometrical displacement toward a more highly coordinated state. The phosphite **4** has a P–S donor distance of 2.876(2) Å, considerably longer than the range of P–S distances from 2.366(3) to 2.495(2) Å obtained for the pentaoxyphosphoranes **1–3**. These data express quantitatively the relative electrophilicity of phosphorus as a function of coordination number and substituent composition.

Introduction

Studies have now been conducted that show that donor atom coordination at phosphorus causes a change in geometry for phosphites² and phosphates² toward trigonal bipyramidal and for oxyphosphoranes^{3–15} toward octahedral. With the use of sulfur,^{3–12} oxygen,^{12–14} and nitrogen¹⁵ as components of flexible ring systems, donor atom–phosphorus distances have varied between the van der Waals sum and the sum of the covalent radii. Specifically, for the most studied series, sulfur donor action with cyclic pentaoxyphosphoranes^{3–7,10–12} has led to P–S distances covering the range from 2.880(1) Å for **A**⁵ to 2.362(2) Å for **B**.⁷ Correspondingly, the pentacoordinate geometries are displaced toward the octahedron, ranging from 44% to 69%. The variation is attributable to electronic and steric contributions



associated with the ligand composition.^{5,7} In this series, the ring containing the sulfur donor atom is in a syn boat–boat conformation. Examples also exist where sulfur coordination is lacking, as in **C**,³ as measured by the long P–S distance of



3.504(3) Å, close to the van der Waals sum of 3.65 Å.¹⁶ Here the ring is in an anti chair–boat conformation.³ A rare example of a ring arrangement is found in **D**,¹⁷ which has two potential sulfur donor atoms contained in rings having syn boat–boat conformations, for which neither of the sulfur atoms coordinates to phosphorus. It has been reasoned¹⁷ that the presence of P–N

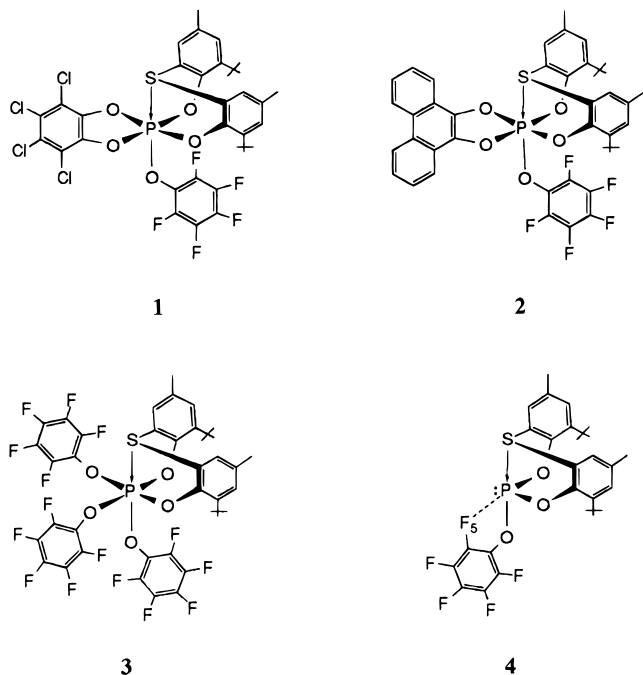
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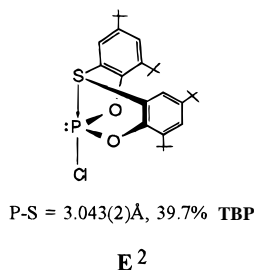
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π back-bonding sufficiently reduces the electrophilicity of phosphorus to prevent additional coordination.

In the present study, we explore the use of the electronegative pentafluorophenoxy ligand and its influence to control sulfur donor action. This has resulted in the synthesis of the pentaoxyphosphoranes **1–3** as well as the phosphite formulation **4**. Although the ligand composition is varied, the eight-



membered ring system is maintained unchanged throughout the series. Phosphite **4** is included in this study to examine the degree to which donor action will take place for comparison with the oxyphosphoranes having the same sulfur-containing cyclic ligand. Previous work² with related phosphites, e.g. **E**,² has shown the presence of donor coordination but to a lesser degree in general than that found for cyclic oxyphosphoranes with sulfur coordination.^{3–12}



Studies of the X-ray structures of these newly synthesized phosphorus compounds are reported as well as solution NMR measurements to determine if any isomeric changes take place.

Experimental Section

Phosphorus trichloride, pentafluorophenol, tetrachloro-1,2-benzoquinone, and phenanthrenequinone were used as supplied by Aldrich. Triethylamine (Eastman) was distilled over potassium hydroxide. Solvents were of HPLC grade and were purified according to standard procedures.¹⁸ 2,2'-Thiobis(4-methyl-6-*tert*-butylphenol)⁵ and *N*-chloro-

diisopropylamine¹⁴ were synthesized according to literature methods. All reactions were performed in a dry nitrogen atmosphere using standard Schlenk-type glassware.¹⁹ 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 CDCl₃ unless otherwise stated. Phosphorus NMR spectra were recorded in toluene unless otherwise stated. Chemical shifts are reported in ppm, downfield positive, relative to tetramethylsilane (¹H) or 85% H₃PO₄ (³¹P). All were recorded at 23 °C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

[2,2'-Thiobis(4-methyl-6-*tert*-butylphenoxy)](pentafluorophenoxy)-(tetrachloro-1,2-benzenedioxy)phosphorane, S[(*t*-Bu)MeC₆H₂O]₂P(OC₆F₅)(O₂C₆Cl₄) (1**).** [2,2'-Thiobis(4-methyl-6-*tert*-butylphenyleneoxy)-*O,O'*](pentafluorophenoxy) phosphite (1.00 g, 1.75 mmol) and tetrachloro-1,2-benzoquinone (0.430 g, 1.75 mmol) were dissolved in dichloromethane (15 mL). A dark red solution formed, which was stirred at room temperature for 2 min. During this time, the solution became colorless. Skelly-C (15 mL) was added and the system concentrated under a flow of nitrogen to yield a crystalline product: mp 183–185 °C (yield: 0.92 g, 64%). ¹H NMR (C₆D₆): 1.44 (s, 18 H, C(CH₃)₃), 1.83 (s, 6 H, CH₃), 6.82 (s, 2 H, Ar(H)), 7.00 (s, 2 H, Ar(H)). ³¹P NMR (toluene): –68.9. Anal. Calcd for C₃₄H₂₈Cl₄F₅O₅SP: C, 50.0; H, 3.43. Found: C, 50.82; H, 4.16.

[2,2'-Thiobis(4-methyl-6-*tert*-butylphenoxy)](pentafluorophenoxy)-(phenanthrenedioxy)phosphorane, S[(*t*-Bu)MeC₆H₂O]₂P(OC₆F₅)(O₂C₁₄H₈) (2**).** [2,2'-Thiobis(4-methyl-6-*tert*-butylphenyleneoxy)-*O,O'*](pentafluorophenoxy) phosphite (2.00 g, 3.51 mmol) and phenanthrenequinone (0.730 g, 3.51 mmol) were dissolved in toluene (50 mL). A bright orange mixture formed, which was heated under reflux for 150 min. The solvent was removed under vacuum and the residue dissolved in a mixture of dichloromethane (25 mL) and Skelly-C (25 mL). The resultant solution was concentrated under a flow of nitrogen to yield an orange solid. The solid was quickly washed with small amounts of cold ether, leaving a colorless crystalline solid: mp 178 °C (yield: 1.23 g, 45%). ¹H NMR: 1.50 (s, 18 H, C(CH₃)₃), 2.24 (s, 6 H, CH₃), 7.19–7.52 (m, 8 H, H(Ar)), 8.16 (s, 2 H, Ar(H)), 8.48 (s, 2 H, Ar(H)). ³¹P NMR (toluene): –61.28. Anal. Calcd for C₄₂H₃₆F₅O₅SP: C, 64.78; H, 4.63. Found: C, 64.50; H, 4.86.

[2,2'-Thiobis(4-methyl-6-*tert*-butylphenoxy)]tris(pentafluorophenoxy)phosphorane, S[(*t*-Bu)MeC₆H₂O]₂P(OC₆F₅)₃ (3**).** To a solution of phosphorus trichloride (1.00 mL, 11.5 mmol) and pentafluorophenol (6.30 g, 34.2 mmol) in dichloromethane (200 mL) was added triethylamine (4.80 mL, 34.5 mmol) with stirring at about 23 °C over 5 min. The solution was stirred for 4 h, and then 2,2'-thiobis(4-methyl-6-*tert*-butylphenol) (4.50 g, 11.5 mmol) was added along with *N*-chlorodiisopropylamine (2.00 mL, 13.6 mmol). The solution was stirred for an additional 21 h. The solution was then washed with water (4 × 100 mL), dried with anhydrous Na₂SO₄, and filtered. Skelly-C (50 mL) was added and the solution left under a nitrogen flow to obtain a crystalline product: mp 150–155 °C (yield: 7.5 g, 70%). ¹H NMR: 1.03 (s, 18 H, *t*-Bu), 2.27 (s, 6 H, aryl-*Me*), 7.10 (s, 2 H, aryl), 7.30 (s, 2 H, aryl). ³¹P NMR (CH₂Cl₂): –100.8. Anal. Calcd for C₄₀H₂₈F₁₅O₅PS: C, 51.29; H, 3.01. Found: C, 51.35; H, 3.62.

[2,2'-Thiobis(4-methyl-6-*tert*-butylphenoxy)](pentafluorophenoxy)phosphite, S[(*t*-Bu)MeC₆H₂O]₂P(OC₆F₅) (4**).** A solution of 2,2'-Thiobis(4-methyl-6-*tert*-butylphenol) (10.26 g, 28.7 mmol) and Et₃N (8.00 mL, 57.6 mmol) in diethyl ether (100 mL) was added dropwise to an ice cold solution of phosphorus trichloride (2.50 mL, 28.7 mmol) in diethyl ether (350 mL). The reaction mixture was stirred for 24 h after the addition was complete and then filtered. A solution of pentafluorophenol (5.27 g, 28.7 mmol) and triethylamine (4.00 mL, 28.8 mmol) in diethyl ether (50 mL) was added dropwise to the filtrate. Stirring was continued for a further 24 h. After filtration, the colorless filtrate was concentrated under a flow of nitrogen and yielded the product as a colorless crystalline mass: mp 172–174 °C (yield: 10.97 g, 67.3%). ¹H NMR: 1.40 (s, *t*-Bu, 18 H), 2.27 (s, Me, 6 H), 7.12–7.32 (m, H(Ar), 4 H). ³¹P NMR (toluene): 138 (t), ⁴J_{PF} 34 Hz. Anal. Calcd for C₂₈H₂₈F₅O₃PS: C, 58.95; H, 4.91. Found: C, 58.66; H, 5.12.

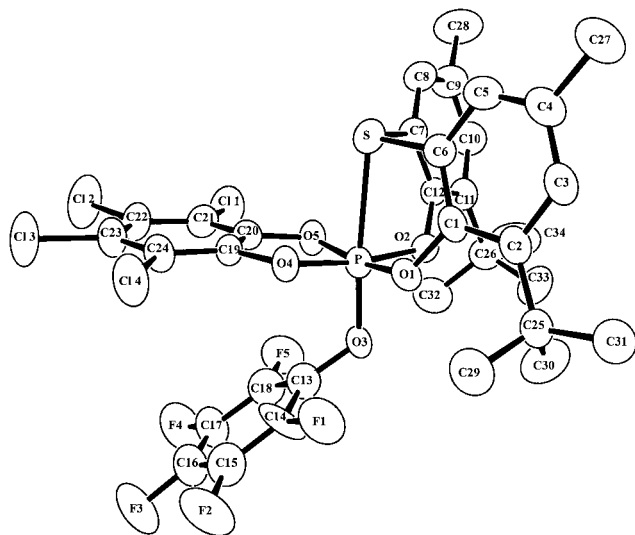
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Table 1. Crystallographic Data for Compounds 1–4

	1	2	3	4
formula	C ₃₄ H ₂₈ Cl ₄ F ₅ O ₅ PS ^{1/2} C ₇ H ₁₆	C ₄₂ H ₃₆ F ₅ O ₅ PS·CH ₂ Cl ₂	C ₄₀ H ₂₈ F ₁₅ O ₅ PS ^{1/2} CH ₂ Cl ₂	C ₂₈ H ₂₈ F ₅ O ₃ PS
fw	866.49	863.66	979.12	570.53
cryst system	monoclinic	triclinic	triclinic	triclinic
space group	C2/c (No. 15)	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
cryst size (mm)	0.60 × 0.32 × 0.15	1.00 × 0.45 × 0.35	0.87 × 0.50 × 0.45	0.70 × 0.45 × 0.35
a (Å)	28.147 (3)	12.667 (3)	12.404 (4)	10.689 (2)
b (Å)	18.039 (7)	17.692 (5)	14.344 (4)	11.999 (2)
c (Å)	16.140 (2)	18.876 (6)	15.459 (6)	12.377 (3)
α (deg)	90	90.98 (3)	116.47 (3)	109.88 (2)
β (deg)	108.47 (1)	107.95 (3)	85.17 (3)	97.03 (2)
γ (deg)	90	92.50 (2)	112.73 (2)	107.77 (2)
V (Å ³)	7773 (3)	4018 (2)	2258 (1)	1375.5 (5)
Z	8	4	2	2
D _{calc} (g/cm ³)	1.481	1.428	1.440	1.377
μ _{Mo Kα} (cm ⁻¹)	4.66	3.22	2.69	2.38
tot. reflns	4461	9154	5173	3148
reflns with I > 2σ _I	2775	5606	3292	2630
R ^a	0.0573	0.0580	0.0744	0.0411
R _w ^b	0.1419	0.1432	0.2057	0.1052

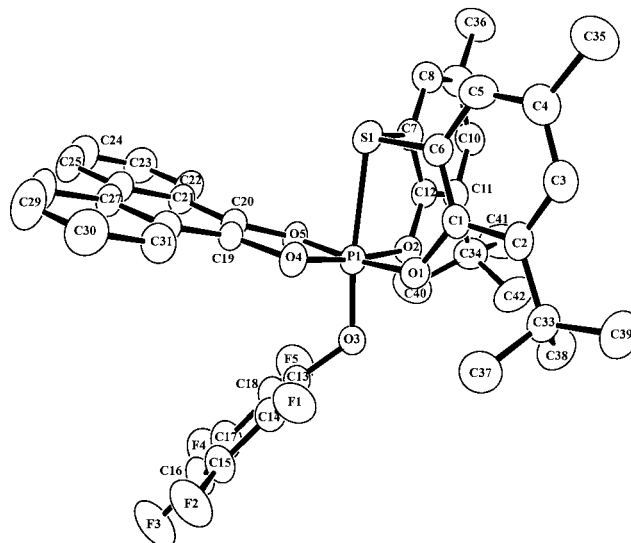
^a R = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b R_w(F_o²) = $[\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.

**Figure 1.** ORTEX diagram of S[(*t*-Bu)MeC₆H₂O]₂P(OC₆F₅)(O₂C₆Cl₄) (1).

X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Details of the experimental procedures have been described previously.²⁰

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 θ - 2θ scan mode with $3^\circ \leq 2\theta_{\text{MoK}\alpha} \leq 43^\circ$ 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 procedures. Refinements were based on F^2 , and computations were performed on a 486/66 computer using SHELXS-86 for solution²¹ and SHELXL-93 for refinement.²² All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding either in 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.

Compound 1 had a highly disordered solvent molecule (heptane) located around the inversion center with four carbons on each side.

**Figure 2.** ORTEX diagram of S[(*t*-Bu)MeC₆H₂O]₂P(OC₆F₅)(O₂C₁₄H₈) (2). Only one of the two molecules is shown. The second molecule is numbered identically.

Each carbon was refined in two positions with half-occupancy while the terminal ones were assigned a quarter-occupancy each. Compound 2 had two independent molecules in each asymmetric unit. Also, there was one dichloromethane molecule with disordered chlorine atoms. In compound 3, two dichloromethane molecules were found and assigned a quarter-occupancy each. None of the solvent hydrogens were included in the model.

Results and Discussion

The atom-labeling schemes for 1–4 are given in the ORTEX plots²³ of Figures 1–4, respectively. Thermal ellipsoids are shown at the 40% probability level. All hydrogen atoms are omitted for clarity. Selected bond parameters are presented in Table 2 for 1–3 and in Table 3 for 4 and related phosphites, E–G, and phosphates H and I.

Syntheses. The sulfur-donor-coordinated pentaoxyphosphoranes 1 and 2 were prepared by the oxidative additions of a cyclic phosphite with tetrachlorobenzoquinone. The reaction to obtain 1 was complete in 2 min at room temperature whereas

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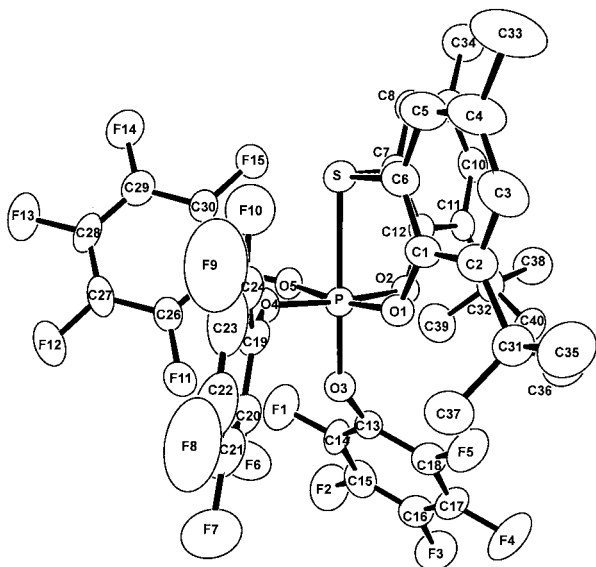
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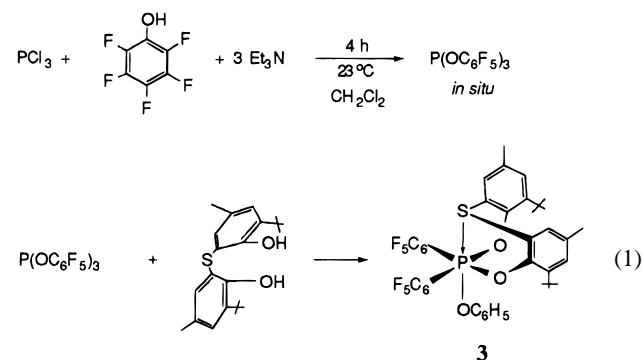
Table 2. Selected Bond Parameters for Cyclic Pentaoxyphosphoranes 1–3 Measuring the Degree of Octahedral Coordination

compd no.	bond distances (Å)					bond angles (deg)				
	P–O5	P–O1	P–O4	P–O2	P–O3	P–S	O5–P–O1 ^a	O4–P–O2 ^a	O3–P–S	% octa ^b
1	1.707(5)	1.652(5)	1.699(4)	1.649(5)	1.640(5)	2.494(3)	170.2(3)	170.9(3)	174.7(2)	68.2
2 (1) ^c	1.685(4)	1.656(4)	1.691(4)	1.663(4)	1.650(4)	2.457(2)	172.8(2)	172.4(2)	173.8(2)	73.2
2 (2) ^c	1.682(4)	1.646(5)	1.687(4)	1.659(4)	1.642(4)	2.495(2)	173.1(2)	169.8(2)	173.9(2)	73.2
3	1.677(5)	1.683(5)	1.688(5)	1.678(5)	1.625(5)	2.366(3)	172.7(3)	173.2(3)	176.9(2)	76.2

^a Relative to a square pyramid, these are trans angle values. The cis angle values for O1–P–O2 are 92.6(2)° for **1**, 91.5(2) and 91.2(2)° for **2**, and 91.2(3)° for **3**, and for O4–P–O5, they are 89.9(2)° for **1**, 90.7(2) and 90.3(2)° for **2**, and 88.4(2)° for **3**. ^b The degree of structural displacement from a square pyramid toward an octahedron is based on the distance of the phosphorus atom from the basal plane of the four oxygen atoms. ^c Compound **2** has two independent molecules in the unit cell.

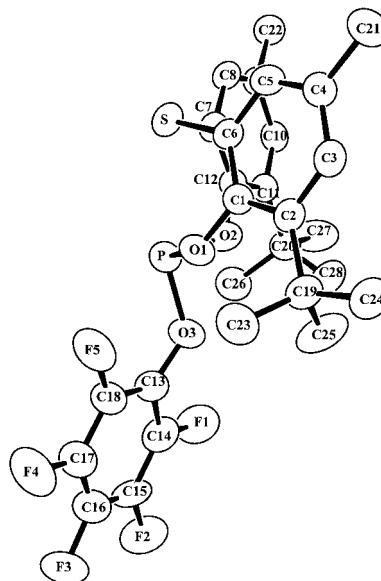
**Figure 3.** ORTEX diagram of S[(*t*-Bu)MeC₆H₂O]₂P(OC₆F₅)₃ (**3**).

refluxing in toluene for 2½ h was required for the formation of **2**. For **3**, the phosphite P(OC₆F₅)₃ was prepared in situ from PCl₃ and pentafluorophenol which was then reacted with the sulfur containing diol to obtain the hexacoordinated product. The process is illustrated in eq 1. The synthesis of phosphite



4 also started with PCl₃ to which the sulfur-containing diol was added with triethylamine in ethyl ether solution, resulting in the in situ formation of the cyclic chlorophosphite intermediate. Condensation of the latter with pentafluorophenol gave **4**. Yields were in the range 64–70% other than that for **2**, which was 45%.

Structure: Hexacoordination. Both of the bicyclic pentaoxyphosphoranes (**1** and **2**) and the monocyclic pentaoxyphosphorane (**3**) exhibit P–S coordination that results in octahedral geometries. Table 2 shows that the P–S distances which vary from 2.494(3) Å for **1** to 2.366(3) Å for **3** are intermediate between the van der Waals sum of 3.65 Å¹⁶ and the sum of the

**Figure 4.** ORTEX diagram of S[(*t*-Bu)MeC₆H₂O]₂P(OC₆F₅)₃ (**4**).

covalent radii of 2.12 Å.²⁴ The values of the P–S distances suggest a high degree of coordination. This is further borne out by noting that the cis O–P–O angles are near 90° and the trans angles are in the range 170–177°.

A more quantitative measure of the degree of octahedral character is obtained by viewing the structure along a displacement coordinate from an ideal square pyramid (SP) toward an ideal octahedron.^{3,7} The square pyramid for use in the calculation is the one formed by the five oxygen atoms attached to phosphorus. In an ideal SP, the trans basal angles are 150° for main group elements.^{25–27} These are the angles O5–P–O1 and O4–P–O2 in Table 2. With the use of an average P–O basal bond distance of 1.676(5) Å for **1–3**, the displacement of the phosphorus atom from the plane of the four basal oxygen atoms is 0.434 Å if the SP is an ideal one. Using the observed trans basal angles in Table 2, the geometrical displacement toward the octahedron results (last column) as a linear measure of the phosphorus atom distance from the basal plane between 0.434 and 0.0 Å. It is seen that the extent of octahedral character varies from 68% to 76% for **1–3** on this basis. The percent octahedral character calculated for **3** is the highest so far deter-

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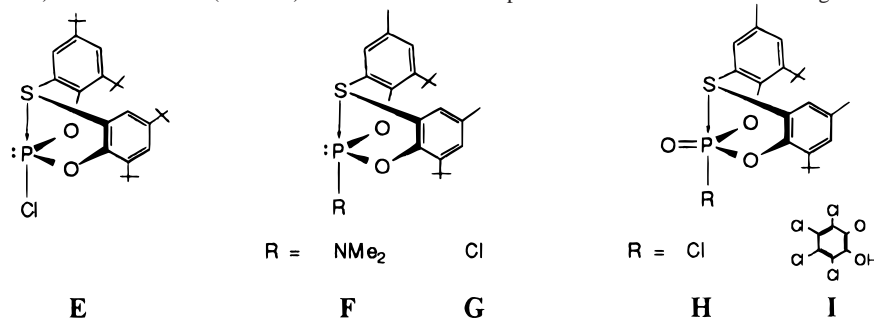
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Table 3. Selected Bond Parameters for Cyclic Phosphites and Phosphates Measuring the Degree of Trigonal Bipyramidal Coordination

compd no. ^{c,d}	bond distances, Å				bond angles (deg)			
	P-O1	P-O2	P-R	P-S	O1-P-O2	R _{ax} -P-S ^a	% TBP ^b	Σ _{eq} (deg) ^a
I (R = O3)	1.571(3)	1.565(3)	1.586(3)	3.177(2)	104.9(2)	162.9(1)	30.9	339.5(2)
H (R = Cl)	1.575(3)	1.561(3)	2.002(2)	3.114(2)	105.9(2)	167.7(1)	35.0	343.6(2)
E (R = Cl)	1.633(3)	1.629(4)	2.303(3)	3.043(2)	100.1(2)	172.2(1)	39.7	
F (R = NMe ₂)	1.66(2)	1.63(2)	1.65(3)	2.952(9)	97.7(9)	173.3(9)	47.1	
4 (R = O3) ^e	1.627(2)	1.626(2)	1.684(3)	2.876(2)	100.3(1)	163.5(1)	50.6	
G (R = Cl)	1.625(3)	1.620(3)	2.119(2)	2.816(2)	101.4(2)	169.2(1)	54.5	

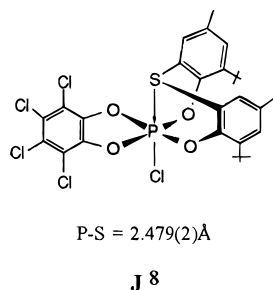
^a With reference to a TBP with sulfur in an axial position and both ring oxygen atoms in equatorial positions. ^b Percent geometrical displacement from a pyramid (**E-G** and **4**) or a tetrahedron (**H** and **I**) toward a TBP. ^c Compound labels refer to the following:



^d All data are from ref 2 except those for **4**, which is part of this work. ^e An additional coordination is present in **4** due to the weak interaction of F5 with phosphorus (Figure 4). A P-F(5) distance of 3.006(3) Å is obtained.

mined for a pentaoxyphosphorane undergoing sulfur coordination.^{3-7,10}

The influence of the pentafluorophenoxy ligand in promoting hexacoordination may be judged by P-S bond distances and the extent of octahedral character displayed by related oxyphosphoranes undergoing sulfur coordination. For example, phosphorane **B**⁷ depicted in the Introduction has trifluoroethoxy ligands in place of the three pentafluorophenoxy ligands of **3** with the same ring arrangement. The P-S distance for **B**, 2.362(2) Å, and displacement toward the octahedron of 69.4% are very similar to these values for **3**. Thus, it is implied that the influences of these two ligands are approximately the same. If steric factors are not involved, then it may be concluded that the OCH₂CF₃ and OC₆F₅ ligands have similar electronegativity effects in acting to enhance the electrophilicity at phosphorus. Another comparison can be made with the closely related composition and geometry found for **J**⁸ and **1**. The P-S

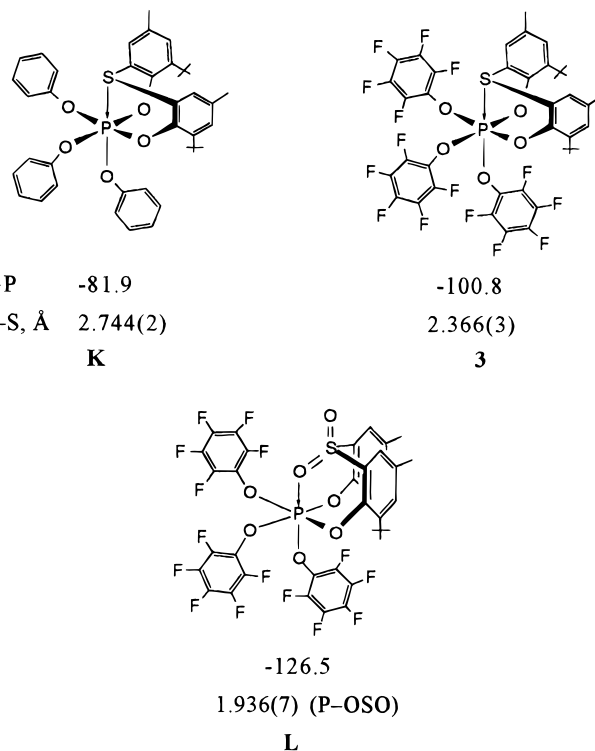


distance for **J** is 2.479(2) Å, within 3σ of the P-S distance for **1**, and the octahedral displacement also is much the same, 71% relative to 68% for **1**. As discussed for the OCH₂CF₃ ligand, the pentafluorophenoxy ligand similarly appears to exert an influence on hexacoordinate formation of oxyphosphoranes comparable to that of the chlorine atom.

³¹P NMR Data. The ³¹P chemical shifts for the bicyclic derivatives **1** and **2** in solution are -68.9 and -61.3 ppm, respectively. These values, which are considerably deshielded compared to that for **3**, -100.8 ppm, are primarily associated with the presence of the bicyclic systems possessing rigid five-

membered rings. It has been commented that the latter less flexible ring systems reduce the extent of P-O π bonding which is a factor that contributes to shielding at phosphorus.^{28,29}

In general, there is not a great change in ³¹P NMR shift for pentaoxyphosphoranes when one compares a similar ring system where only the substituents are varied.²⁸ However, it is noteworthy that a marked increase in ³¹P shielding occurs for the series **K**⁵ < **3** < **L**.¹⁴ This may be related to the strength

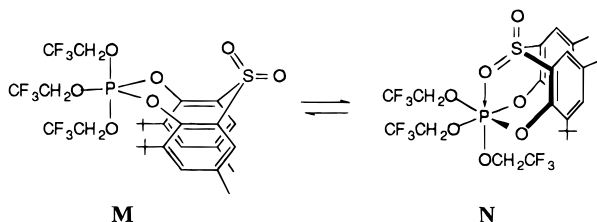


of the P-S donor interaction in **3** relative to that in **K** due to

- (28) Holmes, R. R.; Prakasha, T. K. *Phosphorus, Sulfur Silicon* **1993**, *80*, 1-22 and references therein.
 (29) Sarma, R.; Ramirez, F.; McKeever, B.; Maracek, J. F.; Lee, S. *J. Am. Chem. Soc.* **1976**, *98*, 581 and references therein.

the gain in electrophilicity at phosphorus in the presence of the more electronegative pentafluorophenoxy ligands. These two derivatives exhibit close to the longest and shortest P–S bond interactions. Although the structure of **L** is only slightly more displaced toward an octahedron compared to **3**, 82% and 76%, respectively, the ^{31}P shift for **L** is upfield by an unusual extent. This type of effect has been associated with the greater p–d π bonding of oxygen compared to that of sulfur.^{28,29}

Whether P–S coordination is present in solution for **1–3** has not been addressed in this work. However, earlier studies involving the oxygen atom of the sulfonyl group as a donor have led to the existence of isomers in five different oxyphosphorane derivatives, all of which were subjected to X-ray analysis.^{13,14} Four of the structures were noncoordinating and hence trigonal bipyramidal^{13,14} while the fifth one was octahedral¹⁴ as a result of donor action. For example, **M**,¹³ which is pentacoordinate in the solid, showed ^{31}P chemical shifts at -84.1 ppm in the solid state and -85.5 ppm in CDCl_3 solution. A signal at -73.1 ppm in CDCl_3 was assigned to the hexacoordinate isomer, **N**. The latter structural assignment agreed with



^1H and ^{19}F NMR data.¹³ VT ^1H NMR spectra showed dynamic behavior and led to an activation free energy of 17 kcal/mol for intramolecular interconversion between the penta- and hexacoordinate isomers. On this basis, we feel that structural retention for **1–3** in solution is likely.

Structure: Pentacoordination. Phosphite **4** somewhat surprisingly not only shows evidence of increased coordination as a result of sulfur donor action but has an additional base interaction indicated by the shortness of the P–F5 distance from one of the ortho fluorine atoms of the pentafluorophenoxy ligand. This distance is $3.006(3)$ Å, which compares with 3.40 Å for the van der Waals sum¹⁶ for phosphorus and fluorine and 1.83 Å for the covalent sum.²⁴ Although the shortening is not very large, the phosphorus atom in **4** formally has a lone electron pair in addition to presumed electron density supplied by sulfur atom coordination. The triplet for the ^{31}P resonance ($^4J_{\text{P-F}} = 34$ Hz) in solution implies that both ortho fluorine atoms take part. This is viewed as a result of rapid rotation of the pentafluorophenoxy ligand about the O3–C13 bond. The geometry for **4** may be viewed as a pseudo trigonal bipyramid with the sulfur atom positioned axially and a lone pair located at an equatorial site. Movement toward a TBP geometry is reinforced by the disparity in the P–O bond distances. The axial P–O3 distance of $1.684(3)$ Å is about 0.06 Å longer than the equatorial P–O distances (P–O1 = $1.627(2)$ Å and P–O2 = $1.626(2)$ Å), in agreement with the usual lengthening effect of axial bonds for trigonal bipyramids.²⁶

Structural data for other phosphites (**E–G**) as well as phosphates (**H** and **I**) undergoing sulfur coordination in related geometries² are included in Table 3 for comparison with **4**. For each of these, the structural displacement from a pyramid (**E–G** and **4**) or a tetrahedron (**H** and **I**) toward a trigonal-bipyramidal geometry is listed in the column labeled “% TBP”. A graphical display of the variation of the P–S distance for phosphates and

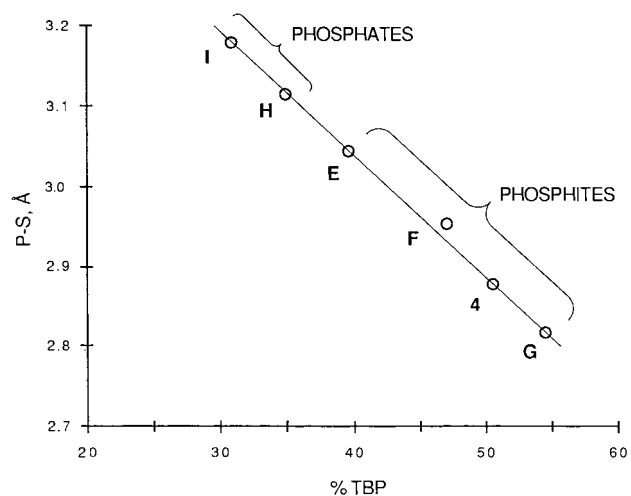


Figure 5. Graphical display of the variation of the P–S distances for phosphates and phosphites listed in Table 3. See ref 30.

phosphites is shown in Figure 5.³⁰ For both the phosphates and the phosphites, the effect of electronegativity is seen in that the axial chlorine ligands are associated with structures having the shortest P–S linkages. The influence of the axial pentafluorophenoxy ligand in **4** approaches that of the chlorine atom in this regard (Table 3). This is similar to the finding for the OC_6F_5 ligand with the oxyphosphoranes **1–3** undergoing hexacoordination.

The composition of phosphate **H** is most comparable to that of phosphite **G**, differing only in the presence of a phosphoryl oxygen atom in place of a lone pair. Associated with these structures, the P–S distance in phosphite **G** is 0.3 Å shorter than that for phosphate **H**, most likely an indication of the phosphoryl back-bonding effect² in decreasing the electrophilicity at phosphorus.

Although, with the limited series studied, phosphates appear to coordinate with sulfur to a lesser degree than phosphites, oxyphosphoranes coordinate to sulfur more strongly than phosphites. For example, the average P–S bond distance for the phosphoranes in Table 2 is $2.453(3)$ Å, which compares with $2.922(4)$ Å for the phosphites in Table 3, a difference of 0.47 Å. The replacement of the lone pair from the phosphorus center of phosphites by additional electronegative ligands increases the ability of phosphorus to undergo stronger coordination in forming hexacoordinated geometries via sulfur donor action. This bond distance effect is even greater when oxyphosphoranes are compared with phosphates in sulfur donor action. Here an average P–S bond difference of nearly 0.8 Å is involved.³¹

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1–4** and a thermal ellipsoid figure for the second independent molecule of **2** (30 pages). See any current masthead page for ordering information.

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(30) The linear variation in Figure 5 is a consequence of the procedure used in the calculation. Thus, the P–S distance is not an independent term relative to the % TBP character. The graphical display is shown here to emphasize the range of P–S distances traversed for phosphates and phosphites in comparison to that for oxyphosphoranes.

(31) Holmes, R. R. *Acc. Chem. Res.*, in press.