Inorg. Chem. **1999,** *38,* 3369−3376 **3369**

Chloro- and Fluoro-Substituted Phosphites, Phosphates, and Phosphoranes Exhibiting Sulfur and Oxygen Coordination[1]

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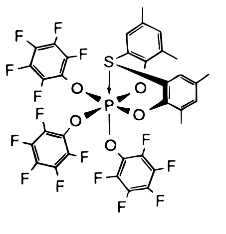
Received January 28, 1999

New cyclic phosphoranes, $O_2S[Me(t\text{-}Bu)C_6H_2O]_2PCl_3$ (**1**), $O_2S[Me(t\text{-}Bu)C_6H_2O]_2P(OC_6H_4\text{-}m\text{-}CF_3)_3$ (**2**), and $O_2S[(t\text{-}Bu)_2C_6H_2O]_2PCl_3$ (**3**), containing sulfone donor groups and halogen substituents were synthesized by oxidative addition reactions of a diol with a tricoordinated phosphorus precursor. Cyclic phosphates, $O_2S[(t\text{-}Bu)_2C_6H_2O]_2P(O)Cl$ (**4**) and $O_2S[Me(t\text{-}Bu)C_6H_2O]_2P(O)(OC_6H_4\text{-}m\text{-}CF_3)$ (**5**), resulted from hydrolysis reactions of **3** and **2**, respectively. Phosphate $O_2S[Me(t\text{-}Bu)C_6H_2O]_2P(O)(OC_6F_5)$ (**6**) was prepared from a known phosphorane precursor and independently from the reaction of an *N*-oxide molecule with a parent phosphite, $O_2S[Me(t\text{-}Bu)C_6H_2O]_2P(OC_6F_5)$. Two additional compounds containing a sulfur atom in place of the sulfone group, a cyclic phosphite, $S[Me_2C_6H_2O]_2P(OC_6F_5)$ (**7**), and a cyclic phosphate, $S[Me_2C_6H_2O]_2P(O)Cl$ (**8**), were synthesized. X-ray analysis and NMR data were obtained on all of these compounds to establish the role of electronegative ligands in promoting donor interaction. Compounds **1**−**3** were hexacoordinate as a consequence of oxygen atom coordination while **7** and **8** were trigonal bipyramidal due to sulfur atom coordination. The chlorine atom and the pentafluorophenoxy group promote similar degrees of coordination in these compounds. The results support the conclusion that the sulfur atom and oxygen atom of the sulfone group show similar coordination abilities in donor action with phosphoranes containing strongly electronegative ligands while in the presence of less electronegative ligands sulfur is the stronger coordinating agent. With phosphates and phosphites the sulfur atom exerts the stronger donor action independent of the electronegativity of the attached ligands.

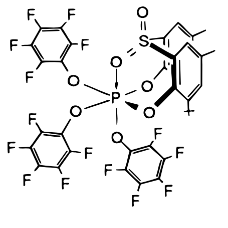
Introduction

Our recent work[2] has demonstrated that pentaoxyphosphoranes substituted with pentafluorophenyl ligands undergo donor action with sulfur that is comparable with the oxygen atom of the sulfonyl group in forming octahedral geometries. This behavior contrasts with earlier studies[3,4] in our laboratory that show that sulfur acts as a stronger donor ligand than oxygen in increasing the coordination geometry at phosphorus in pentaoxyphosphoranes when ligands of lesser electronegativity are employed. For example, the cyclic pentaoxyphosphoranes, **A**[2] and **B**,[3] containing three pentafluorophenoxy ligands show the same degree of octahedral character induced by different donor groups. In contrast, **C**[5] and **D**[3] with phenoxy ligands, of lower electronegativity, have disparate geometries. With sulfur as the donor atom, **C** is hexacoordinate as a result of donor action, while the identically composed sulfone-containing phosphorane **D**, other than insertion of the bridging SO_2 group in place of the sulfur atom, is pentacoordinate, lacking any donor coordination.



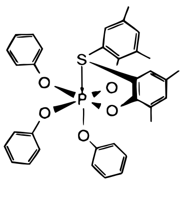
P-S = 2.389(5)Å; 82% octa

A [2]



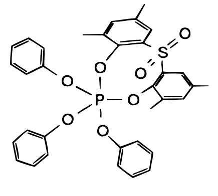
P-OSO = 1.936(7)Å; 82% octa

B [3]



P-S = 2.880(1)Å; 44% octa

C [5]



Ave. P-O = 3.233(5)Å
(2 independent molecules)

D [3]

On examination of structural features of phosphites and phosphates which are known to undergo donor coordination to a more moderate degree compared to pentaoxyphosphoranes, evidence on the donor ability of sulfur and oxygen in the presence of highly electronegative ligands is scant. The only comparison that can be made at this time is between the phoshites **E**[6] and **F**[2] having the same composition other than differing donor atoms. Both contain the pentafluorophenoxy ligand. The geometries are pseudo trigonal bipyramidal (TBP) with a lone pair at an equatorial site. The geometry of **E**, containing a sulfur donor atom, is indicated to be slightly more tightly coordinated than **F**, which possesses an oxygen donor,

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(1) (a) Pentacoordinated Molecules. 128. (b) Part 127: Mercardo, R.-M.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1999**, *18*, 1686.

(2) Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 6329.

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(5) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc*. **1993**, *115*, 2690.

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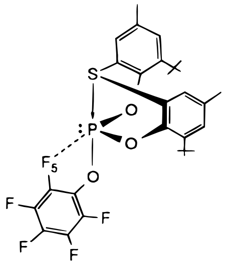
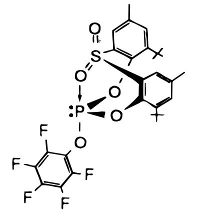
10.1021/ic9901214 CCC: $18.00

as measured by the extent of structural displacement toward an ideal TBP.[2] No information is currently available on similar structural comparisons of phosphates containing different donor atoms or phosphites with donor atoms of reduced electronegativity.


P-S = 2.876(2)Å; 51% TBP

E[6]


P-OSO = 2.652(5)Å; 46% TBP

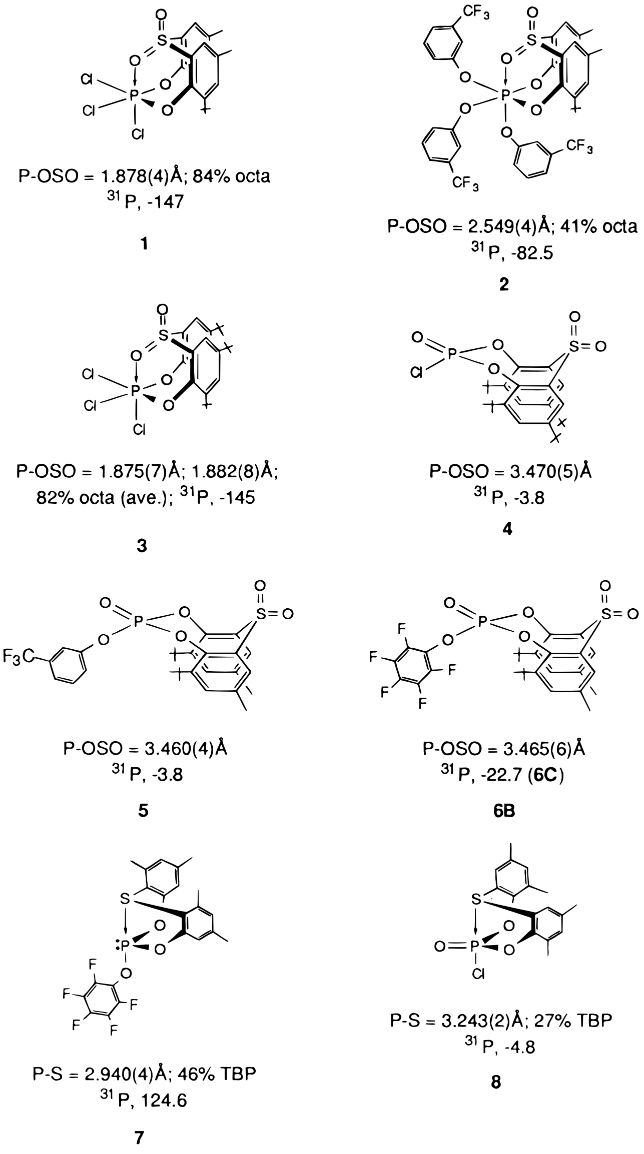
F[2]

To address the problem associated with the comparison of donor ability of sulfur and oxygen ligands as a function of substituent electronegativity in phosphites, phosphates, and oxyphosphoranes, we have synthesized **1**−**8**, which have chloro- and fluoro-containing substituents of varying electronegativity. These are shown schematically in Chart 1. The same types of electronegative substituents used in the phosphoranes, **1**−**3**, also are employed in the lower coordinated phosphates, **4**−**6**, all containing the potential sulfonyl donor group. In addition, the latter donor group has been replaced with a sulfur atom as part of the flexible ring system to contrast its effect on coordination.

Experimental Section

Phosphorus trichloride, pentafluorophenol, 3-trifluoromethylphenol, phosphorus oxychloride (Aldrich), and phenylphosphorus dichloride (Fluka) were used as supplied. Triethylamine (Aldrich) was distilled over potassium hydroxide, and solvents were purified according to standard procedures.[7] Sulfurylbis(4-methyl-6-*tert*-butylphenol),[8] **G**, sulfurylbis(4,6-di-*tert*-butylphenol),[9] **H**, thiobis(4,6-dimethylphenol),[10] **I**, thiobis(3,5-dimethylphenol),[11] **J**, anhydrous methylamino-*N*,*N*-bis-(2-methylene-4,6-dimethylphenol) *N*-oxide,[12] and *N*-chlorodiisopropylamine[3] were synthesized according to literature methods. Light petroleum fractions are referred to as Skelly-B (66−69 °C) or Skelly-F (35−60 °C). All reactions were carried out in a dry nitrogen atmosphere using standard Schlenk type glassware.[13] Melting points are uncorrected. The proton NMR spectra were recorded on a Bruker AC200 FT NMR spectrometer in $CDCl_3$ unless mentioned otherwise. The ^{31}P NMR spectra were recorded on a Bruker MSL300 FT NMR instrument in the sweep-off mode (in CH_2Cl_2 unless mentioned otherwise). Chemical shifts are reported in parts per million, downfield positive, relative to tetramethylsilane (or 85% H_3PO_4 for ^{31}P). All were recorded at around 23 °C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Chart 1


P-OSO = 1.878(4)Å; 84% octa
^{31}P, -147

1

P-OSO = 2.549(4)Å; 41% octa
^{31}P, -82.5

2

P-OSO = 1.875(7)Å; 1.882(8)Å;
82% octa (ave.); ^{31}P, -145

3

P-OSO = 3.470(5)Å
^{31}P, -3.8

4

P-OSO = 3.460(4)Å
^{31}P, -3.8

5

P-OSO = 3.465(6)Å
^{31}P, -22.7 (**6C**)

6B

P-S = 2.940(4)Å; 46% TBP
^{31}P, 124.6

7

P-S = 3.243(2)Å; 27% TBP
^{31}P, -4.8

8

Syntheses. 2,2′-Sulfurylbis(4-methyl-6-*tert*-butylphenoxy)trichlorophosphorane, $O_2S[Me(t\text{-}Bu)C_6H_2O]_2PCl_3$ (1). A solution of sulfuryl diol **G** (4.45 g, 11.4 mmol) and PCl_3 (1.00 mL, 11.5 mmol) in dichloromethane (120 mL) was added together with Pr^i_2NCl (1.80 mL, 12.2 mmol), and the solution was stirred for 5 min and left for crystallization to occur. It formed crystals of amine hydrochloride as needles and the compound as blocks. The crystals of the amine hydrochloride floated while the crystals of **1** stayed at the bottom. After all of the solvent evaporated, the residue was washed quickly with two portions of dichloromethane (100 and 20 mL) and dried under vacuum, mp >240 °C (sealed tube) (yield 2.1 g, 39%). The product is insoluble in ether, which created a problem in its separation from the amine hydrochloride. Hence, the difference in solubility and density was used to separate them. After crystallization, **1** is less soluble in dichloromethane and slower to dissolve than the amine hydrochloride. However, the solvent washes away some of the compound and reduces the yield. No proton NMR was obtained due to its very sensitive nature. ^{31}P NMR of the reaction mixture: −147 (br) ppm. Anal. Calcd for $C_{22}H_{28}Cl_4O_3PS$: C, 50.25; H, 5.37. Found: C, 49.66; H, 5.57.

2,2′-Sulfurylbis(4-methyl-6-*tert*-butylphenoxy)tris(3-trifluoromethylphenoxy)phosphorane, $O_2S[Me(t\text{-}Bu)C_6H_2O]_2P(OC_6H_4\text{-}m\text{-}CF_3)_3$ (2), and 2,2′-Sulfurylbis(4-methyl-6-*tert*-butylphenyl)(3-trifluoromethylphenyl)phosphate, $O_2S[Me(t\text{-}Bu)C_6H_2O]_2P(O)(OC_6H_4\text{-}m\text{-}CF_3)$ (5). To a solution of phosphorus trichloride (1.00 mL, 11.5 mmol) and 3-trifluoromethylphenol (4.20 mL, 34.5 mmol) in dichloromethane (200 mL) was added triethylamine (4.80 mL, 34.5 mmol) with stirring at about 23 °C over 1 min. The solution was stirred for 4 h, and then

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(12) Unpublished work.

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diol **G** (4.45 g, 11.4 mmol) was added along with Pr^i_2NCl (1.80 mL, 12.2 mmol). The solution was stirred for an additional 24 h. The solvent was removed, the residue extracted with ether (200 mL), the mixture filtered, and the solvent removed. The residue was recrystallized from a 1:1 hexane−dichloromethane mixture (100 mL) by slow evaporation under a nitrogen flow, mp 175−180 °C (yield 3.0 g, 29%). ^1H NMR: 1.32 (s, 18 H, *t*-Bu), 2.37 (s, 6 H, aryl−*Me*), 6.7−7.9 (m, 16 H, aryl). ^{31}P NMR: −82.5. Anal. Calcd for $C_{43}H_{40}F_9O_7PS$: C, 57.21; H, 4.47. Found: C, 56.88; H, 4.39. The mother liquor on crystallization from the open atmosphere gave crystals of the hydrolyzed phosphate **5**, mp 229−230 °C (yield 0.5 g, 7.4%). ^1H NMR: 1.37 (s, 18 H, *t*-Bu), 2.37 (s, 6 H, aryl−Me), 7.4−7.9 (m, 8 H, aryl). ^{31}P NMR: −23.0. Anal. Calcd for $C_{29}H_{32}F_3O_6PS$: C, 58.38; H, 5.41. Found: C, 58.24; H, 5.27.

2,2′-Sulfurylbis(4,6-di-*tert*-butylphenoxy)trichlorophosphorane, $O_2S[(t\text{-Bu})_2C_6H_2O]_2PCl_3$ (3), and 2,2′-Sulfurylbis(4,6-di-*tert*-butylphenyl)chlorophosphate, $O_2S[(t\text{-Bu})_2C_6H_2O]_2P(O)Cl$ (4). A solution of sulfuryl diol **H** (4.90 g, 10.3 mmol) and PCl_3 (0.90 mL, 10.4 mmol) in ether (200 mL) was added together with Pr^i_2NCl (2.30 mL, 15.6 mmol), and the solution stirred for 24 h. The mixture was filtered and the filtrate left under a flow of nitrogen to allow crystallization to occur. Only a few crystals of compound **3** were obtained, and they were used to collect X-ray data but soon decomposed before the completion of the data collection. ^{31}P NMR of the reaction mixture: −145 (br) ppm. Attempted recrystallization of the solid product resulted in crystals of the hydrolyzed product **4**, mp >240 °C. ^{31}P NMR (ether): −3.8 ppm.

2,2′-Sulfurylbis(4-methyl-6-*tert*-butylphenyl)(3-pentafluorophenyl)phosphate, $O_2S[Me(t\text{-Bu})C_6H_2O]_2P(O)(OC_6F_5)$ (6). The parent phosphite, **F** (0.40 g, 6.6 mmol), and methylamino-*N*,*N*-bis(2-methylene-4,6-dimethylphenol) *N*-oxide (0.22 g, 7.0 mmol) were dissolved in a 1:1 mixture of Skelly-B and dichloromethane (30 mL) and left under a nitrogen flow. The reaction mixture gave clusters of crystals (**6A**) and a waxy solid. The residue was recrystallized from hot toluene (10 mL) to obtain crystals (**6B**), mp 226−228 °C. The X-ray study performed on crystals **6B** is reported here. The ^{31}P NMR of the reaction mixture showed the presence of at least four phosphates (2.7, −9.7, −16.8, −22.7 ppm in an approximate ratio of 27:13:70:22, respectively). Crystals (**6C**) were obtained from hydrolysis of the mother liquor of sulfurylbis[2-(4-methyl-6-*tert*-butylphenyl)] tris(pentafluorophenoxy)-phosphorane (**B**, a previously known compound[3]). These crystals contained a molecule of pentafluorophenol hydrogen bonded to the phosphoryl oxygen and had a ^{31}P NMR value of −22.7 ppm. Several attempts to synthesize this compound using the usual method of obtaining phosphates starting with $OPCl_3$ were not successful.

2,2′-Thiobis(3,5-dimethylphenyl)(pentafluorophenyl)phosphite, $S[Me_2C_6H_2O]_2P(OC_6F_5)$ (7). A solution of phosphorus trichloride (1.50 mL, 17.2 mmol) and 2,2′-thiobis(3,5-dimethylphenol) (4.72 g, 17.2 mmol) in diethyl ether (450 mL) was cooled to 0 °C. Triethylamine (4.80 mL, 34.4 mmol) in diethyl ether (25 mL) was added dropwise to the cold solution, and the system was then stirred for 24 h and filtered. Pentafluorophenol (3.16 g, 17.2 mmol) and triethylamine (2.40 mL, 17.2 mmol) in diethyl ether (50 mL) was added dropwise to the filtrate, and stirring was continued for 24 h. The system was filtered again and the solution was concentrated to dryness under a flow of nitrogen. The resultant solid was dissolved in a 2:1 mixture of dichloromethane and pentane (150 mL) and concentrated under nitrogen to yield needle-shaped crystals of the product, mp 95 °C (yield 2.00 g, 24%). ^1H NMR: 2.27 (s, 6 H, CH_3), 2.52 (s, 6 H, CH_3), 6.64 (s, 2 H, Ar(H)), 6.80 (s, 2 H, Ar(H)). ^{31}P NMR (deuterated toluene): 124.6 (t, $^4J_{P-F}$ 13 Hz). Anal. Calcd for $C_{22}H_{16}F_5O_3PS$: C, 54.32; H, 3.29. Found: C, 54.76; H, 3.66.

2,2′-Thiobis(4,6-dimethylphenyl)chlorophosphate, $S[Me_2C_6H_2O]_2P(O)Cl$ (8). A solution of phosphorus oxychloride (1.50 mL, 16.1 mmol) and 2,2′-thiobis(4,6-dimethylphenol) (4.41 g, 16.1 mmol) in diethyl ether (350 mL) was cooled to 0 °C. Triethylamine (4.47 mL, 32.3 mmol) in diethyl ether (50 mL) was added dropwise and the mixture stirred for 44 h. The system was then filtered and the solution left under a flow of nitrogen for concentration. A mixture of crystals and oil resulted. The oil was removed by washing with toluene. X-ray analysis of the crystals showed them to be those of compound **8**, mp 160 °C (yield 1.15 g, 20%). ^1H NMR: 2.24 (s, 6 H, CH_3), 2.49 (s, 6 H, CH_3), 6.64 (s, 2 H, Ar(H)), 6.79 (s, 2 H, Ar(H)). ^{31}P NMR (deuterated toluene): −4.75. Anal. Calcd for $C_{16}H_{16}ClO_3PS$: C, 54.16; H, 4.51. Found: C, 55.34; H, 5.40. Attempts at further purification were unsuccessful.

X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Details of the experimental procedures have been described previously.[14]

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. The θ range was $1.5° \leq \theta_{\mathrm{Mo}K\bar{\alpha}} \leq 22°$ at 23 ± 2 °C for crystals of **2**, **4**, **5**, and **7**. The θ range was 1−25° for crystals **1** and **8** and 1−17° for **3** and **6B**. Crystal **6B** retained one-half of a toluene molecule of crystallization. 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[15] and SHELXL-93 for refinement.[16] All of 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 atoms. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$. Crystallographic data are summarized in Table 1.

There was disorder in one of the CF_3 groups for compound **2**. The fluorine atoms were refined in two positions with an occupancy of 60:40. A similar disorder for the CF_3 fluorines was observed for compound **5**. They were refined at a 50:50 occupancy ratio.

The crystals of compound **3** were extremely sensitive and decomposed before the completion of the data collection (a shell of 1−17° only had been collected). During this data collection there was about 62% decay of the standard intensity and a linear isotropic decay correction was applied. There were two independent molecules in each asymmetric unit. In one of the molecules, one of the *tert*-butyl groups was disordered. The methyl carbons were refined at two positions with equal occupancy, and the bonded hydrogen atoms were not included in the calculations. The crystal of **4** suffered a 9% decay during collection. A correction was applied. X-ray data that were collected on **6A** and **6C** showed unit cells that contained solvent molecules of crystallization of $^1/_2$ CH_2Cl_2 and C_6F_5OH, respectively.

Results and Discussion

Tables 2−9 list selected bond parameters for **1**−**8** while Figures 1−8 depict the atom-labeling schemes in the respective ORTEX[17] plots from the crystallographic studies. The thermal ellipsoids are shown at the 40% probability level, and all hydrogen atoms are omitted for clarity.

Synthesis. The use of *N*-chlorodiisopropylamine allowed retention of the chlorine atoms on phosphorus in the reaction of PCl_3 with a diol in forming the cyclic hexacoordinate products **1** and **3**. In contrast, the use of triethylamine with similar reactants, PCl_3 and a diol, causes removal of two of the chlorine atoms from phosphorus in the formation of the cyclic phosphite **7** after displacement of the remaining chlorine atom with pentafluorophenol. These reactions are contrasted in eqs 1 and 2 for the syntheses of **1** and **7**, respectively.

The synthesis of **2**, containing a pentaoxyphosphorane unit, was accompanied by oxidative addition of the preformed phosphite with the sulfuryl-containing diol **G** in the presence of $(i\text{-Pr})_2NCl$. The preformed phosphite was obtained from PCl_3 and 3-trifluoromethylphenol. A similar procedure was followed that led to the known phosphorane **B**.[3] Hydrolysis reactions led

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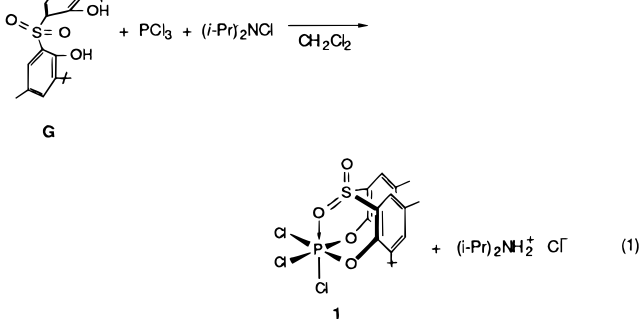
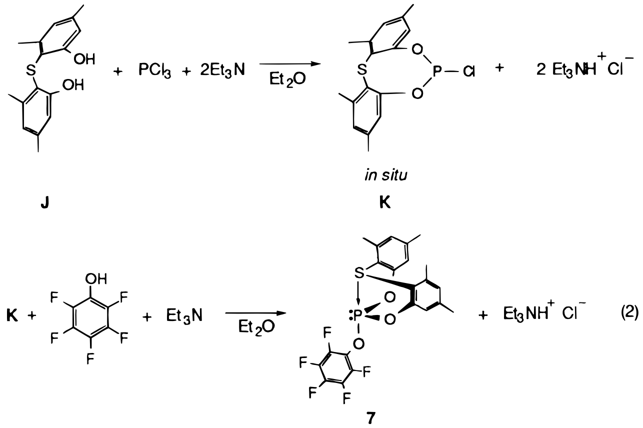
Table 1. Crystallographic Data for Compounds **1**−**8**

	1	**2**	**3**	**4**	**5**	**6B**	**7**	**8**
formula	$C_{22}H_{28}Cl_3O_4PS$	$C_{43}H_{40}F_9O_7PS$	$C_{28}H_{40}Cl_3O_4PS$	$C_{28}H_{40}ClO_5PS$	$C_{29}H_{32}F_3O_6PS$	$C_{28}H_{28}F_5O_6PS\cdot{}^1/_2C_7H_8$	$C_{22}H_{16}F_5O_3PS$	$C_{16}H_{16}ClO_3PS$
fw	525.8	902.8	610.0	555.1	596.6	664.6	486.4	354.8
cryst syst	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$C2/c$	$P2_1/c$	$Pna2_1$
cryst size, mm^3	0.75 × 0.75 × 0.75	0.35 × 0.15 × 0.07	0.35 × 0.20 × 0.10	0.75 × 0.50 × 0.08	0.90 × 0.40 × 0.35	0.75 × 0.20 × 0.10	1.00 × 0.30 × 0.20	1.00 × 0.50 × 0.20
a (Å)	9.473(4)	9.635(4)	14.508(8)	10.881(2)	9.305(3)	21.033(6)	12.709(6)	8.154(3)
b (Å)	16.160(6)	13.754(2)	16.188(11)	18.059(4)	30.950(9)	19.083(4)	16.770(8)	12.133(3)
c (Å)	16.143(6)	16.946(4)	16.595(12)	15.508(4)	10.427(4)	15.645(4)	10.161(4)	16.881(4)
α (deg)	90	98.19(2)	109.60(6)	90	90	90	90	90
β (deg)	94.49(3)	103.17(3)	99.38(5)	90.55(2)	94.56(3)	91.68(2)	91.57(4)	90
γ (Å^3)	90	99.49(2)	114.70(5)	90	90	90	90	90
V (Å^3)	2464(2)	2118(1)	3119(4)	3047(1)	2993(2)	6277(3)	2165(2)	1670.1(8)
Z	4	2	4	4	4	8	4	4
D_{calc} (g/cm^3)	1.418	1.415	1.299	1.210	1.324	1.407	1.492	1.411
$\mu_{MoK\alpha}$ (cm^{-1})	5.48	2.03	4.43	2.80	2.20	2.26	2.88	4.58
total reflns	4324	5183	3640	3469	3652	3828	2634	1527
reflns with $I > 2\sigma_I$	2994	3376	2423	2314	2519	1787	1301	1240
R[a]	0.0819	0.0615	0.0529	0.0780	0.0677	0.0652	0.0964	0.0333
R_w[b]	0.1929	0.1680	0.1250	0.1984	0.1952	0.1295	0.2324	0.0869

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



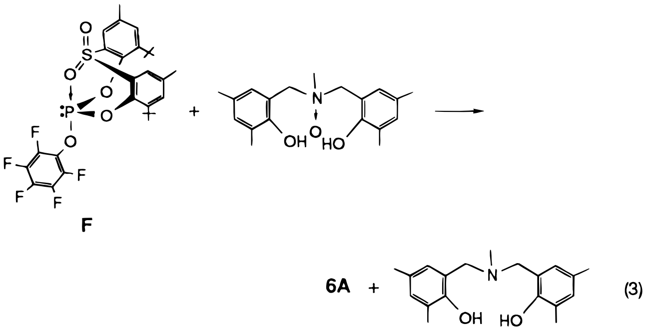


to the formation of the cyclic phosphates **4** and **5** from **3** and **2**, respectively.

The ready hydrolysis of the compounds **2** and **3**, giving the phosphates **5** and **4**, respectively, most likely is associated with the high electrophilicity of phosphorus induced by electronegative ligands in its hexacoordinated state. A previous reactivity study[18] supports this assertion where sulfone donors coordinated to pentaoxyphosphoranes reacted much faster than related sulfone-containing pentaoxyphosphoranes showing no phosphorus−oxygen coordination. Phosphate **6A** was prepared independently by reacting the parent phosphite **F** with the newly synthesized molecule methylamino-*N*,*N*-bis(2-methylene-4,6-dimethylphenol) *N*-oxide,[12] eq 3. In addition, three other phosphates formed which were not identified.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

P−O(1)	1.674(3)	P−Cl(2)	2.119(2)
P−O(2)	1.685(3)	P−Cl(3)	2.133(2)
P−O(3)	1.878(4)	S−O(3)	1.519(3)
P−Cl(1)	2.089(2)	S−O(4)	1.412(4)
O(1)−P−O(2)	90.2(2)	O(3)−P−Cl(2)	84.08(12)
O(1)−P−O(3)	88.4(2)	O(3)−P−Cl(3)	85.62(12)
O(1)−P−Cl(1)	92.36(13)	Cl(1)−P−Cl(2)	91.71(8)
O(1)−P−Cl(2)	88.16(12)	Cl(1)−P−Cl(3)	93.46(7)
O(1)−P−Cl(3)	173.9(2)	Cl(2)−P−Cl(3)	89.78(7)
O(2)−P−O(3)	93.2(2)	O(3)−S−O(4)	114.7(2)
O(2)−P−Cl(1)	90.99(13)	C(1)−O(1)−P	127.6(3)
O(2)−P−Cl(2)	176.88(14)	C(12)−O(2)−P	130.4(3)
O(2)−P−Cl(3)	91.63(12)	S−O(3)−P	118.7(2)
O(3)−P−Cl(1)	175.69(12)		



Due to the difficulty in working with these highly reactive compounds, all having enhanced electrophilicity at phosphorus attributed to the presence of strongly electronegative ligands, elemental analysis for **3**−**5** was not obtained. However, X-ray analyses of all new phosphorus products, **1**−**8**, were performed.

Basic Structures and Structural Displacement. The sulfuryl-containing rings in the phosphorane compounds, **1**−**3**, provide oxygen donor action leading to hexacoordination at phosphorus, Chart 1. Use of a previous method[19] to describe structural displacement from a square pyramid, as viewed in

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[18] Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 459.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

P−O(1)	1.659(3)	P−O(5)	1.640(3)
P−O(2)	1.646(3)	P−O(6)	2.549(4)
P−O(3)	1.599(3)	S−O(7)	1.429(4)
P−O(4)	1.617(4)	S−O(6)	1.441(4)
O(1)−P−O(2)	88.0(2)	O(3)−P−O(6)	177.4(2)
O(1)−P−O(3)	91.4(2)	O(4)−P−O(5)	89.4(2)
O(1)−P−O(4)	88.9(2)	O(4)−P−O(6)	79.2(2)
O(1)−P−O(5)	168.9(2)	O(5)−P−O(6)	82.2(2)
O(1)−P−O(6)	86.63(14)	O(6)−S−O(7)	117.9(2)
O(2)−P−O(3)	101.8(2)	C(1)−O(1)−P	129.8(3)
O(2)−P−O(4)	155.6(2)	C(12)−O(2)−P	130.3(3)
O(2)−P−O(5)	89.0(2)	C(13)−O(3)−P	127.7(3)
O(2)−P−O(6)	76.50(14)	C(20)−O(4)−P	139.7(3)
O(3)−P−O(4)	102.5(2)	C(27)−O(5)−P	130.4(3)
O(3)−P−O(5)	99.8(2)	S−O(6)−P	105.4(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**

P(1)−O(1)	1.673(10)	P(1A)−O(1A)	1.681(9)
P(1)−O(2)	1.674(8)	P(1A)−O(2A)	1.694(9)
P(1)−O(3)	1.875(7)	P(1A)−O(3A)	1.882(8)
P(1)−Cl(1)	2.068(4)	P(1A)−Cl(1A)	2.060(5)
P(1)−Cl(2)	2.109(5)	P(1A)−Cl(2A)	2.099(5)
P(1)−Cl(3)	2.104(5)	P(1A)−Cl(3A)	2.116(5)
S(1)−O(3)	1.507(7)	S(1A)−O(3A)	1.509(7)
S(1)−O(4)	1.425(7)	S(1A)−O(4A)	1.421(7)
O(1)−P(1)−O(2)	90.2(4)	O(1A)−P(1A)−O(2A)	88.7(4)
O(1)−P(1)−O(3)	88.9(4)	O(1A)−P(1A)−O(3A)	92.3(4)
O(1)−P(1)−Cl(1)	91.9(3)	O(1A)−P(1A)−Cl(1A)	91.4(3)
O(1)−P(1)−Cl(2)	88.3(3)	O(1A)−P(1A)−Cl(2A)	92.1(3)
O(1)−P(1)−Cl(3)	174.4(3)	O(1A)−P(1A)−Cl(3A)	175.7(3)
O(2)−P(1)−O(3)	93.1(4)	O(2A)−P(1A)−O(3A)	89.0(4)
O(2)−P(1)−Cl(1)	90.3(3)	O(2A)−P(1A)−Cl(1A)	92.7(3)
O(2)−P(1)−Cl(2)	176.8(3)	O(2A)−P(1A)−Cl(2A)	173.0(4)
O(2)−P(1)−Cl(3)	91.4(3)	O(2A)−P(1A)−Cl(3A)	88.5(3)
O(3)−P(1)−Cl(1)	176.5(3)	O(3A)−P(1A)−Cl(1A)	176.0(3)
O(3)−P(1)−Cl(2)	84.0(3)	O(3A)−P(1A)−Cl(2A)	84.1(3)
O(3)−P(1)−Cl(3)	85.6(3)	O(3A)−P(1A)−Cl(3A)	84.4(3)
Cl(1)−P(1)−Cl(2)	92.6(2)	Cl(1A)−P(1A)−Cl(2A)	94.2(2)
Cl(1)−P(1)−Cl(3)	93.5(2)	Cl(1A)−P(1A)−Cl(3A)	92.0(2)
Cl(2)−P(1)−Cl(3)	89.8(2)	Cl(2A)−P(1A)−Cl(3A)	90.3(2)
O(3)−S(1)−O(4)	114.9(4)	O(3A)−S(1A)−O(4A)	114.7(4)
C(1)−O(1)−P(1)	132.7(10)	C(1A)−O(1A)−P(1A)	134.5(8)
C(12)−O(2)−P(1)	132.4(8)	C(12A)−O(2A)−P(1A)	130.9(10)
S(1)−O(3)−P(1)	121.1(4)	S(1A)−O(3A)−P(1A)	120.5(4)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **4**

P−O(1)	1.583(5)	P−Cl	1.953(3)
P−O(2)	1.566(5)	S−O(4)	1.421(5)
P−O(3)	1.507(5)	S−O(5)	1.443(5)
O(1)−P−O(2)	108.1(3)	O(3)−P−Cl	118.9(2)
O(1)−P−O(3)	112.8(3)	O(4)−S−O(5)	119.1(3)
O(1)−P−Cl	100.6(2)	C(1)−O(1)−P	120.2(4)
O(2)−P−O(3)	114.4(3)	C(12)−O(2)−P	125.4(4)
O(2)−P−Cl	100.3(2)		

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **5**

P−O(1)	1.574(4)	P−O(4)	1.439(4)
P−O(2)	1.583(4)	S−O(5)	1.429(4)
P−O(3)	1.564(4)	S−O(6)	1.437(4)
O(1)−P−O(2)	106.6(2)	O(3)−P−O(4)	114.0(2)
O(1)−P−O(3)	102.4(2)	O(5)−S−O(6)	118.9(2)
O(1)−P−O(4)	115.6(2)	C(1)−O(1)−P	123.4(3)
O(2)−P−O(3)	101.5(2)	C(12)−O(2)−P	122.6(3)
O(2)−P−O(4)	115.0(2)	C(13)−O(3)−P	129.5(3)

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **6**

P−O(1)	1.580(5)	P−O(4)	1.448(6)
P−O(2)	1.569(5)	S−O(5)	1.424(6)
P−O(3)	1.584(6)	S−O(6)	1.435(6)
O(1)−P−O(2)	108.2(3)	O(3)−P−O(4)	115.4(3)
O(1)−P−O(3)	102.0(3)	O(5)−S−O(6)	119.2(4)
O(1)−P−O(4)	115.7(3)	C(1)−O(1)−P	120.8(5)
O(2)−P−O(2)	98.6(3)	C(12)−O(2)−P	122.7(5)
O(2)−P−O(4)	114.9(3)	C(13)−O(3)−P	128.6(5)

Table 8. Selected Bond Lengths (Å) and Angles (deg) for **7**

P−O(1)	1.634(7)	P−O(3′)	1.523(13)
P−O(2)	1.638(6)	P−S	2.940(4)
P−O(3)	1.802(13)		
O(1)−P−O(2)	97.1(3)	O(3′)−P−S	166.7(5)
O(1)−P−O(3)	101.1(5)	C(6)−S−P	81.8(4)
O(1)−P−O(3′)	90.7(6)	C(7)−S−P	81.4(4)
O(2)−P−O(3)	87.9(5)	C(1)−O(1)−P	125.9(6)
O(2)−P−O(3′)	104.7(6)	C(12)−O(2)−P	125.3(6)
O(1)−P−S	76.2(3)	C(13)−O(3)−P	126.7(13)
O(2)−P−S	75.8(2)	C(13)−O(3′)−P	118.4(13)
O(3)−P−S	162.8(5)		

Table 9. Selected Bond Lengths (Å) and Angles (deg) for **8**

P−O(1)	1.573(4)	P−Cl	1.997(2)
P−O(2)	1.563(3)	P−S	3.243(2)
P−O(3)	1.457(4)		
O(1)−P−O(2)	105.9(2)	O(3)−P−Cl	111.5(2)
O(1)−P−O(3)	116.0(2)	O(3)−P−S	87.9(2)
O(1)−P−Cl	101.9(2)	Cl−P−S	160.60(8)
O(1)−P−S	67.8(2)	C(6)−S−P	74.7(2)
O(2)−P−O(3)	119.7(2)	C(7)−S−P	76.6(2)
O(2)−P−Cl	99.2(2)	C(1)−O(1)−P	123.8(3)
O(2)−P−S	69.63(13)	C(12)−O(2)−P	129.4(3)

the absence of the donor atom, toward an octahedron, shows that **1** and **3** are displaced along this coordinate to the extent of 84% and 82%, respectively, whereas **2** is calculated as 41% octahedral. The degree of displacement correlates with the P−OSO donor distance, which is much shorter for **1** (1.878(4) Å) and **3** (1.879(8) Å average) compared to that for **2** (2.549(4) Å). The donor distances for **1** and **3** are very close to the sum of the covalent radii for phosphorus and oxygen, 1.83 Å.[20] The van der Waals sum is 3.35 Å.[21] The more electronegative chlorine ligands present in **1** and **3** compared to the *m*-trifluoromethyl-substituted phenoxy ligand for **2** account for the stronger coordination tendency by increasing the electrophilicity at phosphorus.

For the sulfuryl-containing cyclic phosphates **4**, **5**, and **6B**, the structures are tetracoordinate and do not exhibit any coordination tendencies. When sulfur is incorporated in place of the sulfonyl group, donor coordination occurs, as is apparent in the cyclic phosphite **7** and the cyclic phosphate **8**. Even though the substituents on the aromatic rings supply less of an inductive effect for **7** and **8** compared to the presence of a preponderance of *tert*-butyl groups so situated for **4**, **5**, and **6B** which should enhance the Lewis basicity of the donor atom, the overriding factor appears to be associated with the greater donor ability of the sulfur atom compared to the oxygen atom of the sulfuryl group. This seems to be the case, for example, if one compares the chlorophosphate **4**, lacking donor coordination, with the chlorophosphate **8**, which shows donor coordination.

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(19) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Inorg. Chem.* **1993**, *32*, 4360. In this method, the displacement of the phosphorus atom from the mean plane of the four basal ligands is calculated. This distance is 0.43 Å for a regular square pyramid for main group elements based on trans basal angles of 150°. See ref 26 and the following: Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(20) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Sutton, L., Ed.; Special Publications 11 and 18; The Chemical Society: London, 1958 and 1965.

(21) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

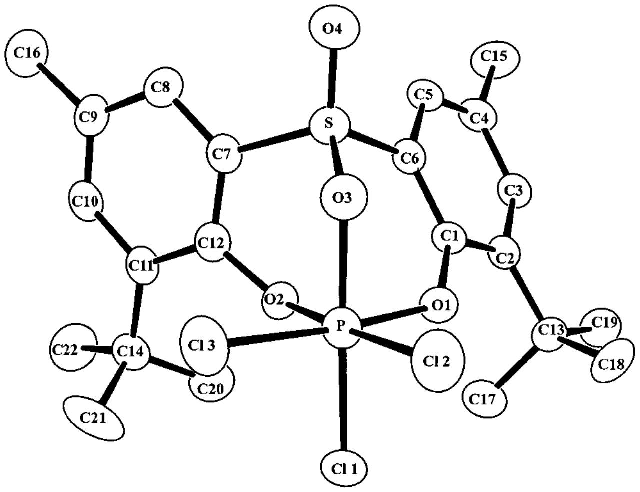


Figure 1. ORTEX diagram of **1**.

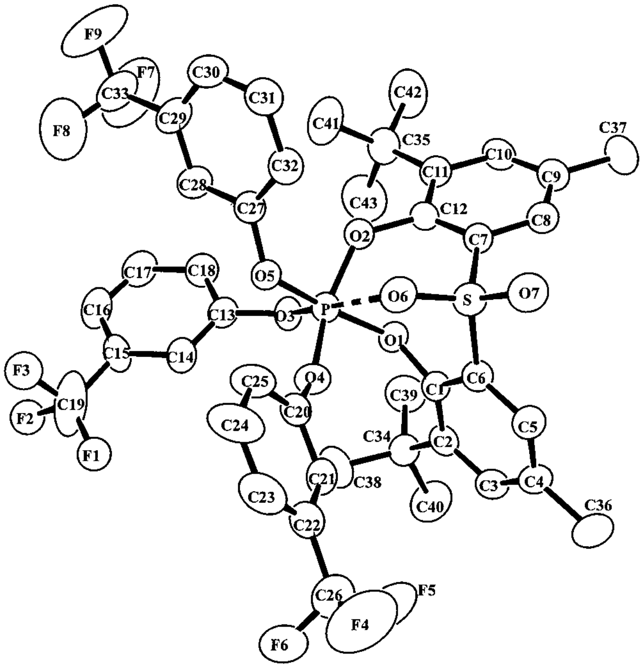
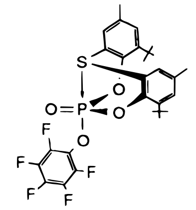


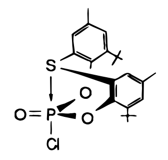
Figure 2. ORTEX diagram of **2**. F1−F3 are disordered, and only one set is shown.

An additional comparison is possible between phosphate **6B** (in Chart 1), which lacks sulfuryl oxygen coordination, and phosphate **L**,[2] which exhibits sulfur coordination. Both of these cyclic phosphates have the same composition, other than the potential donor group, and possess the electronegative pentafluorophenoxy ligand. A comparison is also possible which



P-S = 3.085(2)Å; 37% TBP

L[2]



P-S = 3.114(2)Å; 35% TBP

M[22]

establishes that the electronegativity of the pentafluorophenoxy ligand is very similar to that of the chlorine atom. The cyclic phosphates **L** and **M**[22] have the same composition other than the type of electronegative ligand but differ little in their P−S bond distance or geometrical displacement toward a TBP.

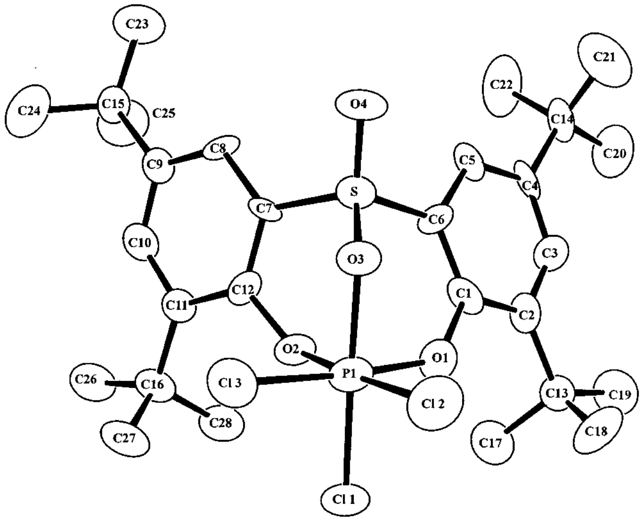


Figure 3. ORTEX diagram of **3**. There is a second independent molecule of **3** which is labeled identically. An ORTEX diagram of it is placed in the Supporting Information. For the latter, the methyl groups on C14A are disordered.

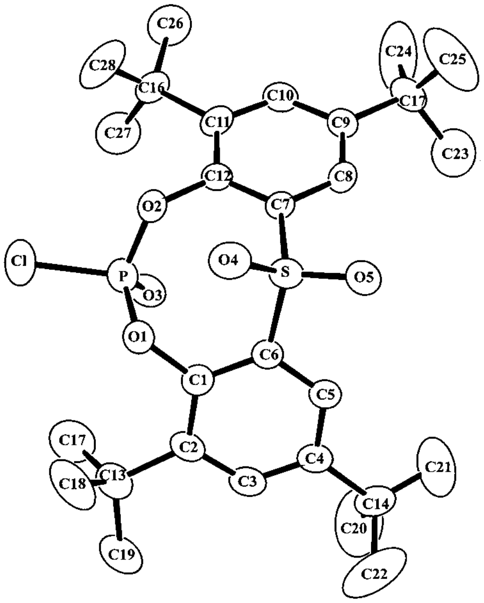


Figure 4. ORTEX diagram of **4**.

The degree of coordination of **7** and **8** can be expressed in terms of a displacement parameter that takes the lower coordinate geometry toward a trigonal bipyramid (TBP). By simply taking the extent to which the phosphorus−donor distance has decreased from the sum of the phosphorus and sulfur van der Waals radii[21] to the covalent sum,[20] a percent TBP can be assigned. For **7**, the geometry is determined to be 46% TBP, which is a considerably greater structural displacement than that for **8**, 27%.

The rationale for the greater donor ability of **7** relative to **8** is based on previous work which shows that phosphites have a tendency to coordinate more strongly than phosphates.[2,4,6,22] For example, the chlorophosphite **N**[22] and the chlorophosphate **M**[22]

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[22] Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1997**, *36*, 5082.

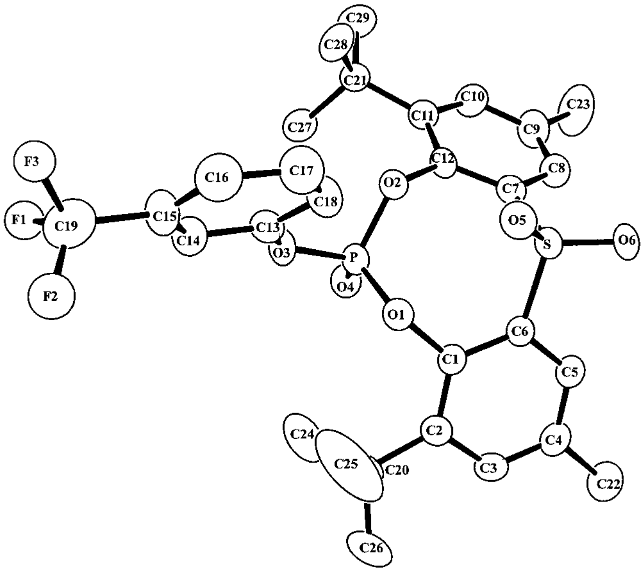


Figure 5. ORTEX diagram of **5**. F1−F3 are disordered, and only one set is shown.

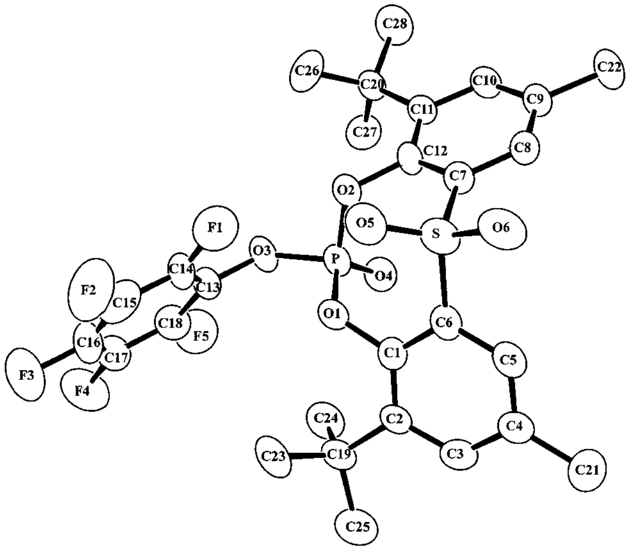
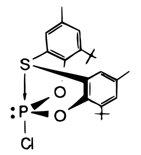


Figure 6. ORTEX diagram of **6B**.

have the same substituents and donor atom but differ appreciably in P−S coordination. As shown by both the P−S distance and the % TBP character, the phosphite **N** coordinates to a greater degree than the phosphate **M**. Hence, in the comparison between **7** and **8**, the mildly differing electronegativities of the chlorine ligand and the pentafluorophenoxy ligand are not the principal structural determinant.



P-S = 2.816(2)Å; 55% TBP

N

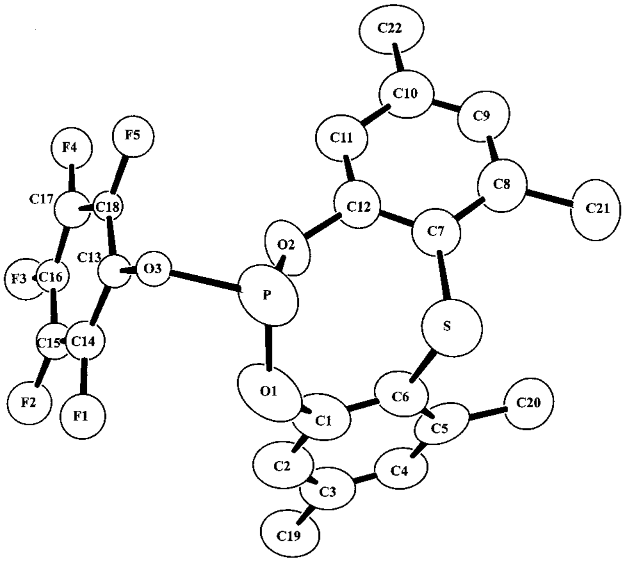


Figure 7. ORTEX diagram of **7**.

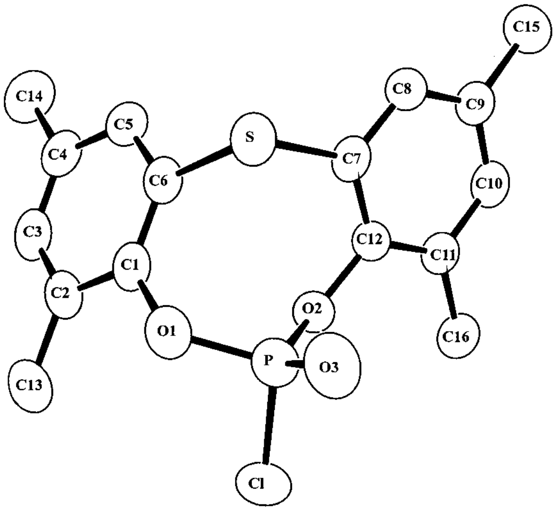


Figure 8. ORTEX diagram of **8**.

Thus, the present work provides the first examples establishing stronger coordination of the sulfur atom vs the oxygen atom of the sulfone group for cyclic phosphates, and this difference is maintained even in the presence of rather electronegative ligands. By contrast, as pointed out in the Introduction, in the presence of OC_6F_5 ligands, the sulfur atom and oxygen atom of the sulfonyl group exercise similar donor abilities for oxyphosphoranes,[2] whereas when ligands of lesser electronegativity are employed, sulfur acts as a stronger donor than oxygen in displacing oxyphosphoranes toward an octahedral geometry.[3,4] In the present work, **1** and **3** (Chart 1) vary only in the substitution of the aromatic ring components and show almost identical P−OSO distances and geometrical displacements toward the octahedron in the presence of chlorine atom ligands. Since the variation in the alkyl groups attached to the aromatic rings offers an inappreciable structural effect and the electronegativities of the chlorine atom and the pentafluorophenoxy ligand are comparable, the fact that **1**, **3**, **A**, and **B** have a nearly identical geometrical displacement toward the octahedron as a result of donor interaction suggests that the sulfur atom and the oxygen atom of the sulfone group exert equal coordination abilities in the presence of strongly electronegative ligands.

The evidence supplied here that cyclic phosphates do not show this same equality in donor action is most likely associated with the presence of a lower number of ligands attached to phosphorus compared to the number present in phosphoranes. It has been amply demonstrated that pentaoxyphosphoranes coordinate with donor atoms much more strongly than phosphates or phosphites.[2−4] This is apparent here by noting the much shorter donor phosphorus distances for **1**, **3**, and **B** compared to **F** for oxygen coordination or **A** compared to **7**, **8**, and **E** for sulfur coordination. With the pentaoxyphosphoranes containing strongly electronegative ligands, it is suggested that the electrophilicity at phosphorus reaches a limit such that reasonable donor groups experience a leveling effect in displaying their coordination abilities.

Solution Structures and Ring Conformations. ^{31}P NMR chemical shifts (Chart 1) are representative values for each of the coordination geometries.[23,24] Increasingly negative values from about 125 ppm to −147 ppm occur as the coordination number increases from phosphite to phosphate to pentaoxyphosphorane. This implies, as is normally the case for phosphorus compounds,[25,26] that the structures are retained in solution.[27] For all of the structures reported here and for the comparisons that have been made, the ring conformation is boatlike when donor interaction is present (a syn conformation) and chairlike in the absence of donor interaction (an anti conformation).[4] These ring conformations are not obvious from the ORTEX plots in Figures 1−8. However, in a different orientation, as shown in Figure 9, the boat form for the hexacoordinate geometry **1**, showing strong donor action (top), is contrasted with that for the hexacoordinate geometry **2**, which has a longer P−OSO coordinate distance and hence lesser donor interaction (middle). In the lower portion of Figure 9 is the skeletal display of the chairlike ring conformation of the chlorophosphate **4**, which lacks any P−OSO donor interaction. Here, the P−O4 distance is 3.470(5) Å, which is greater than the van der Waals sum of 3.35 Å.

Conclusion

Cyclic phosphates and cyclic phosphites exhibit stronger coordination with the sulfur atom situated as part of a flexible ring system compared to the oxygen atom of a sulfone gorup which is located as well in a similar flexible ring system. This comparative donor action is independent of the electronegativity of the ligands. Cyclic pentaoxyphosphoranes exhibit a similar dependence in coordinating more strongly with sulfur compared to that with the oxygen atom of the sulfone group located in the same type of ring system except when the ligand attachments are strongly electronegative. When that is the case, a leveling effect occurs and the two donors provide similar coordination tendencies. The effect causing this leveling is attributed to a saturation in enhancing the electrophilicity at phosphorus that is not experienced by phosphates and phosphites having fewer ligand attachments.

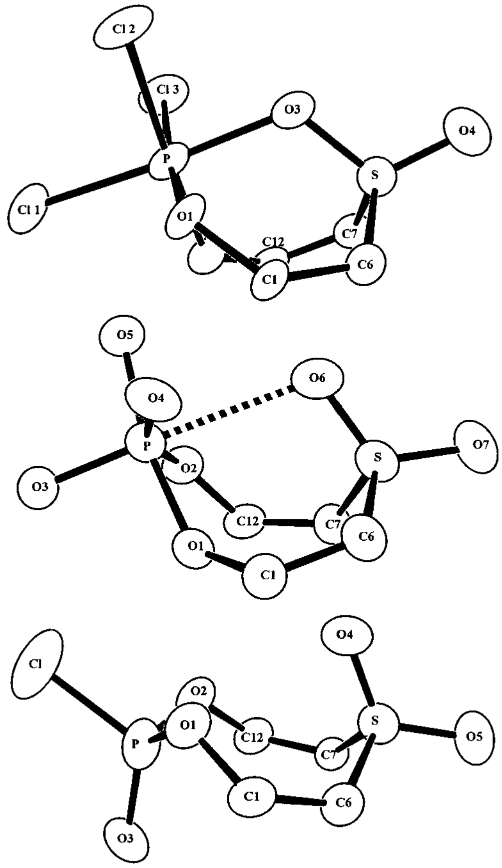


Figure 9. ORTEX displays of the boatlike ring conformations of **1** (top) and **2** (middle) contrasted with that for **4** (bottom), which has a chairlike ring form.

The present study emphasizes the potential importance of the likelihood of donor action from nearby amino acid residues at active sites of phosphoryl transfer enzymes where pentacoordinate phosphorus activated states or intermediates are invoked in mechanistic considerations.[4] In these activated states, the high ligand eletronegativity supplied by phosphate precursors makes such a proposal attractive. Additional coordination which is stronger in the pentacoordinate activated state relative to the phosphate substrate should act as a rate enhancement effect.

Acknowledgment. The support of this research by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1**−**8** and an ORTEX diagram of the second molecule of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9901214

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