Structural Displacement of Phosphites, Phosphates, and Pentaoxyphosphoranes to Higher Coordinate Geometries by Sulfur and Oxygen Donor Action[1]

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New phosphites, $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OC_6F_5)$ (**1**), $S[Me_2C_6H_2O]_2P(OC_6F_5)$ (**3**), and $H_2C[(t\text{-Bu})_2C_6H_2O]_2P(OC_6F_5)$ (**6**), a phosphate, $S[(t\text{-Bu})MeC_6H_2O]_2P(O)(OC_6F_5)$ (**4**), and pentaoxyphosphoranes $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OC_6F_5)(O_2C_6Cl_4)$ (**2**) and $S[Me_2C_6H_2O]_2P(OC_6F_5)_3$ (**5**), all containing pentafluorophenoxy ligands, have been prepared and characterized by NMR and X-ray studies. Starting with either PCl_3 for the phosphites or $POCl_3$ for the phosphate, reactions with diols formed cyclic chlorophosphites or a chlorophosphate, respectively, in situ, followed by condensation with pentafluorophenol to give the products. An oxidative addition reaction of **1** with a quinone produced **2** while **5** was prepared from $P(OC_6F_5)_3$ formed in situ, followed by oxidative addition with a diol. Other than **6**, all contained sulfonyl (**1** and **2**) or sulfur (**3**−**5**) donor groups which coordinated with phosphorus to give pseudo trigonal bipyramidal (**1** and **3**), trigonal bipyramidal (**4**), and octahedral (**2** and **5**) geometries. In the presence of OC_6F_5 ligands, the sulfur atom and oxygen atom of the sulfonyl group exercise similar donor abilities for oxyphosphoranes, which contrasts with previous studies where ligands of lesser electronegativity were employed that showed sulfur to supply stronger donor interaction in displacing oxyphosphoranes toward an octahedral geometry. This leveling effect is attributed to the enhancement of the electrophilicity at phosphorus in the presence of pentafluorophenoxy ligands. In support of earlier work, it is now quantitatively well defined that donor action causes an increase in coordination geometry at phosphorus where the strength of such action increases in the order phosphates < phosphites < oxyphosphoranes.

Introduction

Recent studies have shown that donor action by sulfur,[2−13] oxygen,[12,14−16] and nitrogen[1b] atoms incorporated into flexible ring systems may serve to increase the coordination geometry at phosphorus in the tri-,[2,13,16] tetra-,[2] and pentacoordinated[1b,3−15] states. This effect strongly depends on the electrophilicity at phosphorus provided by its substitutent makeup.[17] For compounds of biological interest, phosphites,[2,13] phosphates,[2] and pentaoxyphosphoranes[1b,3−15] comprise model classes which have met this criterion and have been demonstrated to undergo such coordination changes. The phosphites and phosphates increase their coordination to pseudo trigonal bipyramidal and trigonal bipyramidal (TBP), respectively, while pentaoxyphosphoranes approach octahedral geometry as a result of donor action. Some examples in Chart 1 are **A**−**E**[1b,2,5,13,14] involving sulfur, oxygen, and nitrogen as donor atoms. All of these have the same aromatic ring substituents but vary in the other groups while **C** and **D** differ only in the type of donor ligand. Listed below each formulation are the phosphorus−donor atom distance and the percent displacement toward the geometry associated with its increased coordination. The phosphine **F**[16] is included which shows carbonyl oxygen coordination in the presence of the less electronegative phenyl group.

In all of these compounds, five- or six-membered rings are formed. However, due to the ring flexibility, other structural arrangements are possible, which allows for the absence of donor coordination if factors are unfavorable for its formation. This occurs in **G**−**J**,[1b,14,15,18] for example. That these all lack donor coordination is demonstrated by the phosphorus−donor atom distances, which are all very close to the sum of the van der Waals radii.[19]

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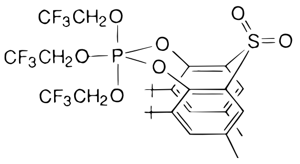
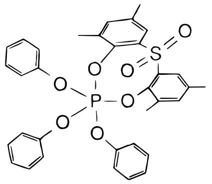
10.1021/ic9804418 CCC: $15.00



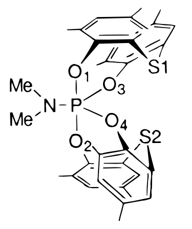
P–OSO = 3.345(4)Å

G [14]



P–OSO = 3.233(5)Å

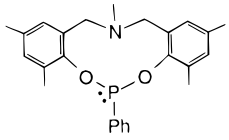
H [15]



P–S$_1$ = 3.652(3)Å

P–S$_2$ = 3.485(4)Å

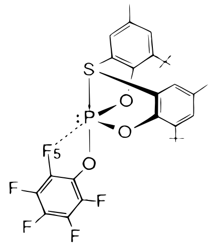
I [18]



P–N = 3.152(3)Å

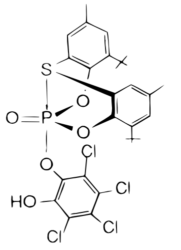
J [1b]

Chart 1



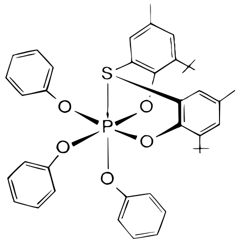
P–S = 2.876(2)Å; 50.6% TBP

A [13]



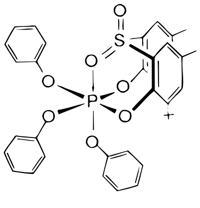
P–S = 3.177(2)Å; 30.9% TBP

B [2]



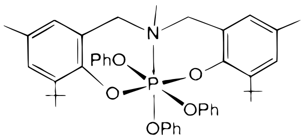
P–S = 2.744(2)Å; 56.6% octa

C [5]



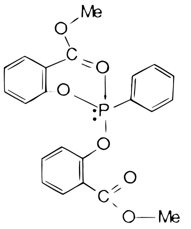
P–OSO = 2.487(3)Å; 44.5% octa

D [14]



P–N = 2.143(3)Å; 73.4% octa

E [1b]



P–O = 2.788(6)Å; 37% TBP

F [16]

Whether or not donor action occurs depends to some extent on the coordination tendency of a particular donor ligand. Indications are that the sulfur atom is a stronger coordinating agent than the sulfonyl oxygen atom;[15,17] e.g., the structure of **C** is displaced further toward the octahedron than **D** (Chart 1). Other comparisons have been made supporting this conclusion.[15] In addition, it has been observed, in a more limited way, that coordination ability increases from phosphates to phosphites to pentaoxyphosphoranes.[13,17]

In the present study, we focus on a series of oxygen ligated phosphorus compounds varying in coordination number from 3 to 5. To quantitatively determine factors responsible for donor interactions, particularly the influence of coordination number on donor strength, the pentafluorophenoxy ligand is utilized as a constant component in all formulations as well as incorporating the same type of eight-membered ring system in each derivative. The work was designed to expand our knowledge of the less studied ability of phosphites and phosphates to undergo donor interaction and to assess the comparative influence of sulfur vs oxygen in their competitive effects in increasing coordination geometry in these states. This resulted in the synthesis and X-ray and NMR studies of **1**−**5**. Phosphite **6**, which does not contain a ring donor atom, was included in the study for comparison of ring conformations with and without donor interactions. The formulations are depicted in Chart 2.

Experimental Section

Phosphorus trichloride, pentafluorophenol, 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.[20] 2,2′-Thiobis(4,6-dimethylphenol),[21] 2,2′-thiobis(4-methyl-6-*tert*-butylphenol),[5] 2,2′-sulfurylbis(4-methyl-6-*tert*-butylphenol),[22] 2,2′-methylenebis(4,6-di-*tert*-butylphenol),[23] and *N*-chlorodiisopropylamine[24] were prepared by literature methods. All reactions were carried out in a dry nitrogen atmosphere using standard Schlenk-type glassware.[25] 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. Proton spectra were recorded in $CDCl_3$ except where otherwise noted. Phosphorus-31 NMR spectra 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 ∼23 °C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. (a) [2,2′-Sulfurylbis(4-methyl-6-*tert*-butylphenyleneoxy)-*O,O*′](pentafluorophenoxy)phosphite, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OC_6F_5)$ (1). A solution of 2,2′-sulfurylbis(4-methyl-6-*tert*-butylphenol) (8.94 g, 22.9 mmol) and phosphorus trichloride (2.00 mL, 22.9 mmol) in diethyl ether (350 mL) was cooled to 0 °C. Triethylamine (6.37 mL, 45.8 mmol) in diethyl ether (50 mL) was added dropwise to the cold mixture which was stirred for 36 h. The system was then filtered, leaving a yellow solution. Pentafluorophenol (4.22 g, 22.9 mmol) and triethylamine (3.19 mL, 25.2 mmol) in diethyl ether (50 mL) were added

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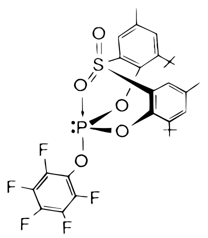
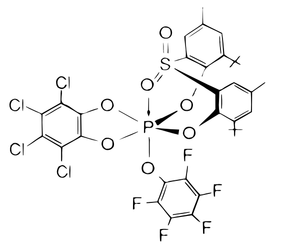
Chart 2



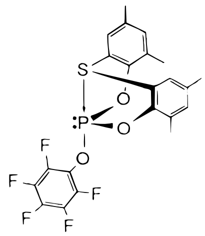
P–OSO = 2.652(5)Å; 46% TBP
^{31}P, 132.0

1



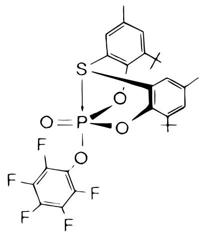
P–OSO = 2.314(5)Å; 68% TBP
^{31}P, -67.0

2



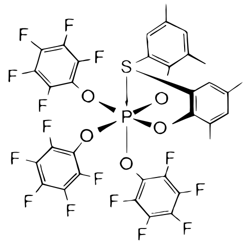
P–S = 2.828(2)Å; 54% TBP
^{31}P, 136.8

3



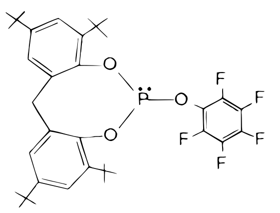
P–S = 3.085(2)Å; 37% TBP
^{31}P, -24.0

4



P-S = 2.389(5); 82% octa
^{31}P, -93.0

5



P–C7 = 3.350(6)Å
^{31}P, 130.7

6

dropwise to the solution with stirring that was continued for 24 h, followed by filtration. The yellow solution was concentrated under a flow of nitrogen, producing a pale yellow solid. This was dissolved in a 1:1 mixture of dichloromethane/Skelly C (80 mL), and the mixture was concentrated under a nitrogen flow to yield the product as large colorless crystals: yield 4.3 g (34%); mp 190 °C. ^{1}H NMR: 1.37 (s, 18 H, C(CH$_3$)$_3$), 2.38 (s, 6 H, CH$_3$), 7.50−7.76 (4 H, Ar). ^{31}P NMR: 132.0 (t, $^4J_{P-F}$ 66 Hz). Anal. Calcd for $C_{28}H_{28}F_5O_5PS$: C, 55.81; H, 4.65. Found: C, 55.35; H, 4.50.

(b) [2,2′-Sulfurylbis(4-methyl-6-*tert*-butyl-*O*-phenyleneoxy)(pentafluorophenoxy)(tetrachloro-1,2-benzenedioxy)phosphorane, O$_2$S-[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(OC$_6$F$_5$)(O$_2$C$_6$Cl$_4$) (2). [2,2′-Sulfurylbis(4-methyl-6-*tert*-butylphenyleneoxy)-*O*,*O*′](pentafluorophenoxy)phosphite (**1**) (1.00 g, 1.66 mmol) and tetrachloro-1,2-benzoquinone (0.41 g, 1.66 mmol) were dissolved in toluene (20 mL), and the solution was heated under reflux for 45 min. The solvent was removed under vacuum and the residue dissolved in dichloromethane (30 mL). Skelly C (30 mL) was added and the solution left under a flow of nitrogen to yield the product as a crop of colorless crystals: yield 0.92 g (65%); mp > 250 °C. ^{1}H NMR: 1.40 (s, 18 H, C(CH$_3$)), 2.37 (s, 6 H, CH$_3$), 7.45−7.79 (m, 4 H, Ar). ^{31}P NMR: −67.04. Anal. Calcd for $C_{34}H_{28}Cl_4F_5O_7PS$: C, 48.12; H, 3.30. Found: C, 48.30; H, 3.39.

(c) [2,2′-Thiobis(4,6-dimethyl-*O*-phenyleneoxy-*O*,*O*′](pentafluorophenoxy)phosphite, S[Me$_2$C$_6$H$_2$O]$_2$P(OC$_6$F$_5$) (3). The procedure for the synthesis of **3** was similar to that for **1**. The compounds (quantities) used were as follows: phosphorus trichloride (1.50 mL, 17.2 mmol) in diethyl ether (300 mL); 2,2′-thiobis(4,6-dimethylphenol) (4.71 g, 17.2 mmol); triethylamine (4.80 mL, 34.4 mmol) in diethyl ether (100 mL); pentafluorophenol (3.16 g, 17.2 mmol); triethylamine (2.40 mL, 17.2 mmol) in diethyl ether (50 mL). Yield: 2.42 g (29%). Mp: 107 °C. ^{31}P NMR: 136.8 (t, $^4J_{P-F}$ 36 Hz). Due to decomposition in solution, the ^{1}H NMR spectrum was not observed. Anal. Calcd for $C_{22}H_{16}F_5O_3PS$: C, 54.32; H, 3.29. Found: C, 54.93; H, 3.40.

(d) [2,2′-Thiobis(4-methyl-6-*tert*-butylphenyleneoxy)-*O*,*O*′](pentafluorophenoxy)phosphine Oxide, S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(O)(OC$_6$F$_5$) (4). To an ice cold solution of phosphorus oxychloride (1.00 mL, 10.7 mmol) in diethyl ether (250 mL) were added 2,2′-thiobis(4-methyl-6-*tert*-butylphenol) (3.84 g, 10.7 mmol) and triethylamine (3.00 mL, 21.6 mmol) dropwise in diethyl ether (50 mL). The system was stirred for 44 h and filtered. Pentafluorophenol (1.97 g, 10.7 mmol) and triethylamine (1.50 mL, 10.7 mmol) in diethyl ether (50 mL) were added dropwise to the filtrate with stirring for a further 24 h. The system was filtered, and the filtrate was left to concentrate under a nitrogen flow. The resultant solid was dissolved in dichloromethane (50 mL), and Skelly-C (50 mL) was added. Concentration yielded the crystalline product: yield 4.27 g (68%); mp 200 °C. ^{1}H NMR: 1.22 (s, 18 H, C(CH$_3$)$_3$), 2.30 (s, 6 H, CH$_3$), 7.17−7.44 (4 H, Ar). ^{31}P NMR: −24.04. Anal. Calcd for $C_{28}H_{28}F_5O_4PS$: C, 57.34; H, 4.78. Found: C, 56.47; H, 5.00.

(e) [2,2′-Thiobis(4,6-dimethylphenoxy)]tris(pentafluorophenoxy)-phosphorane, S[Me$_2$C$_6$H$_2$O]$_2$P(OC$_6$F$_5$)$_3$ (5). Pentafluorophenol (6.33 g, 34.4 mmol) was dissolved in dichloromethane (250 mL), and phosphorus trichloride (1.00 mL, 11.5 mmol) was added. Triethylamine (4.80 mL, 34.4 mmol) was injected via a syringe over the course of 3 min and the solution stirred for 4 h. 2,2′-Thiobis(4,6-dimethylphenol) (3.14 g, 11.5 mmol) was added to the system, and *N*-chlorodiisopropylamine (1.70 mL, 11.5 mmol) was injected with stirring continued for 44 h. The solvent was removed under vacuum, and diethyl ether (200 mL) was added to the residue. The mixture was filtered and the resultant yellow solution concentrated under a stream of nitrogen, producing colorless crystals of the product: yield 1.80 g (18%); mp >250 °C. ^{1}H NMR: 1.98 (s, 6 H, CH$_3$), 2.25 (s, 6 H, CH$_3$), 6.97−7.32 (4 H, Ar). ^{31}P NMR: −93.0. Anal. Calcd for $C_{34}H_{16}F_{15}O_5PS$: C, 47.89; H, 1.88. Found: C, 48.07; H, 1.86.

(f) [2,2′-Methylenebis(4,6-di-*tert*-butyl-*O*-phenyleneoxy-*O*,*O*′]-(pentafluorophenoxy)phosphite, H$_2$C[(*t*-Bu)$_2$C$_6$H$_2$O]$_2$P(OC$_6$F$_5$) (6). The procedure for the synthesis of **6** was similar to that for **1**. The compounds (quantities) used were as follows: 2,2′-methylenebis(4,6-di-*tert*-butylphenol) (7.29 g, 17.2 mmol); phosphorus trichloride (1.50 mL, 17.2 mmol) in diethyl ether (450 mL); triethylamine (4.80 mL, 34.4 mmol) in diethyl ether (40 mL); pentafluorophenol (3.16 g, 17.2 mmol); triethylamine (2.50 mL, 18.0 mmol) in diethyl ether (30 mL). Yield: 6.7 g (61%). Mp: 134 °C. ^{1}H NMR: 1.39 (s, 18 H, C(CH$_3$)$_3$), 1.41 (s, 18 H, C(CH$_3$)$_3$), 4.35−4.44 (dd, 2 H, CH$_2$), 7.27−7.32 (m, 4 H, Ar). ^{31}P NMR: 130.7. Anal. Calcd for $C_{35}H_{42}F_5O_3P$: C, 66.03; H, 6.60. Found: C, 66.52; H, 6.70.

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.[26]

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 $3° \leq 2\theta_{\mathrm{Mo}\ K\bar{\alpha}} \leq 43°$ 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 procedures. Refinements were based on F^2, and computations were performed on a 486/66 computer using SHELXS-86 for solution[27] and SHELXL-93 for refinement.[28] 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

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Table 1. Crystallographic Data for Compounds **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{28}H_{28}F_5O_5PS$	$C_{34}H_{28}Cl_4F_5O_7PS\cdot{}^1/_2CH_2Cl_2$	$C_{22}H_{16}F_5O_3PS$	$C_{28}H_{28}F_5O_4PS$	$C_{34}H_{16}F_{15}O_5PS$	$C_{35}H_{42}F_5O_3P$
fw	602.5	890.9	486.4	586.5	852.5	636.7
cryst syst	triclinic	triclinic	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	*Pbca*	$P2_1/n$
cryst size (mm)	0.90 × 0.35 × 0.35	0.50 × 0.50 × 0.40	1.00 × 0.10 × 0.10	1.00 × 0.40 × 0.25	1.00 × 0.60 × 0.40	0.75 × 0.55 × 0.35
a (Å)	10.547(2)	12.513(5)	4.601(1)	10.561(1)	15.568(4)	17.380(3)
b (Å)	12.419(8)	13.223(2)	19.156(3)	12.057(3)	17.524(10)	9.626(3)
c (Å)	12.905(4)	13.772(5)	23.655(5)	12.816(2)	25.650(12)	20.389(3)
α (deg)	61.79(4)	84.82(2)	90	110.08(2)	90	90
β (deg)	76.76(2)	83.51(3)	94.13(2)	98.70(1)	90	90.73(1)
γ (deg)	75.40(4)	67.82(2)	90	107.78(2)	90	90
V (Å^3)	1429(1)	2094(1)	2079.5(7)	1398.3(4)	6998(6)	3411(1)
Z	2	2	4	2	8	4
D_{calc} (g/cm^3)	1.400	1.413	1.554	1.393	1.618	1.240
$\mu_{Mo\ K\alpha}$ (cm^{-1})	2.38	5.00	3.00	2.39	2.60	1.40
no. of tot. reflns	3266	4767	2380	3198	4011	3897
no. of reflns with $I > 2\sigma_I$	2564	3378	1500	2609	2017	2366
R^a	0.0823	0.0684	0.0385	0.0455	0.1010	0.0699
$R_w{}^b$	0.2382	0.1978	0.0803	0.1147	0.2571	0.1725

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

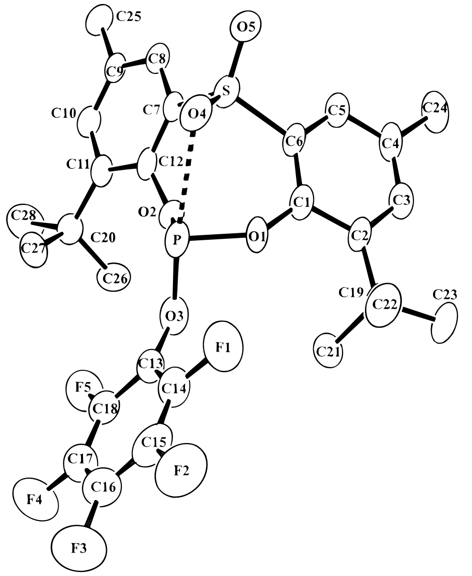

Figure 1. ORTEX diagram of $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OC_6F_5)$ (**1**).

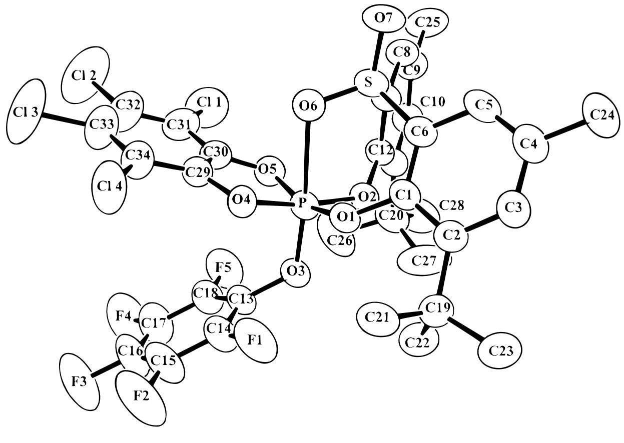

Figure 2. ORTEX diagram of $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OC_6F_5)(O_2C_6Cl_4)$ (**2**).

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 crystals of **2**, one-half of a molecule of a loosely bound dichloromethane molecule was located which was refined isotropically. The hydrogens on the methylene carbon were fixed at the calculated positions. In compound **6**, one of the *tert*-butyl methyl groups was disordered. These carbons were refined isotropically in two positions with equal occupancy (shown in Figure 6 with primed labels) and their hydrogens were not fixed.

Results and Discussion

The atom-labeling schemes for **1**−**6** are given in the ORTEX[29] plots of Figures 1−6, respectively. The thermal ellipsoids are shown at the 40% probability level, and all hydrogen atoms are omitted for clarity. Selected bond parameters are given in Tables 2 and 3.

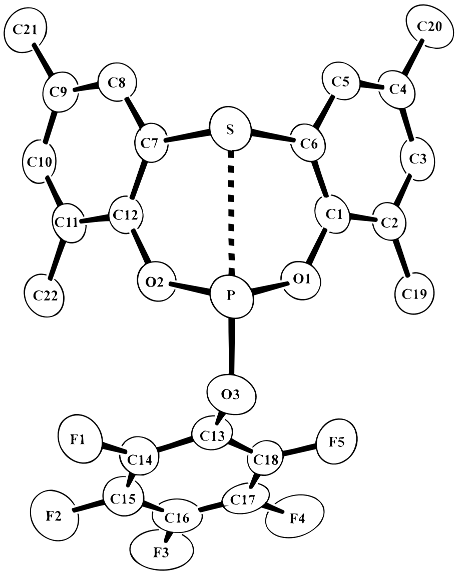

Figure 3. ORTEX diagram of $S[Me_2C_6H_2O]_2P(OC_6F_5)$ (**3**).

Syntheses. The cyclic phosphites **1**, **3**, and **6** were prepared by a common method which involved reaction of a diol with PCl_3 in diethyl ether solution in the presence of Et_3N to first form the cyclic chlorophosphite in situ followed by condensation with pentafluorophenol. The same procedure was used in the formation of the cyclic phosphate **4** except that $POCl_3$ was used

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(29) McArdle, P. *ORTEX 5e*; Crystallography Centre, Chemistry Department, University College Galway: Galway, Ireland, 1996.

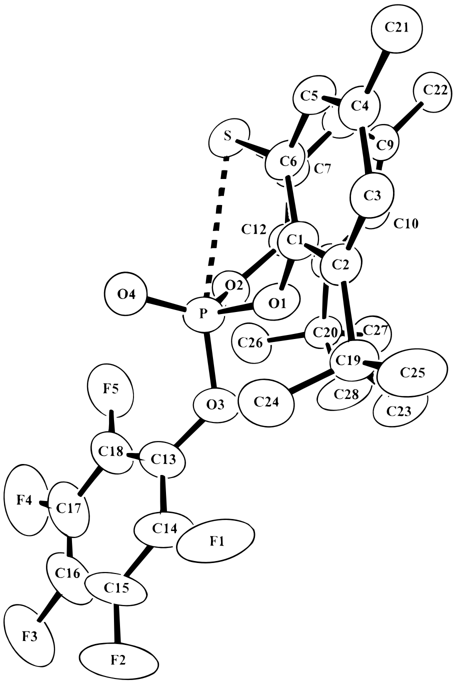


Figure 4. ORTEX diagram of S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(O)(OC$_6$F$_5$) (**4**).

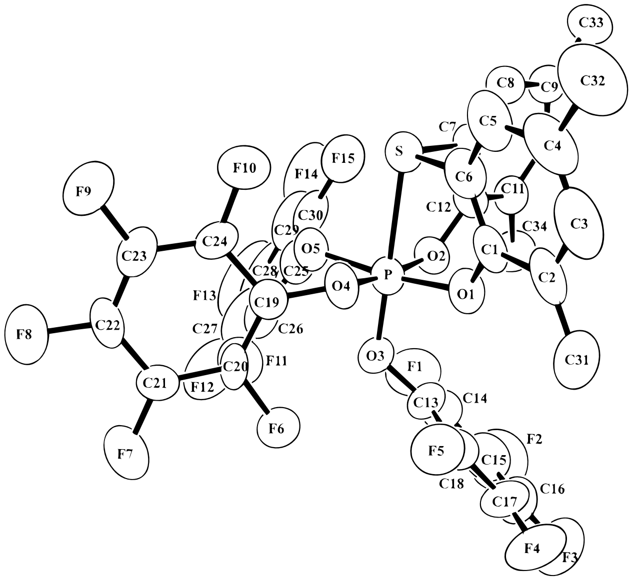


Figure 5. ORTEX diagram of S[Me$_2$C$_6$H$_2$O]$_2$P(OC$_6$F$_5$)$_3$ (**5**).

as the starting reagent instead of PCl$_3$. The reaction is illustrated for the preparation of **4** in eqs 1 and 2.

The cyclic pentaoxyphosphoranes were prepared by different methods. For the bicyclic derivative **2**, an oxidative addition reaction of the phosphite **1** with a quinone led to the product. The formation of the monocyclic derivative **5** was achieved by the condensation reaction of PCl$_3$ with pentafluorophenol in the presence of Et$_3$N in ether solution to give P(OC$_6$F$_5$)$_3$ in situ followed by oxidative addition with a diol in the presence of (*i*-Pr)$_2$NCl. Yields ranged from 18 to 68%.

Basic Structures. The cyclic phosphites **1** and **3** and the cyclic phosphate **4** have structures which are displaced toward trigonal bipyramidal. Each of these have the ring donor atom occupying an axial position and the two ring oxygen atoms occupying equatorial sites. A lone electron pair is assumed to occupy the remaining equatorial site for the phosphites **1** and **3** while the phosphoryl oxygen atom does so for the phosphate **4**. The structures of **2** and **5** are displaced toward an octahedron as a result of donor coordination.

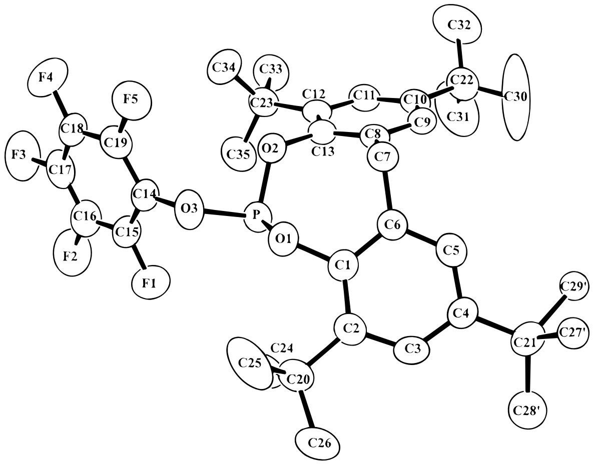
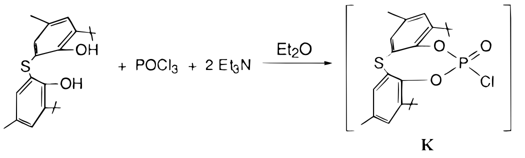
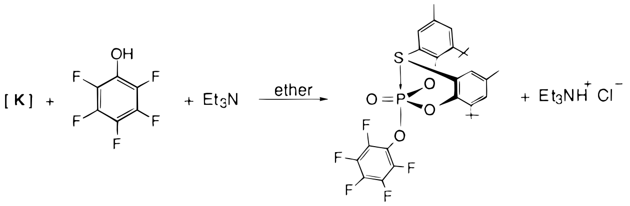


Figure 6. H$_2$C[(*t*-Bu)$_2$C$_6$H$_2$O]$_2$P(OC$_6$F$_5$) (**6**).



(1)



(2)

Solution Structure and Ring Conformations. The ^{31}P chemical shifts in toluene solution that are summarized in Chart 2 are representative values for each of the coordination geometries.[30,31] Increasingly negative values from about +130 to −93 ppm occur as the coordination number increases from phosphite to phosphate to pentaoxyphosphorane. This implies, as is normally the case for phosphorus compounds,[32,33] that the structures are retained in solution.[34] Phosphite **6**, which has no donor coordination tendencies, exhibits a ^{31}P shift comparable to **1**, which exhibits oxygen atom donor coordination from the sulfonyl group. Thus, although donor coordination, which is relatively weak in the lower coordinated states compared to that in oxyphosphoranes,[2] does not appreciably affect ^{31}P chemical shifts,[35] ring conformational changes take place as a result of an increase in coordination geometry. All of the compounds **1**−**5** have ring conformations in syn-boat forms, whereas for **6**, the ring exists in an anti-chair conformation. This results in

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(30) Holmes, R. R.; Prakasha, T. K. *Phosphorus, Sulfur Silicon* **1993**, *80*, 1−22.

(31) Quin, L. D., Verkade, J. G., Eds. *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; VCH Publishers: New York, 1994; see also references therein.

(32) Dennis, L. W.; Bartuska, V. J.; Maciel, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 230.

(33) Holmes, R. R. *Pentacoordinated Phosphorus*—*Structure and Spectroscopy, Vol. I*; ACS Monograph 175; American Chemical Society: Washington, DC, 1980; see also references therein.

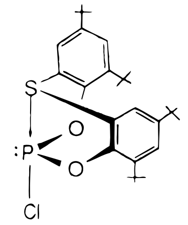
(34) Solid state ^{31}P NMR measurements also confirm the retention of solid-state structure in solution. See ref 3 for comparison between these two states for oxyphosphoranes.

(35) Reference 30, p 179.

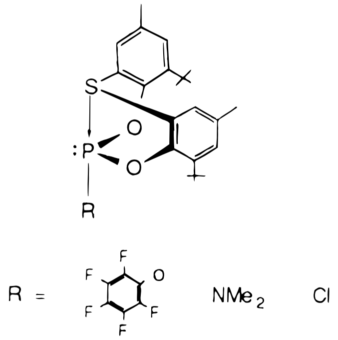
Table 2. Selected Bond Parameters for Cyclic Phosphites and Phosphates Measuring the Degree of Trigonal Bipyramidal Coordination

	bond distances (Å)				bond angles (deg)			
compd[c,d]	P−O1	P−O2	P−R	P−S	O1−P−O2	R$_{ax}$−P−S[a]	% TBP[b]	Σ_{eq} (deg)[a]
B (R = O3)	1.571(3)	1.565(3)	1.586(3)	3.177(2)	104.9(2)	162.9(1)	31	339.5(2)
O (R = Cl)	1.575(3)	1.561(3)	2.002(2)	3.114(2)	105.9(2)	167.7(1)	35	343.6(2)
4 (R = O3)	1.567(3)	1.579(2)	1.601(3)	3.085(2)	105.4(1)	163.7(1)	37	344.6(2)
L (R = Cl)	1.633(3)	1.629(4)	2.303(3)	3.043(2)	100.1(2)	172.2(1)	40	
M (R = NMe$_2$)	1.66(2)	1.63(2)	1.65(3)	2.952(9)	97.7(9)	173.3(9)	47	
A (R = O3)[e]	1.627(2)	1.626(2)	1.684(3)	2.876(2)	100.3(1)	163.5(1)	51	
3 (R = O3)	1.644(3)	1.635(3)	1.670(3)	2.828(2)	99.7(2)	174.9(1)	54	
N (R = Cl)	1.625(3)	1.620(3)	2.119(2)	2.816(2)	101.4(2)	169.2(1)	55	
1 (R = O3)	1.637(4)	1.630(5)	1.668(5)	2.652(5) (P−OSO)	98.9(2)	172.9(2) (R$_{ax}$−P−OSO[a])	46	
6 (R = O3)[f]	1.611(4)	1.625(4)	1.652(5)	3.350(6) (P−CH$_2$)	104.5(2)	123.2(2) (R−P−CH$_2$)		

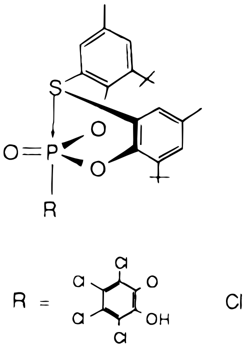
[a] With reference to a trigonal bipyramid with sulfur (or O4 for **1**) in an axial position and both ring oxygen atoms in equatorial positions. [b] Percent geometrical displacement from a pyramid (**1**, **A**, **3**, and **L**−**N**) or a tetrahedron (**B**, **O**, and **4**) toward a TBP. [c] Compound labels refer to the following:



L[2]



A[13] **M**[2] **N**[2]



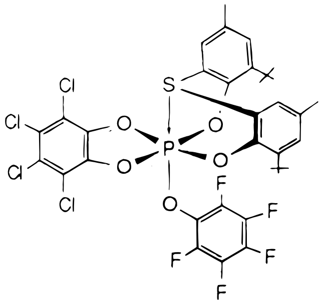
B[2] **O**[2]

[d] References are listed as superscripts below each formula. Data for compounds **1**, **3**, **4**, and **6** are from this work. [e] An additional coordination is present in **A** due to the weak interaction of an ortho fluorine atom with phosphorus. A P−F distance of 3.006(3) Å is obtained. [f] A CH$_2$ group is in place of a donor atom for **6**. Thus, coordination is precluded but is listed here for comparison.

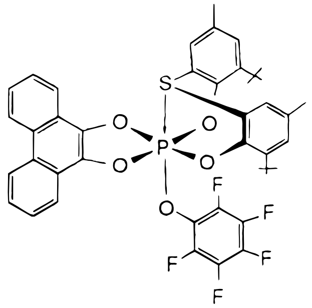
Table 3. Selected Bond Parameters for Cyclic Pentaoxyphosphoranes Measuring the Degree of Octahedral Coordination

	bond distances, Å						bond angles, deg			
compd[a,b]	P−O5	P−O1	P−O4	P−O2	P−O3	P−S	O5−P−O1[c]	O4−P−O2[c]	O3−P−S	% octa[d]
P	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
Q (1)[e]	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
Q (2)[e]	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
5	1.691(10)	1.681(10)	1.678(10)	1.691(10)	1.620(10)	2.389(5)	170.7(5)	171.9(5)	178.6(5)	82
R	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	1.679(5)	1.625(4)	1.688(4)	1.629(4)	1.637(4)	2.314(5) (P−OSO)	160.9(2)	169.6(2)	174.2(2) (O3−P−OSO)	68
S	1.666(7)	1.684(7)	1.688(7)	1.675(7)	1.634(7)	1.936(7) (P−OSO)	172.4(4)	177.1(4)	179.2(3) (O3−P−OSO)	82

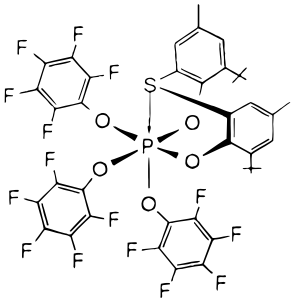
[a] Compound labels refer to the following:



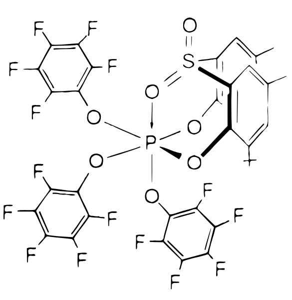
P[13]



Q[13]



R[13]



S[15]

[b] References are listed as superscripts below each formula. Data for compounds **2** and **5** are from this work. [c] Relative to a square pyramid, these are trans angle values. The cis angle values for O1−P−O2 are 92.6(2)° for **P**, 91.5(2) and 91.2(2)° for **Q**, 90.4(5)° for **5**, 91.2(3)° for **R**, and 91.2(2)° for **5**, and for O4−P−O5, they are 89.9(2)° for **P**, 90.7(2) and 90.3(2)° for **Q**, 87.9(5)° for **5**, 88.4(2)° for **R**, and 90.6(2)° for **2**. [d] 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. [e] Compound **Q** has two independent molecules in the unit cell.

a O3−P−C7 angle of 123.2(2)°, which compares with axial angles for **1**, **3**, and **4** that are 172.9(2), 174.9(1), and 163.7(1)°, respectively. There are no other significant structural changes for phosphites and phosphates. The comparison of bond

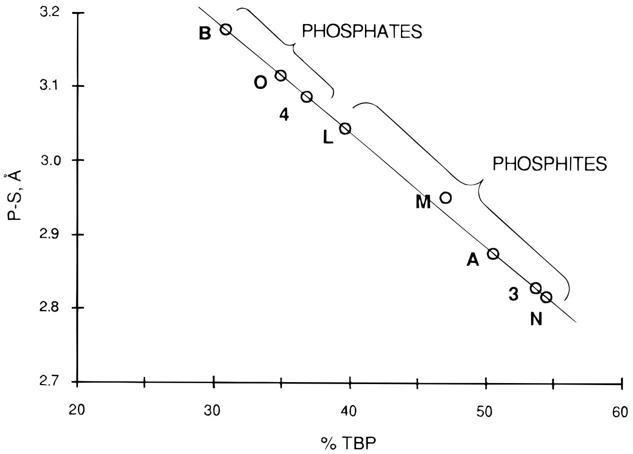


Figure 7. Graphical display of the variation of the P−S distance for phosphates and phosphites listed in Table 2. See ref 37.

parameters for these classes of compounds with that for **6** in Table 2 illustrates this aspect.

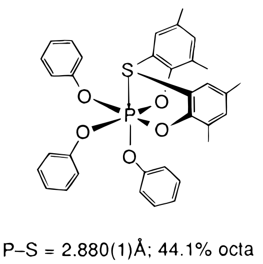
By way of contrast, donor action causes large geometrical changes for oxyphosphoranes which are TBP in the absence of such action. For monocyclic **G** which is TBP and has its ring in an anti-chair conformation, the degree of conformity to a trigonal bipyramid may be expressed by the following angle summations. The average of the three equatorial angles is 120.0(2) ± 2.4°. Their sum is 359.9°, while the axial O−P−O angle is 176.2(2)°. Comparable summations for angles at phosphorus for the monocyclic oxyphosphorane **5** may be made to indicate the geometrical change to hexacoordination induced by sulfur donor action. The average of the eight O−P−O angles is 92.0(5) ± 2.9°. The sum of the four O−P−O angles that lie in a near planar arrangement is 358.8°, while the S−P−O3 angle is 178.6(5)°.

Structural Comparisons. Table 2 lists bond parameters for **1**, **3**, and **4** as well as related cyclic phosphites, **A**, and **L**−**N** and phosphates **B** and **O** for comparison. The extent to which the phosphorus-donor distance is displaced from the sum of the van der Waals radii[19] toward the sum of the covalent radii[36] is used to estimate the percent TBP character. These values are listed in Table 2. It is seen that the phosphates undergo donor action to a lesser degree than the phosphites. The range for the three phosphates extends from 31 to 37% TBP, whereas that for the six phosphites extends from 40 to 55% TBP. Compounds **A** and **4** provide direct comparisons, since the ligand composition is the same except for the presence of the phosphoryl oxygen in **A** in place of the lone electron pair in **4**. The amount of TBP character for phosphate **4** is 37%, and that for phosphite **A** is substantially higher at 51%. Thus, the additional information from the present study strengthens the conclusion reached earlier that the extent of donor interaction increases from phosphates to phosphites.[2] This is portrayed graphically in Figure 7.[37]

A similar effect takes place on going from phosphites to pentaoxyphosphoranes, as demonstrated in Table 3, which lists bond parameters for **2** and **5** and related compounds **P**−**S**. The P−S donor distances are much shorter, spanning the range from 2.37 to 2.49 Å. This compares to the ranges of 2.82−3.04 Å for the phosphites and 3.09−3.18 Å for the phosphates exhibiting P−S distances in Table 2. With the oxygen atom of the sulfonyl group, we can make a comparison between the cyclic phosphite **1** and the cyclic pentaoxyphosphoranes **2** and **S**. The P−O donor distances are 2.652(5) Å for **1**, 2.314(5) Å for **2**, and 1.936(7) Å for **S**, which again shows the heightened donor action for pentaoxyphosphoranes, like that for compounds exhibiting P−S donor interaction.[2,13,17]

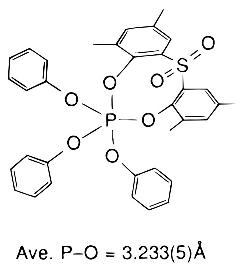
The percent octahedral character listed in Table 3 is derived from a calculation[3,7] of the displacement of the phosphorus atom from the base plane of the four oxygen atoms that would be a part of a square pyramid if we neglect consideration of the presence of the donor group. The P−O bond parameters listed in Table 3 are used for this calculation along with a value of the phosphorus atom displacement for an ideal square pyramid of 0.428 Å.[33,38,39] For all of these phosphoranes containing pentafluorophenoxy groups, the displacement toward the octahedron is quite strong, ranging from 68 to 82%.

The greatest displacement is seen to occur for the monocyclic derivatives **5**, **R**,[13] and **S**,[15] each containing three pentafluorophenoxy groups compared to one for the others. Compounds **5** and **S** have different donor groups but otherwise very similar compositions. They show the same degree of octahedral character, implying that little difference exists between the donor ability of these two ligands, at least when the electrophilicity at phosphorus is increased by the presence of multiple pentafluorophenoxy groups. This behavior differs from earlier studies. As pointed out in the Introduction, indications are that the sulfur atom is a better donor than the sulfonyl oxygen atom in interactions with oxyphosphoranes.[15,17] In these studies, the ligand electronegativity is lower. For example, with sulfur as a donor atom, **T**,[5] with aryl methyl substituents, is hexacoordinate due to sulfur donor action, while the identically composed sulfone-containing phosphorane, **H**,[15] other than insertion of the bridging SO_2 group in place of the sulfur atom, is pentacoordinate lacking any donor coordination. Compare also **C** and **D** in Chart 1 with respect to the degree of coordination in terms of percent displacement toward an octahedron. Consequently, a leveling effect appears to be in operation, as enhancement of the Lewis acidity at the phosphorus atom takes place due to



P−S = 2.880(1)Å; 44.1% octa

T



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

H

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

(37) The linear variation in Figure 7 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, the latter of which are listed in Table 3.

(38) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(39) Holmes, R. R. Five-Coordinated Structures. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley and Sons: New York, 1984; Vol. 32, pp 119−235.

the increased ligand electronegativity offered by the presence of pentafluorophenoxy ligands.

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 and *U*(eq) values, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters and *U*(iso) values for **1**−**6** (27 pages). See any current masthead page for ordering information.

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