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Sulfonyl-Containing Eight-Membered Rings Varying in Ring Conformation in Oxyphosphoranes. Hexacoordination vs Pentacoordination[1]

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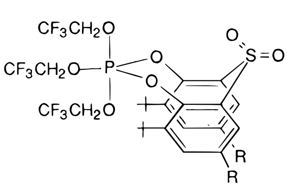
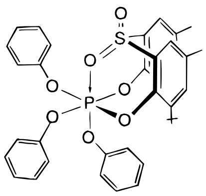
The new cyclic phosphine $O_2S[(t\text{-Bu})MeC_6H_2O]_2PPh$ (**1**) was used to prepare the new cyclic tetraoxyphosphoranes $O_2S[(t\text{-Bu})MeC_6H_2O]_2PPh(O_2C_6Cl_4)$ (**2**) and $O_2S[(t\text{-Bu})MeC_6H_2O]_2PPh(O_2C_6H_4)$ (**3**) by oxidative addition reactions. In similar reactions, the new cyclic pentaoxyphosphoranes $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OCH_2CCl_3)_3$ (**4**), $O_2S[Me_2C_6H_2O]_2P(OPh)_3$ (**5**), and $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OC_6F_5)_3$ (**6**) were formed from acyclic phosphites and the appropriate diol. Yields ranged from 51% to 66%. X-ray studies revealed hexacoordinated representations for **2** and **6** while **3**−**5** are pentacoordinate in trigonal bipyramidal geometries. For **3** and **4**, the eight-membered rings are positioned diequatorially in *anti* chair conformations, whereas for **5**, this ring occupies axial−equatorial sites in a *syn* twist-boat form. Tetraoxyphosphorane **3** is unique in locating the least electronegative ligand, the phenyl group, in an axial position. Oxygen donor action from the sulfone SO_2 group led to a displacement from a square pyramid to an octahedron to the extent of 82.2% for the highly fluorinated member **6** in comparison with 27.9% for the tetrachlorocatecholate derivative **2**. These two pentaoxyphosphoranes provide the longest and shortest P−O distance thus far from a sulfone donor group, 2.646 (5) Å for **2** and 1.936 (7) Å for **6**. In comparison with oxyphosphoranes having bridging sulfur atoms in the eight-membered ring, it is apparent that sulfur atom coordination is greater than oxygen atom coordination from the sulfone group as measured by the tendencies toward hexacoordination. ^{31}P and ^{1}H NMR data indicate the presence of two isomeric forms for each of the phosphoranes **2**−**4**. Structural comparisons are made with related cyclic phosphoranes containing sulfur atoms and sulfone groups relative to steric and electronic factors that influence the formation of hexacoordination.

Introduction

The presence of the sulfonyl group in rings containing oxyphosphoranes has produced two types of geometrical arrangements, a trigonal pyramid (TBP) with the ring in an *anti* (or chairlike) conformation and an octahedron as a result of donor action from one of the sulfonyl oxygen atoms.[2] Here the ring is in a *syn* (or boatlike) conformation. In the former instance, the ring occupies diequatorial positions of the TBP. Examples of these two different structural types are found in **A** and **B**, respectively.[2] When a methylene group is used in place of the sulfonyl group as a ligand bridging the two aryl functions of the cyclic system, another possibility reveals itself. Both **C**[3] and **D**[4] are examples containing this ring conformation where the ring system occupies axial−equatorial positions of a TBP. In these pentaoxyphosphoranes, the ring assumes a twist *syn* or boatlike conformation.

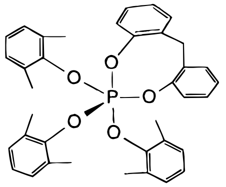


A$_1$ (R = Me)[2]
A$_2$ (R = t-Bu)[2]

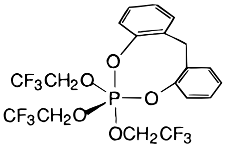


P–OSO = 2.487(3)Å

B[2]



C[3]



D[4]

In studies[4−9] of related cyclic pentaoxyphosphoranes containing potential donor sulfur atoms as bridging groups in place of the sulfonyl group, the same two types of ring conformational orientations as found with use of the sulfonyl group prevail, *i.e.*, the chairlike and boatlike ring conformations giving penta- and hexacoordinated geometries similar to those illustrated for **A** and **B**. Examples with the presence of sulfur atoms are **E**[4] and **F**,[5] representing these two geometrical possibilities, respectively. In addition, we have found one oxyphosphorane, **G**,[10] which has a structure analogous to those

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(1) (a) Pentacoordinated Molecules. 115. (b) Part 114: Sherlock, D.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 1317.

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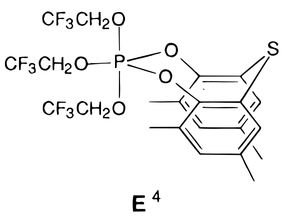
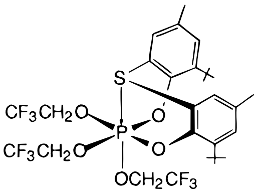


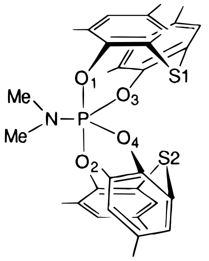
E[4]



P–S = 2.362(2)Å

F[5]

of **C** and **D** where the rings containing the sulfur atoms occupy axial–equatorial sites in a *syn* or boatlike arrangement. However, no P–S interaction exists as the distances are too long.

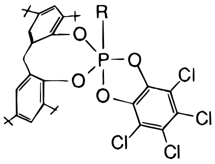


P–S$_1$ = 3.652(3)Å

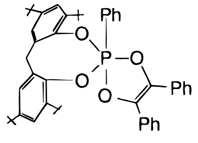
P–S$_2$ = 3.485(4)Å

G[10]

One other feature of interest is that, when an alkyl or aryl group replaces one of the acyclic oxygen containing ligands in ring arrangements having a methylene group as a bridging ligand, as in **C** or **D**, the less electronegative displacing ligand may appear at an axial site of a TBP, *e.g.*, **H**[11,12] and **I**.[12] The latter site is usually reserved for the more electronegative oxygen atoms. The eight-membered rings in these tetraoxy derivatives are in chairlike *anti* conformations.



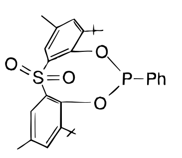
H (R = Ph,[11] Et[12])



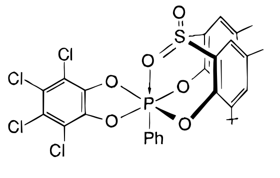
I[12]

To learn the influence of the sulfonyl group in extending the structural and conformational possibilities for tetra- and pentaoxyphosphoranes analogous to **A**–**I**, we report herein the synthesis and X-ray studies of the new oxyphosphoranes **2**–**6**. In addition to the incorporation of the phenyl group in **2** and **3** with the use of the precursor phosphine **1**, the study extends to monocyclic derivatives, **4**–**6**, where the electronic and steric properties of the acyclic ligands are varied.

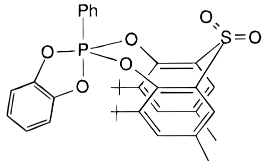
In all of these oxyphosphoranes, the type of eight-membered ring system remains constant. In addition, ^{1}H and ^{31}P NMR spectra are recorded to evaluate solution effects on this closely-related series and to make comparisons with the analogous derivatives **A**–**I** that have sulfur atoms and methylene groups as ring-containing bridging groups.



1



2



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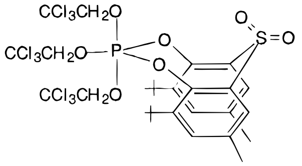

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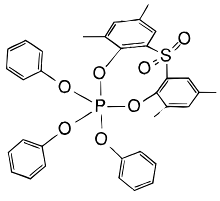

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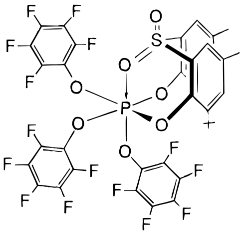

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Experimental Section

Triphenyl phosphite (Eastman), phenyldichlorophosphine (Fluka), tris(2,2,2-trifluoroethoxy) phosphite, phosphorus trichloride and trichloroethanol (Aldrich) were used as supplied. Sulfurylbis[2-(4-methyl-6-*tert*-butylphenol)] (**7**) and sulfuryl bis[2-(4,6-dimethylphenol)] (**8**) were synthesized according to our previous literature method.[13] Solvents were purified according to standard procedures.[14] All the reactions were carried out in a dry nitrogen atmosphere. 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 the spectra were recorded in $CDCl_3$ at 23 °C unless otherwise mentioned. Some ^{31}P NMR spectra were recorded in nondeuterated solvents in sweep-off mode. Chemical shifts are reported in parts per million, downfield positive, relative to tetramethylsilane (for ^{1}H) or 85% H_3PO_4 (for ^{31}P NMR). Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

CAUTION: Phenyldichlorophosphine has an offensive odor, and its vapors present a health hazard. All contaminated areas, flasks, and needles can be treated with 1:1 aqueous nitric acid or 3% hydrogen peroxide.

***N*-Chlorodiisopropylamine**. The following is a procedure modified from a literature method.[15] Diisopropylamine (60 mL) was added to a NaOCl solution (4–6%, 1 L) contained in a 2-L beaker that was cooled with ice. This mixture was stirred for 2 h. The top layer (about 50 mL) was separated with a separatory funnel and stored over anhydrous $CaCl_2$ in the refrigerator overnight. It was filtered using a funnel with a cotton plug and stored over more fresh $CaCl_2$ spheres again in the refrigerator overnight. This twice-dried product was filtered as quickly as possible and then poured into a flask containing molecular sieves (4 Å, 10 g), which had been dried under vacuum over a Bunsen flame for about 10 min and allowed to cool to room temperature under nitrogen. The liquid was purged with nitrogen and kept in the refrigerator for 3 days before use (yield 45 mL, 72%).

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[Sulfurylbis[2-(4-methyl-6-*tert*-butylphenoxy)]]phenylphosphine, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2PPh$ (1). To a solution of diol **7** (14.5 g, 37.1 mmol) and triethylamine (11.0 mL, 79.1 mmol) in dichloromethane (200 mL) was added a solution of $PhPCl_2$ (5.0 mL, 36.8 mmol) in dichloromethane (50 mL) with constant stirring at 23 °C for 75 min. The resultant mixture was stirred for a further period of 24 h and the solution washed with water (4 × 200 mL). The organic layer was dried over anhydrous K_2CO_3, and the solvent was removed under vacuum. Compound **1** was obtained in a 60% yield (11.0 g): mp >260 °C. ^1H NMR: 1.22 (s, 18 H, *t*-Bu), 2.36 (s, 6 H, aryl *Me*), 7.37 (s, 2 H, aryl), 7.57 (m, 5 H, aryl), 7.80 (s, 2 H, aryl), 8.10 (m, 2 H, aryl). ^{31}P NMR: 165.7. Anal. Calcd for $C_{28}H_{33}O_4PS$: C, 67.72; H, 6.70. Found: C, 67.35; H, 6.73.

[Sulfurylbis[2-(4-methyl-6-*tert*-butylphenoxy)]]phenyl(tetrachloro-1,2-benzenedioxy)phosphorane, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2PPh(O_2C_6Cl_4)$ (2). A solution of **1** (0.60 g, 1.2 mmol) and tetrachlorobenzoquinone (0.29 g, 1.2 mmol) in toluene (40 mL) was heated under reflux for 5 min. The reddish solution turned yellowish. The solvent was removed under vacuum, the residue was dissolved in a dichloromethane−hexane (1:1) mixture, and the solution was left under a nitrogen flow. Crystals of **2** were obtained, which were dried under vacuum (yield 0.50 g, 56%): mp >250 °C. ^1H NMR: 1.18 (s, 18 H, *t*-Bu), 2.36 (s, 6 H, aryl *Me*), 7.3−7.7 (br, m, 9 H, aryl). ^1H NMR for the other isomer: 1.22 (s, *t*-Bu). ^{31}P NMR: −39.4, −46.4 (9:1). Anal. Calcd for $C_{34}H_{33}Cl_4O_6PS\cdot 0.5C_6H_{14}$: C, 56.57; H, 5.13. Found: C, 56.46; H, 5.15.

[Sulfurylbis[2-(4-methyl-6-*tert*-butylphenoxy)]]phenyl(1,2-benzenedioxy)phosphorane, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2PPh(O_2C_6H_4)$ (3). To a solution of **1** (0.60 g, 1.2 mmol) and catechol (0.14 g, 1.3 mmol) in ether (170 mL) was added an excess of $Pr^i{}_2NCl$ (0.70 mL, 4.8 mmol) with constant stirring at 23 °C for 1 min. The resultant mixture was stirred for 46 h. The solvent was removed under vacuum and the residue extracted with a hexane−dichloromethane (1:1, 100 mL) mixture and filtered. The filtrate was left under a nitrogen flow to give a crystalline product (yield 0.40 g, 55%): mp >250 °C. ^1H NMR ($CDCl_3$): 1.17 (s, 18 H, *t*-Bu), 2.34 (s, 6 H, aryl *Me*), 6.6−7.8 (m, 13 H, aryl). ^{31}P NMR ($CDCl_3$): −44.7, −54.3 (4.4:1). ^{31}P NMR (toluene): −41.2, −49.8 (4:1). Anal. Calcd for $C_{34}H_{37}O_6PS$: C, 67.53; H, 6.17. Found: C, 67.79; H, 6.24.

[Sulfurylbis[2-(4-methyl-6-*tert*-butylphenoxy)]]tris(2,2,2-trichloroethoxy)phosphorane, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OCH_2CCl_3)_3$ (4). To a solution of phosphorus trichloride (1.00 mL, 11.5 mmol) and 2,2,2-trichloroethanol (3.30 mL, 34.4 mmol) in dichloromethane (200 mL) was added triethylamine (4.80 mL, 34.5 mmol) with stirring at 23 °C for 5 min. The solution was stirred for an additional 6 h, and then diol **7** was added (4.50 g, 11.5 mmol) along with $Pr^i{}_2NCl$ (2.00 mL, 13.6 mmol). The solution was stirred for 48 h. The solvent was removed under vacuum and the residue extracted with ether (200 mL). The ether was removed and the residue dissolved in hot toluene and left at −20 °C to obtain the crystalline product. These crystals had loosely bound toluene molecules which slowly escaped to give an opaque powdery product even at atmospheric pressure. On heating to 80 °C, the toluene escaped and the crystals turned to a powder (yield 6.6 g, 66%): mp >250 °C. The product consisted of two isomers (**4A** and **4B**) in solution. In $CDCl_3$ the isomer ratio **4A**:**4B** was 1:0.64 (^1H and ^{31}P). In $C_6H_5CH_3$ the ratio was 1:1.36 (only by ^{31}P). ^1H NMR ($CDCl_3$): **4A**, 1.50 (s, 18 H, *t*-Bu), 2.35 (s, 6 H, aryl *Me*), 3.79 (d, 2 H, 2.9 Hz), 4.53 (br, 2 H), 4.90 (br, 2 H), 7.37 (s, 2 H, aryl), 7.74 (s, 2 H, aryl); **4B**, 1.42 (s, 18 H, *t*-Bu), 2.30 (s, 6 H, aryl *Me*), 4.90 (br, 6 H), 7.37 (s, 2 H, aryl), 7.55 (s, 2 H, aryl). ^{31}P NMR ($CDCl_3$): **4A**, −85.6; **4B**, −74.3. ^{31}P NMR (toluene): **4A**, −85.6; **4B**, −75.0. Anal. Calcd for $C_{28}H_{34}Cl_9O_7PS$: C, 38.89; H, 3.96. Found: C, 38.89; H, 4.12.

[Sulfurylbis[2-(4,6-dimethylphenoxy)]triphenoxyphosphorane, $O_2S[Me_2C_6H_2O]_2P(OPh)_3$ (5). To a solution of diol **8** (1.20 g, 3.92 mmol) and $P(OPh)_3$ (1.00 mL, 3.81 mmol) in ether (200 mL) was added an excess of $Pr^i{}_2NCl$ (0.60 mL, 4.1 mmol) with constant stirring at 23 °C in 1 min. The resultant mixture was stirred for 24 h and filtered. Hexane (50 mL) was added to the filtrate and the solution left under a nitrogen flow to give a mixture of crystals and oil. The oil was washed off with a heptane−ether (2:1, 60 mL) mixture, and the crystals were dried under vacuum (yield 1.2 g, 51%): mp 205−207 °C. ^1H NMR: 1.68 (s, 6 H, aryl *Me*), 2.28 (s, 6 H, aryl *Me*), 6.9−7.3 (br, m, 17 H, aryl), 7.69 (s, 2 H, aryl). ^{31}P NMR: −83.5. Anal. Calcd for $C_{34}H_{31}O_7PS$: C, 66.44; H, 5.08. Found: C, 65.55; H, 5.43. This compound was the least stable one in this work as indicated by some decomposition during the X-ray study.

[Sulfurylbis[2-(4-methyl-6-*tert*-butylphenoxy)]tris(pentafluorophenoxy)phosphorane, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OC_6F_5)_3$ (6). 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 23 °C for 5 min. The solution was stirred for 5 h, and then diol **7** (4.50 g, 11.5 mmol) was added along with $Pr^i{}_2NCl$ (2.00 mL, 13.6 mmol). The solution was stirred for an additional 41 h. The solution was then washed with water (3 × 100 mL), dried with anhydrous Na_2SO_4, and filtered. Skelly-C (50 mL) was added and the solution left under a nitrogen flow to obtain a crystalline product (yield 7.2 g, 65%): mp >250 °C. ^1H NMR: 1.36 (s, 18 H, *t*-Bu), 2.38 (s, 6 H, aryl *Me*), 7.47 (s, 2 H, aryl), 7.52 (s, 2 H, aryl). ^{31}P NMR: −126.5. Anal. Calcd for $C_{40}H_{28}F_{15}O_7PS$: C, 49.60; H, 2.91. Found: C, 49.34; H, 3.10.

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.[16]

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. Refinements were based on F^2, and computations were performed on a 486/66 computer using SHELXS-86 for solution[17] and SHELXL-93 for refinement.[18] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding 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.

In compound **2** there is a hexane molecule and in compound **4** there is a toluene molecule of solvation. Compound **5** suffered a 13% decay during data collection. An approximate linear decay correction was applied. One of the CH_2CCl_3 groups of compound **4** was disordered. Compound **5** has two independent molecules in each asymmetric unit. Only one figure is given, and the other one is labeled identically.

Results and Discussion

Selected bond parameters for **2**−**6** are given in Tables 2−6, respectively. The atom-labeling schemes for **2**−**6** are shown in the ORTEX[19] plots of Figures 1−5, respectively, with thermal ellipsoids shown at the 40% probability level. All hydrogens are omitted for clarity.

Syntheses. Compound **1**, which is a new compound, as are the cyclic oxyphosphoranes **2**−**6**, was synthesized from the reaction of $PhPCl_2$ with sulfurylbis[2-(4-methyl-6-*tert*-butylphenol)] in the presence of Et_3N in dichloromethane solution. It is highly stable and did not form any phosphate even after several months of exposure to the atmosphere.

Phosphorane **2** was synthesized from **1** in an oxidative addition reaction with tetrachlorobenzoquinone in boiling toluene, whereas phosphorane **3** was obtained from **1** in a reaction with catechol in ether solution in the presence of $(i\text{-}Pr)_2NCl$ to take up the diol hydrogen atoms. Phosphoranes **4**−**6** also were obtained by reactions similar to that used for **3**, *i.e.*, reaction of the appropriate phosphite with a diol in the presence

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Table 1. Crystallographic Data for Compounds **2**−**6**[a]

	2	**3**	**4**	**5**	**6**
formula	$C_{40}H_{33}Cl_4O_6PS{\cdot}C_6H_{14}$	$C_{34}H_{37}O_6PS$	$C_{28}H_{34}Cl_9O_7PS{\cdot}C_7H_8$	$C_{34}H_{31}O_7PS$	$C_{40}H_{28}F_{15}O_7PS$
formula wt	828.61	604.67	956.77	614.62	968.65
cryst syst	triclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
cryst size, mm	0.15 × 0.40 × 0.60	0.45 × 0.75 × 1.00	0.40 × 0.50 × 1.00	0.15 × 0.62 × 1.00	0.12 × 0.42 × 0.52
a (Å)	12.392(4)	14.827(7)	9.649(2)	11.444(4)	10.711(9)
b (Å)	12.834(1)	10.602(3)	22.657(4)	16.316(5)	11.965(5)
c (Å)	14.317(2)	20.254(6)	20.532(3)	18.429(7)	16.094(7)
α (deg)	108.90(1)	90	90	78.48(3)	80.62(3)
β (deg)	98.57(2)	92.05(3)	97.42(2)	73.30(3)	93.25(6)
γ (deg)	86.33(2)	90	90	73.50(3)	102.83(6)
V (Å^3)	2129.8(8)	3182(2)	4451(1)	3134(2)	1984(2)
Z	2	4	4	4	2
D_{calc} (g/cm^3)	1.292	1.262	1.428	1.303	1.622
$\mu_{MoK\alpha}$ (cm^{-1})	4.07	1.95	6.92	2.02	2.44
total reflns	4799	3657	5117	7138	4540
reflns with $I > 2\sigma_I$	3021	2738	3431	3898	2243
R^b	0.0629	0.0523	0.0960	0.0587	0.0775
$R_w{}^c$	0.1601	0.1408	0.2434	0.1136	0.1705

[a] The data were collected using Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 23 ± 2 °C. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w(F_o^2) = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $O_2S[(t\text{-Bu})MeC_6H_2O]_2PPh(O_2C_6Cl_4)$ (**2**)

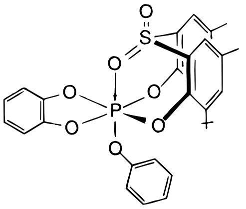
P−O(1)	1.546(4)	P−O(5)	2.646(5)
P−O(3)	1.691(5)	S−O(5)	1.435(5)
P−O(2)	1.695(5)	S−O(6)	1.496(5)
P−O(4)	1.704(5)	S−C(7)	1.725(7)
P−C(13)	1.901(8)	S−C(6)	1.792(7)
O(1)−P−O(3)	155.6(3)	O(4)−P−O(5)	76.9(2)
O(1)−P−O(2)	93.9(2)	C(13)−P−O(5)	172.7(3)
O(3)−P−O(2)	83.4(2)	O(5)−S−O(6)	118.0(3)
O(1)−P−O(4)	84.3(2)	O(5)−S−C(7)	112.5(3)
O(3)−P−O(4)	90.6(2)	O(6)−S−C(7)	102.0(3)
O(2)−P−O(4)	161.2(2)	O(5)−S−C(6)	98.3(3)
O(1)−P−C(13)	93.4(3)	O(6)−S−C(6)	118.6(3)
O(3)−P−C(13)	110.9(3)	C(7)−S−C(6)	107.4(3)
O(2)−P−C(13)	102.9(3)	C(1)−O(1)−P	127.3(5)
O(4)−P−C(13)	95.9(3)	C(12)−O(2)−P	132.1(4)
O(1)−P−O(5)	87.3(2)	C(19)−O(3)−P	113.1(4)
O(3)−P−O(5)	68.3(2)	C(20)−O(4)−P	111.7(4)
O(2)−P−O(5)	84.3(2)	S−O(5)−P	108.3(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $O_2S[(t\text{-Bu})MeC_6H_2O]_2PPh(O_2C_6H_4)$ (**3**)

P−O(1)	1.606(3)	S−O(6)	1.424(3)
P−O(2)	1.622(3)	S−O(5)	1.428(3)
P−O(3)	1.640(3)	S−C(7)	1.778(4)
P−O(4)	1.727(3)	S−C(6)	1.783(4)
P−C(13)	1.840(5)		
O(1)−P−O(2)	116.8(2)	O(6)−S−O(5)	118.3(2)
O(1)−P−O(3)	122.1(2)	O(6)−S−C(7)	105.7(2)
O(2)−P−O(3)	121.2(2)	O(5)−S−C(7)	108.8(2)
O(1)−P−O(4)	89.9(1)	O(6)−S−C(6)	105.7(2)
O(2)−P−O(4)	90.8(1)	O(5)−S−C(6)	108.8(2)
O(3)−P−O(4)	88.8(1)	C(7)−S−C(6)	109.3(2)
O(1)−P−C(13)	91.8(2)	C(1)−O(1)−P	130.6(2)
O(2)−P−C(13)	89.7(2)	C(12)−O(2)−P	128.7(2)
O(3)−P−C(13)	89.0(2)	C(19)−O(3)−P	115.8(3)
O(4)−P−C(13)	177.7(2)	C(20)−O(4)−P	113.1(2)

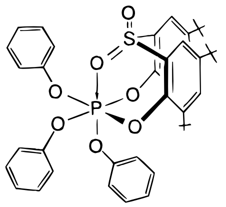
of (i-Pr)$_2$NCl. However, in the case of **4** and **6**, the phosphite, tris(trichloroethyl) phosphite and tris(pentafluorophenyl) phosphites, respectively, were prepared *in situ* from PCl_3 in the presence of Et_3N with Cl_3CCH_2OH (for **4**) and C_6F_5OH (for **6**) using dichloromethane as the solvent. The reaction is illustrated for the synthesis of **6**, eqs 1 and 2 (Scheme 1). Yields ranged from 51% to 66%.

Basic Structures and Structural Displacement. The cyclic oxyphosphoranes **3**−**5** have trigonal bipyramidal geometries with the difference that the sulfone-containing rings of **3** and **4** (shown in Figures 2 and 3) are positioned in diequatorial sites in *anti* or chairlike conformations, whereas this ring in **5** is arranged in axial−equatorial sites in a *syn* or twisted-boat conformation as displayed in Figure 6. By way of contrast, **2** and **6** are hexacoordinate with octahedral geometries as a result of donor action from one of the oxygen atoms of the sulfonyl group. In the case of **6**, the P−O donor bond distance of 1.936(7) Å is the shortest so far observed for coordination with a sulfone group. In contrast, **2** has the longest P−O distance, 2.646(5) Å, for this type of coordination. These distances compare with the sum of the covalent radii of 1.83 Å.[20a] On the basis of our previous method,[5] the extent of displacement of **6** from a square pyramid toward an octahedron is 82.2% while **2** is only 27.9% displaced along this coordinate. For this calculation, the square pyramid is taken as the geometrical arrangement that exists without the presence of the oxygen donor linkage. Other examples that exhibit donor coordination from a sulfone group are the analogous cyclic pentaoxyphosphoranes **B**, **J**, and **K**.[2] The bond parameters for these three oxyphosphoranes indicative of octahedral coordination are compared with those for **2** and **6** in Table 7. In Figure 7, the displacement of the phosphorus atom from the average plane of the four basal atoms of the square pyramid is shown to vary in a linear fashion with the donor P−O distance of the incoming sulfuryl oxygen atom. Earlier we found this same type of correlation[5,6] in which



P–OSO = 2.607(5)Å
P–OSO = 2.605(5)Å

J[2]



P–OSO = 2.546(9)Å

K[2]

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(20) (a) Sutton, L., Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Special Publications 11 and 18; The Chemical Society: London, 1958 and 1965. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Scheme 1

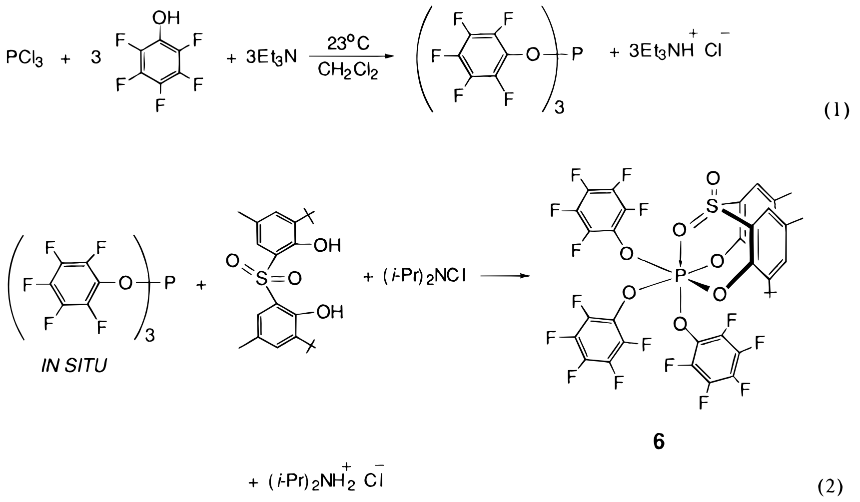


Table 4. Selected Bond Lengths (Å) and Angles (deg) for $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OCH_2CCl_3)_3$ (**4**)

P−O(2)	1.599(6)	S−O(6)	1.421(7)
P−O(1)	1.606(6)	S−O(7)	1.422(7)
P−O(3)	1.613(6)	S−C(7)	1.780(9)
P−O(4)	1.632(6)	S−C(6)	1.78(1)
P−O(5)	1.641(6)		
O(2)−P−O(1)	116.9(3)	C(15′)−O(4)−P	127.3(11)
O(2)−P−O(3)	120.3(3)	C(15)−O(4)−P	128.9(7)
O(1)−P−O(3)	122.7(3)	C(17)−O(5)−P	123.0(6)
O(2)−P−O(4)	94.5(3)	O(3)−P−O(5)	88.6(3)
O(1)−P−O(4)	90.6(3)	O(4)−P−O(5)	176.4(3)
O(3)−P−O(4)	88.9(3)	O(6)−S−O(7)	118.5(4)
O(2)−P−O(5)	88.9(3)	O(6)−S−C(7)	107.9(4)
O(1)−P−O(5)	88.7(3)	O(7)−S−C(7)	105.3(4)
C(1)−O(1)−P	128.6(5)	O(6)−S−C(6)	108.0(4)
C(12)−O(2)−P	128.0(5)	O(7)−S−C(6)	106.0(4)
C(13)−O(3)−P	126.1(6)	C(7)−S−C(6)	111.1(4)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $O_2S[Me_2C_6H_2O]_2P(OPh)_3$ (**5**)

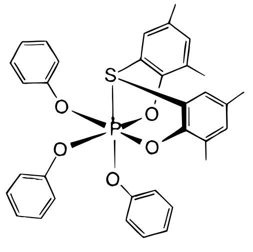
S(1)−O(7)	1.411(5)	S(2)−O(7′)	1.414(5)
S(1)−O(6)	1.416(4)	S(2)−O(6′)	1.420(5)
S(1)−C(6)	1.763(7)	S(2)−C(7′)	1.745(7)
S(1)−C(7)	1.767(7)	S(2)−C(6′)	1.748(7)
P(1)−O(5)	1.590(4)	P(2)−O(5′)	1.587(4)
P(1)−O(4)	1.598(4)	P(2)−O(4′)	1.616(4)
P(1)−O(2)	1.619(4)	P(2)−O(2′)	1.617(4)
P(1)−O(3)	1.640(4)	P(2)−O(3′)	1.644(4)
P(1)−O(1)	1.685(4)	P(2)−O(1′)	1.682(4)
O(7)−S(1)−O(6)	118.5(3)	O(7′)−S(2)−O(6′)	117.7(3)
O(7)−S(1)−C(6)	108.1(3)	O(7′)−S(2)−C(7′)	107.8(3)
O(6)−S(1)−C(6)	108.0(3)	O(6′)−S(2)−C(7′)	109.1(3)
O(7)−S(1)−C(7)	107.8(3)	O(7′)−S(2)−C(6′)	108.3(3)
O(6)−S(1)−C(7)	109.0(3)	O(6′)−S(2)−C(6′)	108.1(3)
C(6)−S(1)−C(7)	104.6(3)	C(7′)−S(2)−C(6′)	105.1(3)
O(5)−P(1)−O(4)	117.6(2)	O(5′)−P(2)−O(4′)	116.9(3)
O(5)−P(1)−O(2)	111.4(2)	O(5′)−P(2)−O(2′)	111.6(2)
O(4)−P(1)−O(2)	131.0(2)	O(4′)−P(2)−O(2′)	131.5(2)
O(5)−P(1)−O(3)	91.6(2)	O(5′)−P(2)−O(3′)	91.2(2)
O(4)−P(1)−O(3)	89.5(2)	O(4′)−P(2)−O(3′)	88.8(2)
O(2)−P(1)−O(3)	88.9(2)	O(2′)−P(2)−O(3′)	89.5(2)
O(5)−P(1)−O(1)	93.3(2)	O(5′)−P(2)−O(1′)	93.4(2)
O(4)−P(1)−O(1)	86.6(2)	O(4′)−P(2)−O(1′)	86.5(2)
O(2)−P(1)−O(1)	91.0(2)	O(2′)−P(2)−O(1′)	91.5(2)
O(3)−P(1)−O(1)	174.8(2)	O(3′)−P(2)−O(1′)	174.6(2)
C(1)−O(1)−P(1)	130.4(4)	C(1′)−O(1′)−P(2)	130.7(4)
C(12)−O(2)−P(1)	128.4(4)	C(12′)−O(2′)−P(2)	127.7(4)
C(13)−O(3)−P(1)	126.0(4)	C(13′)−O(3′)−P(2)	129.4(4)
C(19)−O(4)−P(1)	129.5(4)	C(19′)−O(4′)−P(2)	129.2(4)
C(25)−O(5)−P(1)	134.9(4)	C(25′)−O(5′)−P(2)	133.8(4)

a decrease in the P−S donor distance paralleled an increase in the phosphorus atom displacement toward an octahedron for a series of analogous pentaoxyphosphoranes[4−6] which had a sulfur atom in place of the sulfone group. In the series with the sulfur atom as a donor, the P−S distances varied from 3.04 to 2.33 Å[1b,4−9] with the corresponding displacement toward the octahedron covering the range 24% to 71%, respectively. For the P−S distance, the sum of covalent radii is 2.14 Å[20a] while the van der Waals sum is 3.75 Å.[20b]

Structural Comparisons. All of the hexacoordinated derivatives listed in Table 7 are pentaoxyphosphoranes, except **2**. The presence of the less electronegative phenyl group in **2** in place of a phenoxy ligand most likely reduces the electrophilicity of phosphorus such that Lewis base action is inhibited to some degree in spite of the presence of the electron-withdrawing action of the chlorine substituents on the catechol moiety. At the other end of this series of oxyphosphoranes where **6** exhibits the strongest P−O donor action as reflected in the shortest sulfone oxygen−phosphorus distance, the presence of the three electron-withdrawing pentafluorophenoxy ligands is felt to contribute strongly in enhancing the electrophilicity at phosphorus.

The Lewis acidity of phosphorus in **3** and **4**, both of which have chairlike ring conformations as seen in Figures 2 and 3, respectively, apparently is sufficiently reduced such that sulfone donor action does not take place. The P−OSO distance is 3.312(3) Å for **3** and 3.335(6) Å for **4**. These values compare with the sum of the van der Waals radii of 3.35 Å.[20b] The only difference in the composition of **3** relative to **2** is the deletion of the chlorine atom substituents on the catecholate ring. It seems reasonably certain that the loss of these electronegative attachments is causative in giving a pentacoordinate rather than a hexacoordinate structure. Pentacoordinate **4** is structurally very similar to the sulfone-containing ring system in **A**.[2] The only difference in composition is the presence of the less electronegative trichloroethoxy ligands attached to phosphorus in **4** compared to the presence of trifluoroethoxy ligands in **A**. With this loss of electronegativity for **4**, it would be surprising if a hexacoordinate structure did form.

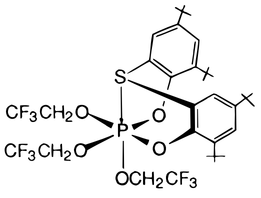
An indication that the sulfone component as a bridge between aryl substituents acts as a poorer donor group compared to a sulfur atom in this position in related derivatives is found by contrasting the geometries of specific members.[4−9] For example, with sulfur as a donor atom, **L**[6] with aryl methyl substituents is hexacoordinate due to sulfur donor action, while the identically composed sulfone-containing phosphorane, **5**, other than insertion of the bridging SO_2 group in place of the sulfur atom, is pentacoordinate lacking any donor coordination.



P–S = 2.880(1)Å

L[6]

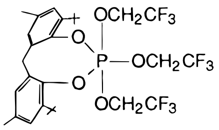
The same conclusion is reached on comparing the trigonal bipyramidal geometries for the ring sulfone members $\mathbf{A_1}$[2] and $\mathbf{A_2}$[2] with octahedral geometries achieved for analogous sulfur donor phosphorane, **F**[5] and **M**.[4]



P–S = 2.504(3)Å

M[4]

A particularly unique feature of **5** is the placement of the eight-membered ring system at axial–equatorial (a–e) sites of a trigonal bipyramid. Here the P–OSO distance is 3.233(5) Å, which is the average for two independent molecules in the unit cell. Previously, this orientation was found only with this type of ring that had a methylene group acting as a bridging ligand, *e.g.*, **C**[3] or **D**,[4] or in the isolated case of sulfur acting as the bridging ligand in the bicyclic phosphorane **G**.[10] The ring conformation in these oxyphosphoranes is the same, that of a very twisted boat. Also it is noted that this ring orientation does not occur if *tert*-butyl groups reside in ortho positions of the aryl groups relative to the location of the ring oxygen atoms. This is the situation in **H**,[11,12] **I**,[12] and **N**.[4] Like **H** and **I**, **N** has



N[4]

a chairlike *anti* ring conformation. It would appear that a steric effect due to the presence of the *tert*-butyl group may operate to destabilize the axial–equatorial ring orientation found for **5**, **C**, and **D**.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OC_6F_5)_3$ (**6**)

P–O(3)	1.634(7)	P–O(6)	1.936(7)
P–O(5)	1.666(7)	S–O(7)	1.406(7)
P–O(2)	1.675(7)	S–O(6)	1.489(7)
P–O(1)	1.684(7)	S–C(6)	1.715(11)
P–O(4)	1.688(7)	S–C(7)	1.737(10)
O(3)–P–O(5)	93.7(4)	O(4)–P–O(6)	86.2(3)
O(3)–P–O(2)	88.4(3)	O(7)–S–O(6)	115.3(4)
O(5)–P–O(2)	89.7(3)	O(7)–S–C(6)	113.0(5)
O(3)–P–O(1)	93.8(4)	O(6)–S–C(6)	103.7(4)
O(5)–P–O(1)	172.4(4)	O(7)–S–C(7)	112.0(5)
O(2)–P–O(1)	89.4(3)	O(6)–S–C(7)	104.8(4)
O(3)–P–O(4)	94.5(3)	C(6)–S–C(7)	107.3(5)
O(5)–P–O(4)	90.3(3)	C(1)–O(1)–P	127.5(6)
O(2)–P–O(4)	177.1(4)	C(12)–O(2)–P	130.1(6)
O(1)–P–O(4)	90.3(3)	C(13)–O(3)–P	129.9(7)
O(3)–P–O(6)	179.2(3)	C(19)–O(4)–P	130.8(6)
O(5)–P–O(6)	86.0(3)	C(25)–O(5)–P	130.5(6)
O(2)–P–O(6)	90.8(3)	S–O(6)–P	119.7(4)
O(1)–P–O(6)	86.4(3)		

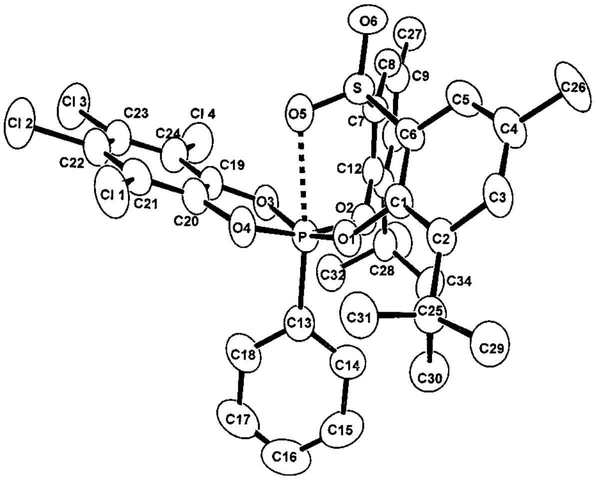


Figure 1. ORTEX diagram of $O_2S[(t\text{-Bu})MeC_6H_2O]_2PPh(O_2C_6Cl_4)$ (**2**).

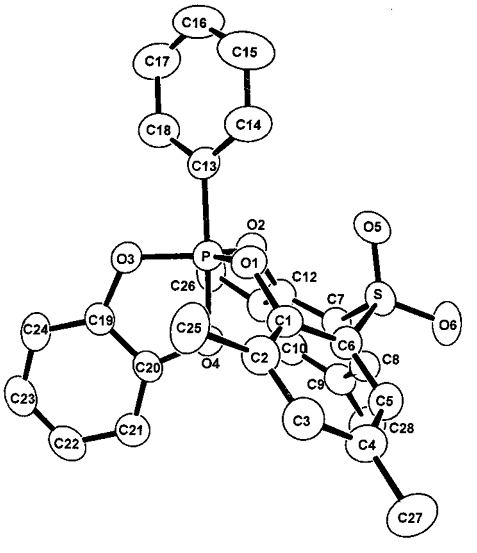


Figure 2. ORTEX diagram of $O_2S[(t\text{-Bu})MeC_6H_2O]_2PPh(O_2C_6H_4)$ (**3**).

Isomerism

^{31}P and ^1H NMR data revealed that phosphoranes **2**–**4** exist in $CDCl_3$ and toluene solution in two forms. They are presumed to be isomeric formulations in each case due to the closeness in the ^{31}P chemical shifts. These are −39.4 and −46.4 ppm (9:1) for **2** in $CDCl_3$; −44.7 and −54.3 ppm (4.4:1) for **3** in $CDCl_3$, −41.2 and −49.8 (4:1) for **3** in toluene; −85.6 and −74.3 ppm (1:0.64) for **4** in $CDCl_3$, and −85.6 and −75.0 ppm (1:1.36) for **4** in toluene. In view of the existence of trigonal bipyramidal geometries in the absence of sulfone donor action and the formation of octahedral geometries as a result of sulfone donor action, it seems most reasonable that the presence of isomers is due to these two isomeric representations. Their energies are close to each other as the above discussion has demonstrated, *i.e.*, the alteration of substituents by way of subtle steric or electronegativity effects may induce the appearance of one form over the other. For example, the requirement to form the hexacoordinated geometry like **2** from the pentacoor-

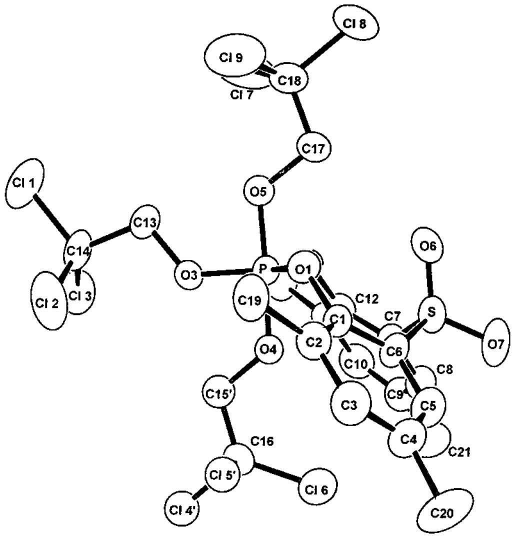


Figure 3. ORTEX diagram of $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OCH_2CCl_3)_3$ (**4**). Only one set of the disordered atoms (with primes) is given. Also the six methyl groups at C19 and C22 have been omitted for clarity.

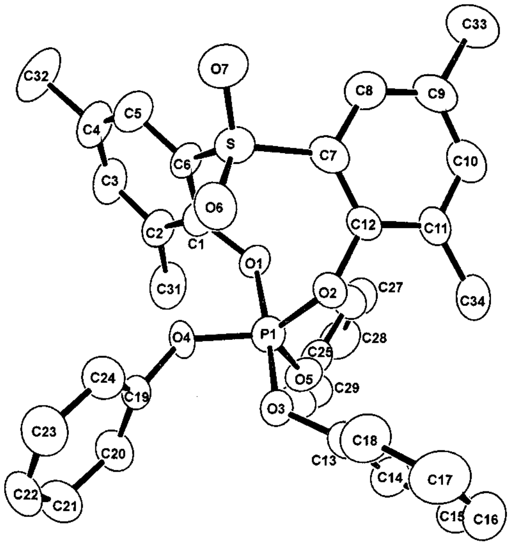


Figure 4. ORTEX diagram of $O_2S[Me_2C_6H_2O]_2P(OPh)_3$ (**5**).

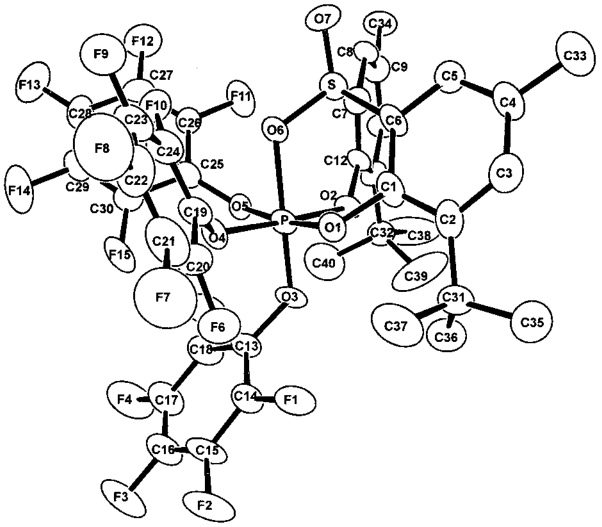


Figure 5. ORTEX diagram of $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OC_6F_5)_3$ (**6**).

dinated geometries like **3** and **4** is for a conformational rearrangement of the eight-membered ring to take place such that the *anti* chairlike form changes to a *syn* boatlike arrangement. This process followed by sulfone donor action or accompanying it would allow conversion to the octahedral isomeric formulation.

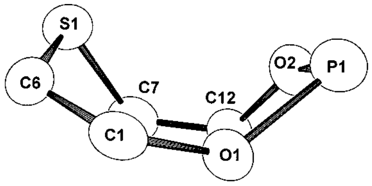


Figure 6. ORTEX diagram showing the conformation of the eight-membered ring in **5**.

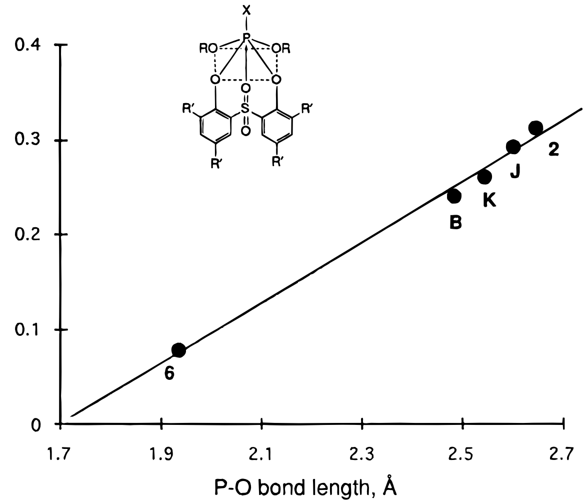


Figure 7. Displacement of phosphorus from the mean plane of four attached oxygen atoms considered to comprise the base of a square pyramid. The displacement is toward the remaining apical atom, which is trans to the approaching oxygen atom, as depicted in the inset. This displacement is represented as a function of the P−O distance for the compounds listed in Table 7.

Table 7. Comparison of Bond Parameters for P−OSO Coordination in Hexacoordinated Cyclic Oxyphosphoranes

compd[a]	P−O, Å	X−P−O, deg[b]	P displacement, Å[c]	% octa[d]
2	2.646(5)	172.7(3)	0.3109	27.9
J	2.606(5)	177.8(2)	0.2916	32.4
K	2.546(9)	177.6(3)	0.2605	39.6
B	2.487(3)	178.3(2)	0.2392	44.5
6	1.936(7)	179.2(3)	0.0769	82.2

[a] Data for compounds **J**, **K**, and **B** are taken from ref 2. Data for **2** and **6** are from this work. [b] This angle refers to the atom trans to the oxygen atom of the sulfone group in the hexacoordinated structure. [c] Displacement of the phosphorus atom from the base plane (defined by the four oxygen atoms cis to the donor oxygen atom) of a square pyramid toward the trans atom (apical position in the square pyramid). [d] Percent displacement from an ideal square pyramid toward an octahedron.

In earlier work, isomers were observed in solution by ^{31}P and ^{1}H NMR for the sulfone-containing ring systems in the pentaoxyphosphoranes $\mathbf{A_1}$ and $\mathbf{A_2}$.[2] As in the present study, it was suggested that a pentacoordinate and a hexacoordinated form existed in solution. The possibility that the isomers are due to the presence of a TBP with the sulfone-containing ring in an a−e arrangement is unlikely since this form has only been observed when the ring substituents are lacking, as in **C**[3] and **D**,[4] or at most are methyl groups, as in **5**. In previous work, ^{31}P NMR measurements showed that the chemical shift, for example for $\mathbf{A_1}$, was nearly the same in the solid and solution states.[2] The ^{31}P shift is −85.4 ppm in solution and −84.1 ppm in the solid. The presence of another isomer in solution is indicated at a ^{31}P shift of −73.5 ppm. The former solution shift is ascribed to the TBP geometry as found in the X-ray structure while the latter solution value was assigned to a hexacoordinate formulation.

At least one of the chemical shifts for each of the phosphoranes **2**−**4** implies retention of the X-ray structure in solution. Further, of the compounds showing evidence for the presence of two isomers in solution, only **2** is hexacoordinate. For this member, the P−O donor bond is 2.645(5) Å, the longest sulfone donor bond as yet observed. Phosphorane **6**, which has the shortest P−O donor bond length, 1.936(7) Å (Table 7), exhibits only one ^{31}P NMR shift in solution. This may serve as evidence that there is a greater energy difference between isomers for **6** than for **2**. The closeness in the chemical shifts for the isomers of **2**−**4** assigned to penta- and hexacoordinated forms is not unreasonable due to the weakness of the P-donor interaction implied by the long P−O distance to the sulfone oxygen atom for **2**. The same is expected for **3** and **4**.

Ab initio studies[21,22] combined with variable temperature NMR measurements[23] yielding activation energies for ring reorientation in trigonal bipyramidal geometries indicate that, as the ring size increases from five- to eight-membered, there is a marked increase in ring placement at diequatorial sites. It is estimated that the strain energy for the eight-membered ring so situated is of the order of 0−2 kcal/mol.[24] This low strain energy should be maintained in the hexacoordinated structure formed via donor atom coordination. *Ab initio* calculations are currently underway to test this hypothesis and hence gain credence for the isomeric representations.

Summary and Conclusion

In comparisons between eight-membered ring systems containing the sulfone group as a bridge between aryl components in oxyphosphoranes and those with sulfur in place of the SO_2 group, it is concluded that the sulfur atom acts as a stronger donor than an oxygen atom of the SO_2 group in promoting hexacoordination. This is evident when comparing the presence of octahedral geometries for the sulfur-containing ring systems in **L**, **F**, and **M** with the trigonal bipyramidal geometries for the sulfone-containing ring systems in **5**, $\mathbf{A_1}$, and $\mathbf{A_2}$, respectively, where the comparison is made between phosphoranes having identical substituents attached to phosphorus other than the difference in the coordinating Lewis base. It is further concluded that electron-withdrawing ligands promote stronger coordination as measured by the phosphorus−donor bond distance. Steric effects supplied by *tert*-butyl groups on the aryl group ortho to the ring oxygen atom bound to phosphorus are conducive in promoting hexacoordination. The closeness in energy of the penta- and hexacoordinate states of phosphorus in these ring-containing systems is indicated from the presence of isomeric forms in solution as demonstrated by ^{31}P NMR as well as the ready change in coordination number supplied by subtle effects resulting from variations in substituent composition. It is becoming increasingly apparent that hexacoordinated phosphorus should play a role at active sites of phosphoryl transfer enzymes[25] through their formation by coordination with donor atoms of nearby residues.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **2**−**6** and figure depicting thermal ellipsoids for the second molecule of **5** (34 pages). Ordering information is given on any current masthead page.

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