Isomeric Intraconversion among Penta- and Hexacoordinate Cyclic Oxyphosphoranes via Oxygen Atom Coordination[1,2]

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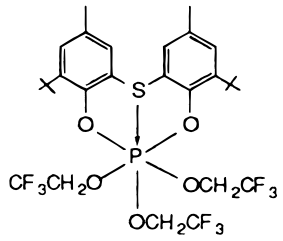
Abstract: The synthesis of a series of cyclic pentaoxyphosphoranes containing a sulfonyl group was carried out by the reaction of either $P(OCH_2CF_3)_3$ or $P(OPh)_3$ with the appropriate diol in an oxidative addition reaction: $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OCH_2CF_3)_3$ (**1**), $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OPh)_3$ (**2**), $O_2S[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)_3$ (**4**), and $O_2S[(t\text{-}Bu)_2C_6H_2O]_2P(OPh)_3$ (**5**). Reaction of **2** with catechol yielded $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OPh)(C_6H_4O_2)$ (**3**). X-ray studies provided the structures of **1**−**5**, although **4** was badly disordered. The geometries of **2**, **3**, and **5** are octahedral due to P−O coordination provided by the sulfonyl group, whereas **1** and **4** are trigonal bipyramidal. Solution ^{31}P, ^{1}H, and ^{19}F NMR spectra demonstrate that **1** and **4** exist in isomeric modifications. These are formulated as a pentacoordinate structure, as in the solid state, and a hexacoordinate structure. This represents the first study establishing intramolecular intraconversion between penta- and hexacoordinate isomers of phosphorus. An activation free energy of 17 kcal/mol for the exchange process for **1** and **4** was obtained from variable temperature ^{1}H NMR spectra.

Introduction

In work in our laboratory, we have employed sulfur atoms to act as donors in promoting hexacoordination in structural studies of cyclic pentaxoyphosphoranes.[3−7] These compounds form a series of structures extending from a square pyramid toward an octahedron ranging from 44 to 70%. The respective P−S distances varied from 2.88 to 2.36 Å. A representative member is **A**.[4]



A[4]

P–S 2.362(2)Å

Recently, Cavell[8] extended this range to 2.33 Å in a related phosphorane having the same type of sulfur ring system but with the use of chlorine ligands in place of OR groups. There also are quite a few X-ray studies identifying hexacoordinated phosphorus formed by oxygen or nitrogen coordination.[9,10]

Our current interest has focused on the use of sulfinyl and sulfonyl groups as Lewis base donors in place of a sulfur atom in the cyclic system present in **A**. We employed this ring system in a variety of organosilanes where the ring donor atom was varied from S[9,11−15] to SO[16] to SO_2.[17] Although the sulfinyl group did not show evidence for increasing the coordination geometry of silicon, the sulfur atom[11−15] and sulfonyl group[17] provided a series of structures displaced along a coordinate from tetrahedral toward trigonal bipyramidal (TBP) as a result of Si−S or Si−O donor action, respectively. Representative members of each of these series are **B**,[14] **C**,[16] and **D**.[17]

With the use of this ring system in oxyphosphoranes, we have found that the sulfonyl group leads to the formation of penta- and hexacoordinate structures which depend on the choice of ligands attached to phosphorus.[18] Thus, the pentaoxyphosphorane **E** having pentafluorophenoxy ligands exhibits a short P−O donor linkage, 1.936(7) Å, in forming an octahedral geometry. This compares with the tetraoxy derivative **F**, which is ligated to a tetrachlorocatecholate unit, where the P−O distance is quite long, 2.646(5) Å. Again, the geometry is octahedral. It is

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(1) (a) Pentacoordinated Molecules 113. (b) For part 112, see Deiters, J. A.; Holmes, R. R. *Ab Initio* Treatment of a Phosphorus Pentafluoride−Pyridine Reaction Coordinate. Submitted for publication.

(2) Presented in part at the 211th American Chemical Society National Meeting, New Orleans, LA, March 24−28, 1996; INOR 189.

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(10) Additional X-ray structures of neutral hexacoordinate phosphorus are found in a recent review: Wong, C. Y.; Kennepohl, D. K.; Cavell, R. G. *Chem. Rev.* **1996**, *96*, 1917.

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(17) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1996**, *15*, 3189.

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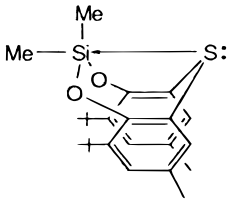
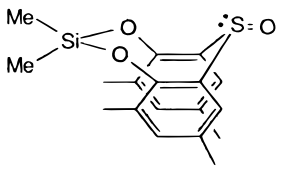


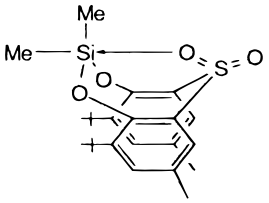
B[14]

Si–S 3.074(1)Å



C[16]

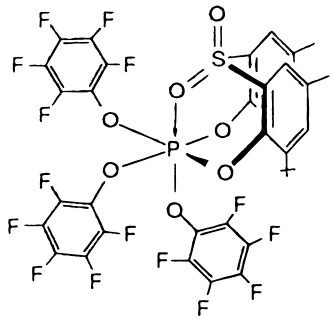
Si–S 3.615(1)Å



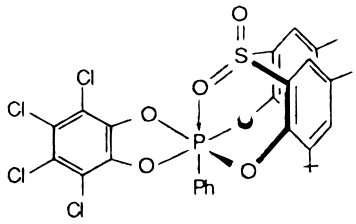
D[17]

Si–O 2.841(2)Å

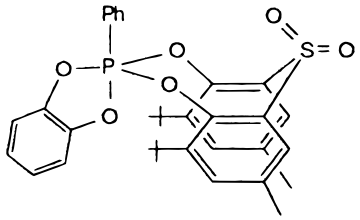
reasoned[18] that the presence of the phenyl group reduces the electrophilicity of phosphorus and serves as a major factor that causes so marked an increase in the donor−acceptor distance relative to **E**. When the chlorine atoms are formally removed from the catechol component of **F**, the tetraoxy derivative **G** results which has a trigonal bipyramidal geometry.[18]



E [18]



F [18]

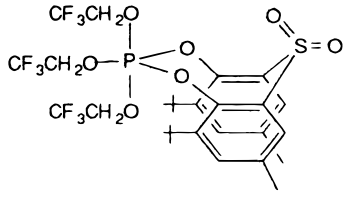


G [18]

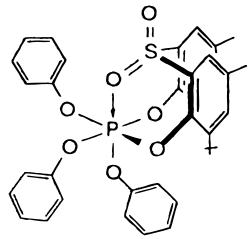
A further feature of interest is that ^{31}P and ^{1}H NMR data indicate the presence of two isomers each for **F** and **G** but not for **E**.[18] With the knowledge that the sulfonyl group coordinates more weakly than a sulfur atom,[18] it may be that an energy balance between pentacoordinated and hexacoordinated forms may be more readily achieved with a suitable ligand combination. The fact that **E** with the more highly electronegative pentafluorophenoxy ligands shows a single ^{31}P peak and hence no isomeric representations suggests that, here, the energy difference between penta- and hexacoordinated forms is substantial.

A number of earlier studies[19] on spirooxyphosphoranes with various bases have shown by ^{31}P NMR that intermolecular P(V) ⇌ P(VI) equilibria are established in solution.

To address this issue in a more quantitative fashion, the synthesis and structural study of the series of cyclic pentaoxyphosphoranes **1**−**5** was undertaken.



1



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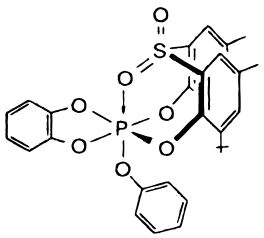

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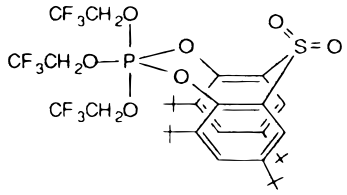

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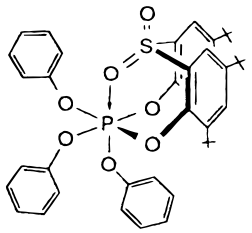

5

In this series, the sulfonyl group is present in the cyclic system in each case. The phosphorus electrophilicity is varied by ligand alterations with the idea of forming isomers. This approach was indicated by the lack of isomers for **E** and by the weaker donor ability of a sulfonyl oxygen atom compared to a sulfur atom as part of the cyclic component to coordinate with oxyphosphoranes. X-ray analyses were performed on **1**−**5** along with ^{31}P, ^{19}F, and variable temperature (VT) ^{1}H NMR measurements. These studies result in the first report indicating the presence of neutral penta- and hexacoordinated isomers of phosphorus that are in equilibrium with one another and undergo exchange by an intramolecular process.

Experimental Section

Tris(2,2,2-trifluoroethoxy)phosphite (Aldrich), triphenylphosphite (Eastman), phenyldichlorophosphine (Fluka), and tetrachloro-1,2-benzoquinone (Aldrich) were used as supplied. 2,2′-Dioxythiobis(4-

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methyl-6-*tert*-butylphenol) (**6**),[17] and *N*-chlorodiisopropylamine[20] were synthesized according to literature methods. Solvents were purified according to the standard procedures.[21] All of 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. Fluorine-19 spectra were recorded on a Bruker DPX-300 spectrometer using $CFCl_3$ as an internal reference. All of the spectra were recorded in $CDCl_3$ unless otherwise mentioned. Chemical shifts are reported in ppm, downfield positive, relative to tetramethylsilane for ^{1}H NMR or 85% H_3PO_4 for ^{31}P NMR, and coupling constants (*J*) are given in hertz All NMR spectra were recorded at 23 °C unless otherwise mentioned. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

(A) Syntheses. Dioxythiobis(4,6-di-*tert*-butylphenol) (7). A solution of hydrogen peroxide (30%, 10.0 mL, 88 mmol) in glacial acetic acid (35 mL) was added with thiobis(di-*tert*-butylphenol)[22] (6.5 g, 15 mmol), and the suspension was heated for 3 h at about 100 °C. The resulting mixture was filtered, and the solid residue was thoroughly washed with water and dried: yield 6.4 g (92%), mp 172−174 °C. ^{1}H NMR: 1.24 (s, 18 H, *t*-Bu), 1.40 (s, 18 H, *t*-Bu), 7.51 (s, 4 H, aryl), 9.41 (s, 2H, O*H*). Anal. Calcd for $C_{28}H_{42}O_4S$: C, 70.85; H, 8.92. Found: C, 71.04; H, 9.16.

[Dioxythiobis(4-methyl-6-*tert*-butylphenoxy)]tris(2,2,2-trifluoroethoxy)phosphorane, $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OCH_2CF_3)_3$ (1). To a solution of diol **6** (1.82 g, 4.61 mmol) and $P(OCH_2CF_3)_3$ (1.00 mL, 4.53 mmol) in ether (150 mL) was added an excess of *i*-Pr_2NCl (1.50 mL, 10.20 mmol) with constant stirring at about 23 °C for 1 min. The resultant mixture was stirred for an additional period of 44 h. The solvent was removed under vacuum, and the residue was extracted with ether (100 mL) and filtered. Hexane (50 mL) was added to the filtrate, and the solution was left under a nitrogen flow to give a mixture of crystals and oil. The oil was washed off with Skelly-F, and the crystals were dried under vacuum: yield 1.6 g (48.5%), mp 200−205 °C. It was found to have two isomers (**1A** and **1B**) in solution. In $CDCl_3$, the isomer ratio **1A**/**1B** was 2:1. In $C_6D_5CD_3$, the ratio was 2:3, and in a 1:1 mixture of $CDCl_3$ and $C_6D_5CD_3$ (only ^{31}P), the ratio was 2:1.5. The isomer ratio was obtained from ^{31}P and ^{1}H NMR signals except as noted for the mixture of $CDCl_3$ and $C_6D_5CD_3$. The isomer ratio was the same in the ^{31}P NMR spectra as that observed in the ^{1}H NMR spectra. The chemical shifts were independent of temperature as determined by ^{31}P NMR spectral measurements. ^{1}H NMR ($CDCl_3$): (**1A**) 1.43 (s, 18 H, *t*-Bu), 2.37 (s, 6 H, aryl-*Me*), 3.21 (qd, 2 H, 8.3, 4.0 Hz), 4.53 (qd, 2 H, 8.3, 2.5 Hz), 4.68 (qd, 2 H, 8.7, 5.1 Hz), 7.39 (s, 2 H, aryl), 7.75 (s, 2 H, aryl); (**1B**) 1.36 (s, 18 H, *t*-Bu), 2.32 (s, 6 H, aryl-*Me*), 4.29 (m, 4 H), 4.43 (qd, 2 H, 6.5, 2.0 Hz), 7.39 (s, 2 H, aryl), 7.56 (s, 2 H, aryl). ^{1}H NMR ($C_6D_5CD_3$): (**1A**) 1.28 (s, 18 H, *t*-Bu), 1.95 (s, 6 H, aryl-*Me*), 3.38 (qd, 2 H, 8.5, 3.6 Hz), 4.52 (qd, 2 H, 8.1, 2.5 Hz), 4.97 (qd, 2 H, 8.9, 5.2 Hz), 7.13 (s, 2 H, aryl), 7.96 (s, 2 H, aryl); (**1B**) 1.32 (s, 18 H, *t*-Bu), 1.87 (s, 6 H, aryl-*Me*), 4.21 (m, 4 H), 4.39 (qd, 2 H, 8.5, 6.5 Hz), 7.18 (s, 2 H, aryl), 7.70 (s, 2 H, aryl). ^{1}H NMR ($C_6D_5CD_3$ at 90 °C): 1.34 (s, 18 H, *t*-Bu), 1.97 (s, 6 H, Me), 4.33 (br, 6 H, OCH_2CF_3), 7.21 (s, 2 H, aryl-CH), 7.76 (s, br, 2 H, aryl-CH). ^{31}P NMR ($CDCl_3$): (**1A**) −85.5; (**1B**) −73.1. ^{31}P NMR ($C_6D_5CD_3$): (**1A**) −85.5; (**1B**) −74.2. ^{31}P NMR ($C_6D_5CD_3$ at 92 °C): (**1A**) −85.2; (**1B**) −74.7. ^{31}P NMR: ($CDCl_3$/$C_6D_5CD_3$ 1:1): (**1A**) −85.3; (**1B**) −73.3. ^{31}P NMR (solid): −82.6 (relative to $CaHPO_4$ at −1.5). ^{19}F NMR: (**1A**) −75.30 (s, 3 F), −75.49 (s, 3 F), −76.89 (s, 3 F); (**1B**) −74.95 (s, 3 F), −75.41 (s, 6 F). Anal. Calcd for $C_{28}H_{34}F_9O_7PS$: C, 46.93; H, 4.78. Found: C, 46.83; H, 4.67.

[**Dioxythiobis(4-methyl-6-*tert*-butylphenoxy)](triphenoxy)phosphorane, $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OPh)_3$ (2).** To a solution of diol **6** (3.00 g, 7.68 mmol) and $P(OPh)_3$ (2.00 mL, 7.63 mmol) in ether (250 mL) was added an excess of (*i*-$Pr)_2NCl$ (1.60 mL, 10.88 mmol) with constant stirring at about 23 °C for 1 min. The resultant mixture was stirred for an additional period of 22 h and filtered. Hexane (50 mL) was added to the filtrate, and the solution was left under a nitrogen flow to give a mixture of crystals and brown oil. The oil was washed off with Skelly-F, and the crystals were dried under vacuum: yield 4.7 g (87.5%), mp 225−230 °C. ^{1}H NMR: 1.30 (s, 18 H, *t*-Bu), 2.30 (s, 6 H, aryl-*Me*), 6.92−7.35 (br m, 17 H, aryl), 7.67 (s, 2 H, aryl). ^{31}P NMR: −80.54. ^{31}P NMR (solid): −76.8 (relative to $CaHPO_4$ at −1.5). Anal. Calcd for $C_{40}H_{43}O_7PS$: C, 68.75; H, 6.20. Found: C, 68.41; H, 6.14.

[Dioxythiobis(4-methyl-6-*tert*-butylphenoxy)](phenoxy)(1,2-benzendioxy)phosphorane, $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OPh)(C_6H_4O_2)$ (3). A solution of phosphorane **2** (1.49 g, 2.13 mmol) and catechol (0.240 g, 2.18 mmol) in toluene (40 mL) was heated under reflux for 1 h. Since the reaction was not complete (^{31}P NMR evidence), it was further refluxed for 11 h. The solvent was removed under vacuum, and the residue was extracted with ether (150 mL). The residue had about 21% of the required phosphorane, and the rest consisted of two phosphates (11.46 and −7.29 ppm; corresponding to 27 and 52%, respectively). The ether extract had 50% of the required phosphorane, and the rest consisted of phosphates (−18.3 and −19.38 ppm; corresponding to 20 and 30%, respectively). Solvent was removed from the extract, and the residue was dissolved in a dichloromethane/hexane (1:1) mixture. The solution was left under a nitrogen flow which resulted in a mixture of crystals and oil. The oil was washed off with Skelly-F, and the crystals were separated by picking manually and dried under vacuum: yield 0.20 g (15%), mp >250 °C. ^{1}H NMR: 1.56 (s, 18 H, *t*-Bu), 2.35 (s, 6 H, aryl-*Me*), 6.67−7.16 (br m, 9 H, aryl), 7.43 (s, 2 H, aryl), 7.61 (s, 2 H, aryl). ^{31}P NMR: −53.7. Anal. Calcd for $C_{34}H_{37}O_7PS$: C, 65.79; H, 6.01. Found: C, 65.38; H, 5.94.

[Dioxythiobis(4,6-di-*tert*-butylphenoxy)]tris(2,2,2-trifluoroethoxy)phosphorane, $O_2S[(t\text{-Bu})_2C_6H_2O]_2P(OCH_2CF_3)_3$ (4). To a solution of diol **7** (2.15 g, 4.53 mmol) and $P(OCH_2CF_3)_3$ (1.00 mL, 4.53 mmol) in ether (200 mL) was added an excess of (*i*-$Pr)_2NCl$ (1.00 mL, 6.80 mmol) with constant stirring at about 23 °C for 1 min. The resultant mixture was stirred for an additional period of 44 h. The solvent was removed under vacuum, and the residue was extracted with ether (100 mL) and filtered. Hexane (50 mL) was added to the filtrate, and the solution left was under a nitrogen flow to give a mixture of crystals and brown oil. The oil was washed off with Skelly-F, and the crystals were dried under vacuum: yield 2.1 g (58%), mp >250 °C. It was found to have two isomers (**4A** and **4B**) in solution. In $CDCl_3$, the isomer ratio **4A**/**4B** was 3.2:1. In $C_6H_5CH_3$ (only ^{31}P), the ratio was 0.87:1, and in a 1:1 mixture of $CDCl_3$ and $C_6H_5CH_3$ (only ^{31}P), the ratio was 1.8:1. The isomer ratio from the ^{31}P NMR spectrum was the same as observed in the ^{1}H NMR spectrum for $CDCl_3$. In the other two solvent systems, only the ^{31}P NMR spectra were recorded. ^{1}H NMR ($CDCl_3$): (**4A**) 1.32 (s, 18 H, *t*-Bu), 1.45 (s, 18 H, *t*-Bu), 3.19 (qd, 2 H, 8.4, 3.0 Hz), 4.53 (qd, 2 H, 8.3, 2.5 Hz), 4.70 (qd, 2 H, 8.9, 5.4 Hz), 7.60 (d, 2 H, 2.5 Hz, aryl), 7.94 (s, 2 H, 2.5 Hz, aryl); (**4B**) 1.32 (s, 18 H, *t*-Bu), 1.39 (s, 18 H, *t*-Bu), 4.28 (qd, 4 H, 8, 6 Hz, poorly resolved), 4.46 (qd, 2 H, 8.3 Hz, J_{PH} not resolved), 7.64 (s, 2 H, aryl), 7.76 (s, 2 H, aryl). ^{1}H NMR ($C_6D_5CD_3$, 298 K): (**4A**) 1.07 (s, 18 H, *t*-Bu), 1.32 (s, 18 H, *t*-Bu), 3.36 (m, 2 H), 4.50 (m, 2 H), 5.00 (m, 2H), 7.64 (s, 2 H, aryl), 8.29 (s, 2 H, aryl); (**4B**) 1.17 (s, 18 H, *t*-Bu), 1.38 (s, 18 H, *t*-Bu), 4.20 (m, 4 H), 4.38 (m, 2 H), 7.55 (s, 2 H, aryl), 8.14 (s, 2 H, aryl). ^{1}H NMR ($C_6D_5CD_3$ at 90 °C (363 K)): 1.16 (s, 18 H, *t*-Bu), 1.38 (s, 18 H, *t*-Bu), 4.39 (br, 6 H, OCH_2CF_3), 7.61 (s, 2 H, aryl-CH), 8.15 (s, br, 2 H, aryl-CH). ^{31}P NMR ($CDCl_3$): (**4A**) −85.7; (**4B**) −73.3. ^{31}P NMR ($C_6H_5CH_3$): (**4A**) −85.3; (**4B**) −73.6. ^{31}P NMR: ($CDCl_3$)/$C_6H_5CH_3$ 1:1): (**4A**) −84.7; (**4B**) −72.6. ^{19}F NMR: (**4A**) −75.31 (s, 3 F), −75.47 (s, 3 F), −77.10 (s, 3 F); (**4B**) −74.96 (s, 3 F), −75.47 (s, 6 F). Anal. Calcd for $C_{34}H_{46}F_9O_7PS$: C, 50.99; H, 5.79. Found: C, 51.14; H, 5.93.

[**Dioxythiobis(4,6-di-*tert*-butylphenoxy)](triphenoxy)phosphorane, $O_2S[(t\text{-Bu})_2C_6H_2O]_2P(OPh)_3$ (5).** To a solution of diol **7** (3.65 g, 7.69 mmol) and $P(OPh)_3$ (2.00 mL, 7.63 mmol) in ether (250 mL) was added an excess of (*i*-$Pr)_2NCl$ (1.60 mL, 10.88 mmol) with constant stirring at about 23 °C for 1 min. The resultant mixture was stirred for an additional period of 22 h and filtered. Hexane (50 mL) was added to the filtrate, and the solution was left under a nitrogen flow to give a mixture of crystals and brown oil. The oil was washed off with Skelly-F, and the crystals were dried under vacuum: yield 5.1 g (87%), mp 213−216 °C. ^{1}H NMR: 1.31 (s, 18 H, *t*-Bu), 1.33 (s, 18 H, *t*-Bu), 6.86−7.86 (br m, 19 H, aryl). ^{31}P NMR: −80.6. Anal. Calcd for $C_{46}H_{55}O_7PS$: C, 70.56; H, 7.08. Found: C, 70.73; H, 7.22.

(20) Bock, H.; Kompa, K. L. *Chem. Ber*. **1996**, *99*, 1347.

(21) (a) Riddick, J. A.; Bunger, W. B., *Organic Solvents*: *Physical Properties and Methods of Purification*, 3rd ed.; Techniques of Chemistry Series; Wiley Interscience: New York, 1970; Vol. II. (b) Vogel, A. I. *Textbook of Practical Organic Chemistry*; Longman: London, 1978.

(22) Pastor, S. D.; Spivak, J. D.; Steinhuebel, L. P. *J. Heterocycl. Chem*. **1984**, *21*, 1285.

Table 1. Crystallographic Data for Compounds **1**−**5**

compound	**1**	**2**	**3**	**5**	**4**
formula	$C_{28}H_{34}F_9O_7PS$	$C_{40}H_{43}O_7PS$	$C_{34}H_{37}O_7PS$	$C_{46}H_{55}O_7PS$	$C_{34}H_{46}F_9O_7PS$
form wt	716.58	698.77	620.67	782.93	800.74
cryst syst	triclinic	triclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$Pcm2_1$ (No. 26)
cryst size (mm)	0.30 × 0.55 × 0.75	0.25 × 0.40 × 0.55	0.15 × 0.50 × 0.90	0.54 × 0.70 × 1.00	0.45 × 0.50 × 1.00
a (Å)	10.319(3)	10.377(1)	12.398(3)	10.564(8)	9.467(4)
b (Å)	11.693(5)	11.672(2)	16.355(5)	10.271(2)	11.145(2)
c (Å)	14.025(2)	15.301(2)	17.521(5)	39.193(7)	18.798(4)
α (deg)	91.58(2)	81.58(1)	70.44(3)	90	90
β (deg)	89.94(2)	85.36(1)	86.78(2)	92.90(3)	90
γ (deg)	102.02(2)	79.91(1)	82.37(3)	90	90
V (Å^3)	1654.5(9)	1802.0(4)	3318(2)	4247(2)	1983(1)
Z	2	2	4	4	2
D_{calcd} (g/cm^3)	1.438	1.288	1.243	1.224	1.341
$\mu_{MoK\alpha}$ (cm^{-1})	2.39	1.84	1.91	1.63	2.07
total reflns	3775	2058	7621	4864	1259
reflns with $I > 2\sigma_I$	3140	1633	4828	3807	1036
R^a	0.0775	0.0306	0.0639	0.1148	0.1950
$R_w{}^b$	0.2051	0.0746	0.1623	0.3165	0.4900

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

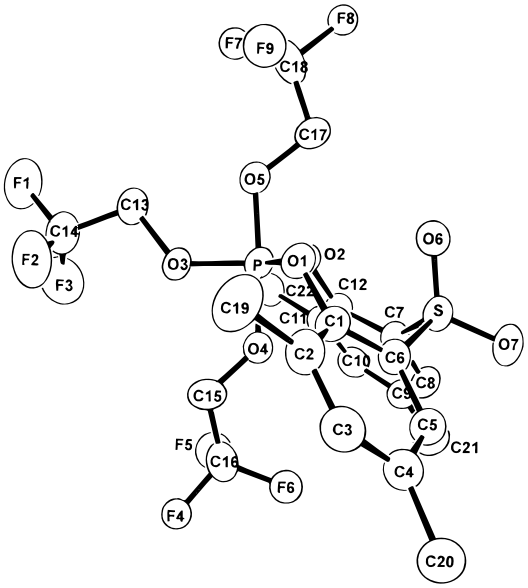


Figure 1. ORTEX diagram of $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OCH_2CF_3)_3$ (**1**). The terminal carbon atoms at C19 and C22 (C23−C28) are omitted for clarity. Only one set of the disordered fluorine atoms on C16 and C18 are shown.

(B) 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.[23]

The crystals, which were all colorless, 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 $3° \le 2\theta_{MoK\bar{\alpha}} \le 43°$ 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[24a] and SHELXL-93 for refinement.[24b] All of the non-hydrogen atoms that were not disordered were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (for methyl hydrogen atoms) on the bonded carbon atoms. The final agreement factors are based on the reflections with $I \ge 2\sigma_I$. Crystallographic data are summarized in Table 1.

(23) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.
(24) (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473. (b) Sheldrick, G. M. *SHELXL-93: program for crystal structure refinement*; University of Gottingen, 1993.

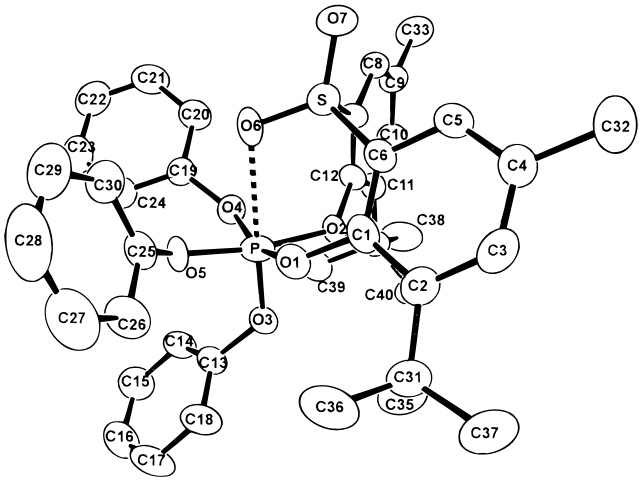


Figure 2. ORTEX diagram of $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OPh)_3$ (**2**).

The fluorines bonded to C16 and C18 of compound **1** have a rotational disorder and were refined in two sets of positions with equal occupancy. All of the C−F distances and angles were restrained to be similar.

Compound **4** has a more complicated disorder. A mirror plane (*x*,0,*z*) passes through the sulfur bisecting the SO_2 oxygen atoms. This places the phosphoranyl moiety, $(CF_3CH_2O)_3PO_2$, on either side of the SO_2 group with equal occupancy. Also, the trifluoroethoxy groups are disordered due to the presence of oppositely facing phosphoranyl moieties in neighboring molecules which have oppositely placed trifluoroethoxy groups. Another mirror plane (*x*,−0.5,*z*) passes through two of the CF_3 carbon atoms and further increases the complication. The *x*,0,*z* plane passes through the remaining CF_3 carbon. Due to these problems, the structure was very unsatisfactory. However, the geometry around the phosphorus atom was adequately resolved and is very similar to that of compound **1**. The bond parameters around the phosphorus atom and around the sulfur atom are given in Table 5. All of the C−C distances and angles of the *tert*-butyl groups excluding the attachments to the phenyl rings were restrained. Similarly, all of the C−F distances were restrained.

Results and Discussion

The atom-labeling schemes for **1**−**3** and **5** are shown in the plots of Figures 1−4, respectively. Selected bond parameters are presented in Tables 2−6 for **1**−**5**, respectively. All figures are ORTEX[25] diagrams with thermal ellipsoids at the 40% probability level. All hydrogen atoms are omitted for clarity.

(25) ORTEX 3.1d; McArdle, P., Crystallography Centre, Chemistry Department, University College Galway, Ireland.

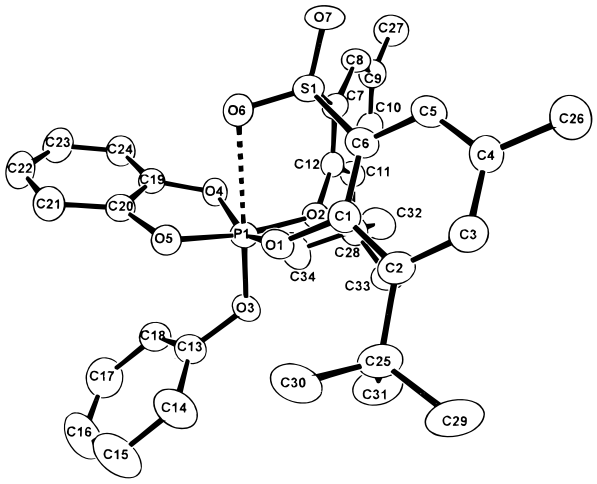


Figure 3. ORTEX diagram of $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OPh)(C_6H_4O_2)$ (**3**).

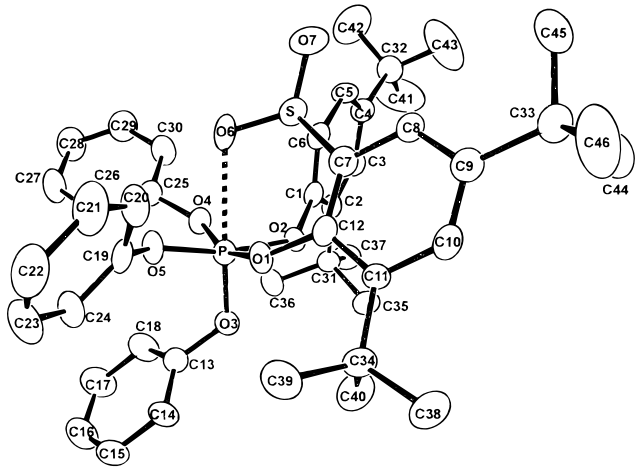
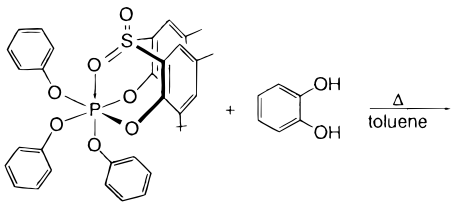
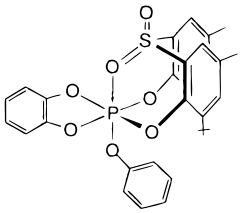


Figure 4. ORTEX diagram of $O_2S[(t\text{-Bu})_2C_6H_2O]_2P(OPh)_3$ (**5**).

Syntheses. The preparation of the pentaoxyphosphoranes **1**, **2**, **4**, and **5** consisted of an oxidative addition reaction of the corresponding phosphite with one of the diols, **6** or **7**, in ether solution in the presence of $(i\text{-Pr})_2NCl$. Yields ranged from 48 to 88%. Synthesis of cyclic phosphorane **3** resulted from a displacement reaction of **2** with catechol in toluene solution as shown in eq 1. The yield in this case was 15%.



2



+ 2PhOH (**1**)

3

Basic Structures. The X-ray studies reveal that **1** has a trigonal bipyramidal geometry with the diequatorially placed ring in an *anti* conformation, *i.e.*, a chair−boat arrangement.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OCH_2CF_3)_3$ (**1**)

P−O2	1.602(4)	P−O4	1.648(4)
P−O3	1.602(4)	S−O7	1.431(4)
P−O1	1.605(4)	S−O6	1.439(4)
P−O5	1.646(4)		
O2−P−O3	122.8(2)	O2−P−O4	91.1(2)
O2−P−O1	116.4(2)	O3−P−O4	88.4(2)
O3−P−O1	120.7(2)	O1−P−O4	93.8(2)
O2−P−O5	89.6(2)	O5−P−O4	176.2(2)
O3−P−O5	88.1(2)	O7−S−O6	118.3(3)
O1−P−O5	89.3(2)		

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OPh_3)$ (**2**)

S−O7	1.433(3)	P−O5	1.652(5)
S−O6	1.452(3)	P−O1	1.671(3)
P−O3	1.604(3)	P−O2	1.707(4)
P−O4	1.637(3)	P−O6	2.487(3)
O7−S−O6	117.7(2)	O4−P−O2	87.5(2)
O3−P−O4	101.7(2)	O5−P−O2	169.7(2)
O3−P−O5	99.1(2)	O1−P−O2	87.5(2)
O4−P−O5	90.9(2)	O3−P−O6	178.3(2)
O3−P−O1	100.5(1)	O4−P−O6	79.7(1)
O4−P−O1	157.3(2)	O5−P−O6	81.7(1)
O5−P−O1	90.1(2)	O1−P−O6	78.0(1)
O(3)−P−O2	91.2(2)	O2−P−O6	87.9(1)

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(O_2C_6H_4)$ (OPh) (**3**)[a]

S1−O7	1.434(4)	S1′−O7′	1.432(4)
S1−O6	1.435(4)	S1′−O6′	1.435(4)
P1−O3	1.601(4)	P1′−O3′	1.591(5)
P1−O1	1.632(4)	P1′−O1′	1.633(5)
P1−O4	1.649(4)	P1′−O4′	1.657(5)
P1−O2	1.656(4)	P1′−O2′	1.663(4)
P1−O5	1.667(4)	P1′−O5′	1.663(5)
P1−O6	2.607(5)	P1′−O6′	2.605(5)
O7−S1−O6	118.5(3)	O7′−S1′−O6′	118.4(3)
O3−P1−O1	103.0(2)	O3′−P1′−O1	101.0(2)
O3−P1−O4	105.4(2)	O3′−P1′−O4′	104.8(2)
O1−P1−O4	151.6(2)	O1′−P1′−O4′	154.2(2)
O3−P1−O2	93.2(2)	O3′−P1′−O2′	93.7(2)
O1−P1−O2	90.1(2)	O1′−P1′−O2	89.8(2)
O4−P1−O2	88.0(2)	O4′−P1′−O2′	87.4(2)
O3−P1−O5	98.6(2)	O3′−P1′−O5′	101.2(2)
O1−P1−O5	84.8(2)	O1′−P1′−O5′	85.4(2)
O4−P1−O5	91.3(2)	O4′−P1′−O5′	90.7(2)
O2−P1−O5	167.9(2)	O2−P1′−O5′	165.0(2)
O3−P1−O6	178.8(2)	O3′−P1′−O6′	176.9(2)
O1−P1−O6	76.5(2)	O1′−P1′−O6′	76.8(2)
O4−P1−O6	75.1(2)	O4′−P1′−O6′	77.5(2)
O2−P1−O6	87.9(2)	O2′−P1′−O6′	88.6(2)
O5−P1−O6	80.3(2)	O5′−P1′−O6′	76.6(2)

[a] Compound **3** has two independent molecules per unit cell.

This is evident in Figure 1. The P−O distance to the nearest sulfone oxygen atom P−O(6) is 3.345(4) Å, essentially the same as the sum of the van der Waals' radii of 3.35 Å.[26a] In contrast, **2** is octahedral due to coordination with an oxygen atom of the sulfonyl group. Here, the ring is in a *syn* conformation, *i.e.*, a boat−boat arrangement (Figure 2). The P−O distance involving the sulfonyl group is 2.487(3) Å, approximately midway between the sum of the P−O covalent radii of 1.83 Å[26b] and the van der Waals' sum, 3.35 Å. Like **2**, cyclic phosphorane **3**, which results from **2** by reaction with catechol, is octahedrally coordinated with a similar conformation for the ring containing the sulfonyl group (Figure 3). The P−O6 distance from an oxygen atom of the sulfonyl group is 2.607(5) Å. Phosphorane **5** which is substituted with an additional *tert*-butyl group on

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

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for $O_2S[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)_3$ (**4**)

S−O6	1.42(2)	P−O1	1.63(3)
P−O4	1.54(2)	P−O2	1.71(2)
P−O5	1.61(3)	P−O3	1.74(4)
O6−S−O6′ [a]	118(2)	O1−P−O2	110(2)
O4−P−O5	176(2)	O4−P−O3	96(1)
O4−P−O1	91(2)	O5−P−O3	85(1)
O5−P−O1	91(2)	O1−P−O3	127(1)
O4−P−O2	92(2)	O2−P−O3	122(1)
O5−P−O2	85(1)		

[a] O(6)′ is generated by *x*, −*y*, *z*.

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for $O_2S[(t\text{-}Bu)_2C_6H_2O]_2P(OPh)_3$ (**5**)[a]

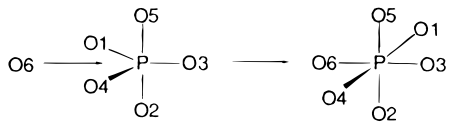
P−O3	1.599(8)	P−O2	1.679(7)
P−O4	1.611(7)	P−O6	2.546(9)
P−O5	1.615(7)	S−O7	1.425(8)
P−O1	1.645(7)	S−O6	1.435(8)
O3−P−O4	102.7(4)	O5−P−O2	166.5(4)
O3−P−O5	101.7(4)	O1−P−O2	86.6(4)
O4−P−O5	90.0(4)	O3−P−O6	177.6(3)
O3−P−O1	99.7(4)	O4−P−O6	79.0(3)
O4−P−O1	156.9(4)	O5−P−O6	79.8(3)
O5−P−O1	90.9(4)	O1−P−O6	78.4(3)
O3−P−O2	91.8(4)	O2−P−O6	86.6(3)
O4−P−O2	87.2(4)	O7−S−O6	117.6(5)

[a] Atoms are labeled to agree with the labeling in Figure 4.

each aryl component compared to **2**, also has a very similar octahedral structural arrangement (Figure 4). Here, the P−O6 distance is 2.546(9) Å. Phosphorane **4**, which is badly disordered, has a molecular geometry like that of **1**, *i.e.*, a trigonal bipyramid with the sulfonyl containing ring located diequatorially. Selected bond parameters are listed in Table 5.

A summary of pertinent bond parameters used to describe the degree of octahedral coordination is given in Table 7. Examination of this data indicates that the displacement toward an octahedron decreases in the order **2** > **5** > **3**, based on the shortness of the P−O interaction formed from the incoming donor oxygen atom of the sulfonyl group, 2.487(3) Å for **2**, 2.546(9) Å for **5**, and 2.606(5) Å for **3**. The latter distances correlate with an increase in the average *trans* basal angles which lie in the order 163.5(2)° for **2**, 161.7(4)° for **5**, and 159.7-(2)° for **3**. The *trans* basal angles refer to a square pyramid consisting of the five oxygen atoms of the pentaoxyphosphorane. The donor oxygen atom of the sulfonyl group then allows the coordinate from the square pyramid to the octahedron to be traversed.

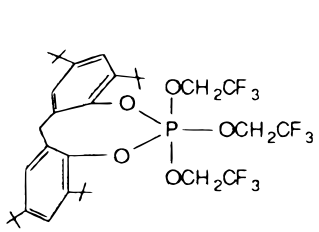
It is also noted that the largest of the two *trans* basal angles, O5−P−O2, for each of these octahedral-like phosphoranes has the longer pair of P−O bond distances. In this sense, the molecules have retained residual trigonal bipyramidal character where O5 and O2 represent axial atoms. The overall coordinate that is followed then is the approach of the incoming donor atom O6, *trans* to O3, in the equatorial plane bisecting the O4−P−O1 angle. This takes the trigonal bipyramid to a square pyramid on the way to an octahedron.



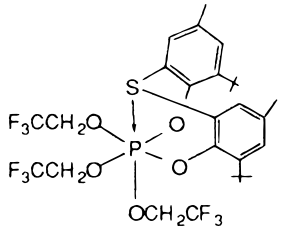
We have performed *ab initio* calculations on the pyridine/PF_5 system and have shown that this trajectory is followed,[1b] *i.e.*, as the pyridine molecule approaches TBP PF_5, it undergoes the Berry[27] bond bending process to form a square pyramid and then on further approach of pyridine, the square pyramid is transferred to the octahedron as the pyridine/PF_5 system reaches the minimum energy configuration.

With a more detailed method that we used[4] with pentaoxyphosphoranes having a graded series of octahedral geometries formed by P−S coordination, the degree of octahedral character, measured from an ideal square pyramid for phosphorus lies in the order **2** > **5** > **3**. In this method, the displacement of the phosphorus atom from the base of the associated square pyramid is determined from the average P−O bond distance to the four basal oxygen atoms and compared with the value of this displacement (0.431 Å) for a square pyramid having *trans* basal angles of 150°.[28−30] This order obtained in a more quantitative fashion agrees with the order toward increasing octahedral character discussed above. These values are included in Table 7 as footnote *a*.

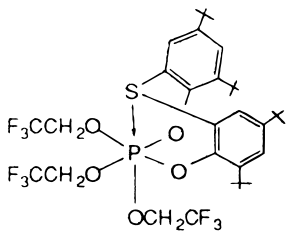
Isomerism. Both **1** and **4**, which have their rings in diequatorial positions in TBP geometries in the solid state, show the presence of two isomeric forms in solution by ^1H and ^{31}P NMR spectroscopy. These data are summarized in Table 8. Also, the ^{19}F NMR data indicate two isomers in $CDCl_3$ solution as is evident from the shifts recorded in the Experimental Section. Athough the isomer ratio varies with solvent for **1**, this ratio is found to be independent of temperature in the solvent examined, toluene-d_8. The fact that the ^{31}P chemical shifts of the two isomers in this solvent do not vary significantly with temperature indicates each structure is remaining unchanged. For each of the two isomers, **1A** and **4A** are assigned to the TBP structure found in the X-ray analysis. The higher of the two ^{31}P chemical shifts in each case has nearly the same value and is in agreement with the solid state ^{31}P shift associated with **1A** in Table 8. Further, the lower values of the three proton signals for **1A** and **4A** listed in Table 8 are assignable to one of the axial methylene resonances of the CF_3CH_2O groups, *i.e.*, those in the range of 3.19−3.38 ppm while the proton signals from 4.52 to 4.97 ppm correspond to the other axial and equatorial methylene resonances of the CF_3CH_2O group. This assignment is based on previous work by Denney and coworkers.[31] For example, in formulation **H**,[31] an upfield value for the methylene resonance of the CF_3CH_2O group was assigned to axial protons which are suggested to be in the shielding region of both aromatic components associated with the eight-membered ring when the ring is oriented in diequatorial sites of a trigonal bipyramid. The other methylene resonances



H [31]



I [4]



J [3]

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Table 7. Selected P−O Bond Parameters Measuring the Degree of Octahedral Coordination[a]

compd no.	bond distances (Å)						bond angles, (deg)		
	P−O(4)	P−O(1)	P−O(5)	P−O(2)	P−O(3)	P−O(6)	O(4)−P−O(1)	O(5)−P−O(2)	O(3)−P−O(6)
3	1.649(4)	1.632(4)	1.667(4)	1.656(4)	1.601(4)	2.607(5)	151.6(2)	167.9(2)	178.8(2)
	1.657(5)	1.633(5)	1.663(4)	1.663(4)	1.591(5)	2.605(5)	154.2(2)	165.0(2)	176.9(2)
5	1.611(7)	1.645(7)	1.615(7)	1.679(7)	1.599(8)	2.546(9)	156.9(4)	166.5(4)	177.6(3)
2	1.637(3)	1.671(3)	1.652(5)	1.707(4)	1.604(3)	2.487(3)	157.3(2)	169.7(2)	178.3(2)

[a] The degree of structural displacement from a square pyramid toward an octahedron based on the distance of the phosphorus atom from the basal plane of four oxygen atoms is 44.5% (**2**), 39.6% (**5**), and 32.4% (**3**).

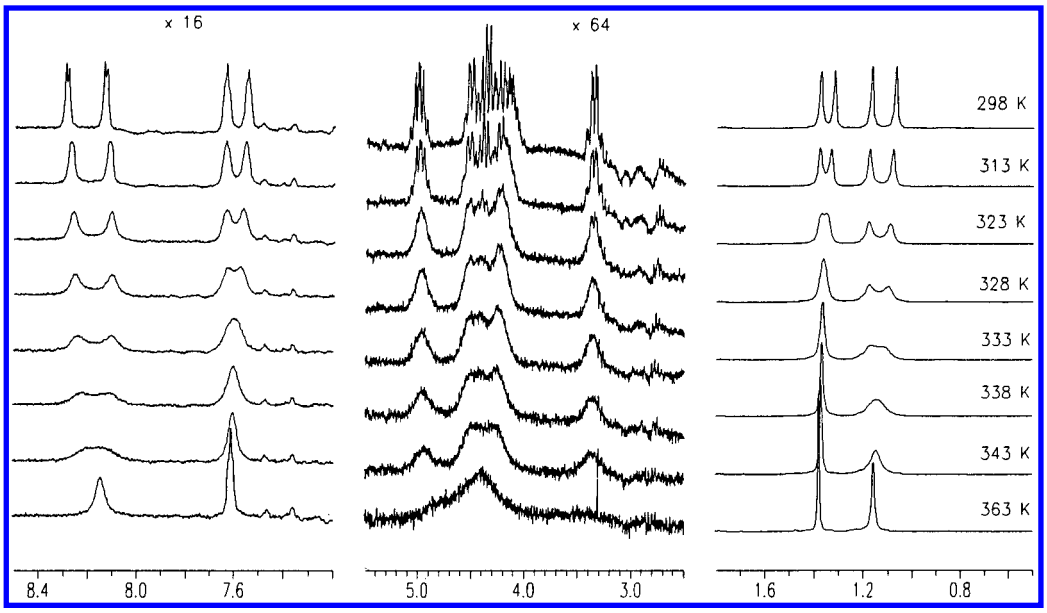

Figure 5. VT ^{1}H NMR spectra of **4** in toluene-d_8. From left to right, the signals displayed are the aromatic ring protons, the methylene protons, and the *tert*-butyl protons. The individual values are cited in the Experimental Section.

of the trifluoroethoxy group are in the 4−5 ppm region. A similar interpretation is involved here as well. As apparent in Figure 1 for **1**, the axial CF_3CH_2O group has C(15) of the methylene unit in the shielding region of the aromatic components. The same holds true for the structure of **4**. The presence of two separate signals for the axial methylene group for both **1A** and **4A** also is consistent with the X-ray structures where the ring in a static conformation has the SO_2 group located closer to one of the axial trifluoroethoxy ligands (Figure 1).

The two methylene ^{1}H NMR signals each for **1B** and **4B** in the intensity ratio of 2:1 are close to those for **I**[4] and **J**.[3] For these hexacoordinate phosphoranes, three equally intense proton signals assignable to the methylene groups of the triflluoroethoxy ligands are at 4.10, 4.28, and 4.69 ppm for **I** and at 4.10, 4.20, and 4.58 ppm for **J**. The ^{31}P NMR signals are at −82.3 ppm for **I** and −82.4 ppm for **J** in $CDCl_3$. A solid state ^{31}P NMR signal for **J** relative to $CaHPO_4$ appeared at −82.9 ppm which indicates that the solid state structure is retained in solution.

The 2:1 intensity ratio and magnitude of the ^{1}H chemical shifts for the methylene protons for **1B** and **4B** relative to **1A** and **4A**, respectively, are consistent with hexacoordinate formulations similar to that known for **I** and **J**. The lower intensity ^{1}H NMR signal for **1B** and **4B** would be expected to be associated with the trifluoroethoxy ligand *trans* to the P−O donor interaction formed from the ring sulfonyl group. The observance of two ^{19}F NMR signals each, assigned to **1A** and

Table 8. ^{31}P NMR and ^{1}H NMR (Methylene Region) Chemical Shifts (ppm) for Isomers of Pentaoxyphosphoranes **1** and **4**

^{31}P NMR

solvent	**1A** (23 °C)	**1A** (92 °C)	**1B** (23 °C)	**1B** (92 °C)	isomer ratio[b] **A/B**
$CDCl_3$	−85.5		−73.1		2:1
$C_6D_5CD_3$	−85.5	−85.2	−74.2	−74.7	2:3
$CDCl_3$:$C_6D_5CD_3$ (1:1)	−85.3		−73.3		2:1.5
solid state	−84.1[a]				
	4A (23 °C)		**4B** (23 °C)		
$CDCl_3$	−85.7		−73.3		3.2:1
$C_6H_5CH_3$	−85.3		−73.6		0.87:1
$CDCl_3$:$C_6H_5CH_3$ (1:1)	−84.7		−72.6		1.8:1

^{1}H NMR

solvent	**1A** (23 °C)	**1B** (23 °C)	isomer ratio[b] **A/B**
$CDCl_3$	3.21 (2H)		2:1
	4.53 (2H)	4.29 (4H)	
	4.68 (2H)	4.43 (2H)	
$C_6D_5CD_3$	3.38 (2H)		2:3
	4.52 (2H)	4.21 (4H)	
	4.97 (2H)	4.39 (2H)	
	4A (23 °C)	**4B** (23 °C)	
$CDCl_3$	3.19 (2H)		3.2:1
	4.53 (2H)	4.28 (4H)	
	4.70 (2H)	4.46 (2H)	

[a] The observed value is −82.6 ppm measured relative to $CaHPO_4$ at −1.5 ppm. The table value is corrected to account for this shift. [b] The isomer ratios for **1** and **4** are the same whether determined from the ^{1}H or ^{31}P NMR spectra.

(28) Holmes, R. R. *Pentacoordination Phosphorus - Structure and Spectroscopy*; ACS Monograph 175; American Chemical Society: Washington, DC, 1980; Vol. I.
(29) 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.
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(31) Abdou, W. M.; Denney, D. B.; Denney, D. Z.; Pastor, S. D. *Phosphorus Sulfur* **1985**, *22*, 99.

Table 9. Variable Temperature ^{1}H NMR Data for **1** and **4** in Toluene-d_8[a]

	compound **1**			compound **4**		
group	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^{\ddagger}$[d]	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^{\ddagger}$[d]
t-Bu	9.38	323	17.03	19.86	338	17.35
R[b]	15.88	333	17.23	10.82	328	17.21
aryl-CH	9.02	323	17.06	17.68	333	17.16
aryl-CH	53.04	353	17.46	31.4	343	17.31
^{31}P	1413	398 ± 6[c]		1461	400 ± 4[c]	

[a] $\Delta G^{\ddagger} = 1.987T_c[23 + \ln(T_c/\Delta\upsilon)]$ (in kcal/mol).[35] [b] R = Me for **1** and *t*-Bu for **4**. [c] Calculated values. [d] Mean $\Delta G^{\ddagger} = 17.2 \pm 0.3$ and 17.3 ± 0.2 kcal/mol for **1** and **4**, respectively.

4A, and three ^{19}F NMR signals each in the ratio of 2:1, assigned to **1B** and **4B**, is in accord with trigonal bipyramidal and octahedral geometries for the **A** and **B** isomers of **1** and **4**, respectively.

A TBP with an axial−equatorial ring arrangement is another possibility for **1B** and **4B**. However, for this structural type, an intensity ratio of methylene proton signals of 2:1 is expected where the higher intensity signal would be associated with the two equatorial trifluoroethoxy ligands. This geometry would give two types of *tert*-butyl signals for **1B**, whereas only one was observed. For **4B**, four types of *tert*-butyl signals would be expected; however, only two were observed.

It is also noteworthy that isomers appear in solution only for phosphoranes containing the SO_2 group[18] which serves as a bridge in the eight-membered ring. Cyclic phosphoranes with methylene[3,32,33] or sulfur[3−7,34] bridges in place of the sulfone group lack evidence for isomeric representations. The sulfur atom acts as a stronger donor in comparison to the sulfone group.[18] Perhaps this factor acts to increase the energy difference between penta- and hexacoordinated structures relative to those with the sulfone group. The lack of appearance of isomers for cyclic phosphoranes with a ring containing methylene bridge is expected since it does not act as a donor group to yield a hexacoordinated isomer.

When the ^{1}H NMR spectra are studied as a function of temperature, coalescence of signals associated with each of the isomers that are present at room temperature is observed for both **1** and **4**. Figure 5 illustrates representative data for **4** over the range from 298 K (25 °C) to 363 K (90 °C). Evaluation of these data yields activation energies ($\Delta G^{\ddagger}$) of 17.2 ± 0.3 kcal/mol for **1** and 17.3 ± 0.2 kcal/mol for **4**. These values were obtained from the separation of signals at 298 K and the coalescence temperatures summarized in Table 9 upon application of the expression $\Delta G^{\ddagger} = 1.987\ T_c\ [23 + \ln(T_c/\Delta\nu)]$.[35] Although the mean values of $\Delta G^{\ddagger}$ from the various line coalescences average to a small deviation, the method used does not allow this accuracy. More likely the uncertainty is of the order of ±1 kcal/mol. From these data, it is estimated that coalescence of ^{31}P NMR signals would take place at approximately 126 ± 6 °C for both **1** and **4**. It is noted that some broadening of the ^{31}P NMR signals occurs when the temperature is increased to 90 °C.

For hexacoordinated isomeric structures of **1B** and **4B**, the exchange process would involve P−O cleavage from the donor sulfonyl group and a ring inversion from a *syn* to an *anti* conformation on going from the octahedral **B** isomers to the trigonal bipyramidal **A** isomers. We have invoked this type of inversion involving the same ring system in cyclic organosilanes containing ring sulfonyl[17] groups where the conformational change was *anti* ⇌ *anti* or *syn* ⇌ *syn* for different members of this series. The $\Delta G^{\ddagger}$ values for these cases are 9.1 and 11.0 kcal/mol, respectively. The latter value applies to silane **D** depicted in the Introduction. In addition, Berry pseudorotation[27] is required for the trigonal bipyramidal **A** isomers to allow equivalence of all the methylene proton signals as indicated at the higher temperature.

Summary and Conclusions

Pentaoxyphosphoranes with ring containing sulfonyl groups exhibit P−O donor action yielding octahedral structures (**2**, **3**, and **5**) when the acyclic ligands are phenoxy. With similar oxyphosphoranes that have trifluoroethoxy ligands (**1** and **4**), trigonal bipyramidal geometries prevail. The latter oxyphosphoranes are present in solution in isomeric forms as shown by NMR studies. The presence of an equilibrium between penta- and hexacoordinate isomers which exchange intramolecularly when heated is demonstrated. It is concluded that the isolation of isomers of phosphorus in solution with different coordination results from taking advantage of appropriate ligand combinations to tune the phosphorus electrophilicity such that the isomer energies are equalized. In this manner, the degree of donor action supplied by the weakly coordinating sulfonyl group is controlled.

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, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for **1**−**5**, and thermal ellipsoid figures for the second independent molecule of **3** and molecule **4** (33 pages). See any current masthead page for ordering and Internet access instructions.

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