

# Pentacoordination and Pseudopentacoordination via Sulfur Donor Action in Cyclic Phosphates and Phosphites<sup>1</sup>

David J. Sherlock, A. Chandrasekaran, Roberta O. Day, and Robert R. Holmes\*

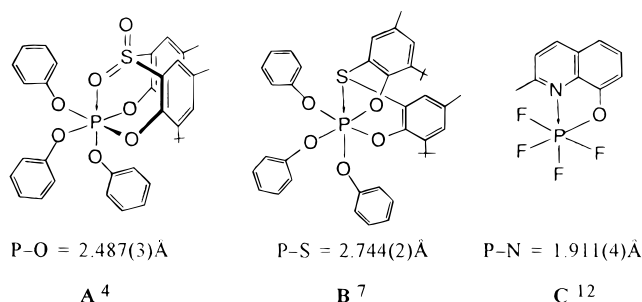
Department of Chemistry, Box 34510, University of Massachusetts, Amherst, Massachusetts 01003-4510

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New cyclic chlorophosphites  $S[(t\text{-Bu})_2\text{C}_6\text{H}_2\text{O}]_2\text{PCl}$  (**3**) and  $\text{CH}_2[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{PCl}$  (**6**) and the cyclic phosphate  $S[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P}(\text{O})\text{Cl}$  (**4**) were synthesized from the reaction of  $\text{PCl}_3$  or  $\text{POCl}_3$  with the appropriate diol. The aminophosphite  $S[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{PNMe}_2$  (**2**) was prepared by a chlorine displacement reaction from  $S[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{PCl}$  (**1**) with  $\text{Me}_2\text{NSiMe}_3$  while  $S[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P}(\text{O})(\text{OC}_6\text{Cl}_4\text{-}o\text{-OH})$  (**5**) resulted as a hydrolysis product of  $S[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{PCl}(\text{O}_2\text{C}_6\text{Cl}_4)$  (**7**). All of the cyclic compounds of tri- and tetraordinated phosphorus compounds **1–5** contained a sulfur atom as part of a flexible eight-membered ring while **6** incorporated a methylene group in place of the sulfur atom. X-ray studies on **1–6** revealed that the cyclic phosphites **1–3** undergo an increase in coordination geometry to a pseudo trigonal bipyramid (TBP) as a result of sulfur donor action while **4** and **5** experience a similar increase in forming a trigonal bipyramid. This is the first series where sulfur donor action results in an increase in coordination geometry for tri- and tetraordinated phosphorus compounds. The structural displacement toward a pseudo-TBP or TBP increased from 30.9% to 54.5% as the P–S distance decreased from 3.177(2) Å for **5** to 2.816(2) Å for **1**. <sup>31</sup>P NMR data support the retention of solid state structures in solution. These results are compared with series of cyclic phosphoranes which become octahedral provided by donor action by sulfur atoms present in similar ring systems. The degree of sulfur interaction in the lower coordinate series presented in this study is less than that for the phosphorane series in line with an increase in phosphorus atom electrophilicity expected for the more highly coordinated series. Comparison is made with other series with nitrogen and oxygen donor action leading to hexacoordination for pentacoordinate phosphorus compounds. The prevalence of donor action by sulfur, nitrogen, and oxygen atoms suggests that mechanistic criteria for nucleophilic displacement reaction may be subject to such action, *e.g.*, at active sites of phosphoryl transfer enzymes.

## Introduction

Previous work has shown that oxygen,<sup>1b,2–4</sup> nitrogen,<sup>2,3</sup> and sulfur ligands<sup>2,3,5–11</sup> function as electron pair donors causing an increase in coordination at phosphorus from pentacoordinate to hexacoordinate. Examples **A–C** illustrate this effect.<sup>4,7,12</sup> In recent work, we have used sulfur atoms<sup>5–10</sup> and sulfonyl groups<sup>1b,4</sup> as part of an eight-membered cyclic system to promote increased coordination in tetra- and penta-oxophosphoranes. For the penta-oxophosphoranes with a sulfur donor atom, a range of P–S distances from 2.88 to 2.33 Å is found<sup>5–9,11</sup> where the respective structural displacements vary from 44% to 70% along



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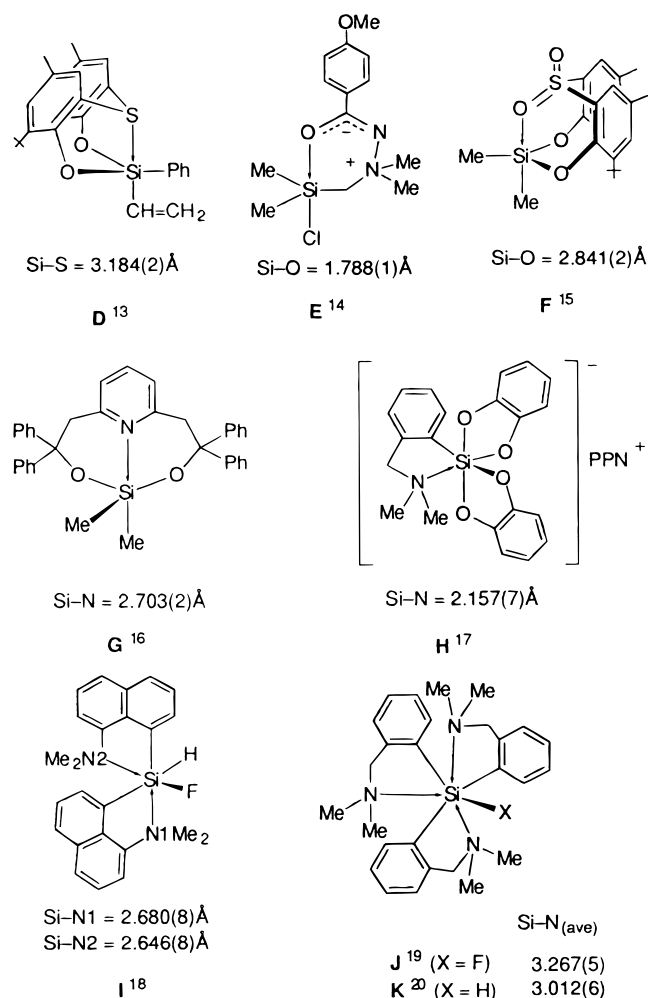
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a coordinate from a square pyramid toward an octahedron.<sup>7,9</sup> In the series of tetra-oxophosphoranes having sulfur coordination, the structural displacements range from 24% to 71% along this same coordinate with the respective P–S distances decreasing from 3.04 to 2.48 Å as octahedral character increases.<sup>10</sup>

Examination of a comparable area of hypervalent silicon chemistry shows that donor action provided by sulfur atoms, oxygen atoms, oxygen atoms of sulfonyl groups, and nitrogen atoms leads to higher coordinate geometries ranging from pentacoordinate to pseudoheptacoordinate. Examples **D–K** illustrate these structural forms.<sup>13–20</sup> As with phosphorus,<sup>2,21,22</sup>

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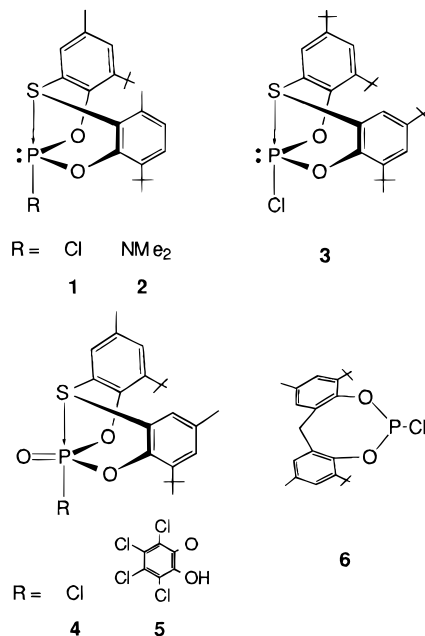
some of these are applicable as models for activated states or intermediates in nucleophilic substitution reactions of silicon.<sup>2,23</sup>



Of particular interest in the present context are series of organosilanes whose structures followed a trajectory from a tetrahedron ( $T_d$ ) toward a trigonal bipyramid (TBP) as a result of donor action by either a sulfur atom<sup>13,24,25</sup> or sulfonyl groups<sup>15</sup> present as part of an eight-membered ring system. **D**<sup>13</sup> and **F**<sup>15</sup>, respectively, are members of these series. In the sulfur series,<sup>24,25</sup> the Si-S distances ranged from 3.292(1) to 2.978(4) Å for members exhibiting this coordination. Linear interpolation between the Si-S van der Waals sum of 3.90 Å<sup>26</sup> and the sum of covalent radii of 2.20 Å<sup>27</sup> gave a displacement  $T_d \rightarrow$  TBP

ranging from 36% to 54%.<sup>13</sup> In the series containing the sulfonyl donor oxygen atom,<sup>15</sup> the Si-O distances for the three members were confined to a narrow range, 2.904(3)–2.841(2) Å, as the displacement  $T_d \rightarrow$  TBP increased from 41.2% to 44.9%. Here the van der Waals sum is 3.60 Å<sup>26</sup> and the sum of the covalent radii for the Si-O coordination is 1.91 Å.<sup>27</sup> Comparable series in phosphorus chemistry involving sulfur donor groups are lacking, although recent work by Corriu and co-workers<sup>28–31</sup> has shown that compounds of three- and four-coordinated phosphorus in constrained ring systems undergo donor action with nitrogen ligands with P-N distances ranging from 2.706(6)<sup>28</sup> to 3.011(4) Å.<sup>29</sup> These results are consistent with the fact that five-coordinated phosphorus has been widely postulated as an activated state in nucleophilic displacements occurring at tetracoordinate phosphorus.<sup>2,21,22,23a,32–34</sup> It seems reasonable that phosphorus in lower coordination states should be receptive to attachment to donor groups due to its inherent electrophilicity. Such action would represent the initial stage in a nucleophilic displacement, *i.e.*, prior to reaching the full pentacoordinated geometry that serves at or near the barrier state.

To investigate the likelihood of this process for phosphorus compounds containing sulfur donor atoms, the series of compounds **1–6** comprising phosphates **4** and **5** and phosphites **1–3**, and **6** was synthesized and the tendency of members to undergo an increase in coordination by sulfur donor action was examined. To accomplish this objective, X-ray analysis of their



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structures was obtained. In addition, <sup>1</sup>H and <sup>31</sup>P NMR spectra

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were obtained to assist in the examination of structural changes encountered in solution. For comparison of ring conformational changes, the X-ray structural study of **6** was carried out where a methylene group was present in place of a sulfur atom.

### Experimental Section

Phosphorus trichloride (Aldrich), (*N,N*-dimethylamino)trimethylsilane (Petrarch), and phosphorus oxychloride (Aldrich) were used as supplied. Triethylamine (Eastman) was distilled over potassium hydroxide. 2,2'-Thiobis(4-methyl-6-*tert*-butylphenol),<sup>7</sup> 2,2'-thiobis(4,6-di-*tert*-butylphenol),<sup>35</sup> 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol),<sup>36</sup> and 2,2'-thiobis(4-methyl-6-*tert*-butylphenyl)] chlorophosphite (**1**),<sup>10</sup> and 2,2'-thiobis[(4-methyl-6-*tert*-butylphenyl)oxy](1,2,3,4-tetrachlorophenylene-5,6-dioxy)chlorophosphorane (**7**)<sup>10</sup> were synthesized according to literature methods. Solvents were purified according to standard procedures.<sup>37</sup> Skelly C, which was employed as a solvent, is a petroleum ether fraction that boils in the 88–99 °C range. All 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 on solutions were recorded on a Bruker MSL300 FT-NMR spectrometer. A Bruker ASX-300 was used to record <sup>31</sup>P solid state NMR spectra. All proton spectra were recorded in CDCl<sub>3</sub>. Phosphorus NMR spectra were recorded in toluene. Chemical shifts are reported in ppm, downfield positive, and relative to tetramethylsilane (<sup>1</sup>H) or 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). All spectra were recorded at around 23 °C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

**S[(*t*-Bu)MeC<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>PNMe<sub>2</sub> (2).** To a solution of **1** (0.74 g, 1.7 mmol) in toluene (25 mL) was added (dimethylamino)trimethylsilane (0.30 mL, 1.8 mmol). The solution was then heated and refluxed for 1 h. The solution was allowed to cool and the solvent removed *in vacuo*. The residue was dissolved in dichloromethane (20 mL). Skelly C (20 mL) was added and the solution left under a stream of nitrogen to obtain the crystalline product (yield 0.38 g, 50%), mp 174–177 °C. <sup>1</sup>H NMR: 1.36 (s, *t*-Bu, 18 H), 2.24 (s, aryl-Me, 6 H), 2.88 (d, 9.4 Hz, NMe<sub>2</sub>, 6 H), 7.14 (d, 2.2 Hz, aryl, 2 H), 7.30 (d, 2.2 Hz, aryl, 2 H). <sup>31</sup>P NMR: 132.46. Anal. Calcd for C<sub>24</sub>H<sub>34</sub>NO<sub>2</sub>PS: C, 66.82; H, 7.89; N, 3.25. Found: C, 66.76; H, 8.05; N, 3.26.

**S[(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>PCl (3).** To a solution of phosphorus trichloride (1.50 mL, 17.2 mmol) in diethyl ether (300 mL) that was stirred at 0 °C were added dropwise 2,2'-thiobis(4,6-di-*tert*-butylphenol) (7.60 g, 17.2 mmol) and triethylamine (5.0 mL, 35.97 mmol) in diethyl ether (50 mL). On completion of the addition, the mixture was allowed to come to room temperature and stirred for 12 h. The solution was filtered and the solvent removed *in vacuo*. The residue was washed with Skelly F (20 mL) and dissolved in dichloromethane (40 mL). Skelly C (40 mL) was added and the solution left under a flow of nitrogen to obtain the crystalline product (yield 5.06 g, 58%), mp 143–147 °C. <sup>1</sup>H NMR: 1.31 (s, *t*-Bu, 18 H), 1.42 (s, *t*-Bu, 18 H), 7.41 (m, aryl, 2 H), 7.54 (d, 2.5 Hz, aryl, 2 H). <sup>31</sup>P NMR: 170.38. Anal. Calcd for C<sub>28</sub>H<sub>40</sub>ClO<sub>2</sub>PS: C, 66.34; H, 7.90. Found: C, 65.77, H, 7.82.

**S[(*t*-Bu)MeC<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>P(O)Cl (4).** To a solution of phosphorus oxychloride (0.53 mL, 5.6 mmol) in diethyl ether (100 mL) that was stirred at room temperature was added dropwise a solution of 2,2'-thiobis(4-methyl-6-*tert*-butylphenol) (2.00 g, 5.6 mmol) and triethylamine (2.00 mL, 14.4 mmol) in diethyl ether (100 mL). On completion of the addition, the mixture was stirred for 20 h. The solution was filtered and the solvent removed *in vacuo*. The residue was washed with Skelly F (30 mL) and dissolved in dichloromethane (50 mL). Skelly C was added and the solution left under a flow of nitrogen to obtain the crystalline product (yield 0.91 g, 37%), mp 184–187 °C.

<sup>1</sup>H NMR: 1.42 (s, *t*-Bu, 18 H), 2.29 (s, Me, 6 H), 7.21 (d, 1.8 Hz, aryl, 2 H), 7.38 (d, 1.8 Hz, aryl, 2 H). <sup>31</sup>P NMR: -9.49. Anal. Calcd for C<sub>22</sub>H<sub>28</sub>ClO<sub>3</sub>PS: C, 60.21; H, 6.39. Found: C, 59.63; H, 6.47.

**S[(*t*-Bu)MeC<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>P(O)(OC<sub>6</sub>Cl<sub>4</sub>-*o*-OH) (5).** Recrystallization of S[(*t*-Bu)MeC<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>PCl(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>), **7** (0.20 g, 0.3 mmol), from dichloromethane (15 mL) and wet acetonitrile (25 mL) gave **5** (yield 0.13 g, 67%), mp 217–220 °C. <sup>1</sup>H NMR: 1.32 (s, *t*-Bu, 18 H), 2.30 (s, Me, 6 H), 6.97 (s, OH, 1 H), 7.20–7.40 (m, aryl, 4 H). <sup>31</sup>P NMR: -16.62. Anal. Calcd for C<sub>28</sub>H<sub>29</sub>Cl<sub>4</sub>O<sub>5</sub>PS: C, 51.71; H, 4.46. Found: C, 51.34; H, 4.55.

**CH<sub>2</sub>[(*t*-Bu)MeC<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>PCl (6).** To a solution of phosphorus trichloride (1.50 mL, 17.2 mmol) in diethyl ether (100 mL) that was stirred at 0 °C was added dropwise a solution of 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol) (5.07 g, 14.9 mmol) and triethylamine (4.30 mL, 30.9 mmol) in diethyl ether (75 mL). On completion of the addition, the solution was allowed to come to room temperature and stirred for 24 h. The solution was filtered and the solvent removed *in vacuo*. The residue was dissolved in dichloromethane (10 mL). Skelly C (15 mL) was added and the solution allowed to stand under a flow of nitrogen to obtain the crystalline product (yield 2.23 g, 38%), mp 145–147 °C. <sup>1</sup>H NMR: not recorded due to decomposition in solution. <sup>31</sup>P NMR: solid state 165.71. Anal. Calcd for C<sub>23</sub>H<sub>30</sub>ClO<sub>2</sub>P: C, 68.24; H, 7.42. Found: C, 68.67; H, 7.49.

**X-ray Studies.** The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Details of the experimental procedures have been described previously.<sup>38</sup>

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  $3^\circ \leq 2\theta_{\text{MoK}\alpha} \leq 43^\circ$  at  $23 \pm 2$  °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<sup>39a</sup> and SHELXL-93 for refinement.<sup>39b</sup> All of 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  $I \geq 2\sigma_I$ . In compound **3** one of the *tert*-butyl methyl groups was disordered. It was refined isotropically in two positions with equal occupancy (shown in Figure 3 with primed labels). Despite repeated attempts, a good quality crystal was not obtained for **2**. The poor quality of the data and the pseudosymmetry in the molecule made it impossible to complete the structure refinement. Hence, it was left at the isotropic level and no hydrogens were included in the calculations.<sup>40</sup> Crystallographic data are summarized in Table 1.

### Results and Discussion

The atom-labeling schemes for **1–6** are given in the ORTEX plots<sup>41</sup> 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 listed in Table 2.

**Syntheses.** The cyclic phosphites **2**, **3**, and **6** and the cyclic phosphates **4** and **5** represent new compounds. The chlorophosphate **1** had been reported previously.<sup>10</sup> The aminophosphate **2** was synthesized by displacement of the chlorine atom in **1** with Me<sub>2</sub>NSiMe<sub>3</sub> in toluene solution. The chlorophosphites **3** and **6** were prepared by treating PCl<sub>3</sub> with the appropriate diol ligand in the presence of Et<sub>3</sub>N in ether solution. A similar

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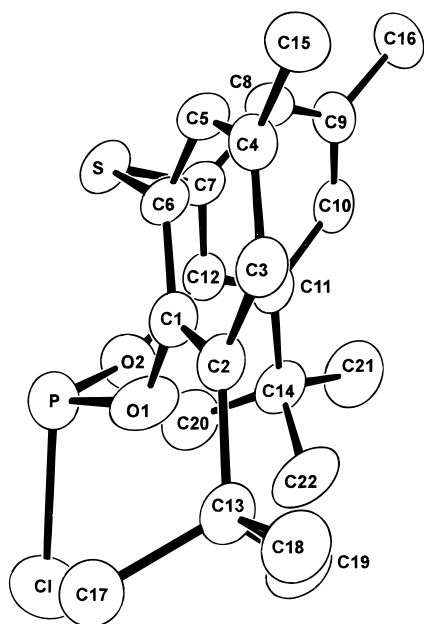
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**Table 1.** Crystallographic Data for Compounds 1–6

	1	2	3	4	5	6
formula	C <sub>22</sub> H <sub>28</sub> ClO <sub>2</sub> PS	C <sub>24</sub> H <sub>34</sub> NO <sub>2</sub> PS	C <sub>28</sub> H <sub>40</sub> ClO <sub>2</sub> PS	C <sub>22</sub> H <sub>28</sub> ClO <sub>3</sub> PS	C <sub>28</sub> H <sub>29</sub> Cl <sub>4</sub> O <sub>5</sub> PS	C <sub>23</sub> H <sub>30</sub> ClO <sub>2</sub> P
fw	422.9	431.5	507.1	438.9	651.3	404.9
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> 2 <sub>1</sub> <i>nb</i> ( <i>Pna</i> 2 <sub>1</sub> ; No. 33)	<i>P</i> 1̄ (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> 1̄ (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)
cryst size, mm	0.40 × 0.45 × 0.80	0.10 × 0.65 × 0.80	0.12 × 0.50 × 0.50	0.60 × 0.65 × 0.70	0.70 × 0.75 × 0.87	0.40 × 0.50 × 1.00
<i>a</i> (Å)	8.398(3)	8.173(2)	11.853(3)	12.593(3)	11.593(4)	14.425(8)
<i>b</i> (Å)	16.135(4)	12.394(3)	11.152(2)	10.635(3)	12.056(2)	10.008(3)
<i>c</i> (Å)	16.434(3)	22.895(7)	13.154(2)	17.711(3)	12.296(3)	16.442(4)
α (deg)	90	90	77.72(2)	90	112.48(2)	90
β (deg)	92.29(2)	90	72.29(2)	105.29(2)	95.28(2)	107.59(3)
γ (deg)	90	90	78.41(2)	90	102.71(2)	90
<i>V</i> (Å <sup>3</sup> )	2225(1)	2319(1)	1601.0(6)	2288.0(9)	1519.1(7)	2263(2)
<i>Z</i>	4	4	2	4	2	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.262	1.236	1.052	1.274	1.424	1.189
μ <sub>MoKα</sub> (cm <sup>-1</sup> )	3.52	2.28	2.54	3.48	5.47	2.54
total reflns	2543	1438	3361	2607	3461	2583
reflns with <i>I</i> > 2σ <sub><i>I</i></sub>	1805	910	2388	1970	2960	1813
<i>R</i> <sup>a</sup>	0.0469	0.1663	0.0599	0.0437	0.0510	0.0526
<i>R</i> <sub>w</sub> <sup>b</sup>	0.1018	0.3817	0.1486	0.1146	0.1285	0.1265

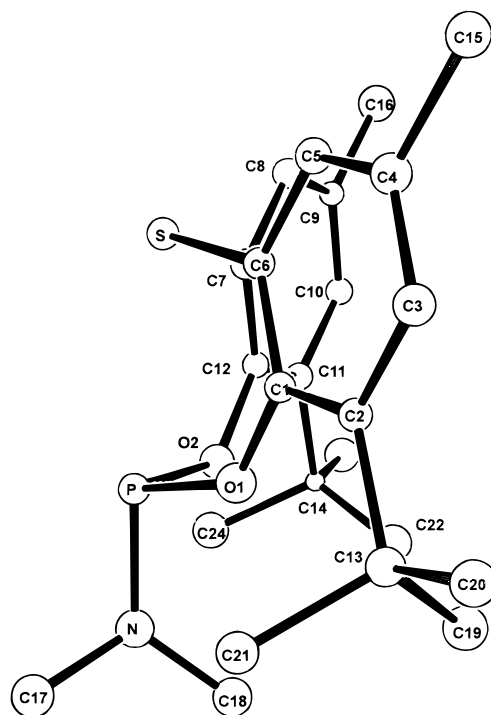
$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w(F_o^2) = \{ \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4 \}^{1/2}.$$

**Figure 1.** ORTEX diagram of S[(*t*-Bu)MeC<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>PCl (1).

process was used to obtain the chlorophosphate **4** with the use of POCl<sub>3</sub> in place of PCl<sub>3</sub>. The cyclic phosphate **5** resulted

(40) Although solution of the structure of compound **2** in the orthorhombic space group *P*2<sub>1</sub>*nb* was facile, some of the refined isotropic thermal parameters were unusually small and attempts at anisotropic refinements resulted in several atoms becoming non-positive definite. In addition, significant residual electron density appeared in locations that were chemically unreasonable. Although the molecule has a pseudo mirror plane passing through the P, S, and N atoms, no unusual correlations between parameters for atoms related by this pseudosymmetry were observed in the refinement, and the orientation of this plane is not commensurate with refinement of the structure with the molecule on a mirror plane in the centric analogue, *Pnma*. Since several exceptions to the *n* glide extinction were noted, a second crystal was examined and an entire hemisphere of data was collected with this crystal.  $\omega$  scans obtained with this crystal were not unusual. Refinements in both orthorhombic and monoclinic space groups that contain only an axial glide were considered. Refinement of the structure was possible with two molecules per asymmetric unit in the monoclinic space group *P*<sub>2</sub>, but this led to insignificant decreases in *R*<sub>int</sub> and *R*<sub>w</sub>, similar residual electron density, and unimproved behavior of the thermal parameters. Therefore we report the partial refinement of the structure, left at the isotropic level with hydrogen atoms omitted, in the space group *P*2<sub>1</sub>*nb*.

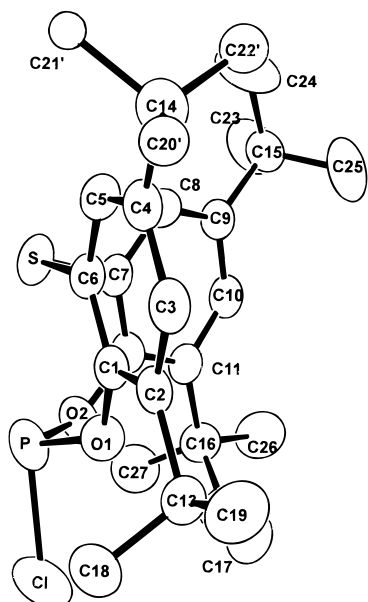
(41) ORTEX 5e, McArdle, P. Crystallography Centre, Chemistry Department, University College Galway, Ireland, 1996.

**Figure 2.** ORTEX diagram of S[(*t*-Bu)MeC<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>PNMe<sub>2</sub> (2).

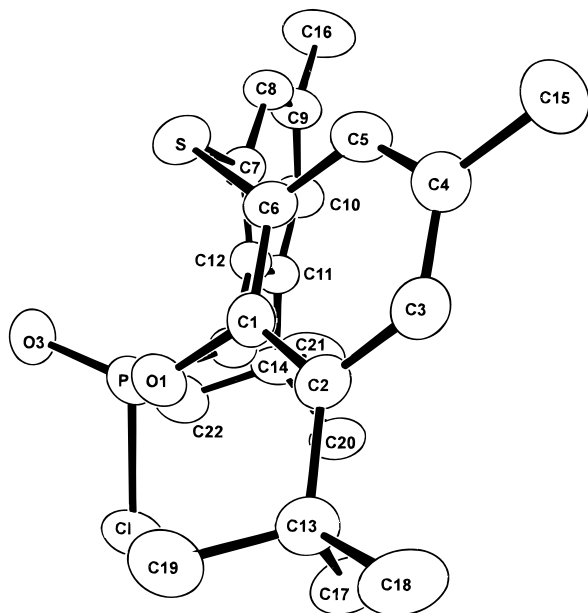
from hydrolysis of the bicyclic precursor **7** in a mixture of dichloromethane and acetonitrile. Yields ranged from 37% to 67%. The compounds are subject to hydrolysis which may have been promoted to some extent by sulfur donor action and the ease of cleavage of the P–Cl bond.

**Structures.** The geometries of the phosphites **1–3** may be regarded as pseudo trigonal bipyramids (TBP), Figures 1–3, and the geometries of the phosphates **4** and **5** as trigonal bipyramids, Figures 4 and 5. In all of these cyclic derivatives, the sulfur atom present as a bridgehead between the two aryl components exhibits coordinative tendencies to phosphorus as expressed by the P–S distance in this series. The latter values range from 3.177(2) Å for **5** to 2.816(2) Å for **1**. This range compares with the sum of the van der Waals radii for phosphorus and sulfur of 3.65 Å<sup>26</sup> and the sum of the covalent radii of 2.12 Å.<sup>27</sup> In all of the derivatives **1–5**, the ring is in

(42) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed., Harper Collins College Publ.: New York, 1993; p 213.



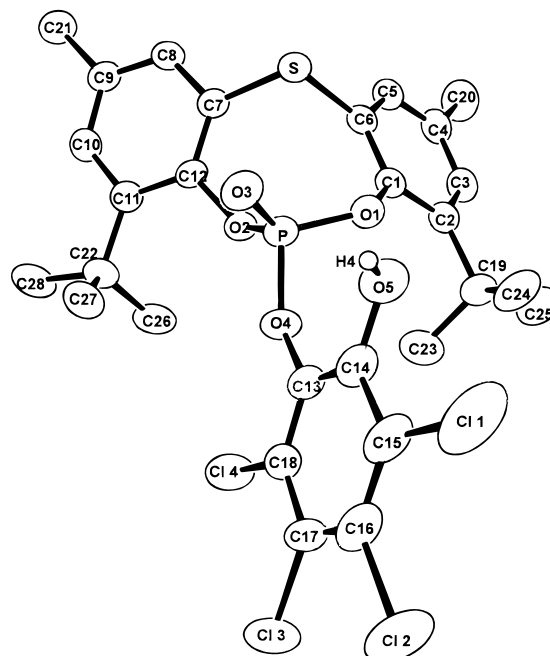
**Figure 3.** ORTEX diagram of  $S[(t\text{-Bu})_2\text{C}_6\text{H}_2\text{O}]_2\text{PCl}$  (**3**); only one set of the disordered methyl groups is shown (with primed labels).



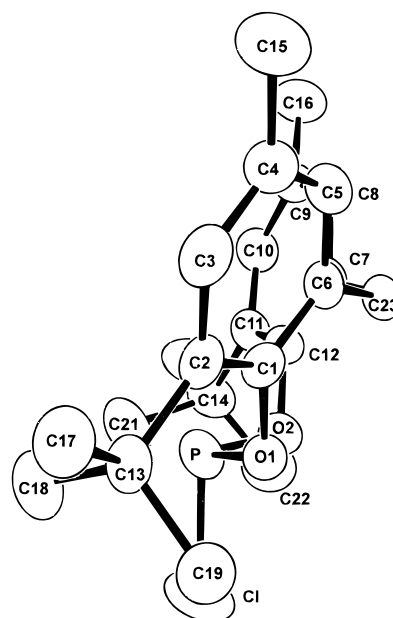
**Figure 4.** ORTEX diagram of  $S[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P(O)Cl}$  (**4**).

a boat-boat conformation (*syn* arrangement). This is apparent, for example, in Figure 1, where the atoms P, O1, C1, C6, S, C7, C12, O2 show this ring orientation. This contrasts with the ring conformation for **6** in Figure 6, which has the same composition as **1** except for the replacement of the sulfur bridgehead atom by a methylene group. Here the ring atoms P, O1, C1, C6, C23, C7, C12, O2 outline a boat-chair or *anti* conformation. The cyclic phosphite **5** exhibits a special property due to the presence of the appended hydroxyl group which interacts intermolecularly to give a hydrogen-bonded dimer as shown in Figure 7. The O3-H4 distance for the hydrogen-bonded linkage O5-H4...O3 is 1.86 Å with the O5-H4 distance fixed at 0.82 Å. The O5-H4...O3 angle is 158°.

The sulfur atom is located in an axial position of the TBP geometries for **1-5**, which then places the lone electron pair in the remaining equatorial site for the phosphites **1-3** and orients the phosphoryl oxygen atom at this site for the phosphates **4** and **5**. The degree to which the TBP is approached can be seen from the axial S-P-R angles for this series. They range from



**Figure 5.** ORTEX diagram of  $S[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P(O)(OC}_6\text{Cl}_4\text{-}o\text{-OH)}$  (**5**).



**Figure 6.** ORTEX diagram of  $\text{CH}_2[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{PCl}$  (**6**).

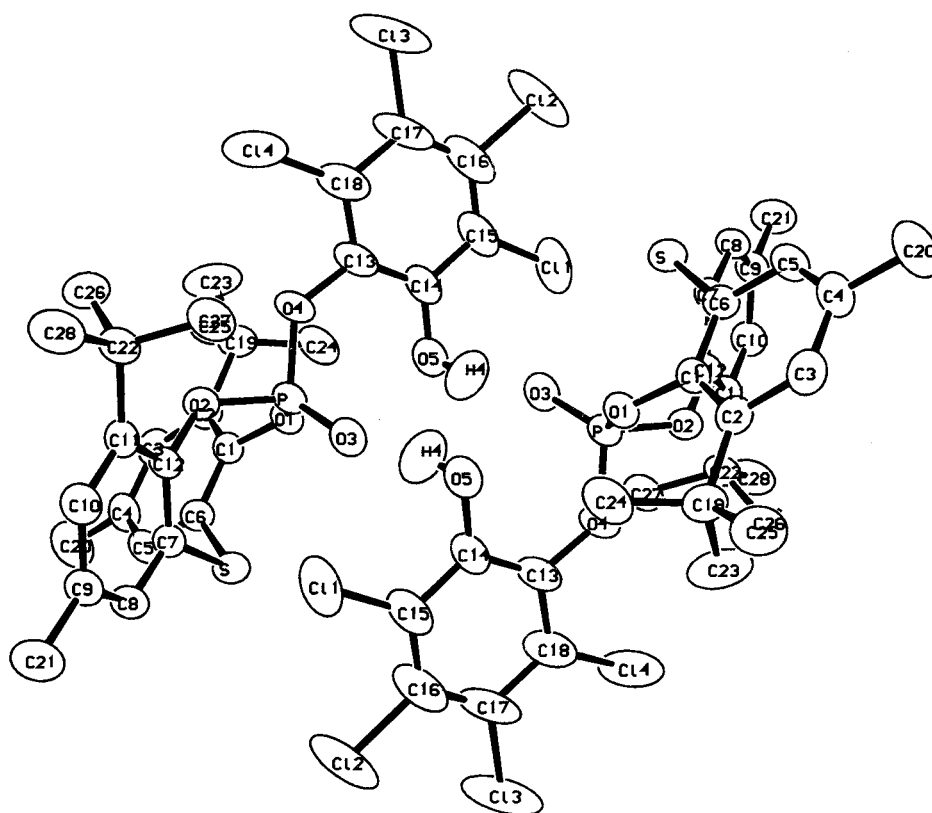
162.9(1)° for **5** to 172.2(1)° for **3**. A better measure of the displacement toward a TBP is one that we have used in earlier studies<sup>13,15,24,25</sup> of sulfur donor atom coordination in cyclic silanes containing the same type of ring system as is present here. In this procedure,<sup>25</sup> the degree of displacement from a pyramidal (for **1-3**) or tetrahedral geometry (for **4** and **5**) toward a TBP is simply estimated from the P-S distance and noting how far it is displaced from the van der Waals sum of 3.65 Å<sup>26</sup> toward the sum of the covalent radii of 2.12 Å.<sup>27</sup> The results are presented in Table 3 as % TBP along with other pertinent bond parameter data indicating increased coordination supplied by sulfur donor action.

A feature negating the operation of a ring strain influence as a contributing factor in determining the P-S distances is the observation that in the absence of a donor atom, as in **6**, the ring assumes an *anti* chair-like conformation in place of the *syn* boat-like conformation that is present for the ring containing

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Compounds 1–6

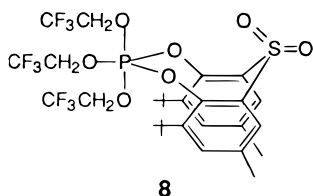
atoms	1	2 <sup>a</sup>	3	4	5	6
P–O1	1.625(3)	1.66(2)	1.633(3)	1.575(3)	1.571(3)	1.624(3)
P–O2	1.620(3)	1.63(2)	1.629(4)	1.561(3)	1.565(3)	1.624(3)
P–O3				1.457(3)	1.443(3)	
P–X <sup>b</sup>	2.119(2)	1.65(3)	2.303(3)	2.002(2)	1.586(3)	2.018(2)
P–S	2.816(2)	2.952(9)	3.043(2)	3.114(2)	3.177(2)	3.323(5) <sup>c</sup>
O1–P–O2	101.4(2)	97.7(9)	100.1(2)	105.9(2)	104.9(2)	103.3(2)
O1–P–O3				117.9(2)	118.1(2)	
O1–P–X	93.4(1)	98.0(10)	95.5(2)	101.1(1)	103.2(2)	95.7(1)
O2–P–O3				119.8(2)	116.5(2)	
O2–P–X	94.0(1)	95.1(10)	95.0(2)	99.9(1)	96.4(2)	95.9(1)
O3–P–X				109.2(1)	114.8(2)	
O1–P–X	79.5(1)	77.8(7)	80.2(1)	72.7(1)	69.8(1)	
O2–P–S	79.6(1)	80.3(6)	79.5(1)	72.3(1)	71.4(1)	
O3–P–S				83.0(1)	81.8(1)	
X–P–S	169.24(7)	173.3(9)	172.22(8)	167.71(7)	162.9(1)	
P–O1–C1	129.2(3)	133(2)	124.8(3)	129.4(2)	127.5(3)	117.3(2)
P–O2–C12	129.0(3)	132(2)	126.4(3)	129.1(2)	126.9(2)	115.6(2)

<sup>a</sup> The structure was refined isotropically only. Hydrogens were not included in the calculations. R1 = 0.1663 and wR2 = 0.3817 for  $I > 2\sigma$ . <sup>b</sup> X = Cl for **1**, **3**, **4**, **6**; X = N for **2**; X = O4 for **5**. <sup>c</sup> P...C23 distance.



**Figure 7.** ORTEX diagram illustrating the hydrogen-bonded dimer formation for **5** as a result of O5–H4...O3 interactions. The two molecules are related by 1 – X, 2 – Y, –Z.

a sulfur donor atom in **1**–**5**. This same type of *anti* ring conformation persists in the presence of a potential donor atom when the electrophilicity at phosphorus is insufficient for donor action to take place, *e.g.*, in **8**.<sup>4</sup>



It is further noted that the TBP geometry of **1** which places the chlorine atom in an axial position has a P–Cl bond distance of 2.119(2) Å, which is about 0.1 Å longer than the P–Cl bond

distance for **6**, which lacks sulfur donor action. This is the expected lengthening effect in going from a lower coordinate geometry to an axial site of a TBP.

The order of the P–S distances listed in Table 3 is consistent with the presence of larger values for the higher coordinate phosphates relative to the values for the phosphites, *i.e.*, the P–S distances for **4** and **5** are longer than those for **1**–**3**. The presence of a phosphoryl bond in an equatorial site of a TBP for **4** and **5** compared to a lone electron pair at this site in **1**–**3** may serve to reduce the ability of sulfur to approach the phosphorus atom due to the presence of  $\pi$  back-bonding. However, the relatively small changes in P–S distances within each series are not amenable to rationalization at present. Somewhat puzzling are the larger values of the axial distances in **3** compared to **1**. Both the axial P–S distance and the axial

**Table 3.** Comparison of P–S Bond Parameters, Ring Conformations, and  $^{31}\text{P}$  Chemical Shifts for Cyclic Phosphites and Phosphates

compd <sup>a</sup>	P–S (Å)	% TBP <sup>b</sup>	S–P–R <sub>ax</sub> , (deg) <sup>c,d</sup>	$\Sigma_{\text{eq}}$ , (deg) <sup>c</sup>	$\delta$ ( $^{31}\text{P}$ ), ppm soln <sup>e</sup> solid
<b>5</b>	3.177(2)	30.9	162.9(1)	339.5(2)	–16.62
<b>4</b>	3.114(2)	35.0	167.71(7)	343.6(2)	–9.49
<b>3</b>	3.043(2)	39.7	172.22(8)		170.38
<b>2</b> <sup>f</sup>	2.952(9)	47.1	173.3(9)		132.46
<b>1</b>	2.816(2)	54.5	169.24(7)		168.37
<b>6</b>					165.71

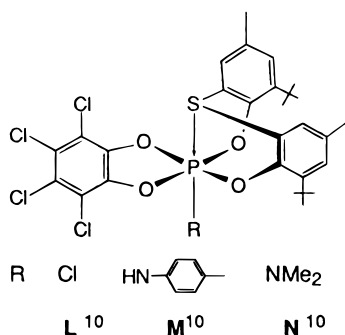
<sup>a</sup> Compounds **1–5** have the eight-membered ring in a *syn* boat conformation, whereas **6** has the ring in an *anti* chair conformation.

<sup>b</sup> Percent geometrical displacement from a pyramid (**1–3**) or a tetrahedron (**4** and **5**) toward a TBP. <sup>c</sup> With reference to a TBP with sulfur in an axial position and both ring oxygen atoms in equatorial positions. <sup>d</sup> R = Cl for **1**, **3**, and **4**. R = NMe<sub>2</sub> for **2**. R = OC<sub>6</sub>Cl<sub>4</sub>-*o*-OH for **5**. <sup>e</sup> All in toluene solution. Decomposition of **6** prevented recording a spectrum. <sup>f</sup> Due to the high degree of thermal motion for **2**, the uncertainty in bond parameters is large.

P–Cl distance for **3**, the latter of which has two additional *tert*-butyl groups as part of the aromatic ring components, suffer an approximate 0.2 Å increase relative to these distances for the less encumbered chlorophosphite **1**. If a steric effect is present in **3** due to the increased bulk of the aryl substituents, its origin is not apparent.

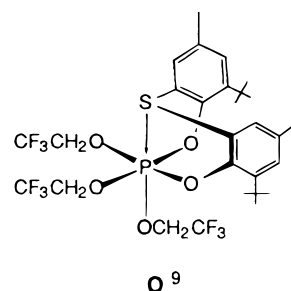
**Comparison with Other Series Showing Sulfur Donor Action.** In a series of related cyclic silanes that underwent a change in geometry from tetrahedral to trigonal bipyramidal as a result of sulfur donor action,<sup>13,24,25</sup> *e.g.*, **D**<sup>13</sup> illustrated in the Introduction, the Si–S distance decreased over the range 3.292(1)–2.978(4) Å as the structural displacement toward a TBP increased from 35.8% to 54.2%. Considering that silicon is larger than phosphorus,<sup>27</sup> a similar range was covered by each of the two series studied so far.

For the two series of phosphoranes that exhibit an increase in coordination toward octahedral geometries, that is, a series of pentaoxyphosphoranes<sup>5–9,11</sup> and a series of tetraoxyphosphoranes<sup>10</sup> discussed in the Introduction, their structural displacements reached considerably closer to the higher coordinate geometry, approximately 70% in each of these series. An example of the pentaoxy series is **B**<sup>7</sup> and representative of the formulations in the tetraoxy series are **L–N**.<sup>10</sup> If we compare

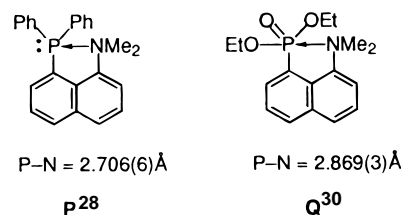


the displacements in the two five-coordinate series with the displacement in the tri- and tetra-coordinate series for equal percentage displacement in each of these series, the P–S distance is approximately 0.1 Å longer in the lower coordinate series. In other words, phosphorus in the pentacoordinate state is more receptive or shows greater electrophilicity in accommodating an incoming donor atom. This is in line with the lower limit for the P–S donor interaction achieved in the tri- and tetra-coordinate series, 2.816(2) Å for **1** compared to the considerably lower values, 2.362(2) Å found for **O** in the

pentaoxyphosphorane series and 2.479(2) Å found for **L** in the tetraoxyphosphorane series. Thus, the ease of sulfur donor atom

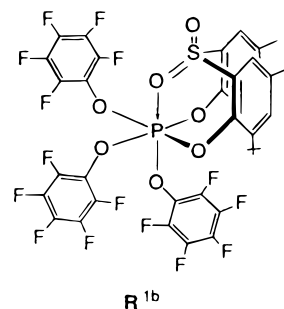


interaction, increasing with an increase in phosphorus atom coordination, is in accord with the increase of Lewis acidity of phosphorus for the higher coordinated state. Actually, it is somewhat surprising that the lower coordinate phosphites **1–3** and phosphates **4–5** as well as the related derivatives studied by Corriu and co-workers<sup>28–31</sup> that exhibit P–N coordination, *e.g.*, **P**<sup>28</sup> and **Q**,<sup>30</sup> have a tendency to accommodate an electron pair donor atom. It is less surprising that coordination occurs in **P** and **Q** with the nitrogen atoms constrained in close proximity to the phosphorus center. The more flexible eight-membered ring employed in this study allows other ring conformations in the absence of donor action. It is known that



phosphorus trihalides act as Lewis bases; *e.g.*, POCl<sub>3</sub>–BCl<sub>3</sub>, PCl<sub>3</sub>–BBR<sub>3</sub>, and PBr<sub>3</sub>–BBR<sub>3</sub> exist but not PCl<sub>3</sub>–BF<sub>3</sub> or PCl<sub>3</sub>–BCl<sub>3</sub>.<sup>43</sup> In this sense, tricoordinate phosphorus shows amphoteric character.<sup>43–46</sup>

In a series of cyclic oxyphosphoranes containing a bridging sulfone group<sup>1b,4</sup> in the ring system, oxygen donor action extended the structural displacement toward the octahedral geometry to 82%. This was found for **R**<sup>1b</sup> with a donor P–O distance of 1.936(7) Å, the shortest in the series. The short distance was attributed to the presence of the electron-withdrawing pentafluorophenoxy ligands acting to enhance the electrophilicity of the phosphorus atom.



These comparisons show that donor coordination at phosphorus is a common property and extends to tri-, tetra-, and pentacoordinate phosphorus molecules leading to an increase in coordination geometry in each case. Similar to increased

(43) Holmes, R. R. *J. Inorg. Nucl. Chem.* **1960**, *12*, 266–275.

(44) Holmes, R. R. *J. Phys. Chem.* **1960**, *64*, 1295–1299.

(45) Holmes, R. R. *J. Am. Chem. Soc.* **1960**, *82*, 5285–5288.

(46) Holmes, R. R.; Wagner, R. P. *Inorg. Chem.* **1963**, *2*, 384–388.

coordination formed for silicon compounds illustrated in the Introduction, sulfur, oxygen, and nitrogen serve as donor atoms in the various series. The present work represents the first study where sulfur donor action leads to an increase in coordination geometry for tri- and tetracoordinated phosphorus molecules. With the knowledge of the tendency of phosphorus to increase its coordination in the presence of suitable donor atoms, it seems reasonable that such action will take place whenever the opportunity presents itself. For example, at active sites of phosphoryl transfer enzymes<sup>21</sup> when nitrogen-, oxygen-, or sulfur-containing residues have donor atoms in appropriate positions, an increase in coordination causing an alteration in phosphorus substrate or activated state geometry may take place.

**<sup>31</sup>P Chemical Shifts.** <sup>31</sup>P chemical shifts summarized in Table 3 are consistent with values expected for tri- and tetracoordinated phosphorus containing electronegative ligands.<sup>47</sup> For example, the value for the cyclic chlorophosphite **1** of 168.4 ppm is seen to undergo an upfield shift of 177.9 ppm on the formal addition of a phosphoryl oxygen to give the cyclic chlorophosphate **4** at a <sup>31</sup>P shift of -9.49 ppm.

No discernible effect is apparent associated with P-S coordination when the comparison is made with compounds that have similar substituents. The <sup>31</sup>P shift for **1** which shows sulfur donor action is nearly the same as that for **6** which has a related composition but lacks the possibility of donor coordination. A solid state value for **6** of 165.7 ppm compares with a solution value of 168.4 ppm for **1**. However, **2**, which has a Me<sub>2</sub>N group in place of the chlorine atom in **1**, shows a more upfield shift, 132.5 ppm compared to 168.4 ppm for **1**. Consistent with this observation is the presence of the more electronegative chlorine atom resulting in electron withdrawal and enhancing sulfur donor action. The P-S distance in **1** is 2.816(2) Å. The upfield shift for **2** possibly is partly due to the ability of nitrogen to  $\pi$  back-bond to phosphorus. The P-N bond distance is 1.65(3) Å which is considerably shorter than the sum of the covalent radii of 1.85 Å,<sup>27</sup> but in the range normally observed for PN compounds. Similarly, the much smaller upfield shift for the

cyclic phosphate **5** (-16.62 ppm) compared to **4** (-9.49 ppm) may be associated partly with P-O  $\pi$  back-bonding in **5**, although countered to some degree by the greater electronegativity due to the chlorination of **4**. For **5**, the P-O<sub>ax</sub> bond distance is 1.586(3) Å, which compares with 1.83 Å for the sum of the covalent radii<sup>27</sup> for phosphorus and oxygen.

### Summary and Conclusion

Cyclic phosphites and cyclic phosphates provide the first series that exhibit sulfur atom coordination from the presence of sulfur as part of a flexible eight-membered ring system. As a consequence, the tri- and tetracoordinate geometries are displaced toward a TBP. The degree of donor coordination is greater for the cyclic phosphites compared to the cyclic phosphates as measured by the P-S distance. In other series using similar ring systems, oxyphosphoranes form hexacoordinate structures via increased sulfur donor action relative to the lower coordinate phosphorus series. The latter is in line with the increase in phosphorus electrophilicity as one proceeds to the higher coordinate series. In all of these series, donor action is enhanced with the use of electronegative ligands. The tendency of electron pair donor groups to increase phosphorus atom coordination even for a relatively basic center as found in the cyclic phosphites suggests that this occurrence may be an important consideration in detailing mechanisms of nucleophilic displacement reactions of phosphorus compounds. In particular, nearby residues at active sites of phosphoryl transfer enzymes having sulfur, nitrogen, or oxygen donor atoms may participate in altering activated state geometries as well as substrates geometries.

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

**Supporting Information Available:** Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1** and **3-6** and tables of crystal and refinement data, atomic coordinates, and bond lengths and angles for **2** (25 pages). Ordering information is given on any current masthead page.

IC970508B

(47) Mann, B. E. *The Common Nuclei*. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; pp 87-104.