

Hexacoordination via Sulfur Donor Action in Nitrogen and Chlorine Bonded Bicyclic Tetraoxyphosphoranes¹

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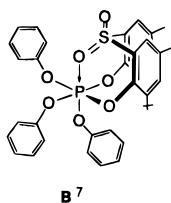
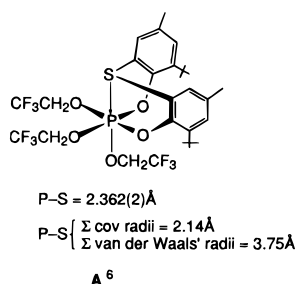
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Abstract: Oxidative addition reactions of a quinone with the sulfur containing cyclic chlorophosphine S[(*t*-Bu)MeC₆H₂O]₂PCl (**1**) yielded the new bicyclic tetraoxyphosphoranes, S[(*t*-Bu)MeC₆H₂O]₂PCl(O₂C₆Cl₄) (**2**) and S[(*t*-Bu)MeC₆H₂O]₂PCl(O₂C₁₄H₈) (**5**). Further new derivatives of this class were prepared by chlorine displacement reactions of **2** and **5** to give S[(*t*-Bu)MeC₆H₂O]₂P(NHC₆H₄Me)(O₂C₆Cl₄) (**3**), S[(*t*-Bu)MeC₆H₂O]₂P(NMe₂)(O₂C₆Cl₄) (**4**), S[(*t*-Bu)MeC₆H₂O]₂P(NHCH₂C₆H₅)(O₂C₁₄H₈) (**6**), and S[(*t*-Bu)MeC₆H₂O]₂P(NMe₂)(O₂C₁₄H₈) (**7**). X-ray studies of **2–6** revealed hexacoordination due to donor action by sulfur which is present as part of an eight-membered ring system. The series **2–6** formed geometries that were displaced along a coordinate from a square pyramid to an octahedron, ranging from 24% to 71%. The respective P–S distance decreased along this series from 3.04 to 2.48 Å as the octahedral character increased. Increased ³¹P NMR shielding accompanied the chloro derivatives **2** and **5**, while increased π P–N back-bonding resulted in the least shielded members **4**, **6**, and **7** containing the less electronegative nitrogen atom. These changes in ³¹P chemical shift correlate with the extent of octahedral character where the more shielded phosphorus atom has the greater octahedral character. The analysis allows a lower limit in the phosphorus atom electrophilicity to be established that will allow hexacoordination in this series of bicyclic tetraoxyphosphoranes provided by a variation in ligand properties.

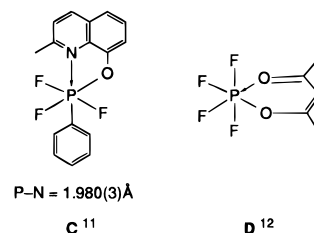
Introduction

In previous work, we have found that sulfur atoms^{2–6} and sulfonyl groups⁷ in ring containing pentaoxyphosphoranes are capable of donor action which leads to neutral hexacoordinated phosphorus. These derivatives form a range of structures along a coordinate from a square pyramid to an octahedral geometry. Representative members of each of these series are **A**⁶ and **B**.⁷



recently reported by Cavell and co-workers.⁸ In a similar fashion, pentaoxyphosphoranes exhibiting additional coordination at phosphorus due to oxygen donor action from the ring containing sulfonyl group provide a range of P–O distances from 2.61 to 2.49 Å.⁷ The respective displacement toward an octahedron varies from 40% to 55%.

Other examples of hexacoordinated phosphorus are known that are formed as a result of donor action from more electronegative nitrogen and oxygen containing ligands,^{9,10} e.g., **C**¹¹ and **D**.¹² In all of these, the ligands attached to phosphorus



For the pentaoxyphosphoranes that have sulfur coordination, the range of P–S distances is 2.88 to 2.33 Å,^{2–6,8} where the respective displacements toward an octahedron vary from 44% to 70%. The latter range includes the shortest P–S distance

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(1) (a) Pentacoordinated Molecules 114. (b) Part 113: Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* Submitted for publication.

(2) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1913–1920.

(3) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 3391–3397.

(4) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 2690–2695.

(5) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Phosphorus, Sulfur, and Silicon* **1993**, *75*, 249–252.

(6) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Inorg. Chem.* **1993**, *32*, 4360–4367.

(7) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* accepted for publication.

(8) Wong, C. Y.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **1996**, *35*, 325–334.

collectively provide a high degree of electronegativity. It is of interest to examine the influence of lowering the electrophilicity at phosphorus with use of the less electronegative sulfur atom as the donor atom along with a decrease in the substituent electronegativity from that which exists in the pentaoxyphosphorane series previously studied. This will allow one to ascertain the ease with which phosphorus achieves the hexacoordinate state in neutral compounds and to establish a lower limit to phosphorus electrophilicity that will provide for an increase in coordinate geometry. Toward this end, we report

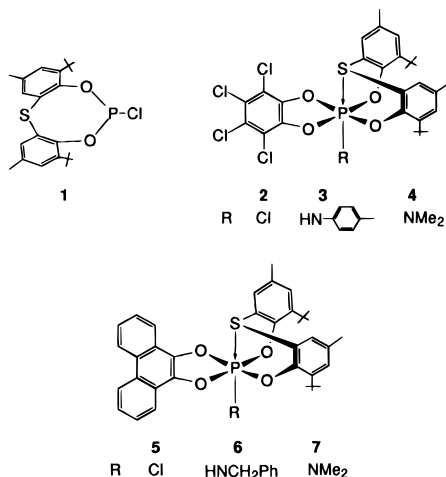
(9) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927–950, and references cited therein.

(10) Wong, C. Y.; Kennepohl, D. K.; Cavell, R. G. *Chem. Rev.* **1996**, *96*, 1917–1951.

(11) John, K.-P.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1974**, 2466.

(12) Sheldrick, W. S.; Hewson, M. J. C. *Z. Naturforsch., B: Anorg. Chem.* **1978**, *33b*, 834.

the tendency of phosphorus to increase its coordination toward an octahedral geometry in a series of sulfur containing tetraoxyphosphoranes, **2–7**, that have either the less electronegative nitrogen or chlorine ligands as the fifth substituent in place of an oxygen atom. For the synthesis of this series, it was necessary to prepare the sulfur containing cyclic chlorophosphine **1** to provide a convenient route for their formation. X-ray structural studies of **2–6** are reported along with ^1H and ^{31}P NMR data to learn if there are indications of structural change on going from the solid to the solution state.



Experimental Section

Phosphorus trichloride (Aldrich), tetrachlorobenzoquinone (Aldrich), phenanthrenequinone (Aldrich), *p*-toluidine (Eastman), *N,N*-dimethylaminotrimethylsilane (Petrarch), and benzylamine (Aldrich) were used as supplied. Triethylamine (Eastman) was distilled over potassium hydroxide. 2,2'-Thiobis(4-methyl-6-*tert*-butylphenol) was synthesized according to a literature method.⁴ Solvents were purified according to standard procedures.¹³ 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 were recorded on a Bruker MSL300 FT-NMR spectrometer. All proton spectra were recorded in CDCl_3 except where otherwise noted. Phosphorus-31 NMR were recorded in toluene. Chemical shifts are reported in ppm, downfield positive, relative to tetramethylsilane (^1H) or 85% H_3PO_4 (^{31}P). All were recorded at around 23 °C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses: $\text{S}[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{PCl}$ (**1**). To a solution of phosphorus trichloride (2.00 mL, 22.9 mmol) in diethyl ether (100 mL) at 0 °C was added dropwise over 1 h a solution of 2,2'-thiobis(4-methyl-6-*tert*-butylphenol) (7.12 g, 19.9 mmol) and triethylamine (6.20 mL, 44.6 mmol) in diethyl ether (75 mL). On completion of the addition, the mixture was allowed to come to room temperature and stirred for 15 h. The solution was filtered, and the solvent was removed *in vacuo*. The residue was washed with hexane (10 mL) and dissolved in dichloromethane (30 mL). Hexane (100 mL) was added, and the solution was left under a nitrogen flow to obtain the crystalline product (yield 4.56 g, 54%): mp 174–176 °C. ^1H NMR: 1.40 (s, *t*-Bu, 18 H), 2.28 (s, Me, 6 H), 7.14–7.36 (m, aryl, 4 H). ^{31}P NMR (CDCl_3): 168.37. Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{ClO}_2\text{PS}$: C, 62.47; H, 6.67. Found: C, 61.74; H, 6.73.

$\text{S}[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{PCl}(\text{O}_2\text{C}_6\text{Cl}_4)$ (**2**). A solution of **1** (1.53 g, 3.63 mmol) and tetrachlorobenzoquinone (0.89 g, 3.63 mmol) in 1:1 dichloromethane and hexane (50 mL) was stirred for 30 min and left under a flow of nitrogen to obtain the crystalline product (yield 2.24

g, 92%): mp > 250 °C. ^1H NMR: 1.32 (s, *t*-Bu, 18 H), 2.30 (s, Me, 6 H), 7.20 (s, aryl, 2 H), 7.39 (s, aryl, 2 H). ^{31}P NMR: –57.62. Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{Cl}_5\text{O}_4\text{PS}$: C, 50.28; H, 4.22. Found: C, 49.96; H, 4.45.

$\text{S}[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P}(\text{NHC}_6\text{H}_4\text{Me})(\text{O}_2\text{C}_6\text{Cl}_4)$ (**3**). A solution of **2** (0.77 g, 1.15 mmol) and *p*-toluidine (0.35 g, 2.32 mmol) in diethyl ether (75 mL) was stirred for 20 h at room temperature. The solution was filtered, and the solvent was removed *in vacuo*. The residue was washed with hexane (10 mL) and dissolved in a 1:1 mixture of dichloromethane and hexane (25 mL). The solution was left under a flow of nitrogen to obtain the crystalline product (yield 0.52 g, 61%): mp 127–130 °C. ^1H NMR: 1.37 (s, *t*-Bu, 18 H); 2.24 (s, toluidine Me, phenol Me, 9 H), 4.95 (d, NH, 1 H, 6.86 Hz), 6.98–7.24 (m, aryl, 8 H). ^{31}P NMR: –55.15. Anal. Calcd for $\text{C}_{35}\text{H}_{36}\text{Cl}_4\text{NO}_4\text{PS}\cdot 1/2(\text{C}_6\text{H}_{14})$: C, 58.32; H, 5.54; N, 1.79. Found: C, 57.85; H, 5.62; N, 1.84.

$\text{S}[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P}(\text{NMe}_2)(\text{O}_2\text{C}_6\text{Cl}_4)$ (**4**). To a solution of **2** (0.50 g, 0.75 mmol) in toluene (50 mL) was added *N,N*-dimethylaminotrimethylsilane (0.13 mL, 0.79 mmol). The solution was heated in an oil bath to 140 °C over 1 h and then allowed to reflux for a further 30 min. After cooling to room temperature, the solvent was removed *in vacuo*. The solid residue was washed with hexane and dissolved in dichloromethane (20 mL). Hexane (30 mL) was added to the solution which was left under a flow of nitrogen to obtain the crystalline product (yield 0.23 g, 45%): mp > 250 °C. ^1H NMR: 1.43 (s, *t*-Bu, 18 H), 2.24 (s, Me, 6 H), 2.87 (d, N-Me, 6 H, 12.28 Hz), 7.17–7.29 (m, aryl, 4 H). ^{31}P NMR: –46.88. Anal. Calcd for $\text{C}_{30}\text{H}_{34}\text{Cl}_4\text{NO}_4\text{PS}$: C, 53.19; H, 5.06; N, 2.07. Found: C, 53.22; H, 5.13; N, 1.92.

$\text{S}[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{PCl}(\text{O}_2\text{C}_{14}\text{H}_8)$ (**5**). A solution of **1** (0.51 g, 1.2 mmol) and phenanthrenequinone (0.25 g, 1.2 mmol) in toluene (50 mL) was refluxed for 2 hours in an oil bath at 140 °C and then cooled to room temperature. Solvent was removed *in vacuo*. The residue was washed with hexane (10 mL) and dissolved in dichloromethane (20 mL) and hexane (30 mL). The resulting solution was left under a flow of nitrogen to obtain the crystalline product (yield 0.30 g, 40%): mp > 250 °C. ^1H NMR: 1.21 (s, *t*-Bu, 9 H), 1.52 (s, *t*-Bu, 9 H), 2.25 (s, Me, 3 H), 2.29 (s, Me, 3 H), 7.15–8.67 (m, aryl, 12 H). ^{31}P NMR: –49.78. Anal. Calcd for $\text{C}_{36}\text{H}_{36}\text{ClO}_4\text{PS}$: C, 68.52; H, 5.71. Found: C, 68.51; H, 5.75.

$\text{S}[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P}(\text{NHCH}_2\text{C}_6\text{H}_5)(\text{O}_2\text{C}_{14}\text{H}_8)$ (**6**). To a solution of **5** (0.58 g, 1.0 mmol) in diethyl ether (50 mL) at room temperature was added benzylamine (0.30 mL, 2.7 mmol). The mixture was stirred for 12 h and filtered, and the solvent was removed *in vacuo*. The resulting oil was dissolved in dichloromethane (10 mL) and hexane (15 mL). The solution was left under a flow of nitrogen to obtain the crystalline product (yield 0.22 g, 35%): mp 240–245 °C. ^1H NMR (CD_2Cl_2): 1.48 (s, *t*-Bu, 18 H), 2.21 (s, Me, 6 H), 4.40 (brs, CH_2 , 2 H), 7.08–7.29 (m, aryl, 9 H), 7.47–7.69 (m, aryl, 6 H), 8.61–8.66 (m, aryl, 2 H). ^{31}P NMR: –43.60. Anal. Calcd for $\text{C}_{43}\text{H}_{44}\text{NO}_4\text{PS}$: C, 73.61; H, 6.28; N, 2.00. Found: C, 73.11; H, 6.51; N, 2.13.

$\text{S}[(t\text{-Bu})\text{MeC}_6\text{H}_2\text{O}]_2\text{P}(\text{NMe}_2)(\text{O}_2\text{C}_{14}\text{H}_8)$ (**7**). To a solution of **5** (0.53 g, 0.94 mmol) in toluene (50 mL) was added *N,N*-dimethylaminotrimethylsilane (0.25 mL, 1.5 mmol). The solution was heated under reflux in an oil bath at 140 °C for 45 min. After cooling to room temperature, the solvent was removed *in vacuo*. The solid residue was washed with hexane, but all attempts to grow a single crystal suitable for X-ray analysis failed (yield 0.52 g, 87%): mp > 250 °C. ^1H NMR: 1.53 (s, *t*-Bu, 18 H), 2.19 (s, Me, 6 H), 2.94 (d, NMe, 6 H, 12.28 Hz), 7.10–8.68 (m, aryl, 12 H). ^{31}P NMR: –43.17. Anal. Calcd for $\text{C}_{38}\text{H}_{42}\text{NO}_4\text{PS}$: C, 71.34; H, 6.62; N, 2.19. Found: C, 71.44; H, 6.69; N, 1.90.

X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Details of the experimental procedures have been described previously.¹⁴

The colorless crystals were mounted in thin-walled glass capillaries which were sealed to protect the crystals from the atmosphere as a precaution. Data were collected using the θ – 2θ scan mode with $3^\circ \leq 2\theta_{\text{MoK}\alpha} \leq 43^\circ$ at $23 \pm 2^\circ \text{C}$. No corrections were made for absorption. All of the data were included in the refinement. The structures were

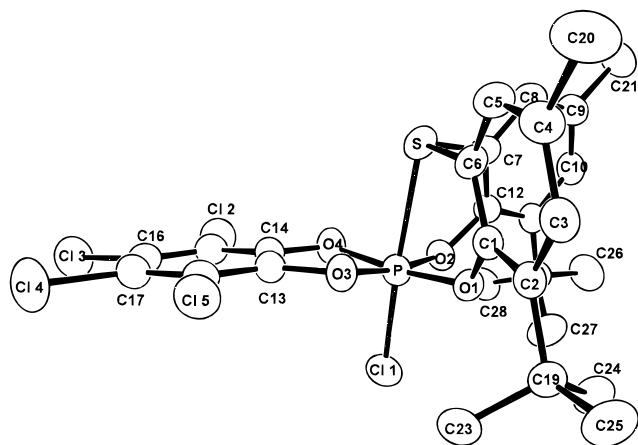
(13) (a) Organic Solvents. Chapter V. In *Techniques of Chemistry*; Riddick, J. A., Bunger, W. B., Eds.; Wiley Interscience: New York, 1970; Vol. II. (b) Vogel, A. I. *Textbook of Practical Organic Chemistry*; Longman: London, 1978.

(14) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

Table 1. Crystallographic Data for Compounds 2–6

| compd | 2 | 3 | 4 | 5 | 6 |
|---|---|--|--|---|--|
| formula | C ₂₈ H ₂₈ Cl ₅ O ₄ PS | C ₃₅ H ₃₆ Cl ₄ NO ₄ PS· ¹ / ₂ C ₆ H ₁₄ | C ₃₀ H ₃₄ Cl ₄ NO ₄ PS | C ₃₆ H ₃₆ ClO ₄ PS | C ₄₃ H ₄₄ NO ₄ PS |
| formula weight | 668.8 | 782.6 | 677.4 | 631.1 | 701.8 |
| crystal system | triclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | <i>P</i> $\bar{1}$ (no. 2) | <i>P</i> 2 ₁ / <i>n</i> (no. 14) | <i>P</i> 2 ₁ / <i>c</i> (no. 14) | <i>P</i> 2 ₁ / <i>n</i> (no. 14) | <i>P</i> 2 ₁ / <i>n</i> (no. 14) |
| crystal size, mm | 0.40 × 0.50 × 0.80 | 0.25 × 0.27 × 0.77 | 0.45 × 0.55 × 0.75 | 0.30 × 0.55 × 0.55 | 0.50 × 0.75 × 0.80 |
| <i>a</i> (Å) | 7.831(6) | 13.783(2) | 8.945(2) | 10.066(3) | 9.751(3) |
| <i>b</i> (Å) | 9.360(1) | 13.294(3) | 18.889(6) | 18.858(3) | 21.242(10) |
| <i>c</i> (Å) | 21.237(3) | 21.547(2) | 19.479(5) | 17.109(3) | 18.517(6) |
| α (deg) | 100.60(1) | 90 | 90 | 90 | 90 |
| β (deg) | 93.58(4) | 90.85(1) | 98.90(2) | 92.88(2) | 100.94(3) |
| γ (deg) | 95.01(4) | 90 | 90 | 90 | 90 |
| <i>V</i> (Å ³) | 1519(1) | 3948(1) | 3252(2) | 3244(1) | 3766(2) |
| <i>Z</i> | 2 | 4 | 4 | 4 | 4 |
| <i>D</i> _{calc} (g/cm ³) | 1.462 | 1.317 | 1.384 | 1.292 | 1.238 |
| μ _{MoKα} (cm ⁻¹) | 6.32 | 4.32 | 5.13 | 2.70 | 1.71 |
| total reflns | 3476 | 4527 | 3695 | 3686 | 4268 |
| reflns with <i>I</i> > 2 σ _{<i>I</i>} | 2843 | 2498 | 2729 | 2457 | 2641 |
| <i>R</i> ^a | 0.0384 | 0.0486 | 0.0434 | 0.0479 | 0.0888 |
| <i>R</i> _w ^b | 0.1032 | 0.0814 | 0.1069 | 0.1058 | 0.2188 |

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

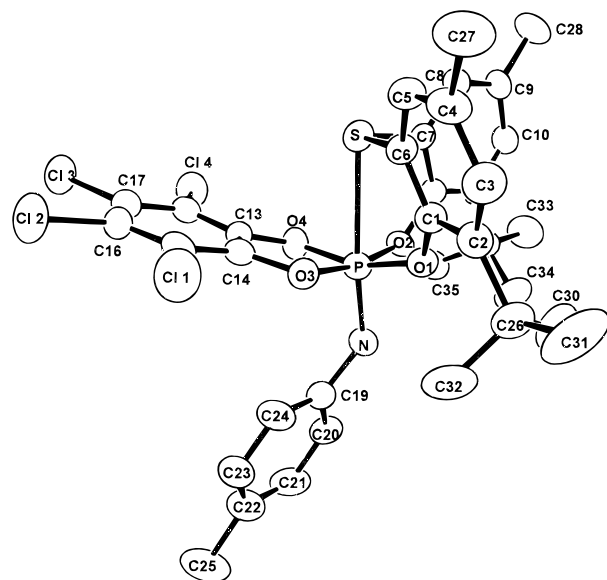
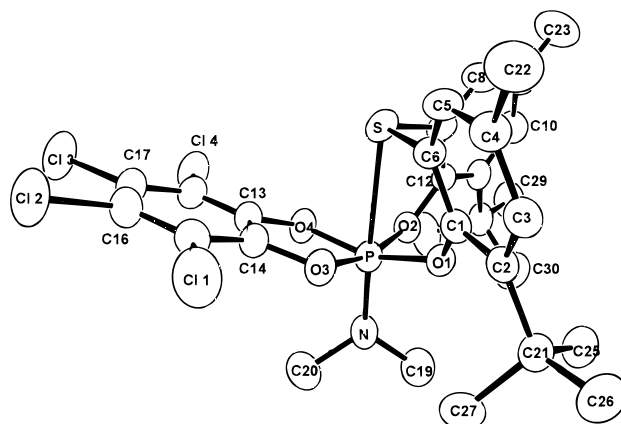
**Figure 1.** ORTEX diagram of S[(*t*-Bu)MeC₆H₂O]₂PCl(O₂C₆Cl₄) (2) with thermal ellipsoids at 40% probability level. All hydrogen atoms are omitted for clarity.

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 solution¹⁵ and SHELXL-93 for refinement.¹⁶ All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded carbon atoms. In the case of 3, a solvent molecule of hexane was located at the inversion center. The final agreement factors are based on the reflections with *I* ≥ 2 σ _{*I*}. Crystallographic data are summarized in Table 1.

Results and Discussion

The atom-labeling schemes for 2–6 are given in the ORTEX¹⁷ plots of Figures 1–5, respectively. Thermal ellipsoids are all shown at the 40% probability level. Selected bond parameters are presented in Table 2 for 2–6, respectively.

Syntheses. All preparations are a result of an oxidative addition reaction of a quinone with the sulfur containing cyclic chlorophosphine 1 (for the synthesis of 2 and 5) or a chlorine

**Figure 2.** ORTEX diagram of S[(*t*-Bu)MeC₆H₂O]₂P(NHC₆H₄Me)-(O₂C₆Cl₄) (3) with thermal ellipsoids at 40% probability level. All hydrogen atoms are omitted for clarity.**Figure 3.** ORTEX diagram of S[(*t*-Bu)MeC₆H₂O]₂P(NMe₂)(O₂C₆Cl₄) (4) with thermal ellipsoids at 40% probability level. All hydrogen atoms are omitted for clarity.

displacement reaction involving either 2 or 5 by an amine reagent (for the synthesis of 3, 4, 6, and 7). The general reaction scheme is illustrated in eqs 1–3 for the synthesis of 1–3.

(15) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

(16) Sheldrick, G. M. SHELXL-93; program for crystal structure refinement; University of Gottingen, 1993.

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

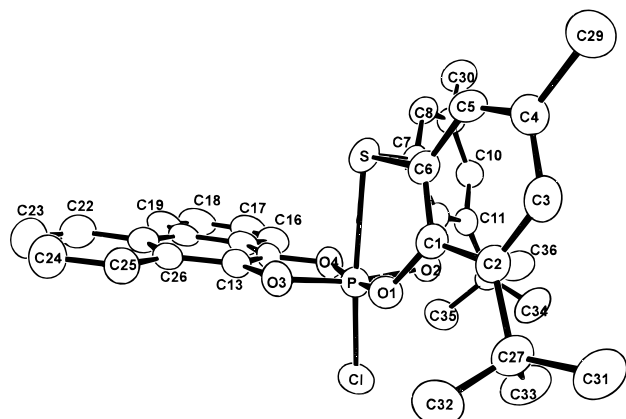
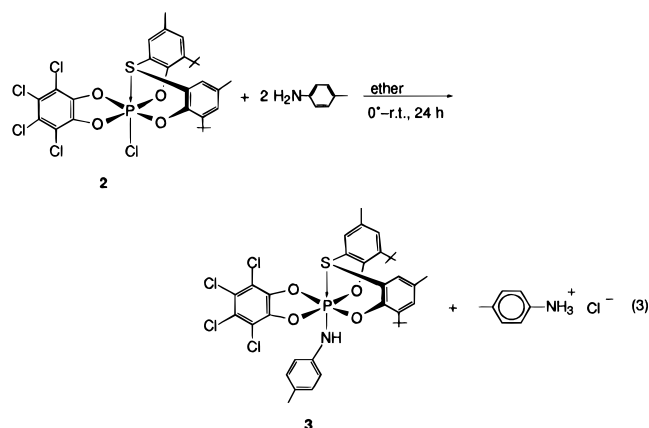
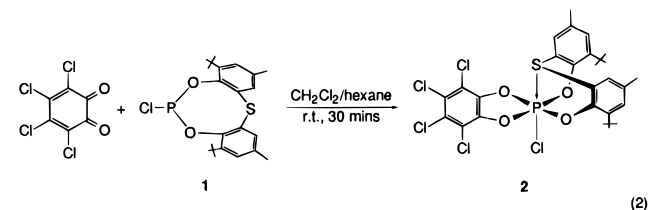
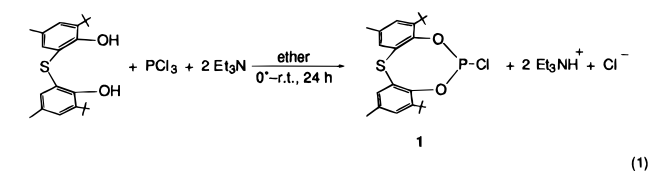


Figure 4. ORTEX diagram of $S[(t\text{-Bu)MeC}_6\text{H}_2\text{O}]_2\text{PCl}(\text{O}_2\text{C}_{14}\text{H}_8)$ (**5**) with thermal ellipsoids at 40% probability level. All hydrogen atoms are omitted for clarity.

Yields range from 35% to 92%. Since the chloro derivatives **2** and **5** are reactive, care must be exercised to prevent hydrolysis.



Basic Structures. Despite lowering the electronegativity of the fifth ligand from oxygen ($\chi = 3.44^{18}$) to nitrogen ($\chi = 3.04^{18}$) or chlorine ($\chi = 3.16^{18}$) in the bicyclic tetraoxaphosphoranes, **2–6**, hexacoordination still occurs via sulfur donor action. The general form of the structures obtained from the X-ray studies are distorted octahedral arrangements as depicted, schematically, in the Introduction. In all cases, the acyclic chlorine or nitrogen containing ligands are located *trans* to the P–S linkages. As shown in Figures 1–5, the eight-membered rings that contain the sulfur atoms are all in *syn* conformations, *i.e.*, boat–boat arrangements.

(18) Pauling values by Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.

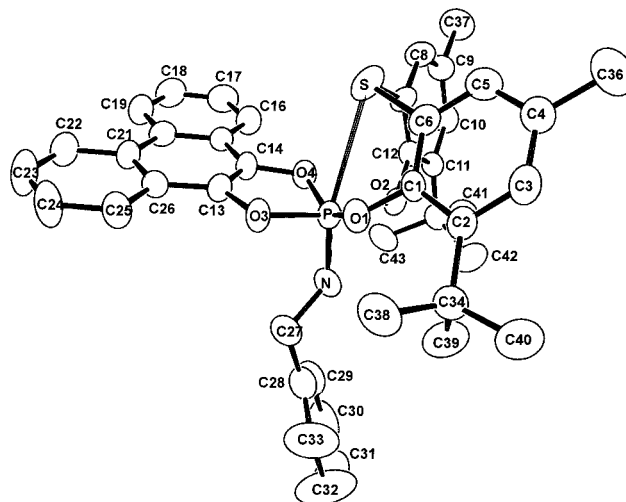


Figure 5. ORTEX diagram of $S[(t\text{-Bu)MeC}_6\text{H}_2\text{O}]_2\text{P}(\text{NHCH}_2\text{C}_6\text{H}_5)(\text{O}_2\text{C}_{14}\text{H}_8)$ (**6**) with thermal ellipsoids at 40% probability level. All hydrogen atoms are omitted for clarity.

For the purpose of evaluating geometrical distortions more quantitatively, Table 2 lists selected bond parameter data for **2–6**. Based on the approach of the sulfur atom to phosphorus, which extends from 3.041(3) Å to 2.479(2) Å, the displacement toward an octahedron increases in the order **6** < **4** < **3** < **5** < **2**. This order parallels the increase in *trans* basal angles O4–P–O1 and O3–P–O2 from an average value of 157.4(3)° for **6** to 171.4(1)° for **2**. The oxygen atoms involved in the latter *trans* angles may be considered to form the base of a square pyramid with the R group as the apical ligand. The donor sulfur atom then allows the coordinate from the square pyramid to the octahedron to be traversed.

Displacement Coordinate. Based on a more detailed method that we have used to evaluate octahedral coordination with a series of pentaoxyphosphoranes exhibiting sulfur donor action⁶ and a series of pentaoxyphosphoranes having oxygen donor action via a sulfonyl group,⁷ we determine the degree of octahedral character as listed in the last column of Table 2. The increase in the series from 23.8% to 70.8% parallels the decrease in P–S distance from 3.041(3) Å to 2.479(2) Å. 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°. ^{19–21}

Compared to the bicyclic tetraoxaphosphoranes in this work, the monocyclic pentaoxyphosphoranes having P–S coordination that were studied earlier^{2–6,8} show a similar range of P–S distances from 2.88 to 2.33 Å. In each series the P–S distance changes about 0.55 Å. However, in the series reported here, the extent of the coordinate traversed from a square pyramid to an octahedron is much greater. In the series of pentaoxyphosphoranes,^{2–6,8} the range extends from 44.1% to 70.8%, whereas here it is 23.8% to 70.8%. Perhaps the use of a greater variety of ligands included in the tetraoxaphosphorane series that vary in size and electronegativity is largely responsible.

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

(20) Holmes, R. R. *Pentacoordinated Phosphorus -- Structure and Spectroscopy*. ACS Monograph 175, American Chemical Society: Washington, DC, 1980; Vol. 1.

(21) 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.

Table 2. Selected Bond Parameters for Bicyclic Tetraoxyphosphoranes Measuring the Degree of Octahedral Coordination

| compd no. | bond distances, Å | | | | | | bond angles, deg | | | % octa ^b |
|-------------------|-------------------|----------|----------|----------|----------|----------|----------------------|----------------------|----------|---------------------|
| | P–O4 | P–O1 | P–O3 | P–O2 | P–R | P–S | O4–P–O1 ^a | O3–P–O2 ^a | R–P–S | |
| 6 (R = N) | 1.675(5) | 1.651(5) | 1.694(5) | 1.670(5) | 1.630(7) | 3.041(3) | 145.3(3) | 169.4(3) | 165.4(2) | 23.8 |
| 4 (R = N) | 1.723(3) | 1.670(3) | 1.716(3) | 1.659(3) | 1.645(4) | 2.731(2) | 159.3(2) | 163.8(2) | 177.6(1) | 37.1 |
| 3 (R = N) | 1.714(4) | 1.656(4) | 1.693(4) | 1.638(4) | 1.662(5) | 2.665(2) | 160.9(2) | 168.0(2) | 174.7(2) | 47.4 |
| 5 (R = Cl) | 1.677(3) | 1.654(3) | 1.680(3) | 1.667(3) | 2.064(2) | 2.581(2) | 171.3(2) | 166.7(2) | 175.0(1) | 62.9 |
| 2 (R = Cl) | 1.695(3) | 1.648(3) | 1.704(3) | 1.645(3) | 2.061(2) | 2.479(2) | 172.2(1) | 170.6(1) | 176.5(1) | 70.8 |

^a Relative to a square pyramid, these are *trans* angle values. For **2–6**, respectively, *cis* angle values for O1–P–O2 are 93.5(1), 91.9(2), 90.9(2), 91.2(2), and 92.0(3), and for O3–P–O4, they are 90.0(1), 89.0(2), 88.4(2), 91.1(2), and 89.6(3). ^b 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 the four oxygen atoms.

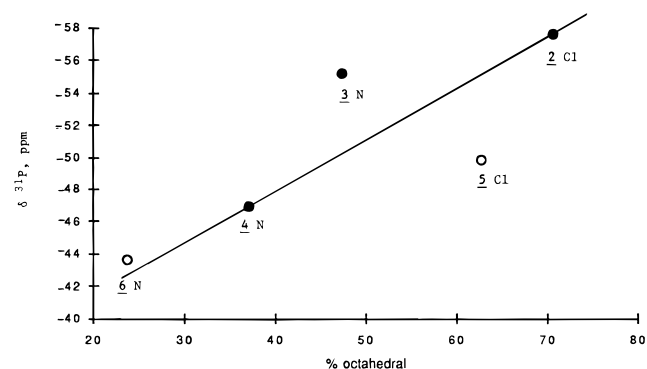


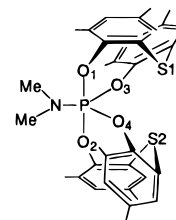
Figure 6. Variation in the ³¹P chemical shift ($\delta^{31}\text{P}$) with the percent octahedral character of the hexacoordinated bicyclic tetraoxyphosphoranes, **2–6**. The filled circles refer to derivatives containing the tetrachlorocatechol ligand. The open circles refer to derivatives which have the phenanthrene moiety. The symbols Cl and N refer to the attached acyclic ligand.

³¹P Shielding and Ligand Electronegativity. As a reflection of the variation in the acyclic ligands in **2–6**, it is noteworthy that there is a correlation between an increase in ³¹P shielding for **2–6** and an increase in octahedral character. In Figure 6, the ³¹P chemical shift for this series plotted vs. the percent displacement toward an octahedron yields a reasonable linear relation. Over the series for **2–6**, the ³¹P chemical shift changes 14 ppm. This change contrasts with the ³¹P shifts for the series of pentaoxyphosphoranes showing P–S coordination^{2–6,8} where the values are nearly the same, averaging 82.2 ± 0.5 ppm for members whose geometries are displaced toward an octahedron from 44% to 71%.

Actually there are two series portrayed in Figure 6, one that has the tetrachlorocatechol ligand, *i.e.*, **2**, **3**, and **4**, and one that comprises **5** and **6** which has phenanthrene moiety. The chlorine ligands are more electron withdrawing, a feature that enhances sulfur donor action which leads to greater octahedral character. The *p*-toluidine ligand in **3** has less electronegativity than chlorine. However, the aliphatic amines in **4** and **6** are relatively inductive in supplying electron density, particularly via π back bonding to phosphorus. At least, this correlates with the P–N bond distances which decrease from **3** to **4** to **6**, Table 2. The shortest P–N distance in the series, 1.630(7) Å for **6**, compares with the sum of the single bond covalent radii of 1.85 Å thus implying some measure of double bond character. In contrast, the P–Cl distances, 2.064(2) Å for **5** and 2.061(2) Å for **2**, are nearly the same as the sum of the covalent radii of 2.05 Å.

Structural Comparisons. The bicyclic sulfur containing tetraoxyphosphorane **E**,²² that has a Me₂N group as the fifth ligand, shows no tendency for P–S coordination even though the rings are in *syn* boat–boat conformation. The P–S distances

are close to the sum of the van der Waals' radii of 3.75 Å.²³ The sum of the covalent radii is 2.14 Å.²⁴ When donor action

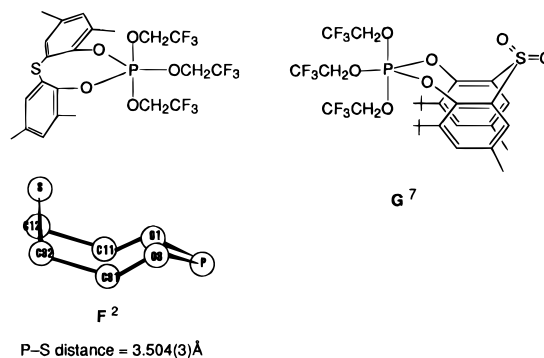


P–S₁ = 3.652(3)Å

P–S₂ = 3.485(4)Å

E²²

is lacking, we find that the ring containing donor atom normally is in a *anti* chair–boat conformation, *e.g.*, **F**² and **G**.⁷ The P–N distance in **E** is 1.644(7) Å, the same value as found in the



P–S distance = 3.504(3)Å

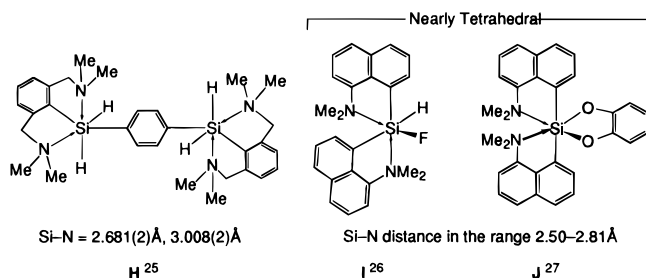
Me₂N derivative **4** (Table 2) which exhibits P–S coordination. The lack of sulfur donor action in **E** was attributed²² to the presence of P–N π back-bonding which sufficiently reduced the electrophilicity of phosphorus to prevent additional coordination. In the analogous bicyclic tetraoxyphosphorane **4**, the presence of the more electron withdrawing tetrachlorocatechol ligand apparently increases the Lewis acidity of phosphorus to allow hexacoordination via sulfur donor action. Thus, it is seen that a crossover in coordination geometry from hexacoordination to pentacoordination occurs in the series of related tetraoxyphosphoranes, **2–6** and **E**, when the ligand electronegativity requirements are sufficiently relaxed, and the ligand π bonding characteristics are increased.

Comparison with Neutral Hexacoordinated Silicon. It is of interest to compare **2–6** with related neutral hexacoordinated silicon formed via nitrogen donor action. Structural work by Corriu and co-workers gives geometries that are best described

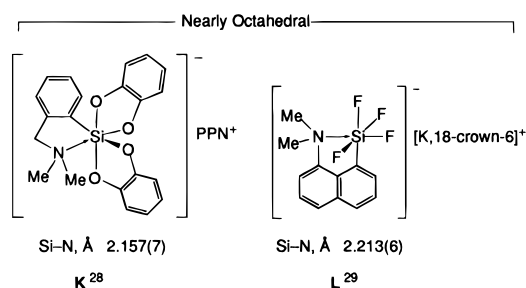
(23) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

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

as bicapped tetrahedrons, e.g., **H**,²⁵ **I**,²⁶ and **J**.²⁷ The Si–N



distances for these silanes are all higher than the sum of the covalent radii of 1.93 Å²⁴ but considerably less than the van der Waals' sum of 3.65 Å.²³ Apparently the nitrogen coordination does not provide sufficient energy to alter the basic tetrahedral geometry toward an octahedral one. If additional electron density is provided as in anionic silicon derivatives like **K**²⁸ and **L**,²⁹ which are then isoelectronic with the phosphoranes **2–6**, octahedral geometries result due to nitrogen donor action.



It also is of interest to compare axial bond distances in a series of chlorosilanes^{30–32} that exist as trigonal bipyramids as

(25) Carré, F.; Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reye, C. *Organometallics* **1995**, *14*, 2754–2759.

(26) Breliere, C.; Carré, F.; Corriu, R. J. P.; Poirier, M.; Royo, G.; Zwecker, J. *Organometallics* **1989**, *8*, 1831.

(27) Carré, F.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *New J. Chem.* **1992**, *16*, 63.

(28) Carré, F.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 489.

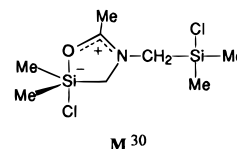
(29) Breliere, C.; Carré, F.; Corriu, R. J. P.; Douglas, W. E.; Poirier, M.; Royo, G.; Wong Chi Man, M. *Organometallics* **1992**, *11*, 1586.

(30) Onan, K. D.; McPhail, A. T.; Yoder, C. H.; Hillyard, R. W. *J. Chem. Soc., Chem. Commun.* **1978**, 209.

(31) Macharashvili, A. A.; Baukov, Yu. I.; Kramarova, E. P.; Oleneva, G. I.; Pestunovich, V. A.; Struchkov, Yu. T.; Shklover, V. E. *Zh. Strukt. Khim.* **1987**, *28*, 114; *Chem. Abstr.* **1988**, *108*, 29802x.

(32) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Oleneva, G. I.; Kramarova, E. P.; Shipov, A. G.; Baukov, Yu. I. *J. Chem. Soc., Chem. Commun.* **1988**, 683.

a result of oxygen donor action. As the Si–O_{ax} donor coordination increases, as judged by a progressive decrease in the associated Si–O_{ax} distance from 2.43 to 1.92 Å, the Si–Cl_{ax} distance increases from 2.15 to 2.35 Å, respectively. The sum of the covalent radii for Si–Cl is 2.17 Å,²⁴ and the van der Waals' sum is 3.90 Å.²³ The member of the series with the shortest Si–O distance is **M**.³⁰ It is representative in that the series is composed of monocyclic dimethyl silanes having the same directly attached atoms. The variation in composition of the five members is provided by alterations in the cyclic components. Although the series under study in this work has



octahedral geometries, a similar trans effect operates. This is seen with the nitrogen ligands in Table 2 for the cyclic phosphoranes **3**, **4**, and **6**. As the P–S donor distance decreases over the series from 3.041(3) for **6** to 2.731(2) for **4** to 2.665(2) Å for **3**, the P–N distances increase from 1.630(7) to 1.645(4) to 1.662(5) Å, respectively.

Summary

A series of neutral sulfur containing bicyclic tetraoxophosphoranes exhibited hexacoordinated structures due to sulfur donor action. The geometries were displaced along a coordinate extending from a square pyramid toward an octahedron. The degree of octahedral character was enhanced by increased electronegativity of the acyclic ligand (Cl > N) and decreased by the presence of the acyclic ligand π back-bonding (N=P) at phosphorus. A lower limit to the electrophilicity of phosphorus provided by variation in the ligand properties that will induce the formation of a hexacoordinated geometry is determined in this series of bicyclic tetraoxophosphoranes. There also is a correlation between the ³¹P chemical shift and octahedral character with ³¹P shifts becoming increasingly more negative as the structure approaches an ideal octahedron.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters and figures showing thermal ellipsoids for **2–6** (30 pages). See any current masthead page for ordering and Internet access instructions.

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