

Seven-Membered Rings in Pentaoxyphosphoranes Containing Trifluoroethoxy Groups¹T. K. Prakasha, Sara D. Burton,² Roberta O. Day, and Robert R. Holmes*

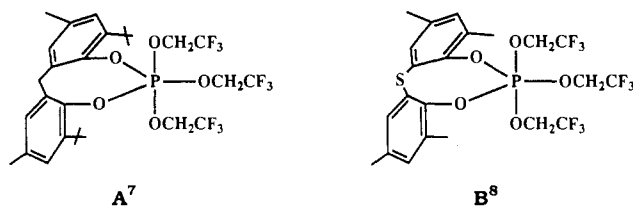
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

Received June 10, 1992

The formation of the new cyclic tetraoxyphosphoranes $(C_{12}H_8O_2)_2P(Ph)(O-Xyl)_2$ (**3**) and $[(t-Bu)_4C_{12}H_4O_2]P(Ph)(C_{12}H_8O_2)_2$ (**4**) and the new cyclic pentaoxyphosphoranes $(C_{12}H_8O_2)_2P(OCH_2CF_3)$ (**5**) and $[(t-Bu)_4C_{12}H_4O_2]P(OCH_2CF_3)_3$ (**6**) resulted from the reactions of $PhPCl_2$ or $P(OCH_2CF_3)_3$ with the appropriate diol in the presence of *N*-chlorodiisopropylamine in ether solution. X-ray studies of **5** and **6** revealed trigonal bipyramidal (TBP) structures with the seven-membered rings positioned at axial-equatorial sites in spite of the greater preference of the electronegative OCH_2CF_3 groups for axial occupancy and the steric inducement of *tert*-butyl substituents to orient the rings in diequatorial positions. ¹H, ¹⁹F, and ³¹P NMR data obtained in toluene-*d*₈ solution were consistent with retention of the solid-state structures in solution. In the case of the monocyclic derivative **6**, rapid ligand exchange (pseudorotation) was indicated over the temperature range of 67.0 to -48.9 °C. In CDCl₃ solution decomposition was indicated for both **5** and **6** by both ¹⁹F and ¹H NMR spectroscopy. It is concluded that the energy barrier to ring placement in diequatorial sites of a TBP for the particular seven-membered cyclic system used is greater than that for related eight-membered rings in pentaoxyphosphoranes. The latter ring system exists in diequatorial sites in two compounds studied earlier. The spirocyclic derivative **5** crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.259$ (3) Å, $b = 12.662$ (3) Å, $c = 14.817$ (4) Å, $\beta = 96.42$ (2)°, and $Z = 4$. The monocyclic compound **6** crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.370$ (4) Å, $b = 25.338$ (6) Å, $c = 12.770$ (4) Å, $\beta = 118.42$ (3)°, and $Z = 4$. The final conventional unweighted residuals are 0.041 (**5**) and 0.089 (**6**).

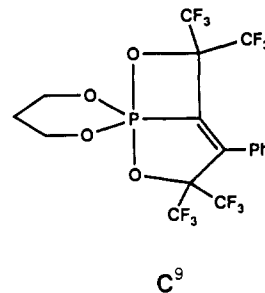
Introduction

Work in our laboratory has centered on the synthesis and structural characterization of new cyclic pentaoxyphosphoranes^{3,4} and isoelectronic anionic silicates^{5,6} having ring sizes larger than five-membered. Recently, we reported the first pentaoxyphosphoranes, **A**⁷ and **B**,⁸ with eight-membered rings positioned at

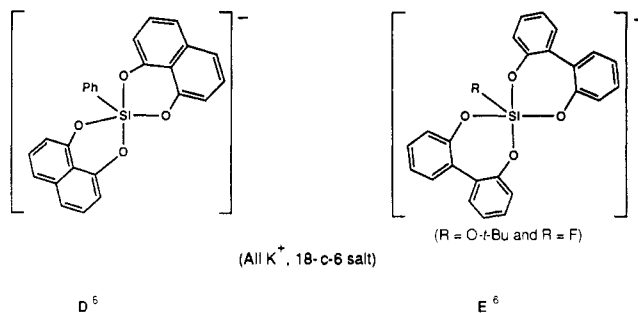


diequatorial sites (e-e) of a trigonal bipyramid (TBP) rather than the more conventional axial-equatorial orientation, (a-e). Bentrude and co-workers⁹ reported the polycyclic tetraoxyphosphorane **C** with a constrained bicyclic system that had a six-membered ring located at e-e sites.

For the less developed but more reactive analogous silicon chemistry, isolation of the first anionic five-coordinated silicates



with six- and seven-membered oxygen-containing rings in tetraoxy and pentaoxy derivatives, **D** and **E**, was recently achieved.⁶

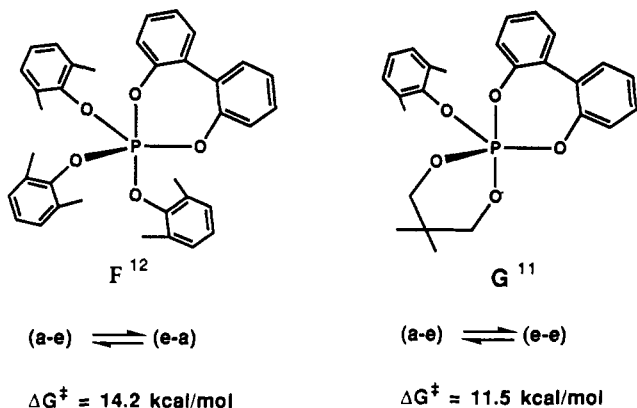


- (1) (a) Pentacoordinated Molecules. 94. (b) Part 93: Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 3391.
- (2) Taken in part from the Ph.D. Thesis of Sarah D. Burton, University of Massachusetts, Amherst, MA, 1991.
- (3) Holmes, R. R.; Day, R. O.; Deiters, J. A.; Kumara Swamy, K. C.; Holmes, J. M.; Hans, J.; Burton, S. D.; Prakasha, T. K. *Cyclic Oxyphosphoranes. Models for Reaction Intermediates*. In *Phosphorus Chemistry Developments in American Science*; Walsh, E. N., Griffiths, E. J., Parry, R. W., Quin, L. D., Eds.; ACS Symposium Series 486; American Chemical Society: Washington, DC, 1992; pp 18-40.
- (4) Kumara Swamy, K. C.; Burton, S. D.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *Phosphorus, Sulfur Silicon* **1990**, *53*, 437.
- (5) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17.
- (6) Kumara Swamy, K. C.; Sreelatha, C.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3126.
- (7) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 725.
- (8) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1913.
- (9) Huang, Y.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1991**, *113*, 7800.

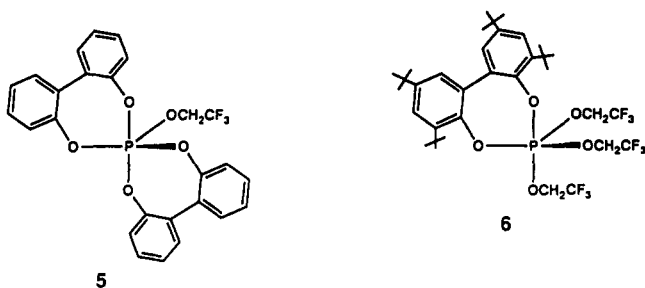
In continuance of the development of oxygen-ligated penta-coordinated phosphorus^{3,4,10-15} and silicon species^{5,16,17} as models for intermediates and transition states in nucleophilic substitution

- (10) Schomburg, D.; Hacklin, H.; Rösenthaller, G.-V. *Phosphorus Sulfur Relat. Elem.* **1988**, *35*, 241.
- (11) Kumara Swamy, K. C.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6095.
- (12) Burton, S. D.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6104.
- (13) Holmes, R. R.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O. *Inorg. Chem.* **1991**, *30*, 1052.
- (14) Yu, J. H.; Sopchik, A. E.; Arif, A. M.; Bentrude, W. G. *J. Org. Chem.* **1990**, *55*, 3444.
- (15) Yu, J. H.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1990**, *112*, 7451.

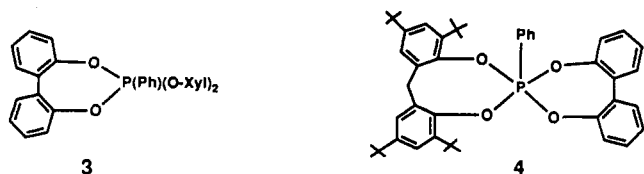
reactions,^{3,5,18} we concentrate here on oxyphosphoranes containing seven-membered ring systems. Previously, the structural characterization of pentaoxyphosphoranes having this ring size has been sparse. The first examples that have had their X-ray structures reported are F¹² and G¹¹ containing the same seven-membered ring. These rings are located in a-e sites of a TBP.



In an effort to ascertain factors favoring the location of seven-membered rings at e-e sites of a TBP, we report pentaoxyphosphoranes **5** containing two such rings and **6** having a steric



component provided by the *tert*-butyl groups substituted on this same ring. In addition, the use of the electronegative trifluoroethoxy groups serving as acyclic ligands should facilitate attainment of an e-e ring orientation, especially since this factor apparently assisted in allowing placement of eight-membered rings in this orientation in A⁷ and B.⁸ X-ray crystal studies and NMR measurements are used to structurally characterize these new members. Also the new tetraoxyphosphoranes **3** and **4** were synthesized and their NMR data reported.



The depictions for A-G and **5** and **6** are meant to reflect their basic structures, whereas those for **3** and **4** do not.

Experimental Section

Chemicals were obtained from Aldrich, Fisher Scientific, or Fluka and used without further purification. Solvents were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.¹⁹

¹H, ¹⁹F, and ³¹P NMR spectra were recorded on a Varian XL-300 FT-NMR spectrometer. ¹H and ¹⁹F chemical shifts are reported in ppm relative to tetramethylsilane and fluorotrichloromethane (external), respectively. Chemical shifts for ³¹P NMR spectra were obtained by setting triphenyl phosphate (CDCl₃) at -18.0 ppm²⁰ and are referenced to 85% H₃PO₄ with negative shifts upfield. All NMR spectra were obtained at 21 °C unless otherwise stated.

All the reactions were carried out in a dry nitrogen atmosphere using standard Schlenk-type glassware.²¹ Melting points are uncorrected.

Syntheses. **Bis(2,6-dimethylphenoxy)phenylphosphine, (O-Xyl)₂PPh (1).** A mixture of 2,6-dimethylphenol (7.65 g, 62.6 mmol) and triethylamine (10.45 mL, 7.59 g, 75.0 mmol) in diethyl ether (100 mL) was added dropwise to a solution of dichlorophenylphosphine (4.2 mL, 5.54 g, 31.0 mmol) in diethyl ether (50 mL), which was kept at 0 °C. The reaction mixture was stirred at room temperature for 18 h. Removal of Et₃NHCl by filtration followed by evaporation of the solvent under reduced pressure gave an oily material. The extraction of the oily material with a 1:1 mixture of Et₂O/hexane (50:50 mL) and slow evaporation of the solvent mixture afforded **1**, mp 82–84 °C (yield 10.7 g, 99%). ¹H NMR (CDCl₃): 2.10 (s, 12H, CH₃), 6.9–8.0 (m, 11H, H(Ar)). ³¹P NMR (CDCl₃): 165.70. Anal. Calcd for C₂₂H₂₃O₂P: C, 75.42; H, 6.57. Found: C, 75.37; H, 6.65.

[2,2'-Methylenebis(4,6-*tert*-butylphenyleneoxy)-O,O'-phenylphosphine, [CH₂(*t*-Bu)₄C₁₂H₄O₂]PPh (2). A procedure similar to that for the preparation of **1** was followed. Quantities used were as follows: PhPCl₂ (5.00 mL, 6.60 g, 36.9 mmol); 2,2'-methylenebis(4,6-di-*tert*-butylphenol)²² (15.62 g, 36.9 mmol); Et₃N (11.29 mL, 8.21 g, 81.1 mmol); diethyl ether (200 mL). Mp: 190–191 °C. Yield: 15.6 g, 80%. ¹H NMR (CDCl₃): 1.20 (s, 18H, C(CH₃)₃), 1.26 (s, 18H, C(CH₃)₃), 3.45 (d, ²J_{HH} = 12.5 Hz, 1H, CH₂), 4.52 (d, ²J_{HH} = 12.7 Hz, 1H, CH₂), 7.10–8.00 (m, 9H, H(Ar)). ³¹P NMR (CDCl₃): 164.20. Anal. Calcd for C₃₃H₄₇O₂P: C, 79.25; H, 8.87. Found: C, 79.07; H, 9.83.

(Biphenylene-2,2'-dioxy)bis(2,6-dimethylphenoxy)phenylphosphorane, (C₁₂H₈O₂)(O-Xyl)₂PPh (3). To a mixture of bis(2,6-dimethylphenoxy)phenylphosphine (1.00 g, 2.86 mmol) and 2,2'-biphenol (0.532 g, 2.86 mmol) in diethyl ether (50 mL) maintained at -70 °C was added dropwise a solution of *N*-chlorodiisopropylamine (0.46 mL, 0.43 g, 3.15 mmol) in diethyl ether (20 mL) over a period of 10 min with continuous stirring. The reaction mixture was stirred at 25 °C for 16 h. After the removal of (*i*-Pr)₂NH₂⁺Cl, the solvent was evaporated under reduced pressure to afford **3**, mp 135–137 °C (decomposes) (yield 1.22 g, 80%). ¹H NMR (CDCl₃): 2.08 (br, 12H, CH₃), 6.82–8.00 (m, 19H, H(Ar)). ³¹P NMR (CDCl₃): -42.97. Anal. Calcd for C₃₄H₃₁O₄P: C, 76.4; H, 5.80. Found: C, 76.2; H, 5.87.

[2,2'-Methylenebis(4,6-di-*tert*-butylphenyleneoxy)-O,O'][(biphenylene-2,2'-dioxy)phenylphosphorane, (C₁₂H₈O₂)[CH₂(*t*-Bu)₄C₁₂H₄O₂]PPh (4). A procedure similar to that for the preparation of **3** was followed. Quantities used were as follows: **2** (0.50 g, 0.94 mmol); 2,2'-biphenol (0.18 g, 0.94 mmol); *N*-chlorodiisopropylamine (0.17 mL, 0.15 g, 1.15 mmol); diethyl ether (100 mL). Mp: 210 °C (decomposes without melting). Yield: 1.31 g, 76%. ¹H NMR (CDCl₃): 1.10–1.50 (m, 36H, C(CH₃)₃), 3.61 (m, 1H, CH₂), 4.10 (m, 1H, CH₂), 6.60–7.60 (m, 17H, H(Ar)). ³¹P NMR (CDCl₃): -43.9. Anal. Calcd for C₄₇H₅₅O₄P: C, 78.9; H, 7.7. Found: C, 78.1; H, 8.1.

Bis(biphenylene-2,2'-dioxy)(2,2,2-trifluoroethoxy)phosphorane, (C₁₂H₈O₂)₂P(OCH₂CF₃) (5). A procedure similar to that for the preparation of **3** was followed. Quantities used were as follows: Tris(2,2,2-trifluoroethyl) phosphite (1.00 mL, 1.49 mg, 4.53 mmol); 2,2'-biphenol (0.843 g, 4.53 mmol); *N*-chlorodiisopropylamine (0.80 mL, 0.74 g, 5.4 mmol); diethyl ether (100 mL). **5** was crystallized by slowly

(16) Holmes, R. R.; Day, R. O.; Payne, J. S. *Phosphorus Sulfur Silicon* **1989**, *42*, 1.

(17) Kumara Swamy, K. C.; Chandrasekhar, V.; Harland, J. J.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2341.

(18) (a) Holmes, R. R. *Pentacoordinated Phosphorus-Structure and Spectroscopy, Vol. I*; ACS Monograph 175; American Chemical Society: Washington, DC, 1980; 479 pp. (b) Holmes, R. R. *Pentacoordinated Phosphorus-Reaction Mechanisms, Vol. II*; ACS Monograph 176; American Chemical Society: Washington, DC, 1980; 237 pp.

(19) (a) Riddick, J. A.; Bunger, W. G., Eds. *Organic Solvents in Physical Methods in Organic Chemistry*; Weissberger, Wiley Interscience: New York, 1970; Vol. II. (b) Vogel, A. I. *Textbook of Practical Organic Chemistry*; Longman: London, 1978.

(20) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Wiley: New York, 1976; p 82.

(21) Shriver, D. F.; Drezdson, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(22) Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Bini, D.; Rodebaugh, R. K. *Phosphorus Sulfur* **1984**, *19*, 285.

evaporating the ether solution under a stream of nitrogen, mp 200–203 °C (yield 0.90 g, 40%). ¹H NMR (toluene-*d*₈, 67.0 °C): 4.17 (m, 2H, OCH₂CF₃), 6.90–7.50 (m, 16H, H(Ar)). ¹⁹F NMR (toluene-*d*₈): –74.50 (s, OCH₂CF₃). ³¹P NMR (CDCl₃): –47.34. Anal. Calcd for C₂₆H₁₈F₃O₃P: C, 62.65; H, 3.61. Found: C, 62.51; H, 3.75.

Variable-temperature ¹H and ¹⁹F NMR spectra were recorded in the range 67.0 to –48.9 °C. The single sharp triplet pattern at 67 °C in the methylene region at 4.17 ppm, which is interpreted as an overlapping doublet of quartets, broadened as the temperature was lowered. The coupling was lost and the peak width at half-height more than doubled from 67 to –48.9 °C. The sharp peaks in the multiplet pattern in the aromatic region (7.5–6.9 ppm) remained so. No appreciable shift in the resonances occurred. The ¹⁹F single resonance was essentially invariant over this temperature range. The peak at –74.50 ppm at 67.0 °C shifted to –74.96 ppm at –48.9 °C.

3,3',5,5'-Tetra-*tert*-butylbiphenylene-2,2'-dioxytris(2,2,2-trifluoroethoxy)phosphorane,²³ [(*t*-Bu)₄C₁₂H₈O₂]P(OCH₂CF₃)₃ (**6**). A procedure similar to that for the preparation of **3** was followed. Quantities used were as follows: Tris(2,2,2-trifluoroethyl) phosphite (2.00 mL, 2.97 g, 9.07 mmol); 3,3',5,5'-tetra-*tert*-butylbiphenyl-2,2'-diol²⁴ (3.72 g, 9.07 mmol); *N*-chlorodiisopropylamine (1.60 mL, 1.47 g, 1.09 mmol); diethyl ether (150 mL). The addition of (*i*-Pr)₂NCl in Et₂O was done at –70 °C, and then the reaction mixture was stirred at 25 °C for 62 h. **6** was crystallized from a Et₂O/hexane (50:100 mL) mixture, mp 210 °C (decomposes) (yield 5.34 g, 80%). ¹H NMR (toluene-*d*₈, 67 °C): 1.50 (s, 18H, C(CH₃)₃), 1.65 (s, 18H, C(CH₃)₃), 4.35 (br, 6H, OCH₂CF₃), 7.15 (s, 1H, H(Ar)), 7.25 (s, 1H, H(Ar)), 7.50 (s, 1H, H(Ar)), 7.70 (s, 1H, H(Ar)). ¹⁹F NMR (toluene-*d*₈): –74.96 (s, OCH₂CF₃). ³¹P NMR (CDCl₃): –68.34. ³¹P NMR (toluene-*d*₈): –67.67. Anal. Calcd for C₃₄H₄₆F₉O₃P: C, 55.40; H, 6.30. Found: C, 55.43; H, 6.25.

Variable-temperature ¹H and ¹⁹F NMR spectra were recorded in toluene-*d*₈ in the range 67.0 to –48.9 °C. The singlet proton resonance observed at 4.35 ppm for the methylene protons at 67.0 °C broadened and split into two signals on cooling. At –48.9 °C, the somewhat broad peaks of equal intensity appeared at 4.10 and 4.60 ppm, which average to 4.35 ppm, the value observed at 67.0 °C for the single unsplit peak. The remainder of peaks in the proton spectrum which were assigned to the *tert*-butyl groups and aromatic protons were essentially invariant over the temperature range covered. The same is true for the ¹⁹F spectrum. The latter spectrum which contained a single sharp peak at 67.0 °C (–74.96 ppm) showed only a small shift to –75.10 ppm at –48.9 °C.

X-ray Studies. All X-ray crystallographic studies were done with an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation. Details of the experimental procedures have been described previously.²⁵ Crystals were mounted in thin-walled glass capillaries which were sealed as a precaution against moisture sensitivity. Data were collected using the θ – 2θ scan mode. No corrections were made for absorption. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least squares.²⁶

All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. Crystallographic data are summarized in Table I.

X-ray Study for (C₁₂H₈O₂)₂P(OCH₂CF₃)₃ (5**).** The colorless plate used for the study was cut to dimensions of 0.20 × 0.38 × 0.48 mm. A total of 2437 independent reflections were measured (+*h*, +*k*, ±*l*; 3° ≤ 2 θ _{M₀K α} ≤ 42°). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as fixed isotropic scatterers in ideal positions. The final refinement was based on the 1505 reflections with *I* > 3 σ _{*I*}.

X-ray Study for [(*t*-Bu)₄C₁₂H₈O₂]P(OCH₂CF₃)₃ (6**).** Crystals of **6** were large frosted opaque polycrystalline chunks and were deliquescent. The crystal used for the study was cut to approximate dimensions of 0.38 × 0.45 × 0.55 mm. The Niggli-matrix for the monoclinic cell suggested transformation to a C-centered orthorhombic cell, but the systematic extinctions and diffraction symmetry did not support that assignment. A total of 4334 independent reflections was measured (+*h*, +*k*, ±*l*; 3° ≤ 2 θ _{M₀K α} ≤ 43°).

Table I. Crystallographic Data for **5** and **6**

	compound	
	5	6
formula	C ₂₆ H ₁₈ F ₃ O ₃ P	C ₃₄ H ₄₆ F ₉ O ₃ P
fw	498.367	736.702
cryst system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> , Å	12.259 (3)	13.370 (4)
<i>b</i> , Å	12.662 (3)	25.338 (6)
<i>c</i> , Å	14.817 (4)	12.770 (4)
β , deg	96.42 (2)	118.42 (3)
<i>V</i> , Å ³	2285 (2)	3805 (4)
<i>Z</i>	4	4
<i>T</i> , °C	23 ± 2	23 ± 2
λ , Å	0.710 73	0.710 73
<i>D</i> _{calc} , g cm ^{–3}	1.448	1.286
μ , cm ^{–1}	1.743	1.470
<i>R</i> (<i>F</i> _o) ^a	0.041	0.089
<i>R</i> _w (<i>F</i> _o) ^a	0.054	0.119

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o| \text{ and } R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}.$$

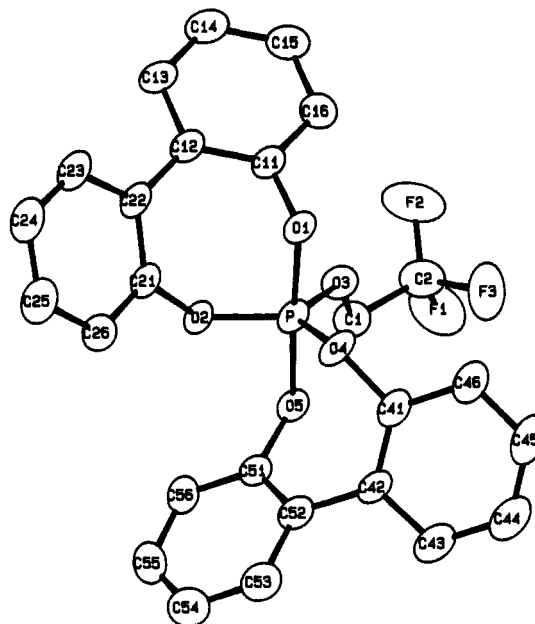


Figure 1. ORTEP plot of (C₁₂H₈O₂)₂P(OCH₂CF₃)₃ (**5**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Solution of the structure was complicated by disorder in two of the CF₃ groups and in one of the *t*-Bu groups. Two sets of positions were found for the three fluorine atoms bound to C2 and for the three carbons atoms bound to C21 (rotational disorder). For the fluorine atoms bound to C6 only F9 had two positions which could be resolved (tipping disorder, with F7 and F8 nearly superposed). Non-hydrogen atoms were refined anisotropically except for those disordered atoms in partial occupancy which were refined isotropically. Hydrogen atoms bound to well-defined species were included in the refinement in ideal positions as fixed isotropic scatterers (24 H atoms). The remaining hydrogen atoms were omitted. The final refinement was based on the 2654 reflections with *I* ≥ 3 σ _{*I*}. The maximum density on a final difference Fourier synthesis (0.608 e/Å³) was in the immediate vicinity of the disordered *t*-Bu group.

Results

The atom-labeling scheme for **5** is shown in the ORTEP plot of Figure 1. Selected atomic coordinates are given in Table II, and selected bond lengths and angles are given in Table III. The corresponding material for **6** is given in Figure 2 and in Tables IV and V.

Discussion

Syntheses. The acyclic and cyclic phenylphosphines (O-Xyl)₂PPh (**1**) and [CH₂(*t*-Bu)₄C₁₂H₈O₂]PPh (**2**), respectively,

- (23) This is the first isolation of **6**. The formation of **6** in dichloromethane-*d*₂ solution by a different method was reported: Abdou, W. M.; Denney, D. B.; Denney, D. Z.; Pastor, S. D. *Phosphorus Sulfur* **1985**, *22*, 99.
 (24) Müller, E.; Mayer, R.; Narr, B.; Rieker, A.; Scheffler, K. *Ann. Chem.* **1961**, *645*, 25.
 (25) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.
 (26) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oL_p/\sigma_l$.

Table II. Selected Atomic Coordinates and B_{equiv} Values in Crystalline $(\text{C}_{12}\text{H}_8\text{O}_2)_2\text{POCH}_2\text{CF}_3$ (**5**)^a

atom ^b	x	y	z	B_{equiv} , \AA^2
P	0.8777 (1)	0.1508 (1)	0.73389 (9)	3.74 (3)
O1	1.0043 (3)	0.1183 (2)	0.7773 (2)	3.90 (8)
O2	0.8404 (2)	0.1870 (2)	0.8291 (2)	3.74 (7)
O3	0.9296 (3)	0.2349 (3)	0.6711 (2)	4.27 (8)
O4	0.8634 (3)	0.0287 (3)	0.7078 (2)	4.36 (8)
O5	0.7530 (2)	0.1828 (2)	0.6841 (2)	3.66 (7)
C1	0.8743 (4)	0.3149 (4)	0.6157 (3)	4.6 (1)
C11	1.0749 (4)	0.1938 (4)	0.8190 (3)	3.9 (1)
C12	1.0666 (4)	0.2204 (4)	0.9095 (3)	3.9 (1)
C13	1.1417 (4)	0.2931 (4)	0.9513 (4)	4.6 (1)
C14	1.2207 (4)	0.3374 (4)	0.9056 (4)	5.4 (1)
C15	1.2295 (4)	0.3090 (5)	0.8162 (5)	5.7 (1)
C16	1.1561 (4)	0.2368 (5)	0.7730 (4)	5.1 (1)
C21	0.8771 (4)	0.1486 (4)	0.9171 (3)	3.8 (1)
C22	0.9809 (4)	0.1705 (4)	0.9582 (3)	3.9 (1)
C23	1.0048 (4)	0.1405 (4)	1.0505 (3)	4.8 (1)
C24	0.9266 (5)	0.0917 (4)	1.0958 (3)	5.3 (1)
C25	0.8230 (5)	0.0707 (4)	1.0518 (4)	5.9 (2)
C26	0.7967 (4)	0.1003 (4)	0.9607 (4)	4.8 (1)
C41	0.8058 (4)	-0.0134 (4)	0.6287 (3)	4.1 (1)
C42	0.6934 (4)	-0.0161 (4)	0.6159 (3)	3.8 (1)
C43	0.6437 (5)	-0.0725 (4)	0.5399 (4)	5.3 (1)
C44	0.7080 (5)	-0.1203 (4)	0.4807 (4)	6.2 (2)
C45	0.8200 (5)	-0.1138 (4)	0.4935 (4)	6.5 (2)
C46	0.8719 (5)	-0.0608 (4)	0.5692 (4)	5.4 (1)
C51	0.6582 (4)	0.1382 (4)	0.7103 (3)	3.7 (1)
C52	0.6252 (4)	0.0405 (4)	0.6757 (3)	4.2 (1)
C53	0.5253 (5)	-0.0001 (5)	0.6966 (4)	5.8 (2)
C54	0.4601 (5)	0.0580 (6)	0.7484 (4)	6.8 (2)
C55	0.4953 (5)	0.1568 (5)	0.7820 (3)	6.3 (2)

^a Numbers in parentheses are estimated standard deviations. ^b Atoms are labeled to agree with Figure 1. ^c Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

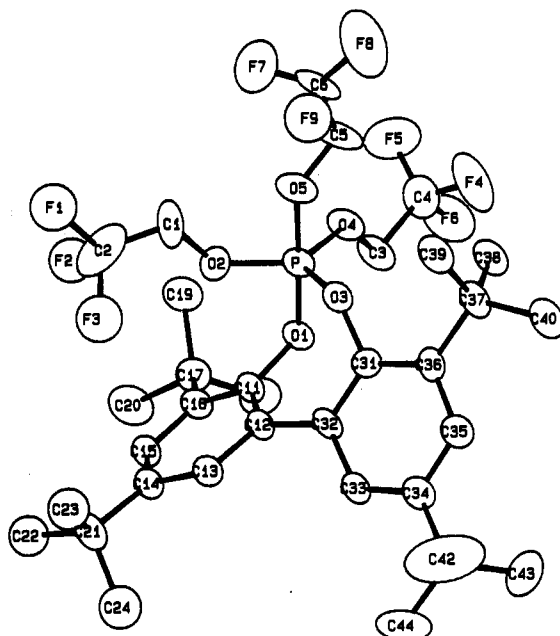
Table III. Selected Distances (\AA) and Angles (deg) in $(\text{C}_{12}\text{H}_8\text{O}_2)_2\text{POCH}_2\text{CF}_3$ (**5**)^a

Distances			
P-O1	1.664 (3)	O1-C11	1.388 (6)
P-O2	1.598 (3)	O2-C21	1.417 (5)
P-O3	1.593 (4)	O3-C1	1.427 (6)
P-O4	1.598 (3)	O4-C41	1.404 (5)
P-O5	1.671 (3)	O5-C51	1.386 (6)
C11-C12	1.396 (7)	C21-C22	1.377 (7)
C41-C42	1.370 (7)	C51-C52	1.382 (7)
C12-C22	1.481 (7)	C42-C52	1.471 (7)
Angles			
O1-P-O2	94.4 (2)	O3-P-O5	89.2 (2)
O1-P-O3	88.5 (2)	O4-P-O5	93.3 (2)
O1-P-O4	85.8 (2)	P-O1-C11	120.7 (3)
O1-P-O5	176.5 (2)	P-O2-C21	128.4 (3)
O2-P-O3	119.7 (2)	P-O3-C1	128.0 (3)
O2-P-O4	117.2 (2)	P-O4-C41	126.9 (3)
O2-P-O5	89.0 (2)	P-O5-C51	122.1 (3)
O3-P-O4	123.0 (2)	O1-C11-C12	119.0 (4)
O2-C21-C22	121.4 (4)	O4-C41-C42	122.0 (4)
O5-C51-C52	118.7 (4)	C11-C12-C22	119.8 (4)
C12-C22-C21	122.8 (4)	C41-C42-C52	122.3 (4)
C42-C52-C51	119.8 (4)		

^a Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1.

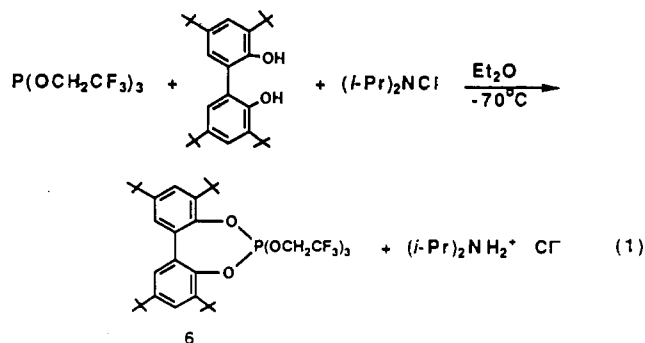
are conveniently prepared in over 80% yield by the reaction of PhPCl_2 with the appropriate phenol in the presence of Et_3N in ether solution at 0°C .

The cyclic phenyltetraoxyphosphoranes, **3** and **4**, illustrated in the Introduction, result from reaction of the tricoordinated phosphines **1** and **2**, respectively, with the corresponding diols at -70°C in the presence of *N*-chlorodiisopropylamine in ether solution with yield greater than 75%. The cyclic pentaoxyphosphoranes, **5** and **6**, were prepared by similar reactions of $\text{P}(\text{OCH}_2\text{CF}_3)_3$ with diols. The reaction is illustrated for **6** in eq 1.

**Figure 2.** ORTEP plot of $[(t\text{-Bu})_4\text{C}_{12}\text{H}_8\text{O}_2]\text{P}(\text{OCH}_2\text{CF}_3)_3$ (**6**) with thermal ellipsoids at the 30% probability level. Only one set of positions for the disordered atoms is shown, and hydrogen atoms are omitted for clarity.**Table IV.** Selected Atomic Coordinates and B_{equiv} Values in Crystalline $[(t\text{-Bu})_4\text{C}_{12}\text{H}_8\text{O}_2]\text{P}(\text{OCH}_2\text{CF}_3)_3$ (**6**)^a

atom ^b	x	y	z	B_{equiv} , \AA^2
P	0.1400 (2)	0.06151 (9)	0.8078 (2)	4.31 (5)
O1	0.0434 (3)	0.0485 (2)	0.8530 (4)	4.0 (1)
O2	0.0395 (4)	0.0797 (2)	0.6825 (4)	5.0 (1)
O3	0.2050 (4)	0.1062 (2)	0.9043 (4)	4.3 (1)
O4	0.1863 (4)	0.0020 (2)	0.8401 (4)	5.2 (1)
O5	0.2315 (4)	0.0705 (2)	0.7561 (5)	6.1 (2)
C1	0.0505 (8)	0.1075 (5)	0.5927 (8)	8.1 (3)
C3	0.1547 (7)	-0.0380 (3)	0.8965 (8)	6.2 (3)
C5	0.3258 (7)	0.0475 (5)	0.7771 (8)	11.2 (3)
C11	-0.0467 (5)	0.0831 (3)	0.8227 (6)	4.0 (2)
C12	-0.0210 (5)	0.1323 (3)	0.8768 (6)	3.7 (2)
C13	-0.1078 (6)	0.1697 (3)	0.8363 (6)	4.2 (2)
C14	-0.2168 (6)	0.1599 (3)	0.7497 (6)	4.3 (2)
C15	-0.2406 (6)	0.1076 (4)	0.7094 (6)	4.7 (2)
C16	-0.1584 (6)	0.0673 (3)	0.7457 (6)	4.4 (2)
C31	0.1940 (5)	0.1265 (3)	1.0002 (6)	3.9 (2)
C32	0.0870 (5)	0.1426 (3)	0.9842 (6)	3.8 (2)
C33	0.0837 (6)	0.1690 (3)	1.0800 (6)	4.1 (2)
C34	0.1794 (6)	0.1799 (3)	1.1846 (7)	4.6 (2)
C35	0.2845 (6)	0.1625 (3)	1.1981 (7)	4.7 (2)
C36	0.2945 (6)	0.1359 (3)	1.1051 (6)	4.0 (2)

^a Numbers in parentheses are estimated standard deviations. ^b Atoms are labeled to agree with Figure 2. ^c Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.



In the case of the formation of the spirocyclic derivative **5**, the reaction is more complicated. Instead of the expected monocyclic

Table V. Selected Distances (Å) and Angles (deg) for [(*t*-Bu)₄C₁₂H₄O₂]₂P(OCH₂CF₃)₃ (**6**)^a

Distances			
P–O1	1.679 (6)	O1–C11	1.388 (9)
P–O2	1.591 (4)	O2–C1	1.41 (1)
P–O3	1.593 (5)	O3–C31	1.40 (1)
P–O4	1.607 (5)	O4–C3	1.42 (1)
P–O5	1.659 (7)	O5–C5	1.30 (1)
C11–C12	1.37 (1)	C12–C32	1.466 (8)
C31–C32	1.41 (1)		

Angles			
O1–P–O2	89.0 (3)	O3–P–O5	88.6 (3)
O1–P–O3	95.8 (3)	O4–P–O5	87.9 (3)
O1–P–O4	89.6 (3)	P–O1–C11	119.2 (5)
O1–P–O5	175.6 (3)	P–O2–C1	126.7 (5)
O2–P–O3	117.4 (3)	P–O3–C31	133.8 (5)
O2–P–O4	124.6 (3)	P–O4–C3	128.9 (6)
O2–P–O5	89.4 (3)	P–O5–C5	133.2 (7)
O3–P–O4	117.8 (2)	O1–C11–C12	116.9 (6)
C11–C12–C32	121.7 (6)	O3–C31–C32	120.2 (5)
C31–C32–C12	124.5 (7)		

^a Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 2.

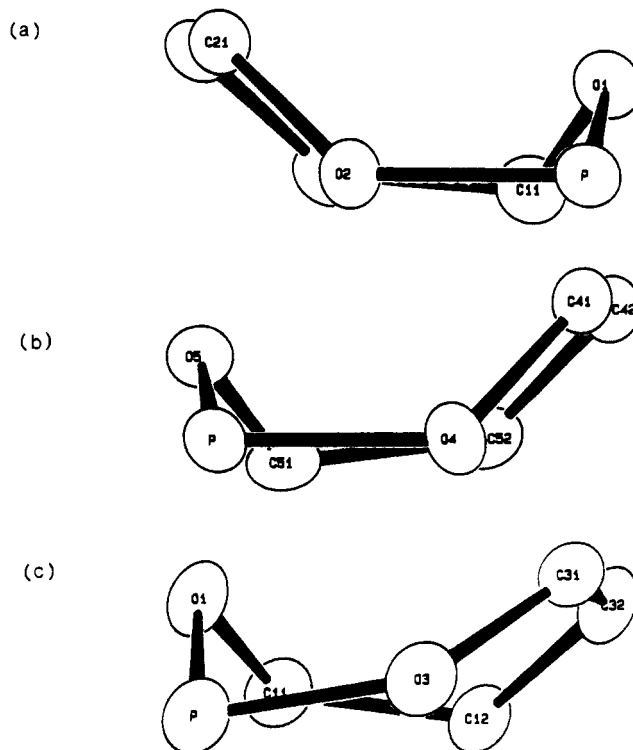
phosphorane containing a seven-membered ring and three trifluoroethoxy groups, a disproportionation reaction likely ensued yielding **5** due to an enhanced stability. The presence of *tert*-butyl substituents on the diol component in the formation of **6** may cause inhibition of a similar reaction. The yield for **5** was only 40%.

Solid-State Structures. X-ray analysis showed that the geometry about the phosphorus atom in both **5** and **6** can be referred to a trigonal bipyramid (TBP) with the seven-membered ring systems spanning axial–equatorial sites. As is to be expected, P–O_{ax} bonds are longer than P–O_{eq} bonds. The value for **5** is 0.07 Å. The average P–O_{ax} bond length is 1.668 (3) Å, while the average P–O_{eq} bond length is 1.596 (3) Å. For **6** these values are 1.669 (7) and 1.597 (5) Å.

Distortions away from ideal TBP geometry are not large. For the monocyclic **6**, these distortions follow the Berry pseudorotation coordinate²⁷ connecting the TBP to a rectangular pyramid (RP) in which the equatorial ring oxygen atom, O3, is in the apical position. By use of the dihedral angle method²⁸ to assess displacement, the geometry is displaced 13.5% (13.3% with unit vectors) from the TBP toward the RP. For the more constrained spirocyclic species, **5**, an average percent displacement of 10.3% (9.93% with unit vectors) is obtained, where the pivotal atom, O2, is also an equatorial ring oxygen atom.

Ring Conformations. The conformation of the seven-membered rings in **5** and **6** is that of a row boat (Figure 3). For the ring system containing O1 and O2 in **5**, the four atoms comprising the floor of the boat (P, O2, C11, C12) are coplanar to within ±0.031 (5) Å. Prow atom O1 is displaced from this plane by a distance of 0.667 (3) Å, while stern atoms C21 and C22 are displaced in the same direction by 0.835 (5) and 0.797 (4) Å, respectively. For the other ring system in **5** the corresponding values are ±0.048 (5), 0.645 (3), 0.841 (5), and 0.818 (5) Å. For **6** the corresponding values are ±0.110 (7), 0.735 (4), 0.777 (7), and 0.602 (7) Å.

In all pentacoordinate structures containing this ring system thus far,^{11,12,29} the ring has spanned axial–equatorial sites of a TBP and has had this same conformation. The similar conformations may be understood in terms of the rigidity of the system, in which the greatest degree of freedom is an out-of-plane rotation of the phenyl rings about the bond which connects them. The extent of this rotation is constrained by the bite at phosphorus. For the two ring systems in **5** this rotation is 38.4 (2)° for the

**Figure 3.** ORTEP plots showing the conformations of the seven-membered rings: (a, b) in (C₁₂H₈O₂)₂P(OCH₂CF₃)₃ (**5**); (c) in [(*t*-Bu)₄C₁₂H₄O₂]₂P(OCH₂CF₃)₃ (**6**).**Table VI.** Dihedral Angles (deg) between the Equatorial Plane and the P–O_{eq}–C Planes

	compd	
	5	6
seven-membered ring	57.9 (3) for C21 56.2 (2) for C41	86.4 (6)
acyclic group	75.1 (3)	88.3 (6) for C3 73.3 (7) for C1

C12–C22 bond as measured by the dihedral angle between the phenyl rings and 37.6 (2)° for the C42–C52 bond. These values lie in the range, 35.6 (5)–41.3 (3)°, previously observed for this ring system.^{11,12,29} The value for **6**, 45.7 (3)°, is somewhat larger. This may reflect the steric demands of the *tert*-butyl groups which are seen here for the first time as substituents on the phenyl groups in this ring system.

It is interesting that the dihedral angles between the equatorial plane and the plane of the P–O_{eq}–C ring atoms for the spirocyclic compound **5** center near 57° (Table VI). In general, this angle tends toward 90°,^{11,13,30–32} which is the value that maximizes P–O_{eq} π bonding.³³ Perhaps ring adjustments are required for the least steric strain to accommodate the two row boat conformations in **5** which are flipped over relative to each other in their attachment at phosphorus.

Solution-State NMR Behavior. The ³¹P spectra of **5** and **6** exhibit a single sharp peak for each with resonances in the pentacoordinate region, at –47.34 ppm for **5** and –68.34 ppm for **6**, both in CDCl₃ solution. Likewise, the ¹⁹F NMR spectra for **5** and **6** in toluene-*d*₈ solution have single sharp peaks. These resonances remain essentially invariant over the temperature range of 67.0 to –48.9 °C. Although consistent with the solid-state structure for **5**, which contains a single equatorial OCH₂CF₃

(27) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.(28) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.(29) Hans, J.; Day, R. O.; Howe, L.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1279.(30) Hans, J.; Day, R. O.; Howe, L.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3132.(31) Day, R. O.; Kumara Swamy, K. C.; Fairchild, L.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 1627.(32) Hans, J.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3928.(33) Trippett, S. *Pure Appl. Chem.* **1974**, *40*, 595.

group, rapid ligand exchange is indicated for **6** since two ^{19}F resonances are expected for a static structure. We observe no such low-temperature behavior in the ^{19}F spectrum.³⁴

As mentioned in the Experimental Section, the ^1H NMR spectrum of **6** has a single resonance void of discernible coupling at 67 °C which separates to two equal intensity peaks as the temperature is lowered to -48.9 °C. The remainder of the ^1H spectrum remains unaltered over this temperature range and indicates the presence of two types of *tert*-butyl groups. The ^1H NMR data at low temperature are consistent with the solid-state structure having an a-e ring orientation that undergoes rapid pseudorotation over the temperature range studied but with a stoppage of rotation around the C-O bond of the trifluoroethoxy groups. This would allow the maintenance of two types of *tert*-butyl groups while giving rise to two types of methylene protons at the lower temperatures.

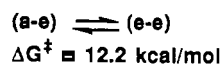
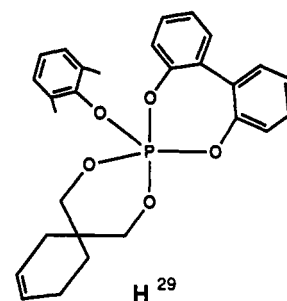
The ^1H NMR spectrum of the spirocyclic phosphorane **5** shows no change over the temperature region 67.0 °C to -48.9 °C other than a broadening and loss of coupling in the peak associated with the methylene protons of the single equatorial OCH_2CF_3 group. This resonance is interpreted (Experimental Section) in terms of an overlapping doublet of quartets due to 3J coupling with the phosphorus atom and the fluorines of the CF_3 group.

Whether ligand exchange is occurring in this molecule cannot be established from the NMR data at hand. On the basis of the work on related molecules, e.g., **G**,¹¹ where a-e \rightleftharpoons e-a ring exchange is slowed only below -70 °C, similar a-e ring exchange also may be taking place in **5**.

In the case of the spirocyclic tetraoxyphosphorane **4**, the presence of two bridge methylene resonances associated with the eight-membered ring in the ^1H NMR spectrum obtained in CDCl_3 solution at 21 °C does not allow a structural conclusion of whether exchange is occurring or not.

Structural Comparisons. Even though a steric factor was introduced in **6** and electronegativity factors were present in both **5** and **6**, all designed to promote diequatorial ring formation, the solid-state structures for these two derivatives maintained the seven-membered rings in a-e sites of TBP geometries. As cited

in the Introduction, both **F**¹² and **G**,¹¹ lacking these requirements, have X-ray structures with the ring positioned at a-e sites. A more recent but analogous example, **H**,²⁹ likewise has the ring arrangement established by an X-ray study. Thus, X-ray evidence establishing a seven-membered ring in diequatorial positions of a TBP for a pentaoxyphosphorane has yet to be obtained.



The greater conformational flexibility of eight-membered rings, such as that present in **A**⁷ and **B**,⁸ has been cited^{1b} as a major factor stabilizing a diequatorial ring orientation found in these pentaoxyphosphoranes. This suggests that the use of seven-membered rings having greater conformational freedom than the ones in **5**, **6**, and **F-H** may overcome the energy barrier toward a diequatorial ring orientation in a TBP. An additional factor that has assisted formation of this geometry for eight-membered rings has been the inclusion of *tert*-butyl substituents.⁷ As apparent in the a-e ring structure reported for **6**, this steric factor was insufficient in bringing about an e-e orientation in this instance. Additional work will focus on factors enhancing the likelihood of the formation of a diequatorial orientation in oxyphosphoranes containing rings of various sizes and conformational requirements.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE 91-22352) is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **5** (Tables S1-S4) and **6** (Tables S5-S8) (19 pages). Ordering information is given on any current masthead page.

(34) Perhaps the difficulty arises due to decomposition. We note when using CDCl_3 as an NMR solvent that both **5** and **6** have complex ^1H and ^{19}F NMR spectra indicating decomposition. For example, in the methylene region of the OCH_2CF_3 group of **6**, five multiplets are present extending over the region 3.0-4.5 ppm at 21 °C. The ^{19}F spectrum in this solvent at 21 °C for **6** shows four peaks with triplet character for the OCH_2CF_3 groups instead of the one seen in toluene-*d*₆.