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Conformational Preference and Donor Atom Interaction Leading to Hexacoordination vs Pentacoordination in Bicyclic Tetraoxyphosphoranes[1]

David J. Sherlock, A. Chandrasekaran, T. K. Prakasha, Roberta O. Day, and Robert R. Holmes*

Department of Chemistry, Lederle Graduate Research Tower 701, Box 34510, University of Massachusetts, Amherst, Massachusetts 01003-4510

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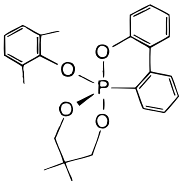
New bicyclic tetraoxyphosphoranes all containing a six-membered oxaphosphorinane ring, $C_6H_8(CH_2O)_2P(OC_{12}H_8)$(OXyl) (**1**), $(C_6H_4O)_2P(OC_{12}H_8)$(OXyl) (**2**), $CH_2[(t\text{-Bu})_2C_6H_2O]_2P(OC_{12}H_8)$(OXyl) (**3**), $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(OC_{12}H_8)$(OXyl) (**4**), and $S[(t\text{-Bu})MeC_6H_2O]_2P(OC_{12}H_8)$(OXyl) (**5**), were synthesized by the oxidative addition reaction of the cyclic phosphine $P(OC_{12}H_8)$(OXyl) (**6**) with an appropriate diol in the presence of *N*-chlorodiisopropylamine. X-ray analysis revealed trigonal bipyramidal (TBP) geometries for **1**−**4** where the dioxa ring varied in size from six- to eight-membered. With a sulfur donor atom as part of an eight-membered ring in place of a potential oxygen donor atom of a sulfone group as in **4**, the X-ray study of **5** showed the formation of a hexacoordinated structure via a P−S interaction. Ring constraints are evaluated to give an order of conformational flexibility associated with the (TBP) tetraoxyphosphoranes **4** > **3** ∼ **1** > **2** which parallels the degree of shielding from ^{31}P NMR chemical shifts: **4** > **3** > **1** > **2**. The six- and seven-membered dioxa rings in **1** and **2**, respectively, are positioned at axial−equatorial sites, whereas the eight-membered dioxa ring in **3** and **4** occupies diequatorial sites of a TBP. *V*−*T* ^{1}H NMR data give barriers to xylyl group rotation about the C−OXyl bond. The geometry of **5** is located along a coordinate from square pyramidal toward octahedral to the extent of 60.7%. Achieving hexacoordination in bicyclic tetraoxyphosphoranes of reduced electrophilicity relative to bicyclic pentaoxyphosphoranes appears to be dependent on the presence of a sufficiently strong donor atom.

Introduction

Previous work[2] revealed members of a new class of bicyclic oxyphosphoranes (**A**−**C**) containing a six-membered oxaphosphorinane ring. The molecular structures were trigonal bipyramidal (TBP) with the rings occupying axial−equatorial (a−e) positions. Other work has shown that oxyphosphoranes are able to increase their coordination from pentacoordinate to hexacoordinate as a result of donor action by oxygen,[3−6] sulfur,[4,5,7−13] and nitrogen[4,5] containing ligands. Examples **D**−**F** illustrate this effect.[3,10,14] In the presence of Lewis base interaction, some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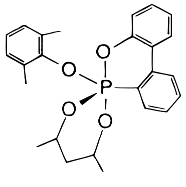
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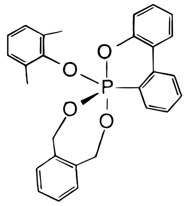
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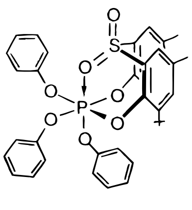
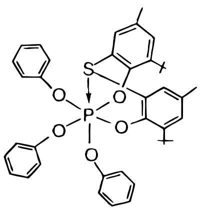
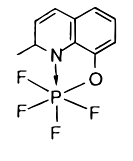

P–O = 2.487(3)Å

D [3]


P–S = 2.744(2)Å

E [10]


P–N = 1.911(4)Å

F [14]

oxyphosphoranes remain pentacoordinate, *e.g.*, **G**[8] and **H**.[6] The

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(1) (a) Pentacoordinated Molecules 118. (b) Part 117. Chandresekaran, A.; Day, R. O.; Holmes, R. R.; Houalla, D. *Phosphorus, Sulfur Silicon Relat. Elem.*, accepted for publication.

(2) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1994**, 116, 8095−8104.

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

(4) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927−950.

(5) Wong, C. Y.; Kennepohl, D. K.; Cavell, R. G. *Chem. Rev.* **1996**, *96*, 1917−1951, and references cited therein.

(6) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1997**, *36*, 2578.

(7) (a) Sherlock, D.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 1317−1322. (b) Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R., submitted for publication.

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

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

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

(11) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *75*, 249−252.

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

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

(14) John, K.-P.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1974**, 1841.

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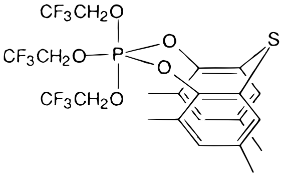
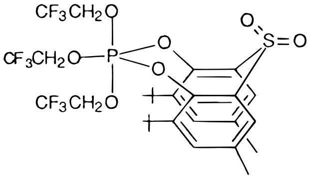
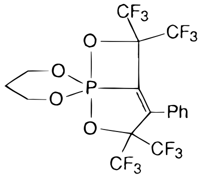


G[8]



H[6]

reason for the retention of TBP geometry for **G** and **H** is associated with the presence of a more flexible eight-membered ring system relative to smaller ring sizes. It has been shown[15] that little energy difference exists between a−e ring occupancy and diequatorial (e−e) ring occupancy when an eight-membered ring system such as that present in **G** and **H** is employed. When smaller size rings are used, this energy difference increases due to an increase in strain energy of the rings situated in e−e sites. In fact, thus far no six-membered ring has been located in e−e sites of a TBP of a pentaoxyphosphorane. Using special ring constraints, Bentrude and coworkers[16] have obtained the TBP geometry of a tetraoxyphosphorane (**I**) with a six-membered ring in this orientation.

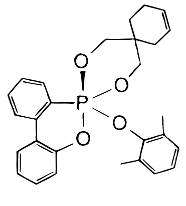


I

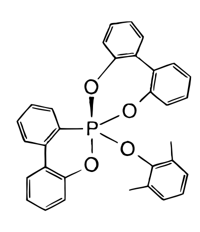
With a view of examining the structural versatility of the new class of bicyclic oxyphosphoranes, **A**−**C**, the ring system size was varied from six- to seven- to eight-membered while the oxaphosphorinane ring was maintained throughout the series. This work resulted in the synthesis and X-ray structures of **1**−**5** complemented by a variable-temperature NMR study to examine ligand exchange processes.

Phosphoranes **1**−**3** were chosen to learn the likelihood of diequatorial ring placement as a function of ring size. In addition, **4** and **5** contain donor atoms which could lead to an increase of coordination geometry even though the electrophilicity of phosphorus is reduced in tetraoxyphosphoranes compared to pentaoxyphosphoranes. Depending on substituents, the latter class are known to form hexacoordinated structures, *e.g.*, **D**[3] and **E**.[10]

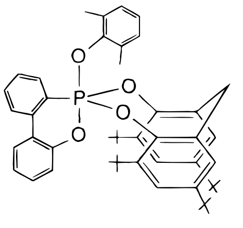
The compounds chosen for study also exhibit interesting optical (**1**−**5**) and geometrical (**5**) isomeric possibilities. ^{31}P chemical shifts (ppm) are indicated in parentheses.



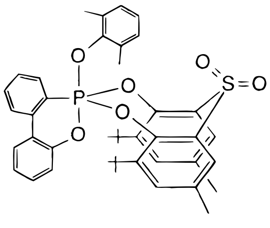
1 (^{31}P, -61.6)



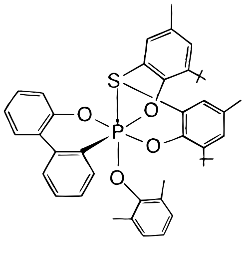
2 (^{31}P, -49.3)



3 (^{31}P, -72.4)



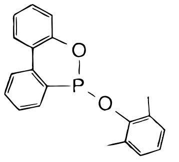
4 (^{31}P, -77.3)



5 (^{31}P, -85.0, -88.9)

Experimental Section

Phosphorus trichloride (Aldrich), 4,4-bis(hydroxymethyl)-1-cyclohexene (Fluka), and 2,2′-biphenol (Aldrich) were used as supplied. N-Chlorodiisopropylamine was prepared by a literature method.[17] Triethylamine (Eastman) was distilled over potassium hydroxide. Solvents were purified according to standard procedures.[18] All reactions were carried out in a dry nitrogen atmosphere using standard Schlenk-type glassware.[19] Phosphine **6** was prepared from a procedure[2] modified from that of Pastor et al.[20] 2,2′-Methylenebis(4,6-di-*tert*-butylphenol) (**7**),[21] 2,2′-dioxythiobis(4-methyl,6-*tert*-butylphenol) (**8**),[22] and 2,2′-thiobis(4-methyl,6-*tert*-butylphenol) (**9**)[10] were prepared as previously described. 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 $CDCl_3$ unless otherwise stated. Phosphorus NMR spectra were recorded in toluene unless otherwise stated. Chemical shifts are reported in parts per million, downfield positive, relative to tetrameth-



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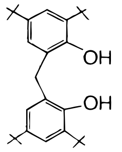

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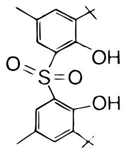

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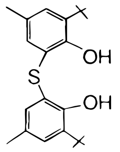

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(15) Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1995**, *34*, 1243.

(16) Huang, Y.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1991**, *113*, 7800.

(17) Bock, H.; Kompa, K. L. *Chem. Ber.* **1966**, *99*, 1347.

(18) (a) Weissberger. Organic Solvents. In *Physical Methods in Organic 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.

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

(20) Pastor, S. D.; Spivack, J. D.; Steinhuebel, L. P. *Phosphorus Sulfur Relat. Elem.* **1987**, *31*, 71.

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

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

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

	1	**2**	**3**	**4**	**5**
formula	$C_{28}H_{29}O_4P$	$C_{32}H_{25}O_4P$	$C_{49}H_{59}O_4P$	$C_{42}H_{45}O_6Ps$	$C_{42}H_{45}O_4PS$
fw	460.48	504.49	742.93	708.81	676.81
cryst syst	triclinic	orthorhombic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
cryst size, mm	0.30 × 0.37 × 0.62	0.27 × 0.42 × 0.45	0.25 × 0.42 × 0.50	0.40 × 0.40 × 0.80	0.50 × 0.50 × 0.50
a (Å)	12.073(4)	11.837(3)	10.712(3)	14.583(4)	9.772(3)
b (Å)	13.190(3)	13.159(3)	14.298(5)	19.355(3)	23.147(4)
c (Å)	15.248(3)	16.626(4)	15.027(8)	13.428(4)	16.128(3)
α (deg)	87.29(2)	90	99.67(4)	90	90
β (deg)	85.71(2)	90	93.65(3)	102.41(2)	100.86(2)
γ (deg)	89.18(2)	90	106.38(3)	90	90
V (Å^3)	2418(1)	2590(1)	2162(2)	3702(2)	3583(1)
Z	4	4	2	4	4
D_{calc} (g/cm^3)	1.265	1.294	1.141	1.272	1.255
$\mu_{\mathrm{Mo\ K\alpha}}$ (cm^{-1})	1.46	1.43	1.06	1.78	1.77
total reflns	5522	1706	4930	4207	4099
reflns with $I > 2\sigma_I$	3226	1301	2977	2778	2899
R^a	0.0553	0.0341^c	0.0942	0.0436	0.0389
$R_w{}^b$	0.1125	0.0746^c	0.2335	0.0994	0.0875

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o{}^2) = \{\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4\}^{1/2}$. [c] These values are for the configuration having the lower R_w.

ylsilane (^{1}H) or 85% H_3PO_4 (^{31}P). All were recorded at 23 °C unless otherwise noted. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. The syntheses were all carried out by the reaction of phosphine **6** with the respective diol in ether solution (100 mL) in the presence of *N*-chlorodiisopropylamine in ether solution (50 mL) either at −78 °C (for **1**, **2**, and **5**) or at room temperature (for **3** and **4**). The former reactions were brought to room temperature and stirred for a further 24−48 h. The latter reactions were stirred for an additional 20 h. The detailed preparation is given for **1**. For the others, quantities used are given along with the recrystallization procedure which was initiated after the stirring time referred to above.

$C_6H_8(CH_2O)_2P(OC_{12}H_8)$(OXyl) (1). To a solution of phosphine **6** (1.00 g, 3.29 mmol) and 4,4-bis(hydroxymethyl)-1-cyclohexene (0.46 g, 3.29 mmol) in diethyl ether (100 mL) at −78 °C was added dropwise a solution of *N*-chlorodiisopropylamine (0.47 mL, 3.20 mmol) in diethyl ether (50 mL) with stirring. The resulting solution was allowed to come to room temperature and stirred for a further 48 h. The solution was then filtered and the filtrate left under a slow flow of nitrogen to yield the crystalline product (yield 0.56 g, 37%), mp 150−153 °C. ^{1}H NMR: 1.35−2.25 (br m, CH_2, Me, 12 H), 3.5−3.9 (br m, CH_2, 4 H), 5.47−5.59 (br d, cyclohexene, 2 H), 6.58−7.83 (m, aryl, 10 H), 8.32 (dd, 14.8 Hz, 8.64 Hz, aryl, 1 H). ^{1}H NMR (27 °C, CD_2Cl_2): 1.0−2.1 (br m, CH_2, 6 H), 1.83 (s, OXyl Me, 3H), 2.57 (s, OXyl Me, 3 H), 3.2−4.5 (br m, CH_2, 4 H), 5.3−5.8 (br m, cyclohexene, 2 H), 6.57−8.33 (m, aryl, 11 H). ^{1}H NMR (77 °C, C_6D_6): 1.1−2.8 (m, CH_2, Me, 12 H), 3.3−4.3 (m, CH_2, 4 H), 5.4−5.7 (br m, cyclohexene, 2 H), 6.54−8.35 (m, aryl, 11 H). ^{31}P NMR ($CDCl_3$): −61.58. Anal. Calcd for $C_{28}H_{29}O_4P$: C, 73.03; H, 6.35. Found: C, 73.07; H, 6.48.

$(C_6H_4O)_2P(OC_{12}H_8)$(OXyl) (2). Quantities: **6** (1.00 g, 3.29 mmol); 2,2′-biphenol (0.61 g, 3.28 mmol); in N-chlorodiisopropylamine (0.50 mL, 3.40 mmol). After filtering, Skelly C, a hydrocarbon fraction boiling in the range 88−99 °C (20 mL) was added to the filtrate and the resulting solution left under a slow flow of nitrogen to obtain the crystalline product (yield 0.85 g, 51%), mp 235 °C. ^{1}H NMR: 1.80 (s, OXyl Me, 3 H), 2.06 (s, OXyl Me, 3 H), 5.79 (d, 7.9 Hz, aryl, 1 H), 6.68−7.91 (m, aryl, 17 H), 8.57 (dd, 14.4 Hz, 6.8 Hz, aryl, 1 H). ^{1}H NMR (25 °C, C_6D_6): 2.04 (s, OXyl Me, 3 H), 2.13 (s, OXyl Me, 3 H), 6.71−7.67 (br m, aryl, 18 H), 8.67 (dd, 14.5 Hz, 8 H, aryl, 1 H). ^{1}H NMR (45 °C, C_6D_6): 2.07 (br s, OXyl Me, 6 H), 6.77−7.68 (br m, aryl, 18 H), 8.67 (dd, 14.5 Hz, 8 Hz, aryl, 1 H). ^{31}P NMR ($CDCl_3$): −49.33. Anal. Calcd for $C_{32}H_{25}O_4P$: C, 76.18; H, 4.99. Found: C, 75.85; H, 5.06.

$CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(OC_{12}H_8)$(OXyl) (3). Quantities: **6** (1.01 g, 3.33 mmol); 2,2′-methylenebis(4,6-di-*tert*-butylphenol) (**7**) (1.41 g, 3.33 mmol); *N*-chlorodiisopropylamine (0.50 mL, 3.40 mmol). After filtering, the solvent was removed *in vacuo* from the filtrate. The resulting solid was dissolved in dichloromethane (10 mL) and Skelly C (15 mL). The resulting solution was left under a slow flow of nitrogen to yield the crystalline product (yield 0.71 g, 29%), mp >250 °C. ^{1}H NMR ($C_6D_5CD_3$): 1.07 (s, *t*-Bu, 18 H), 1.32 (s, *t*-Bu, 18 H), 2.51 (s, OXyl Me, 6 H), 3.46 (d, 13.72 Hz, CH_2, 1 H), 4.61 (d, 13.72 Hz, CH_2, 1 H), 6.4−7.5 (m, aryl, 14 H), 9.47 (dd, 14.4 Hz, 7.58 Hz, 1 H). ^{31}P NMR ($C_6H_5CH_3$): −72.41. Anal. Calcd for $C_{49}H_{59}O_4P$: C, 79.24; H, 7.95. Found: C, 78.88; H, 8.24.

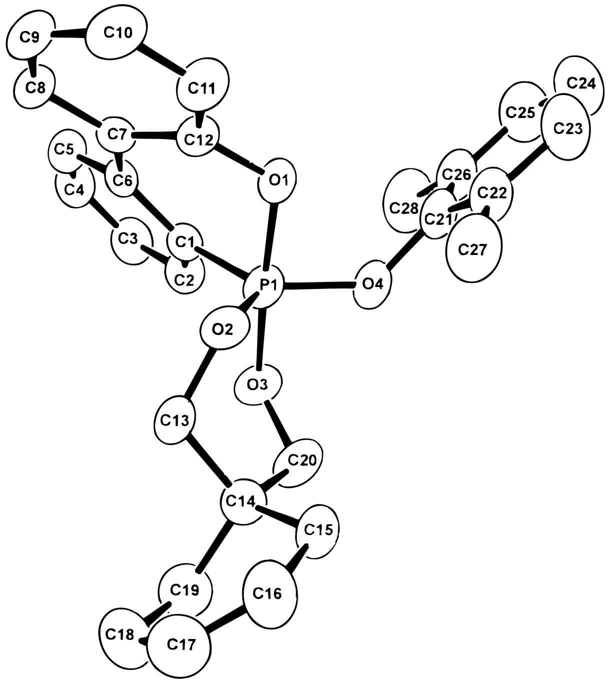


Figure 1. ORTEX diagram for $C_6H_8(CH_2O)_2P(OC_{12}H_8)$(OXyl) (**1**).

$O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OC_{12}H_8)$(OXyl) (4). Quantities: **6** (1.00 g, 3.29 mmol); 2,2′-dioxythiobis(4-methyl-6-*tert*-butylphenol) (**8**) (1.28 g, 3.29 mmol); *N*-chlorodiisopropylamine (0.60 mL, 4.08 mmol). After filtering, the solid residue was dissolved in a 50/50 mixture of dichloromethane and Skelly C (30 mL) and left under a slow flow of nitrogen. After 12 h the solution was filtered again and the filtrate left under a slow flow of nitrogen to yield the crystalline product (yield 0.91 g, 40%), mp 195−199 °C. ^{1}H NMR: 0.93 (s, *t*-Bu, 18 H), 2.12 (s, Me, 6 H), 2.26 (s, Me, 6 H), 6.7−7.9 (br m, aryl, 15 H). ^{31}P NMR (CH_2Cl_2): −77.25. Anal. Calcd for $C_{42}H_{45}O_6PS$: C, 71.18; H, 6.36. Found: C, 70.62; H, 6.46.

$S[(t\text{-}Bu)MeC_6H_2O]_2P(OC_{12}H_8)$(OXyl) (5). Quantities: **6** (1.00 g, 3.29 mmol); 2,2′-thiobis(4-methyl-6-*tert*-butylphenol) (**9**) (1.07 g, 3.29

mmol); *N*-chlorodiisopropylamine (0.47 mL, 3.20 mmol). After filtering the solvent removed *in vacuo*. The resulting solid was recrystallized from a 1:4 mixture of dichloromethane and Skelly C (30 mL) (yield 1.04 g, 47%), mp 230 °C. ^{1}H NMR: 0.62 (s, *t*-Bu, 9 H), 1.08 (s, *t*-Bu, 9 H), 1.45 (s, *t*-Bu, 9 H), 1.62 (s, *t*-Bu, 9 H), 1.69 (s, Me, 3 H), 1.70 (s, Me, 3 H), 2.10 (s, Me, 3 H), 2.17 (s, Me, 3 H), 2.19 (br s, Me, 6 H), 2.20 (s, Me, 3 H), 2.22 (s, Me, 3 H), 5.77 (d, 8.28 Hz, aryl, 1 H), 5.01 (d, 7.92 Hz, aryl, 1 H), 6.77−7.93 (m, aryl, 26 H), 8.41 (dd, 16.56 Hz, 6.78 Hz, aryl, 1 H), 8.64 (dd, 14.31 Hz, 7.14 Hz, aryl, 1 H). ^{31}P NMR (CH_2Cl_2): −85.00, −88.93. Anal. Calcd for $C_{42}H_{45}O_4PS$: C, 74.56; H, 6.66. Found: C, 74.62; H, 7.11.

X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Details of the experimental procedures have been described previously.[23]

The colorless crystals were mounted in thin-walled glass capillaries which were sealed to protect the crystals from the atmosphere as a precaution. Data were collected using the $\theta-2\theta$ scan mode with $3° \leq 2\theta_{\mathrm{Mo\ K\alpha}} \leq 43°$ at 23 ± 2 °C. No corrections were made for absorption. All of the data were included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least squares. Refinements were based on F^2, and computations were performed on a 486/66 computer using SHELXS-86 for solution[24] and SHELXL-93 for refinement.[25] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding either in ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded carbon atoms. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$. Crystallographic data are summarized in Table 1.

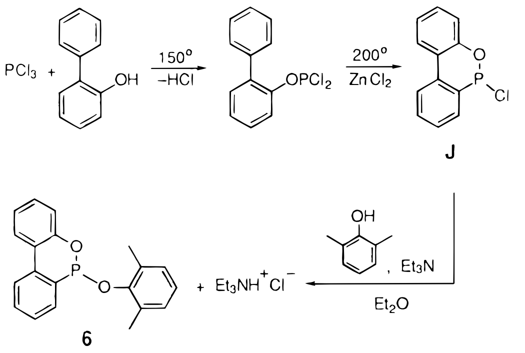
Results and Discussion

The atom labeling schemes for **1**−**5** are given in the ORTEX plots[26] of Figures 1−5, respectively. Thermal parameters are shown at the 40% probability level, and all hydrogens and *tert*-butyl methyl carbons are omitted for clarity. Selected bond parameters are presented in Tables 2−6 for **1**−**5**, respectively.

There are two independent molecules in each asymmetric unit for compound **1**; only one of them is shown in Figure 1. For **2**, only one of the chiral isomers was found in the crystal, as revealed by the chiral space group. In compound **3**, one of the *tert*-butyl methyl groups (C44−C46, attached to C36 of Figure 3) is disordered. This was refined isotropically in two positions with equal occupancy.

Syntheses. Cyclic phosphine **6** was prepared[2] by a route based on a procedure by Pastor and co-workers[20] which involved heating the reactants in the absence of solvent followed by a cyclization step in the presence of $ZnCl_2$ as a catalyst to give **J**. The latter chlorophosphine underwent halide displacement on reaction with 2,6-dimethylphenol *in situ* in diethyl ether at 25 °C using Et_3N as an acid acceptor to give **6** (Scheme 1). Phosphine **6** then served as the starting material for preparing **1**−**5** on reaction in ether solution with the appropriate diol in the presence of *N*-chlorodiisopropylamine. Yields varied from 29 to 51%. The reaction is illustrated for the synthesis of **5** (eq 1).

Scheme 1



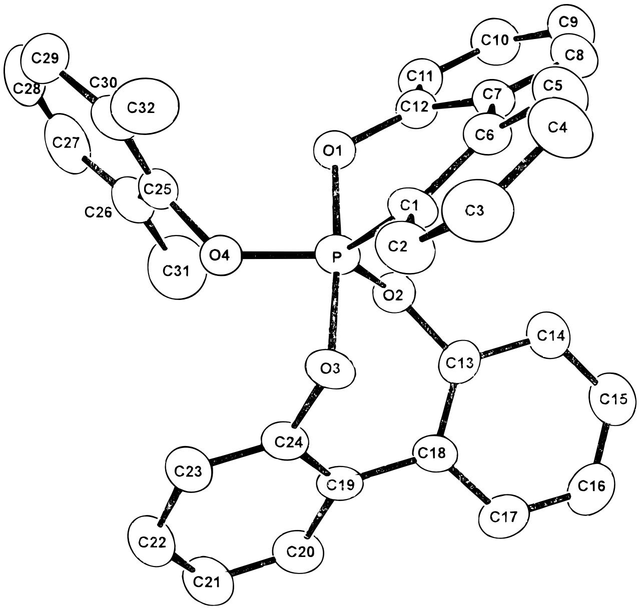
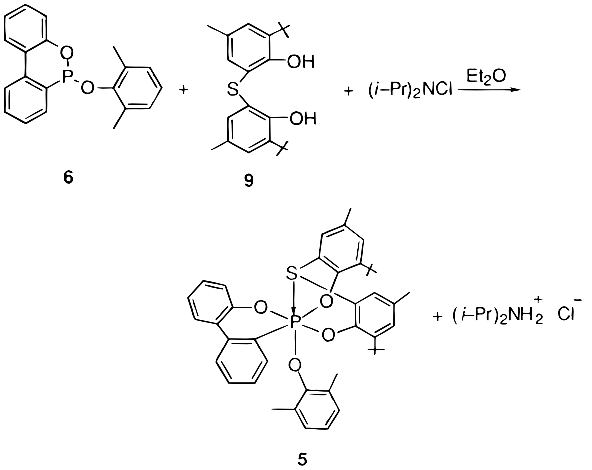


Figure 2. ORTEX diagram for $(C_6H_4O)_2P(OC_{12}H_8)(OXyl)$ (**2**).



(1)

Structural Aspects

Basic Structures. The bicyclic oxyphosphoranes **1** and **2**, containing dioxy six- and seven-membered rings, respectively, are TBP with both rings occupying a−e positions. With the larger eight-membered ring, like **G**[8] and **H**,[6] this ring occupies e−e positions of a TBP in **3** and **4**. When a sulfur atom is introduced as part of the eight-membered ring, a hexacoordinate structure is obtained due to P−S interaction. The sulfur atom acts as a stronger donor compared to the oxygen atom of the sulfone group.[6] The P−S distance in **5** is 2.562(1) Å, well below the sum of the van der Waals' radii of 3.65 Å.[27] Thus, one is able to maintain sufficient electrophilicity at the phosphorus center to form a hexacoordinated geometry for

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[23] Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

[24] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[25] Sheldrick, G. M. *SHELXL-93*: *Program for crystal structure refinement*; University of Gottingen: Gottingen, Germany, 1993.

[26] McArdle, P. *ORTEX 5e*; Crystallography Centre, Chemistry Department, University College: Galway, Ireland, 1996.

[27] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

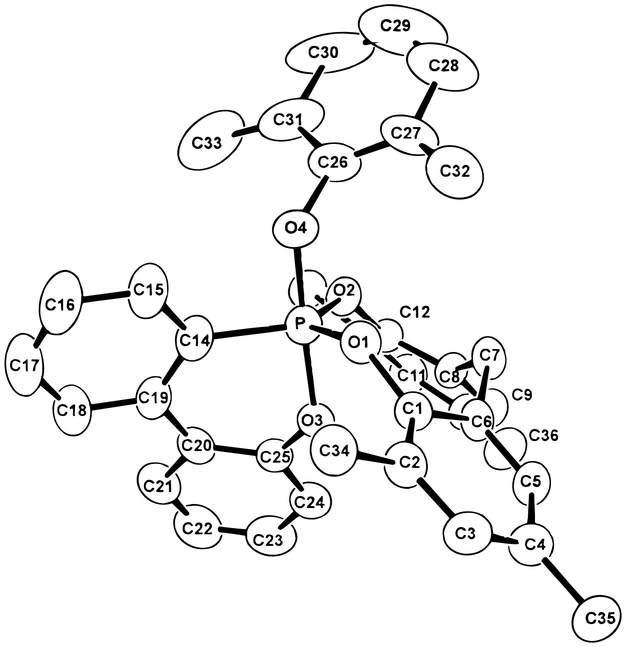


Figure 3. ORTEX diagram for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(OC_{12}H_8)(OXyl)$ (**3**).

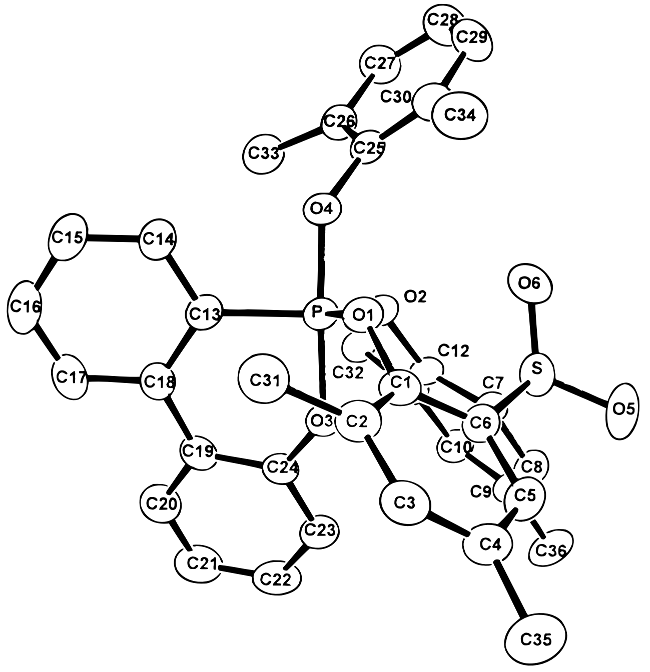


Figure 4. ORTEX diagram for $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OC_{12}H_8)$(OXyl) (**4**).

tetraoxyphosphoranes in comparison with the relative ease of additional coordination for pentaoxyphosphoranes[4,5,7b,8−13] provided that a strong enough donor atom is available to enter the coordination sphere. The most closely analogous bicyclic pentaoxyphosphorane to **5** that exists in a hexacoordinate structure is **K**.[7b] The P−S distance is 2.509(1) Å, somewhat shorter compared to that for **5** as might be expected for a phosphorus atom attached to five oxygens.

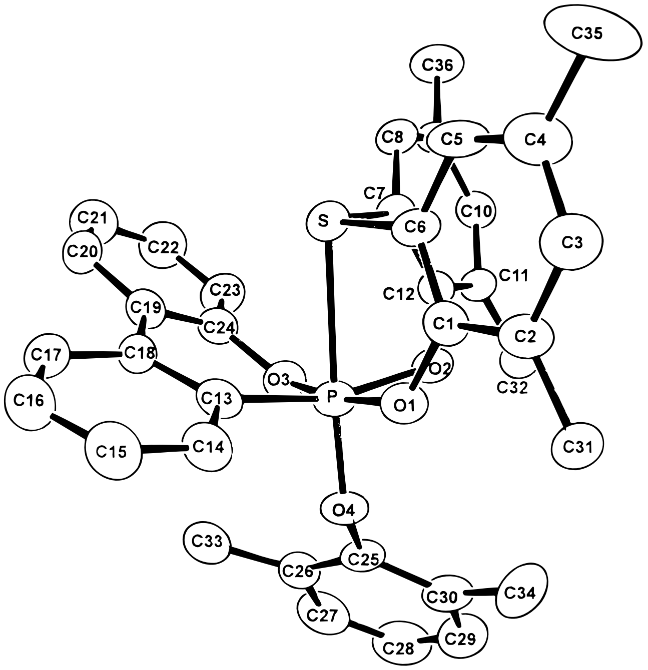
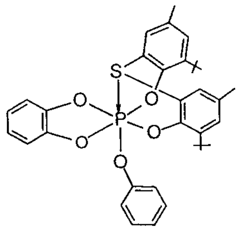


Figure 5. ORTEX diagram for $S[(t\text{-}Bu)MeC_6H_2O]_2P(OC_{12}H_8)(OXyl)$ (**5**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $C_6H_8(CH_2O)_2P(OC_{12}H_8)(OXyl)$ (**1**)

P1−O2	1.598(4)	P2−O6	1.602(4)
P1−O4	1.616(4)	P2−O8	1.605(4)
P1−O3	1.665(4)	P2−O7	1.665(4)
P1−O1	1.698(4)	P2−O5	1.715(3)
P1−C1	1.813(5)	P2−C31	1.811(5)
O2−P1−O4	119.4(2)	O6−P2−O8	120.1(2)
O2−P1−O3	93.7(2)	O6−P2−O7	93.5(2)
O4−P1−O3	88.7(2)	O8−P2−O7	89.3(2)
O2−P1−O1	87.5(2)	O6−P2−O5	86.9(2)
O4−P1−O1	87.8(2)	O8−P2−O5	87.9(2)
O3−P1−O1	176.4(2)	O7−P2−O5	177.0(2)
O2−P1−C1	118.7(2)	O6−P2−C31	120.6(2)
O4−P1−C1	121.9(2)	O8−P2−C31	119.3(2)
O3−P1−C1	90.5(2)	O7−P2−C31	90.4(2)
O1−P1−C1	91.9(2)	O5−P2−C31	92.0(2)

We have found that the geometry of cyclic oxyphosphoranes lies along a trajectory connecting a square pyramid (SP) with an octahedron.[4,7,12] The SP is represented by the atom attachments to phosphorus other than the sulfur atom. Calculation of the displacement of the phosphorus atom from the average base plane formed by O1, O2, O3, and C13 of **5**, a method previously used,[8−10,12] we find that **5** is displaced from the SP toward the octahedron (SP → Octa) to the extent of 60.7%.



K

In the calculation, an average P−O distance found for cyclic oxyphosphoranes undergoing donor atom coordination was used, 1.665 Å, to obtain the distance of the phosphorus atom from the basal plane of an "ideal" square pyramid, 0.431 Å.[12] In general, for phosphoranes,[28,29] as with other main group elements

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

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

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(C_6H_4O)_2P(OC_{12}H_8)(Oxyl)$ (**2**)

P−O4	1.602(4)	P−O3	1.694(3)
P−O2	1.618(3)	P−C1	1.805(5)
P−O1	1.680(3)		
O4−P−O2	120.4(2)	O1−P−O3	174.8(2)
O4−P−O1	88.6(2)	O4−P−C1	123.0(2)
O2−P−O1	88.1(2)	O2−P−C1	116.6(2)
O4−P−O3	86.7(2)	O1−P−C1	94.0(2)
O2−P−O3	92.6(2)	O3−P−C1	90.2(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $CH_2[(t\text{-Bu})_2C_6H_2O]_2P(OC_{12}H_8)(Oxyl)$ (**3**)

P−O1	1.623(5)	P−O3	1.692(5)
P−O2	1.636(4)	P−C14	1.829(8)
P−O4	1.662(5)	P−C7	3.216(7)
O1−P−O2	120.2(2)	O4−P−O3	176.3(3)
O1−P−O4	88.5(2)	O1−P−C14	115.5(3)
O2−P−O4	89.5(2)	O2−P−C14	124.3(3)
O1−P−O3	87.9(2)	O4−P−C14	90.1(3)
O2−P−O3	91.8(2)	O3−P−C14	92.1(3)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $O_2S[(t\text{-Bu})_2C_6H_2O]_2P(OC_{12}H_8)(OXyl)$ (**4**)

P−O1	1.618(3)	P−O3	1.699(3)
P−O2	1.633(3)	P−C13	1.835(4)
P−O4	1.660(3)	P−O5	3.313(3)
O1−P−O2	119.5(2)	O4−P−O3	175.7(2)
O1−P−O4	88.0(1)	O1−P−C13	114.9(2)
O2−P−O4	89.7(1)	O2−P−C13	125.5(2)
O1−P−O3	87.8(1)	O4−P−C13	90.1(2)
O2−P−O3	91.5(1)	O3−P−C13	92.5(2)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $S[(t\text{-Bu})_2C_6H_2O]_2P(OC_{12}H_8)(OXyl)$ (**5**)

P−O4	1.613(2)	P−O2	1.717(3)
P−O3	1.674(3)	P−C13	1.852(4)
P−O1	1.707(2)	P−S	2.5618(14)
O4−P−O3	96.40(13)	O−P−C13	92.5(2)
O4−P−O1	89.58(12)	O2−P−C13	163.71(14)
O3−P−O1	170.60(13)	O4−P−S	174.35(10)
O4−P−O2	98.92(12)	O3−P−S	89.22(9)
O3−P−O2	85.53(12)	O1−P−S	84.77(9)
O1−P−O2	86.38(12)	O2−P−S	80.81(9)
O4−P−C13	97.32(14)	C13−P−S	82.90(11)
O3−P−C13	93.9(2)		

assuming this geometrical form, the *trans* basal angle is 150°.[30] For **5**, the phosphorus atom is displaced from the base plane by a distance of 0.173(3) Å in a direction toward the apical O4 atom. A fairly linear correlation is found between a decrease in the P−S distance and the approach of the phosphorus atom to the basal plane of the SP for previously studied members whose structures are hexacoordinate as a result of sulfur donor action.[12] A similar series of hexacoordinate structures is formed with the sulfone donor group, where the displacement, SP → Octa, varies from 28 to 82%.[6]

Table 7 lists bond lengths of the bicyclic tetraoxyphosphoranes **1**−**4** for comparison with similar data for the analogous oxyphosphoranes **A**−**C**, all with TBP geometries. As expected, the axial P−O bond lengths are longer than the related equatorial P−O distances. The dioxa P−O axial ring values for **1**−**4** average 1.675(4) Å, while those for **A**−**C** average 1.656(3) Å. These compare with average values for dioxa P−O equatorial ring distances for **1**−**4** of 1.618(4) and 1.599(3) Å for **A**−**C**. The average P−O equatorial distance involving the O−Xyl group for **1**−**4** have the same average values as that for **A**−**C**, *i.e.*, 1.608(4) Å. The latter average equatorial P−OXyl distance is not significantly different from the dioxa $P-O_{eq}$ ring distances for **1**−**4** or **A**−**C**. The longer P−O axial bond distance associated with the oxaphosphorinane ring for **1**, 1.698(4) Å, compared to the P−O axial distance associated with the dioxa ring system, 1.665(4) Å, is likely due to the greater ring strain for the relatively planar portion of the six-membered ring containing an sp^2 carbon atom compared to that in the more conformationally flexible saturated dioxa ring system. This was the same observation cited previously[2] for the longer oxa ring P−O axial distances (1.712(2) Å average) observed for **A**−**C** compared to the dioxa ring P−O axial distances (1.656(3) Å average), Table 7. This assertion is supported by noting for **2**, which contains two relatively rigid planar rings, that the oxa ring P−O axial distance, 1.680(3) Å, is now slightly shorter, but not significantly so, compared to the dioxa ring P−O axial distance, 1.694(3) Å. For the hexacoordinate structure **5**, the P−O ring distances (P−O3 = 1.674(3) Å, P−O1 = 1.707(2) Å, and P−O2 = 1.717(3) Å) fall in the range for axial P−O ring distances found for the pentacoordinate phosphoranes **1**−**4** and **A**−**C**. This type of observation has been used in comparing the reactivity of penta- and hexacoordinate oxyphosphoranes.[3]

All the pentacoordinate structures, **1**−**4**, are very close to trigonal bipyramidal. The O−P−O axial angles fall in the range 175−177°. The sum of all three equatorial angles is 360°, which shows that the $C-PO_2$ equatorial ligand set is planar for **1**−**4**. The equatorial angles fall in the range of 115−126°. For an ideal SP of a main group element, the angles are 150 and 105°,[30] which contrasts with 180 and 120° for an ideal TBP.

Dihedral Angles and Ring Conformations. An additional feature of interest concerns the dihedral angle between the equatorial plane and the plane formed by the $P-O_{eq}-C$ atoms that are part of either the dioxa ring system or the xylyloxy group. These data are listed in Table 8 for **1**−**4** along with the biphenyl twist angle. We have found that this dihedral angle tends toward 90° in monocyclic[31] and bicyclic oxyphosphoranes[32] that have flexible ring systems of varying sizes. With reference to six-membered saturated rings incorporated in oxyphosphoranes at axial−equatorial sites, Trippett[33] suggested that the boat conformation is the one that is most favorable in allowing the lone pair of the equatorial heteroatom bonded to phosphorus to reside near the equatorial plane. This occurs at a dihedral angle of 90°. Thus, larger rings which are capable of this orientation may take advantage of this extra stabailization. Presumably the latter orientation allows maximum π bonding with phosphorus d orbitals. As is apparent in Table 8, the dihedral angles associated with the xylyloxy groups consistently approach 90° more so than the ring systems. This is not surprising since there are no ring constraints to interfere with the optimal geometry. Least in accord with the notion of orienting the oxygen lone pair in the equatorial plane is that for compound **2,** which has the least conformationally flexible dioxa ring system. Here, the dihedral angle is only 56.3°. Even in **3** and **4** with the eight-membered dioxa rings positioned diequatorially rather than axial−equatorially, the tendency is to orient the rings in order to take advantage of the lone pair effect. Thus, the dihedral angles listed in Table 8 for **3** and **4**

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[30] Holmes, R. R. Five-Coordinated Structures. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1984; Vol. 32, pp 119−235.

[31] Burton, S. D.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6104.

[32] Kumara Swamy, K. C.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6095.

[33] Trippett, S. *Pure Appl. Chem.* **1974**, *40*, 595.

Table 7. Bond Length Comparisons for Trigonal Bipyramidal Bicyclic Tetraoxyphosphoranes (Å)

	axial			equatorial		
compd	P−O(dioxa)	P−O(oxa)	P−O(Xyl)	P−O(dioxa)	P−C	P−O(Xyl)
1A	1.665(4)	1.698(4)		1.598(4)	1.813(5)	1.616(4)
1B	1.665(4)	1.715(3)		1.602(4)	1.811(5)	1.605(4)
2	1.694(3)	1.680(3)		1.618(3)	1.805(5)	1.602(4)
3		1.692(5)	1.662(5)	1.636(4) 1.623(5)	1.829(8)	
4		1.699(3)	1.660(3)	1.633(3) 1.618(3)	1.835(4)	
av **1**−**4**	1.675(4)	1.697(4)	1.661(4)	1.618(4)	1.819(5)	1.608(4)
av **A**−**C**	1.656(3)	1.712(2)		1.599(3)	1.811(3)	1.608(2)

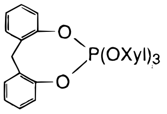
Table 8. Dihedral Angles between P−O$_{eq}$−C Bonds and Equatorial Planes for Bicyclic Tetraoxyphosphoranes (deg)

compd	ring	xylyloxy group	biphenyl twist angle[b]
1A[a]	73.4(2)	82.1(4)	23.6(1)
1B[a]	70.6(3)	88.7(5)	24.6(2)
2	56.3(3)	88.3(3)	21.1(2) 40.7(1)[c]
3	74.5(4) 69.9(4)		23.0(3)
4	79.9(2) 73.4(2)		20.2(1)
A1[a]	71.4(2)	86.2(2)	
A2[a]	68.7(2)	86.2(2)	
B	82.4(2)	84.8(2)	
C	86.0(1)	87.1(2)	

[a] Two independent molecules per unit cell. [b] The biphenyl twist angles for **A**−**C** are very similar to each other and fall in the range from 22.1(5) to 23.6(5)°. [c] This value refers to the seven-membered dioxa ring.

fall in a range similar to those for **1**, **A**, and **B**. The conformational flexibility of the eight-membered dioxa rings has been shown to be such that they will reside at e−e sites of a TBP at the expense of allowing a less electronegative phenyl or ethyl group to be preferentially placed at an axial position.[34] The latter is normally reserved for the more electronegative ligand.

There is a variation of ^{31}P chemical shifts for these tetraoxyphosphoranes with ring flexibility. As shown for the formulations of **1**−**5** in the Introduction, the ^{31}P chemical shift shows shielding at phosphorus in the order **5** > **4** > **3** > **1** > **2**. For the TBP compounds **1**−**4**, this order parallels the order of approach to 90° for the dihedral angles listed in Table 8: **4** > **3** ~ **1** > **2**. Previously it has been established that shielding increases with ring size and accompanying conformational flexibility for a series of monocyclic pentaoxyphosphoranes **L**−**O**.[35] Here as well, a reduction in P−O π bonding with increasing ring constraint was offered to rationalize the loss of shielding on going from eight- to five-membered rings.[35a] The π-bonding effect was mentioned earlier by Ramirez and coworkers[36] in accounting for a reduction in ^{31}P shielding with five-membered rings that replaced phenoxy groups in a series of pentaoxyphosphoranes. It is noted that **M** containing a saturated ring is more conformationally flexible than **N** even though **N** has a larger ring size than **M**. This same effect was apparent between **1** and **2** in this study.



L (^{31}P, -87.4)

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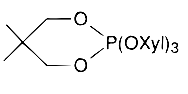

M (^{31}P, -77.5)

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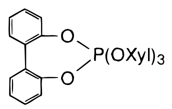

N (^{31}P, -68.3)

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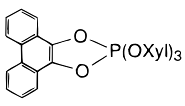
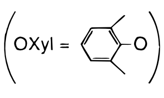


O (^{31}P, -57.0)



The ring conformations that produce these dihedral angles are a boat form when the dioxa ring occupies a−e sites of a TBP and a chair form when the dioxa ring occupies e−e sites. The middle section of Figure 6 and the lower section of Figure 7 show the boat conformations situated at a−e sites for the dioxa rings of **1** and **2**, respectively, whereas the chair conformation is apparent in Figures 3 and 4 for the orientation of the dioxa rings of **3** and **4** situated at e−e sites of a TBP. Likewise, the previously studied dioxa ring conformations of **A**−**C** situated at a−e sites are boat forms.[2] For the six-membered oxa ring common to all the oxyphosphoranes **1**−**4**, as in **A**−**C**, a slightly twisted half-chair results. This is illustrated for **1** and **2** in the upper parts of Figures 6 and 7, respectively.

Symmetry Considerations. The phosphorus atom in the starting materials **J** and **6** in Scheme 1 is chiral. In the compounds studied here, symmetry is lacking such that **1**−**5** are racemates. In the X-ray studies of the crystals, **1**, **3**, and **4** have D/L forms as there is a center of symmetry in each of the unit cells. Also, the two independent molecules in the asymmetric unit for **1** are themselves mirror images. However, the crystal used in the X-ray study of **2** had only one of the D/L forms as it crystallizes in a chiral space group ($P2_12_12_1$). In the case of **5**, in addition to having optical isomers, three geometrical isomers are possible depending on which atom is located *trans* to the sulfur atom in the octahedral geometry. These are either the carbon or oxygen atom of the six-membered oxa ring or the oxygen atom of the xylyloxy group. As displayed in Figure 5, the latter possibility is the one obtained in the X-ray study. However, in solution, two isomers are evident from signals in both the ^{1}H and ^{31}P NMR spectra. The additional isomer is likely one of the former isomers, but which one is not apparent from the spectra.

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(34) (a) Timosheva, N. V.; Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1995**, *34*, 4525. (b) Timosheva, N. V.; Chandarsekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 6552.

(35) (a) Holmes, R. R.; Prakasha, T. K. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *80*, 1. (b) Holmes, R. R.; Prakasha, T. K.; Pastor, S. D. Phosphorus(III) and Phosphorus(V) Heterocyclic Compounds. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH: New York, 1994; pp 27−39.

(36) Sarma, R.; Ramirez, F.; McKeever, B.; Marecek, J. F.; Lee, S. *J. Am. Chem. Soc.* **1976**, *98*, 581, and references cited therein.

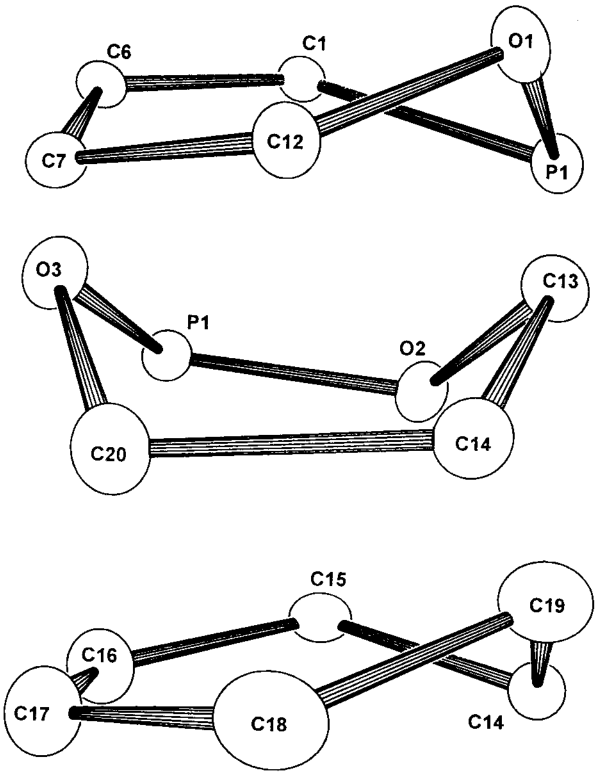

Figure 6. ORTEX diagram showing the conformations of the oxaphosphorinane ring (upper), the saturated six-membered ring (middle), and the appended cyclohexene ring (lower) of compound **1** that is exhibited in Figure 1.

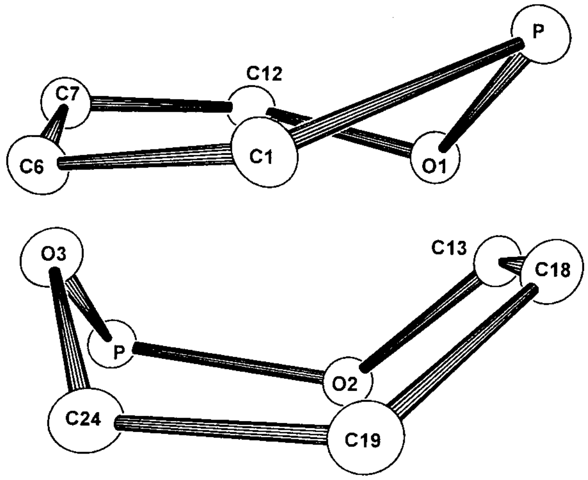

Figure 7. ORTEX diagram showing the conformation of the oxaphosphorinane ring (upper) and the seven-membered ring (lower) of compound **2** that is exhibited in Figure 2.

Variable−Temperature ^{1}H NMR Measurements. The ^{1}H NMR spectrum of **2** gave evidence of fluxional behavior. The two xylyloxy methyl groups gave independent signals at 25 °C but coalesced to one peak at 45 °C, Figure 8. This is the principal temperature dependent feature of interest for this molecule. All of the other protons are aromatic and did not allow definitive assignments. Similar coalescence behavior was observed in the variable-temperature ^{1}H NMR spectra for **1** in the xylyloxy methyl region. An estimate of the barrier to rotation of the xylyl group about the C−O bond is given in Table 9.[37,38] It is not known if this is the only fluxional process occurring in **1** and **2**. In the related tetraoxyphosphoranes **A**−**C**, additional ^{1}H NMR data[2] showing coalescence of independent proton signals of methyl and methylene groups that were part of the saturated rings provided barriers for intramolecular ligand exchange processes. These were outlined in terms of Berry[39] pseudorotations. Thus, it is reasonable at least for the more flexible molecule **1**, which most resembles **A**−**C**, that a similar intramolecular ligand exchange process is coupled to the xylyl group rotation. The lower barrier (Table 9) for the latter rotation for **1** is consistent with its more flexible structure as discussed above. This barrier for **1** is also consistent with the value for xylyl group rotation in **A**, the molecule most analogous to **1**. This value was also 11.3 kcal/mol.[2]

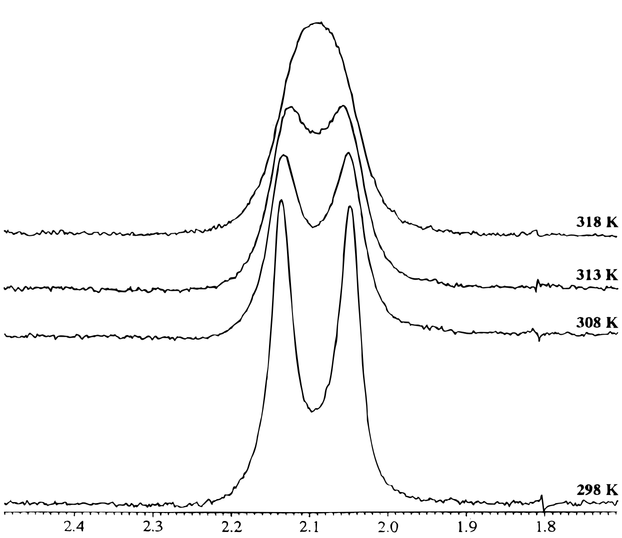

Figure 8. Variable-temperature ^{1}H NMR spectrum of **2** covering the xylyloxy methyl region.

Table 9. Barriers to C−O Bond Rotation of the Xylyl Groups in Bicyclic Tetraoxyphosphoranes

compd	T_c (K)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger\,a}$ (kcal/mol)
1	250	145.8	11.7
2	318.2	17.54	16.4

[a] Values are estimated to be accurate to within ±1.5 kcal/mol. See ref 37.

Structural Comparisons. Figure 9 displays the variation in the P−S donor distance with the extent of geometrical displacement toward an octahedron for the bicyclic tetraoxyphosphoranes that have been structurally characterized. These are **L**−**Q**[7a,40] (Chart 1) from previous work and **5** here. As already discussed,[7a] it is clear that the electron withdrawing chlorine atoms in **M** and **P** cause an increase in donor action and, as a consequence, an increase in the displacement further along the coordinate toward an octahedron. In contrast, the members **N, O**, and **Q** that have P−N bonding from amine ligands exhibit weaker P−S coordination and suffer less geometrical displacement toward an octahedron. The decrease in phosphorus electrophilicity has been associated with π P−N back-bonding.[7a] The degree of P−S coordination and octahedral formation are similar for **5** and **L**.[40] What is interesting in the present context is the *cis* orientation of the least electronegative ligand in **5** relative to the position of the sulfur atom. In all other bicyclic tetraoxyphosphoranes, the least electronegative ligand is located *trans* to sulfur. In nucleophilic displacement

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(37) Calculated from the equation $\Delta G^\ddagger = (4.57 \times 10^{-3})T_c(10.32 + \log(T_c\sqrt{2}/\pi\Delta\nu))$ following: Kessler, H. *Angew. Chem.* **1970**, *82*, 237. See also ref 38.

(38) Buono, G.; Llinas, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 4532.

(39) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(40) Sood, P.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.*, in press.

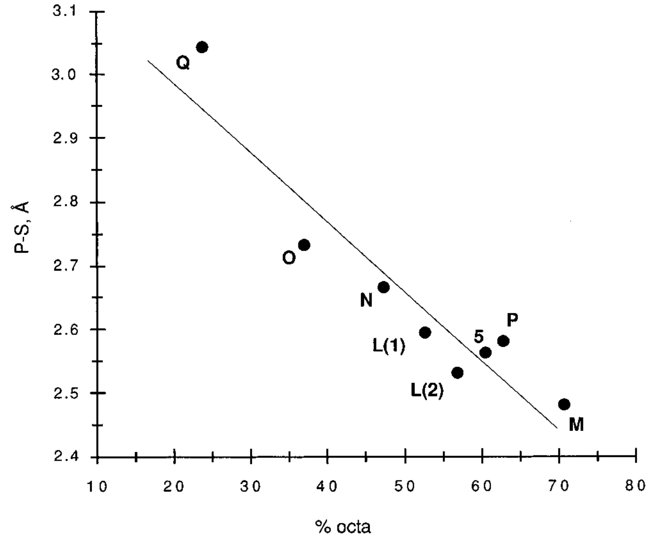


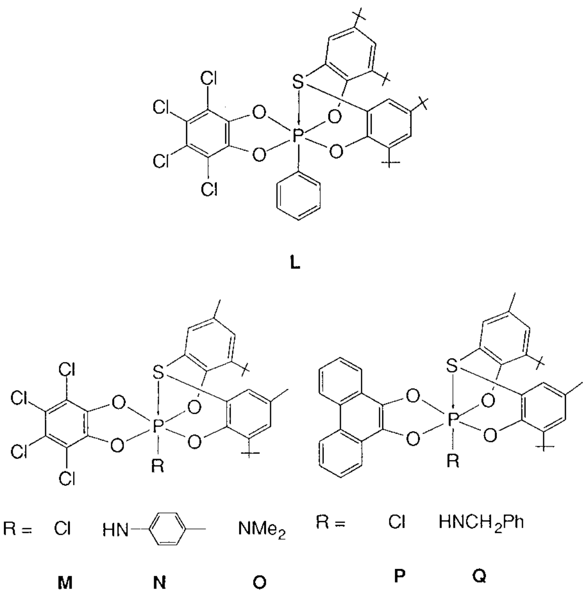
Figure 9. Variation of the P−S distance with the percent octahedral character of the bicyclic tetraoxyphosphoranes **L**−**Q** (Chart 1) and **5**.

reactions at phosphorus where a hexacoordinate activated state may appear, such positioning may have an important influence on whether ring opening or ring retention would preferentially take place (cf. **5** and **L**), assuming sulfur is the incoming nucleophile in these models for mechanistic intermediates.

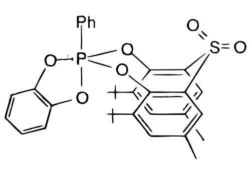
It is evident that even though bicyclic tetraoxyphosphoranes render phosphorus less electrophilic relative to pentaoxy analogues, a range of coordination strength is implied from Figure 9 which centers on P−S donor action. When sulfur in **5** is replaced by the sulfone group resulting in **4**, no coordination occurs. The same situation prevails in the electronically analogous molecule **R**.[6] However, by placing chlorine substituents on the cyclic phenyl group, **S**[6] is obtained which is displaced 28% toward an octahedron. This compares with **L** that has P−S donor coordination. In **L**, the average displacement toward an octahedron is 55% and is greater that that in **S** due to the presence of the stronger sulfur donor atom.

It is apparent that donor action is strongest in pentaoxyphosphoranes[40] and decreasingly so in tetraoxyphosphoranes, especially as the unique ligand electronegativity is decreased or the donor capacity of the coordinating group is decreased. As a result, strong candidates for the formation of hexacoordinate phosphorus in nucleophilic displacements are phosphate reactions that occur at enzyme active sites where nearby residues may supply the necessary coordinating atom.

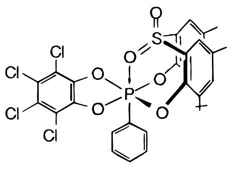
Chart 1. Bicyclic Tetraoxyphosphoranes[a]



[a] **L** is from ref 40, and the remainder are from ref 7a.



R



P-OSO = 2.646(5)Å

S

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters and hydrogen atom parameters for **1**−**5** (29 pages). Ordering information is given on any current masthead page.

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