Axial Site Occupancy by the Least Electronegative Ligands in Trigonal Bipyramidal Tetraoxyphosphoranes[1]

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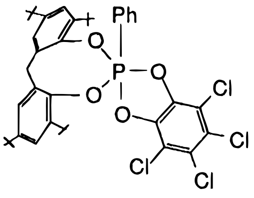
Analogous to the formation of $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Ph)(O_2C_6Cl_4)$ (**1**), the new bicyclic tetraoxyphosphoranes $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Et)(O_2C_6Cl_4)$ (**3**) and $CH_2[ClC_6H_3O]_2P(Ph)(O_2C_6Cl_4)$ (**4**) were synthesized by the oxidative addition of the appropriate cyclic phosphines with *o*-tetrachlorobenzoquinone. For the formation of $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Ph)(O_2C_2Ph_2)$ (**2**), a similar reaction was followed with the use of benzil (PhCOCOPh) in place of *o*-tetrachlorobenzoquinone. X-ray analysis of **1**−**3** revealed trigonal bipyramidal geometries and provided evidence for the first series of complexes in the absence of ring strain in which the least electronegative group, ethyl or phenyl, is located in an axial position, in violation of the electronegativity rule. Thus, the two oxygen-containing ring systems occupied two different sets of positions in the trigonal bipyramid (TBP) with the eight-membered rings at diequatorial sites. X-ray analysis of **4** revealed a trigonal bipyramidal geometry with electron-withdrawing chlorine substituents on each ring assumed the more conventional geometry with the rings occupying axial−equatorial positions and the phenyl group located in the remaining equatorial site. The fact that molecular mechanics calculations favorably reproduced the observed geometries suggests that a steric contribution associated with the ring *tert*-butyl groups for **1**−**3** is partly responsible in favoring diequatorial ring occupancy for the eight-membered ring. NMR data supported rigid pentacoordinated structures in solution at 23 °C. Phosphorane **1** crystallizes in the orthorhombic space group *Fdd*2 with $a = 44.787(5)$ Å, $b = 34.648(8)$ Å, $c = 10.3709(9)$ Å, and $Z = 16$. Phosphorane **2** crystallizes in the orthorhombic space group $Pna2_1$ with $a = 20.658(8)$ Å, $b = 10.342(2)$ Å, $c = 19.879(6)$ Å, and $Z = 4$. Phosphorane **3** crystallizes in the orthorhombic space group *Pcmn* with $a = 9.807(2)$ Å, $b = 16.632(4)$ Å, $c = 23.355(3)$ Å, and $Z = 4$. Phosphorane **4** crystallizes in the monoclinic space group *C*2/*c* with $a = 35.699(5)$ Å, $b = 12.187(2)$ Å, $c = 14.284(3)$ Å, $\beta = 107.08(1)°$, and $Z = 8$. The final conventional unweighted residuals are 0.0395 (**1**), 0.0518 (**2**), 0.0540 (**3**), and 0.0868 (**4**).

Introduction

In a recent communication[2] we reported a unique geometry for a pentacoordinated cyclic tetraoxyphosphorane. X-ray analysis showed the least electronegative ligand, a phenyl group, occupying the axial position of a trigonal bipyramid (TBP) for **1**. This provided the first example for this class of molecules that are in violation of the electronegativity rule[3,4] which gives preference to the axial site occupancy by the most electronegative ligands. Only when ring strain effects are present such as in pentacoordinate phosphorus molecules containing four- and five-membered rings, have exceptions been noted. Some examples are found in **A**−**C**.[5−9] In the case of **1**, which has an eight-membered ring present, a phenyl group resides at an axial position.[2]



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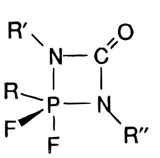
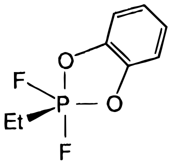
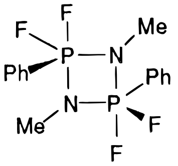


A[5-7]



B[8]



C[9]

In our previous work,[10] we have found that a lack of ring strain exists for this same type of eight-membered ring in other cyclic oxyphosphoranes. Thus, X-ray analysis of the pentaoxyphosphoranes, **D**−**F**,[10−12] shows that the rings are located in diequatorial positions of a TBP. By way of contrast, when alkyl

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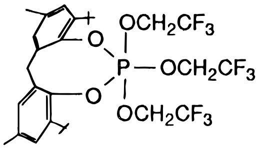
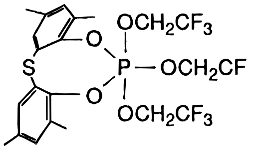
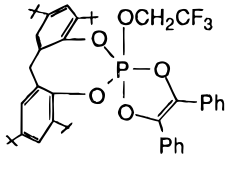
substituents on the aryl components of the rings are removed, as in **G**[12] and **H**,[13] the TBP structures have the rings occupying axial−equatorial sites. Here, the electronegativities of the trifluoroethoxy and xylyloxy groups and the ring O−aromatic component are not expected to be too different.



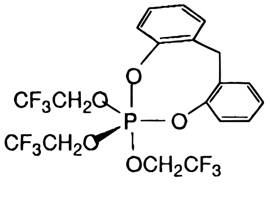
D[11,12]



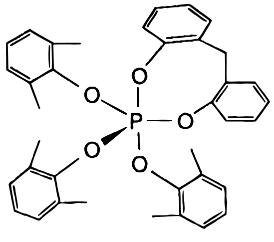
E[12]



F[10]



G[12]

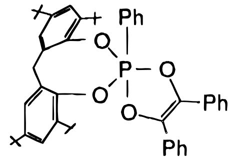


H[13]

To explore the generality of the exception to the "electronegativity rule" found for **1** and perhaps to gain an understanding of the factors involved, we have extended the study to a series of related tetraoxyphosphoranes **2**−**4** containing this type of eight-membered ring where the ring components are varied. In addition, the less electronegative ethyl and phenyl groups are introduced to examine the extent to which this phenomena may occur. For this purpose, it was necessary to synthesize two new phosphines, **5** and **6**, to allow preparation of the cyclic tetraoxyphosphoranes, **2**−**4**. In addition to a study of their X-ray structures, ^{1}H and ^{31}P NMR measurements were carried out to ascertain if structural changes are encountered in solution.

Experimental Section

Tetrachloro-*o*-benzoquinone, benzil (PhCOCOPh), dichloroethylphosphine (Aldrich), and dichlorophenylphosphine (Fluka) were used as supplied. 2,2′-Methylenebis(4-chlorophenol) (Aldrich) was recrystallized from ether. 2,2′-Methylenebis(4,6-di-*tert*-butylphenol)[14] and [2,2′-methylenebis((4,6-di-*tert*-butylphenyl)oxy)]phenylphosphine, $CH_2[(t\text{-}Bu)_2C_6H_2O]_2PPh$ (**7**),[15] were synthesized according to literature methods. Solvents were purified according to standard procedures.[16,17] All of the reactions were carried out in a dry nitrogen atmosphere. Proton NMR spectra were recorded on a Bruker AC200 FT-NMR spectrometer. Phosphorus-31 NMR spectra were recorded on a Bruker MSL300 FT-NMR spectrometer. All of the spectra were recorded in $CDCl_3$ solution. Chemical shifts are reported in ppm, downfield positive, and relative to tetramethylsilane (^{1}H) or 85% H_3PO_4 (^{31}P). All were recorded at 23 °C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.



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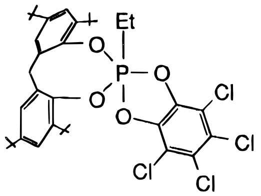

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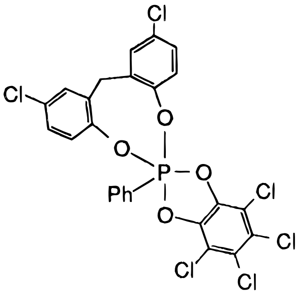

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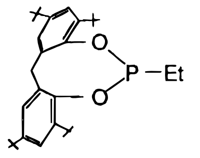

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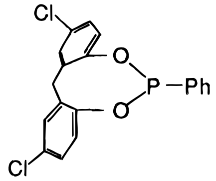

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Syntheses. [2,2′-Methylenebis((4,6-di-*tert*-butylphenyl)oxy)ethylphosphine, $CH_2[(t\text{-}Bu)_2C_6H_2O]_2PEt$ (5). To a solution of 2,2′-methylenebis(4,6-di-*tert*-butylphenol) (8.17 g, 19.2 mmol) and triethylamine (5.50 mL, 39.5 mmol) in diethyl ether (650 mL) was added dichloroethylphosphine (2.00 mL, 19.2 mmol) at 0 °C. After the reaction mixture came to room temperature, it was stirred for a further period of 45 h. The amine hydrochloride was filtered off. Hexane (100 mL) was added to the filtrate and left under a nitrogen flow to give a colorless powdery solid, mp > 260 °C (yield 4.2 g, 46%). ^{1}H NMR: 1.30 (s, 18 H, *t*-Bu), 1.39 (s, 18 H, *t*-Bu), 1.45 (overlapping multiplet, PCH_2CH_3), 2.11 (quintet, 2 H, PCH_2, $^{2}J_{P-H} = {}^{3}J_{P-H} = 8$ Hz), 3.40 (d, 1 H, CH_2, $^{2}J_{H-H} = 13$ Hz), 4.36 (d, 1 H, CH_2, $^{2}J_{H-H} = 13$ Hz), 7.22 (s, 2 H, aryl), 7.33 ppm (s, 2 H, aryl). ^{31}P NMR: 188.8 ppm. Anal. Calcd for $C_{31}H_{47}O_2P$: C, 77.14; H, 9.81. Found: C, 77.07; H, 9.77.

[2,2′-Methylenebis((4-chlorophenyl)oxy)]phenylphosphine, $CH_2(ClC_6H_3O)_2PPh$ (6). To a solution of 2,2′-methylenebis(4-chlorophenol) (6.0 g, 22.3 mmol) and triethylamine (6.20 mL, 44.6 mmol) in diethyl ether (700 mL) was added dichlorophenylphosphine (3.00 mL, 22.3 mmol) at 0 °C. After the reaction mixture came to room temperature, it was stirred for a further period of 48 h. The amine hydrochloride was filtered off. The filtrate was left under a nitrogen flow to give a colorless powdery solid, mp 149−152 °C (yield 4.5 g, 52%). ^{1}H NMR: 3.44 (d, 1 H, CH_2, $^{2}J_{H-H} = 13$ Hz), 4.48 (dd, 1 H, CH_2, $^{2}J_{H-H} = 13$ Hz, $^{5}J_{P-H} = 3$ Hz), 6.9−8.0 ppm (m, 11 H, aryl). ^{31}P NMR: 168.5 ppm. Anal. Calcd for $C_{19}H_{13}Cl_2O_2P$: C, 60.83; H, 3.49. Found: C, 59.76; H, 3.59.

[2,2′-Methylenebis((4,6-di-*tert*-butylphenyl)oxy)](1,2-diphenylethylene-1,2-dioxy)phenylphosphorane, $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Ph)(O_2C_2Ph_2)$ (2). A mixture of **7** (0.50 g, 0.94 mmol) and excess benzil (0.600 g, 2.85 mmol) was heated to 155 °C for 3 h with stirring. The excess benzil was sublimed off under vacuum. After cooling to room

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Table 1. Crystallographic Data for Compounds **1**−**4**

	1	**2**	**3**	**4**
formula	$C_{41}H_{47}Cl_4O_4P$	$C_{49}H_{57}O_4P$	$C_{37}H_{47}Cl_4O_4P$	$C_{25}H_{13}Cl_6O_4P{\cdot}CH_2Cl_2$
formula weight	776.56	740.92	728.50	706.00
crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	*Fdd*2 (No. 43)	*Pna*2$_1$ (No. 33)	*Pcmn* (No. 62)	*C*2/*c* (No. 15)
a (Å)	44.787(5)	20.658(8)	9.807(2)	35.699(5)
b (Å)	34.648(8)	10.342(2)	16.632(4)	12.187(2)
c (Å)	10.3709(9)	19.879(6)	23.355(3)	14.284(3)
β (deg)				107.08(1)
V (Å^3)	16093(4)	4247(2)	3809.4(1)	5940(2)
Z	16	4	4	8
T (°C)	23 ± 2	23 ± 2	23 ± 2	23 ± 2
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
D_{calc} (g/cm^3)	1.282	1.159	1.267	1.579
$\mu_{Mo\ K\alpha}$ (cm^{-1})	3.73	1.07	3.89	8.50
R^a	0.0395	0.0518	0.0540	0.0868
$R_w{}^b$	0.0773	0.1301	0.1231	0.2136

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

temperature, the yellow solid was crystallized from hot acetonitrile to obtain colorless crystals, mp 235−236 °C (yield 0.50 g, 71%). ^{1}H NMR: 1.27 (s, 18 H, *t*-Bu), 1.30 (s, 18 H, *t*-Bu), 3.63 (d, 1 H, CH_2, $^2J_{H-H} = 13$ Hz), 4.63 (d, 1 H, CH_2, $^2J_{H-H} = 13$ Hz), 6.30−8.30 ppm (m, 19 H, aryl). ^{31}P NMR: −47.4 ppm. Anal. Calcd for $C_{49}H_{57}O_4P$: C, 79.43; H, 7.75. Found: C, 79.25; H, 7.45.

[2,2′-Methylenebis((4,6-di-*tert*-butylphenyl)oxy)](1,2,3,4-tetrachlorophenylene-5,6-dioxy)ethylphosphorane, $CH_2[(t\text{-}Bu)_2(C_6H_2O)]_2P(Et)(O_2C_6Cl_4)$ (3). A solution of **5** (0.500 g, 1.04 mmol) and tetrachlorobenzoquinone (0.250 g, 1.02 mmol) in toluene (30 mL) was heated under reflux for 1 h. Solvent was removed under vacuum to give an orange−yellow solid. It was recrystallized from a 1:1 mixture of dichloromethane:hexane using slow evaporation under a nitrogen flow. The resultant crystals were washed with Skelly-F and dried under vacuum, mp 241−243 °C dec (yield 0.50 g, 67%). ^{1}H NMR: 1.13 (s, 18 H, *t*-Bu), 1.29 (s, 18 H, *t*-Bu), 1.45 (m, PCH_2CH_3, overlapped with *t*-Bu), 2.38 (m, 2 H, PCH_2), 3.60 (d, 1 H, CH_2, $^2J_{H-H} = 12$ Hz), 4.43 (d, 1 H, CH_2, $^2J_{H-H} = 12$ Hz), 7.10 (s, 2 H, aryl), 7.37 ppm (s, 2 H, aryl). ^{31}P NMR: −23.94 ppm. Anal. Calcd for $C_{37}H_{47}O_4Cl_4P$: C, 61.00; H, 6.50. Found: C, 61.18; H, 6.61.

[2,2′-Methylenebis((4-chlorophenyl)oxy)](1,2,3,4-tetrachlorophenylene-5,6-dioxy)phenylphosphorane, $CH_2[ClC_6H_3O]_2P(Ph)(O_2C_6Cl_4)$ (4). The procedure was similar to that for **3** (**6** (1.5 g, 4.0 mmol); tetrachlorobenzoquinone (0.98 g, 4.0 mmol)). Mp 120−125 °C (yield 1.0 g, 40.3%). ^{1}H NMR: 3.52 (d, 1 H, CH_2, $^2J_{H-H} = 14.5$ Hz), 4.18 (d, 1 H, CH_2, $^2J_{H-H} = 14.5$ Hz), 6.96−8.14 ppm (m, 11 H, aryl). ^{31}P NMR: −32.29 ppm.

X-ray Experimental Work. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation. Details of the experimental procedures have been described previously.[18]

The crystals were mounted in thin-walled glass capillaries and sealed to protect the crystal from the atmosphere as a precaution. Data were collected using the $\theta-2\theta$ scan mode with $3° \le 2\theta_{Mo\ K\bar{\alpha}} \le 43°$. 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[19] and SHELXL-93 for refinement.[20] Crystallographic data are summarized in Table 1.

X-ray Study for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Ph)(O_2C_6Cl_4)$ (1). The colorless crystal used for the study had approximate dimensions of 0.15 × 0.25 × 0.62 mm. A total of 2460 independent reflections (+*h*,+*k*,+*l*) were measured. 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 the methyl hydrogen atoms) on the bonded carbon atoms. The final agreement factors are based on the 1578 reflections with $I \ge 2\sigma_I$.

X-ray Study for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Ph)(O_2C_2Ph_2)$ (2). The colorless crystal used for the study had approximate dimensions of 0.50 × 0.75 × 0.75 mm. A total of 2495 independent reflections (+*h*,+*k*,+*l*) were measured. 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 the methyl hydrogen atoms) on the bonded carbon atoms. The final agreement factors are based on the 2058 reflections with $I \ge 2\sigma_I$.

X-ray Study for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Et)(O_2C_6Cl_4)$ (3). The colorless crystal used for the study had approximate dimensions of 0.25 × 0.50 × 0.80 mm. A total of 2273 independent reflections (+*h*,+*k*,+*l*) were measured. The molecule has a crystallographic mirror plane which passes through the phosphorus, the methylene carbon, the ethyl carbons, and all of the atoms of the tetrachlorobenzoquinone moiety. 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 the methyl hydrogen atoms) on the bonded carbon atoms. The final agreement factors are based on the 1437 reflections with $I \ge 2\sigma_I$.

X-ray Study of $CH_2[ClC_6H_3O]_2P(Ph)(O_2C_6Cl_4)$ (4). The colorless crystal used for the study had approximate dimensions of 0.25 × 0.25 × 0.64 mm. A total of 3464 independent reflections (+*h*,+*k*,±*l*) were measured. 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 the methyl hydrogen atoms) on the bonded carbon atoms. A disordered dichloromethane molecule was found and the non-hydrogen atoms of this molecule were refined isotropically. The final agreement factors are based on the 1860 reflections with $I \ge 2\sigma_I$.

Results and Discussion

The atom-labeling schemes for **1**−**4** are given in Figures 1−4, respectively. Selected atomic coordinates are provided in Tables 2−5 and selected bond parameters are presented in Tables 6−9 for **1**−**4**, respectively.

Syntheses. The cyclic phosphines **5** and **6** were prepared by the reaction of a chlorophosphine with a diol in the presence of triethylamine in an ether solution at room temperature. The cyclic tetraoxyphosphoranes, **3** and **4**, were synthesized by the reaction of *o*-tetrachlorobenzoquinone with the respective phosphines, **5** and **6**, in refluxing toluene. This followed the same synthetic route previously used for the synthesis of **1**[2] where the same quinone was reacted with phosphine **7**, $CH_2[(t\text{-}Bu)_2C_6H_2O]_2PPh$. For the formation of **2**, it was necessary to conduct the reaction of the phosphine **7** with benzil at 155 °C in the absence of solvent since no reaction took place in a

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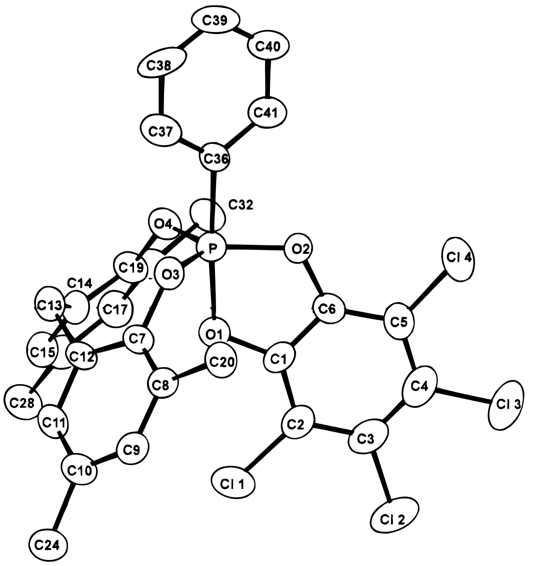


Figure 1. Molecular geometry and atom-labeling scheme for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Ph)(O_2C_6Cl_4)$ (**1**); methyl carbons of the *tert*-butyl groups and hydrogen atoms are omitted for clarity.

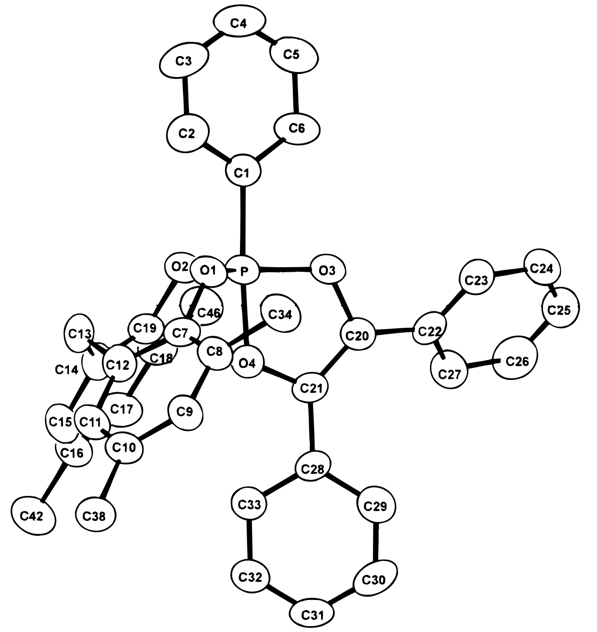


Figure 2. Molecular geometry and atom-labeling scheme for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Ph)(O_2C_2Ph_2)$ (**2**); methyl carbons of the *tert*-butyl groups and hydrogen atoms are omitted for clarity.

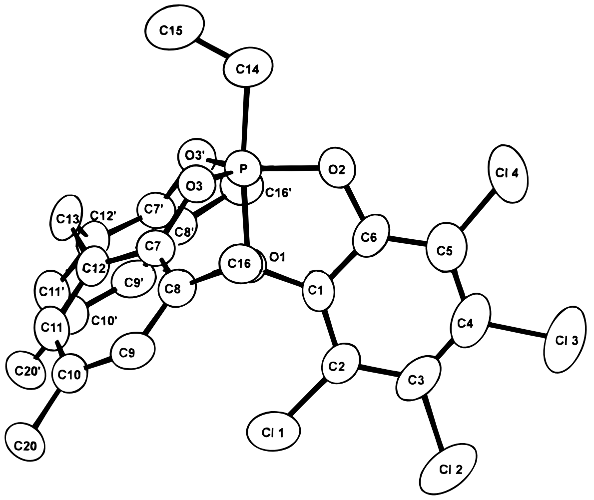
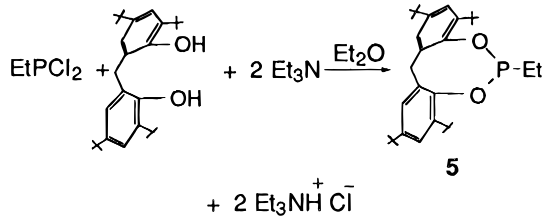
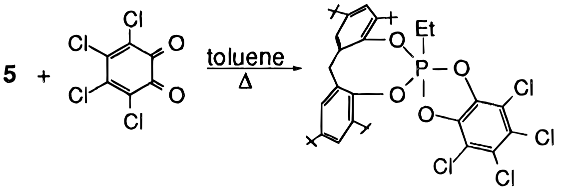


Figure 3. Molecular geometry and atom-labeling scheme for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Et)(O_2C_6Cl_4)$ (**3**); methyl carbons of the *tert*-butyl groups and hydrogen atoms are omitted for clarity. The primed atoms are generated by x, $^1/_2 - y$, z.



5

(1)



3

(2)

refluxing toluene solution. The process is illustrated for the formation of **3** in eqs 1 and 2. The yields of **2**−**4** were in the range of 40−71%, which was considerably lower than the 99% yield obtained for **1**. Phosphoranes **1**−**3** were relatively stable in water. For example, when **2** was dissolved in an immiscible $CDCl_3/H_2O$ mixture, only 54% had undergone hydrolysis after 2 weeks. However, **4**, with chlorine substituents, hydrolyzed rapidly in the presence of traces of moisture. During repeated attempts for the recrystallization of **4** under a dry nitrogen atmosphere, ^{31}P NMR showed hydrolysis leading to the formation of phosphates. The presence of *tert*-butyl groups in **1**−**3** with their hydrophobic tendency, instead of the more reactive chlorine substituents in **4**, most likely accounts for the difference in hydrolytic stability.

Basic Structures. X-ray studies reveal that **2**−**4**, like **1**, have trigonal bipyramidal structures, Figures 1−4. The ligand arrangements for the bicyclic derivatives **2** and **3** are unique in two ways. The finding agrees with that communicated earlier for **1**[2] that the least electronegative ligand occupies the axial position. This leaves the two cyclic components occupying two different sets of positions in the TBP,[10] the same as is observed for **1**.[2] The eight-membered ring is situated in diequatorial (e−e) sites while the five-membered ring in each case resides at axial−equatorial (a−e) sites. For **4**, which has a trigonal bipyramidal geometry, the more conventional ligand arrangement is found for a spirocyclic derivative. Here, both the five- and eight-membered rings are located at axial−equatorial positions, and the least electronegative ligand, the phenyl group, is located at the remaining equatorial position.

Accompanying these geometries, the diequatorial eight-membered rings of **1**−**3** are all of the same type. They possess a symmetrical chairlike *anti* conformation as depicted in Figures 5−7. In contrast, the conformation of the axial−equatorially oriented eight-membered ring of **4** is a distorted *syn* arrangement, or twisted boat, as shown in Figure 8. This is similar to the conformation observed earlier for the other a−e eight-membered rings of this kind that are contained in trigonal bipyramidal oxyphosphoranes, *i.e.*, **G**[12] and **H**.[13]

A constraint that is important for saturated six-membered rings in establishing site occupancy in a TBP is its ability to situate the $P-O_{eq}-C$ ring angle near 90° relative to the equatorial plane.[21] Trippett[21] concluded that this angle is most

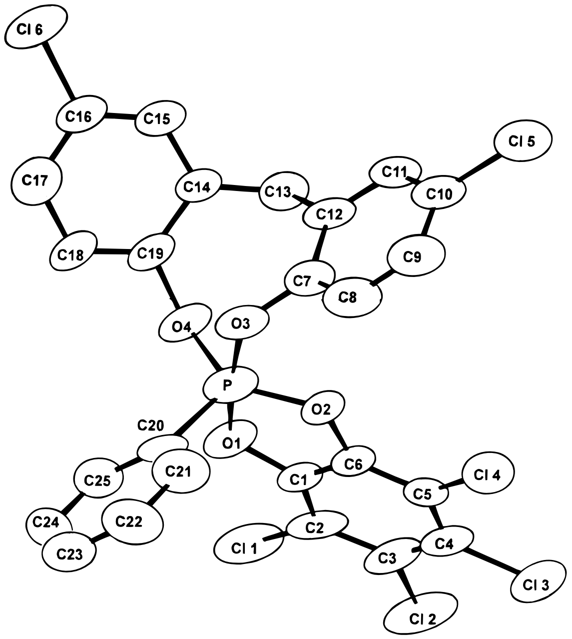


Figure 4. Molecular geometry and atom-labeling scheme for $CH_2[ClC_6H_3O]_2P(Ph)(O_2C_6Cl_4)$ (**4**) with hydrogen atoms omitted for clarity.

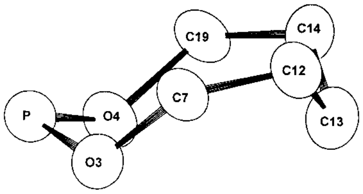


Figure 5. SNOOPI plot showing the conformation of the eight-membered ring in **1**.

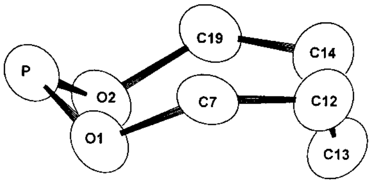


Figure 6. SNOOPI plot showing the conformation of the eight-membered ring in **2**.

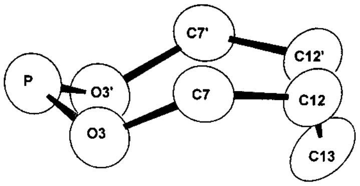


Figure 7. SNOOPI plot showing the conformation of the eight-membered ring in **3.**

Table 2. Atomic Coordinates ($\times 10^4$) for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Ph)(O_2C_6Cl_4)$ (**1**)[a]

	x	*y*	*z*	*U*(eq)
Cl(1)	3582(1)	1024(1)	5123(3)	62(1)
Cl(2)	4258(1)	1104(1)	6022(3)	70(1)
Cl(3)	4612(1)	1851(1)	5360(3)	87(1)
Cl(4)	4307(1)	2503(1)	3676(3)	82(1)
P	3330(1)	2124(1)	2501(2)	36(1)
O(1)	3408(1)	1705(1)	3402(6)	39(2)
O(2)	3672(1)	2271(2)	2878(6)	42(2)
O(3)	3055(1)	2223(2)	3431(5)	36(2)
O(4)	3255(1)	1859(1)	1268(6)	39(2)
C(1)	3679(2)	1701(3)	3942(8)	34(2)
C(2)	3800(2)	1416(2)	4703(8)	36(2)
C(3)	4091(2)	1460(3)	5122(10)	48(3)
C(4)	4256(2)	1797(3)	4812(10)	58(3)
C(5)	4125(2)	2086(3)	4053(10)	48(3)
C(6)	3841(2)	2026(2)	3628(9)	37(2)
C(7)	2925(2)	1978(3)	4355(9)	35(2)
C(8)	2938(2)	2083(2)	5656(9)	38(2)
C(9)	2821(2)	1815(2)	6517(9)	37(2)
C(10)	2686(2)	1475(2)	6124(10)	41(2)
C(11)	2655(2)	1405(2)	4818(9)	40(2)
C(12)	2770(2)	1657(2)	3909(8)	33(2)
C(13)	2725(2)	1577(2)	2485(9)	43(2)
C(14)	2952(2)	1315(2)	1844(9)	35(2)
C(15)	2906(2)	923(3)	1809(9)	41(2)
C(16)	3101(2)	674(2)	1180(10)	42(2)
C(17)	3342(2)	834(3)	558(9)	46(2)
C(18)	3402(2)	1228(2)	528(9)	38(2)
C(19)	3207(2)	1453(2)	1238(9)	37(2)
C(20)	3076(2)	2472(2)	6128(9)	41(2)
C(21)	3413(2)	2465(3)	5982(11)	64(3)
C(22)	2995(2)	2536(3)	7561(10)	72(3)
C(23)	2939(2)	2810(2)	5371(10)	64(3)
C(24)	2567(2)	1172(2)	7128(9)	47(3)
C(25)	2604(3)	1303(3)	8503(11)	94(4)
C(26)	2746(3)	801(3)	6924(13)	98(4)
C(27)	2239(2)	1095(3)	6861(11)	80(4)
C(28)	3036(2)	234(2)	1208(11)	55(3)
C(29)	3284(2)	4(3)	551(12)	88(4)
C(30)	2744(2)	151(2)	508(12)	75(4)
C(31)	3012(3)	95(3)	2607(12)	93(4)
C(32)	3667(2)	1386(2)	−244(9)	43(2)
C(33)	3850(2)	1056(3)	−876(10)	67(3)
C(34)	3889(2)	1601(3)	604(10)	57(3)
C(35)	3557(2)	1651(3)	−1328(10)	71(3)
C(36)	3277(2)	2568(2)	1559(8)	33(2)
C(37)	2995(2)	2722(3)	1373(10)	55(3)
C(38)	2952(2)	3049(3)	636(9)	58(3)
C(39)	3185(3)	3231(3)	65(11)	60(3)
C(40)	3463(2)	3078(3)	230(11)	62(3)
C(41)	3507(2)	2751(3)	949(10)	56(3)

[a] Atoms are labeled to agree with Figure 1. *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

favorable in allowing the lone pair of the equatorial oxygen atom bonded to phosphorus to reside near the equatorial plane and was achievable only for a boat conformation positioned at a−e sites. Thus far, for saturated six-membered ring systems this has held true for monocyclic[13,22,23] and bicyclic[22−25] pentaoxyphosphoranes. However, with eight-membered rings, due to their greater flexibility, Trippett's condition can be met equally well for rings located in e−e sites, as found for **1**−**3**, or a−e sites, as exists for **4**. Table 10 lists the values for this dihedral angle for eight-membered rings. These values fall in the range 71−85°. It is seen that the values for **1**−**3**, **D**, and **E** with diequatorial rings do not, in general, vary appreciably from that for **4**, **G**, and **H** with a−e orientations. These dihedral angles compare with a range of values of 76−87° found from X-ray studies[13,24] on six pentaoxyphosphoranes containing saturated six-membered rings in boat conformations located at a−e positions of a TBP.

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Table 3. Atomic Coordinates ($\times 10^4$) for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Ph)(O_2C_2Ph_2)$ (**2**)[a]

	x	*y*	*z*	*U*(eq)
P	7012(1)	385(2)	1985(1)	39(1)
O(1)	6606(2)	−103(5)	2628(2)	42(1)
O(2)	7004(2)	1935(4)	1890(2)	44(1)
O(3)	7411(2)	−528(5)	1461(2)	45(1)
O(4)	6351(2)	160(5)	1482(2)	45(1)
C(1)	7746(3)	516(7)	2523(3)	40(2)
C(2)	7705(4)	965(9)	3171(5)	74(3)
C(3)	8229(4)	1132(11)	3579(5)	79(3)
C(4)	8828(4)	774(9)	3353(5)	68(2)
C(5)	8890(4)	360(10)	2718(5)	76(3)
C(6)	8357(4)	206(10)	2306(5)	71(3)
C(7)	5926(3)	−301(7)	2676(3)	41(2)
C(8)	5692(3)	−1526(7)	2792(4)	45(2)
C(9)	5023(3)	−1635(7)	2838(4)	48(2)
C(10)	4604(3)	−585(8)	2796(4)	49(2)
C(11)	4872(3)	615(8)	2707(4)	49(2)
C(12)	5541(3)	800(7)	2649(4)	44(2)
C(13)	5819(4)	2165(7)	2598(4)	50(2)
C(14)	5921(3)	2730(6)	1911(4)	44(2)
C(15)	5410(4)	3407(7)	1593(4)	53(2)
C(16)	5484(4)	3999(7)	984(4)	50(2)
C(17)	6104(4)	3980(7)	700(4)	56(2)
C(18)	6629(3)	3317(7)	973(4)	48(2)
C(19)	6500(3)	2664(7)	1571(4)	42(2)
C(20)	7109(3)	−813(7)	856(3)	42(2)
C(21)	6485(3)	−411(7)	885(3)	40(2)
C(22)	7533(3)	−1374(7)	348(4)	42(2)
C(23)	8020(4)	−2202(7)	534(4)	53(2)
C(24)	8454(4)	−2675(9)	69(5)	65(2)
C(25)	8410(4)	−2320(9)	−582(5)	67(2)
C(26)	7944(4)	−1490(10)	−782(4)	69(3)
C(27)	7495(4)	−1011(9)	−324(4)	59(2)
C(28)	5947(3)	−468(7)	401(3)	42(2)
C(29)	5901(4)	−1391(8)	−100(4)	59(2)
C(30)	5392(4)	−1359(9)	−556(4)	62(2)
C(31)	4922(4)	−437(9)	−504(5)	64(2)
C(32)	4957(4)	444(10)	−16(5)	81(3)
C(33)	5455(4)	452(9)	446(5)	68(3)
C(34)	6134(4)	−2729(7)	2896(4)	58(2)
C(35)	5739(4)	−3951(8)	3051(6)	82(3)
C(36)	6579(5)	−2480(10)	3499(6)	93(3)
C(37)	6527(5)	−3009(9)	2259(6)	81(3)
C(38)	3861(4)	−821(8)	2850(4)	60(2)
C(39)	3487(4)	437(10)	2884(6)	82(3)
C(40)	3716(4)	−1590(12)	3481(6)	91(3)
C(41)	3657(4)	−1550(10)	2218(6)	86(3)
C(42)	4930(4)	4770(9)	660(5)	68(2)
C(43)	5060(5)	5063(13)	−76(6)	102(4)
C(44)	4838(5)	6038(10)	1035(6)	94(3)
C(45)	4294(4)	3992(10)	700(7)	94(4)
C(46)	7301(3)	3451(7)	644(4)	54(2)
C(47)	7308(5)	4373(14)	60(7)	118(5)
C(48)	7788(6)	3956(15)	1158(7)	124(5)
C(49)	7541(5)	2155(11)	395(7)	109(4)

[a] Atoms are labeled to agree with Figure 2. *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

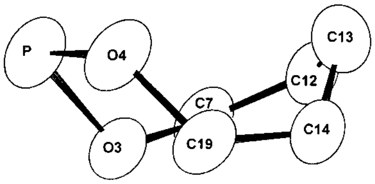

Figure 8. SNOOPI plot showing the conformation of the eight-membered ring in **4**.

Table 4. Atomic Coordinates ($\times 10^4$) for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Et)(O_2C_6Cl_4)$ (**3**)[a]

	x	*y*	*z*	*U*(eq)
P	2538(2)	2500	3199(1)	49(1)
Cl(1)	−2118(2)	2500	2578(1)	75(1)
Cl(2)	−2200(3)	2500	1220(1)	94(1)
Cl(3)	536(4)	2500	536(1)	110(1)
Cl(4)	3346(3)	2500	1209(1)	97(1)
O(1)	798(5)	2500	3014(2)	49(2)
O(2)	2877(6)	2500	2497(2)	57(2)
O(3)	2335(4)	1677(2)	3541(2)	49(1)
C(1)	575(9)	2500	2451(4)	46(2)
C(2)	−661(10)	2500	2176(4)	52(2)
C(3)	−661(11)	2500	1576(4)	59(3)
C(4)	559(13)	2500	1271(4)	69(3)
C(5)	1807(11)	2500	1560(4)	66(3)
C(6)	1759(10)	2500	2142(4)	52(2)
C(7)	1127(6)	1334(4)	3758(2)	46(2)
C(8)	699(6)	582(4)	3555(2)	46(2)
C(9)	−501(6)	286(4)	3801(3)	52(2)
C(10)	−1244(6)	683(4)	4233(2)	48(2)
C(11)	−708(6)	1399(4)	4422(2)	51(2)
C(12)	467(6)	1733(3)	4198(2)	44(2)
C(13)	1024(10)	2500	4454(3)	55(2)
C(14)	4385(9)	2500	3312(4)	69(3)
C(15)	4850(11)	2500	3922(5)	105(4)
C(16)	1509(6)	74(4)	3127(3)	54(2)
C(17)	1680(7)	513(4)	2551(3)	76(2)
C(18)	788(7)	−726(4)	2995(3)	87(2)
C(19)	2913(6)	−128(4)	3369(3)	75(2)
C(20)	−2525(6)	299(4)	4479(3)	55(2)
C(21)	−3506(8)	72(8)	4032(3)	147(5)
C(22)	−2131(8)	−430(5)	4829(4)	125(4)
C(23)	−3221(9)	855(6)	4907(4)	124(4)

[a] Atoms are labeled to agree with Figure 3. *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

In previous papers,[10,26] where we conducted a ring strain analysis for rings varying in size from five- to eight-membered, it was estimated that an unsubstituted eight-membered ring of the type used in this study would show little energy difference between the two sets of positions in a TBP.[10] Thus, one must consider other factors that influence the orientation of rings of this size.

Electronic vs Steric Effects. In an electronegativity scale constructed by Huheey,[27,28] the Pauling value for a phenyl group is 2.49,[28] considerably less than that for an oxygen atom, 3.4.[29] The ethyl group with a value of 2.29[27] is still capable of displacing an oxygen atom from its preferred axial position as found in the tetraoxyphosphorane **3**. However, when the more electronegative chlorine substituents are present on the aryl components of the eight-membered ring instead of *tert*-butyl groups, *i.e.*, in **4** the ring is positioned at a−e sites with the phenyl group displaced to an equatorial location. The implication is that we have now increased the electronegativity of the axial oxygen atom in **4** by use of a *p*-chloro substituent. However, the position *ortho* to the oxygen has a hydrogen atom which has replaced a *tert*-butyl group that was present in phosphoranes **1**−**3**. Hence, a combination of an increase in electronegativity and steric reduction may be responsible for the structural representation found by **4**. As noted, the monocyclic pentaoxyphosphoranes **G**[12] and **H**[13] which lack ring substituents provided the only other examples of trigonal bipyramids with this type of eight-membered ring positioned at a−e sites.

To gain additional insight regarding the change in ring orientation from e−e observed for **1**−**3** to a−e in **4**, we used a molecular mechanics approach via the program HyperChem[30] using the MM^+ routine. The calculations showed, in agreement

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Table 5. Atomic Coordinates ($\times 10^4$) for $CH_2[ClC_6H_3O]_2P(Ph)(O_2C_6Cl_4)$ (**4**)[a]

	x	*y*	*z*	*U*(eq)[b]
P	6195(1)	−1379(3)	2387(2)	58(1)
Cl(1)	5833(1)	2443(3)	2219(3)	77(1)
Cl(2)	4917(1)	2606(3)	1219(3)	89(1)
Cl(3)	4420(1)	465(4)	676(3)	87(1)
Cl(4)	4844(1)	−1838(3)	1020(3)	77(1)
Cl(5)	5423(1)	−5442(3)	−1145(3)	83(1)
Cl(6)	7887(1)	−3546(4)	1581(4)	105(2)
O(1)	6103(2)	31(6)	2351(6)	55(2)
O(2)	5731(2)	−1582(6)	1827(5)	46(2)
O(3)	6263(2)	−2701(6)	2202(6)	51(2)
O(4)	6563(2)	−982(7)	2036(6)	59(2)
C(1)	5712(4)	257(11)	1976(8)	45(3)
C(2)	5549(4)	1284(10)	1866(9)	55(4)
C(3)	5143(4)	1325(13)	1443(9)	64(4)
C(4)	4919(4)	386(13)	1173(9)	56(4)
C(5)	5102(4)	−633(11)	1306(8)	46(3)
C(6)	5494(4)	−658(10)	1687(8)	46(3)
C(7)	6064(4)	−3328(10)	1378(10)	51(3)
C(8)	5806(4)	−4114(11)	1494(10)	63(4)
C(9)	5614(4)	−4788(10)	749(11)	64(4)
C(10)	5681(4)	−4656(11)	−145(10)	57(3)
C(11)	5945(4)	−3903(11)	−247(9)	57(4)
C(12)	6147(4)	−3199(10)	500(9)	49(3)
C(13)	6427(4)	−2321(11)	342(9)	57(4)
C(14)	6813(3)	−2296(10)	1083(9)	49(3)
C(15)	7132(4)	−2855(11)	1009(10)	61(4)
C(16)	7487(4)	−2833(12)	1713(11)	68(4)
C(17)	7532(5)	−2198(12)	2554(12)	79(4)
C(18)	7211(4)	−1640(11)	2660(11)	65(4)
C(19)	6868(4)	−1666(10)	1941(10)	53(3)
C(20)	6327(4)	−1467(10)	3699(8)	47(3)
C(21)	6162(4)	−2333(13)	4111(11)	77(4)
C(22)	6241(5)	−2407(15)	5109(11)	83(5)
C(23)	6466(5)	−1644(14)	5697(11)	73(4)
C(24)	6641(4)	−817(14)	5303(11)	75(4)
C(25)	6554(4)	−725(11)	4294(11)	65(4)
C(1S)	1977(8)	556(27)	3373(23)	233(15)*
Cl(1S)	1697(3)	−568(10)	3167(9)	268(5)*
Cl(2S)	2355(6)	438(20)	4319(17)	252(10)*
Cl(3S)	2138(8)	936(23)	4619(17)	283(12)*

[a] Atoms are labeled to agree with Figure 4. *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] An asterisk (*) indicates isotropic thermal parameters for the disordered CH_2Cl_2 molecule. Occupancies for Cl(2S) Cl(3S) are 0.5 each.

with the X-ray results for **1**−**3** containing *tert*-butyl substituents, that the structures with the eight-membered ring in the e−e orientations were of lower energy than that for a−e ring orientations. For **4**, the opposite was true and the a−e ring orientation was lower in energy, again in agreement with the results of the X-ray study. Furthermore, the ring conformations, as well as other features of the observed structures, were quite well reproduced. The calculated and X-ray structures are compared in Figure 9. Only in the case of **4** was a significant difference found. The computed eight-membered ring conformation was an *anti* a−e ring, whereas the X-ray ring conformation was a *syn* a−e arrangement. The fact that the calculations favorably reproduce observed geometries suggests that packing is not important in causing observed geometries and also indicates that some measure of a steric term supplied by the presence of *tert*-butyl groups *ortho* to the ring P−O bond favors the e−e ring orientation and hence contributes to the stabilization of the least electronegative groups in axial sites of the trigonal bipyramids for **1**−**3**. However, the relative importance of steric vs electronic effects associated with ring substituents is not established at this time.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Ph)(O_2C_6Cl_4)$ (**1**)

P−O(3)	1.602(6)	O(3)−C(7)	1.406(10)
P−O(4)	1.610(6)	O(4)−C(19)	1.421(9)
P−O(2)	1.662(5)	C(1)−C(6)	1.377(11)
P−O(1)	1.760(6)	C(7)−C(12)	1.391(11)
P−C(36)	1.838(8)	C(12)−C(13)	1.516(12)
O(1)−C(1)	1.339(9)	C(13)−C(14)	1.516(11)
O(2)−C(6)	1.377(9)	C(14)−C(19)	1.387(11)
O(3)−P−O(4)	116.1(3)	C(6)−O(2)−P	116.6(5)
O(3)−P−O(2)	120.1(3)	C(7)−O(3)−P	126.8(5)
O(4)−P−O(2)	123.8(3)	C(19)−O(4)−P	127.8(5)
O(3)−P−O(1)	90.5(3)	O(1)−C(1)−C(6)	111.6(8)
O(4)−P−O(1)	89.6(3)	O(2)−C(6)−C(1)	110.6(7)
O(2)−P−O(1)	86.9(3)	C(12)−C(7)−O(3)	117.5(8)
O(3)−P−C(36)	92.3(3)	C(12)−C(13)−C(14)	116.6(7)
O(4)−P−C(36)	91.6(3)	C(14)−C(19)−O(4)	117.1(7)
O(2)−P−C(36)	89.3(3)	C(41)−C(36)−P	122.4(7)
O(1)−P−C(36)	176.1(3)	C(37)−C(36)−P	121.2(6)
C(1)−O(1)−P	114.3(5)	C(37)−C(36)−C(41)	116.3(8)

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 1.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Ph)(O_2C_2Ph_2)$ (**2**)[a]

P−O(1)	1.610(5)	O(4)−C(21)	1.354(8)
P−O(2)	1.614(5)	C(7)−C(12)	1.391(10)
P−O(3)	1.630(5)	C(12)−C(13)	1.528(10)
P−O(4)	1.710(5)	C(13)−C(14)	1.500(10)
P−C(1)	1.860(7)	C(14)−C(19)	1.375(10)
O(1)−C(7)	1.421(8)	C(20)−C(21)	1.356(10)
O(2)−C(19)	1.434(8)	C(20)−C(22)	1.458(10)
O(3)−C(20)	1.386(8)	C(21)−C(28)	1.471(10)
O(1)−P−O(2)	113.5(3)	C(6)−C(1)−C(2)	115.6(7)
O(1)−P−O(3)	126.1(3)	C(6)−C(1)−P	123.6(6)
O(2)−P−O(3)	120.4(3)	C(2)−C(1)−P	120.8(6)
O(1)−P−O(4)	90.3(2)	C(12)−C(7)−O(1)	116.4(6)
O(2)−P−O(4)	93.4(2)	C(7)−C(12)−C(13)	122.9(6)
O(3)−P−O(4)	87.2(2)	C(14)−C(13)−C(12)	118.3(6)
O(1)−P−C(1)	89.6(3)	C(19)−C(14)−C(13)	123.3(6)
O(2)−P−C(1)	90.2(3)	C(14)−C(19)−O(2)	116.2(6)
O(3)−P−C(1)	89.8(3)	C(21)−C(20)−O(3)	109.0(6)
O(4)−P−C(1)	176.2(3)	C(21)−C(20)−C(22)	136.3(6)
C(7)−O(1)−P	127.9(4)	O(3)−C(20)−C(22)	114.6(5)
C(19)−O(2)−P	125.6(4)	O(4)−C(21)−C(20)	111.5(6)
C(20)−O(3)−P	116.8(4)	O(4)−C(21)−C(28)	115.8(6)
C(21)−O(4)−P	114.1(4)	C(20)−C(21)−C(28)	132.8(7)

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 2.

Bond Parameters. As usual, with TBP geometries of main group elements, the axial bonds are longer than equatorial bonds,[4,31] *cf.* P−C(Ph) in **1** and **2** with **4** and axial and equatorial P−O bond lengths in either the five- or eight-membered rings for **1**−**4**. Indicative of the lower amount of strain for eight-membered rings relative to five-membered rings is the presence of shorter bond P−O bond lengths for the eight-membered rings. In particular, it is noted for **4** that the P−O axial length for the eight-membered ring, 1.661(8) Å, is 0.086 Å shorter than that for the five-membered ring, 1.747(8) Å. On average, the P−O axial−equatorial bond length difference is 0.093(6) Å for the five-membered rings in **1**−**4**, whereas it is considerably less, 0.056(7) Å, for the eight-membered rings in **4**, **G**, and **H**.

The effect of the more electronegative chlorine atoms as substituents on the aryl components of the five-membered rings is apparent in the increase of the P−O ring bond lengths contained therein for **1** and **3** compared to **2**. In **4**, the

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(30) *HyperChem Release 4 for Windows: Software for Molecular Modeling*, Hypercube Inc.: Ontario, Canada, 1995.

(31) 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 8. Selected Bond Lengths (Å) and Angles (deg) for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(Et)(O_2C_6Cl_4)$ (**3**)[a]

P−O(3)	1.598(4)	O(3)−C(7)	1.410(6)
P−O(2)	1.672(6)	C(1)−C(6)	1.368(12)
P−O(1)	1.760(6)	C(7)−C(12)	1.382(7)
P−C(14)	1.830(9)	C(12)−C(13)	1.511(7)
O(1)−C(1)	1.334(9)	C(14)−C(15)	1.496(13)
O(2)−C(6)	1.376(10)		
O(3)−P−O(3′)	117.9(3)	C(6)−O(2)−P	115.7(5)
O(3)−P−O(2)	121.0(1)	C(7)−O(3)−P	129.1(3)
O(3)−P−O(1)	90.1(2)	O(1)−C(1)−C(6)	112.4(8)
O(2)−P−O(1)	87.3(3)	C(1)−C(6)−O(2)	111.0(7)
O(3)−P−C(14)	92.9(2)	C(12)−C(7)−O(3)	117.8(5)
O(2)−P−C(14)	86.8(4)	C(7)−C(12)−C(13)	122.0(6)
O(1)−P−C(14)	174.2(4)	C(12)−C(13)−C(12′)	115.2(7)
C(1)−O(1)−P	113.6(5)	C(15)−C(14)−P	116.1(8)

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 3.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for $CH_2[ClC_6H_3O]_2P(Ph)(O_2C_6Cl_4)$ (**4**)[a]

P−O(4)	1.611(8)	O(3)−C(7)	1.407(14)
P−O(2)	1.633(8)	O(4)−C(19)	1.409(14)
P−O(3)	1.661(8)	C(1)−C(6)	1.35(2)
P−O(1)	1.747(8)	C(7)−C(12)	1.38(2)
P−C(20)	1.798(12)	C(12)−C(13)	1.53(2)
O(1)−C(1)	1.369(13)	C(13)−C(14)	1.47(2)
O(2)−C(6)	1.388(13)	C(14)−C(19)	1.41(2)
O(4)−P−O(2)	134.1(5)	C(7)−O(3)−P	126.7(7)
O(4)−P−O(3)	94.2(4)	C(19)−O(4)−P	125.1(8)
O(2)−P−O(3)	87.1(4)	C(6)−C(1)−O(1)	112.5(11)
O(4)−P−O(1)	81.9(4)	C(1)−C(6)−O(2)	110.7(10)
O(2)−P−O(1)	88.8(4)	C(12)−C(7)−O(3)	120.6(11)
O(3)−P−O(1)	169.7(4)	C(7)−C(12)−C(13)	122.6(12)
O(4)−P−C(20)	110.7(5)	C(14)−C(13)−C(12)	115.1(10)
O(2)−P−C(20)	114.8(5)	C(19)−C(14)−C(13)	119.9(11)
O(3)−P−C(20)	95.8(5)	C(25)−C(20)−C(21)	119.1(12)
O(1)−P−C(20)	94.5(5)	C(25)−C(20)−P	123.1(11)
C(1)−O(1)−P	111.7(8)	C(21)−C(20)−P	117.6(10)
C(6)−O(2)−P	115.8(7)		

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 4.

Table 10. Dihedral Angles between $P-O_{eq}-C$ Bonds and Equatorial Planes for Oxyphosphoranes (deg)[a]

1	79.4(5) 78.7(5)	**D**[11,12]	77.7(2)
2	81.5(4) 82.4(4)	**E**[12]	76.8(5)
3	71.4(5)	**G**[12]	85.0(4)
4	79(1)	**H**[13]	76.9

[a] Superscripts refer to reference numbers.

substitution of chlorine and hydrogen atoms in place of *tert*-butyl groups on the eight-membered rings results in a competitive reduction of the P−O bond lengths of the five-membered rings. We might assume that a strengthening of the P−O bonds in the latter ring has occurred by the presence of chlorine atoms on the eight-membered ring causing a shift in the electron density away from the tetrachlorocatecholate moiety.

NMR Data. The ^{31}P chemical shifts in $CDCl_3$ solution indicate retention of the pentacoordinate geometries. In ppm, they are −40.77 (**1**),[2] −47.4 (**2**), −23.94 (**3**), and −32.29 (**4**). A solid state ^{31}P value for **1**, −40.20 ppm,[2] nearly the same as the solution value, suggests that the geometry in solution is retained from that observed in the X-ray study.

The observance of two methylene proton signals at 23 °C for **1**−**4** indicates the absence of ligand exchange. By way of contrast, both **G**[12] and **H**,[13] which are monocyclic pentaoxyphosphoranes rather than bicyclic tetraoxyphosphoranes, undergo rapid intramolecular exchange at room temperature. The presence of a group of considerably different electronegativity is known to raise the energy of the intermediates involved in the pseudorotational process.[32] In a study[26] of a series of bicyclic tetraoxyphosphoranes containing oxaphosphorinane rings, *e.g.*, **I**, a rigid geometry was indicated at 25 °C which exhibited fluxional behavior on heating, *i.e.*, Berry pseudorotation.[33]

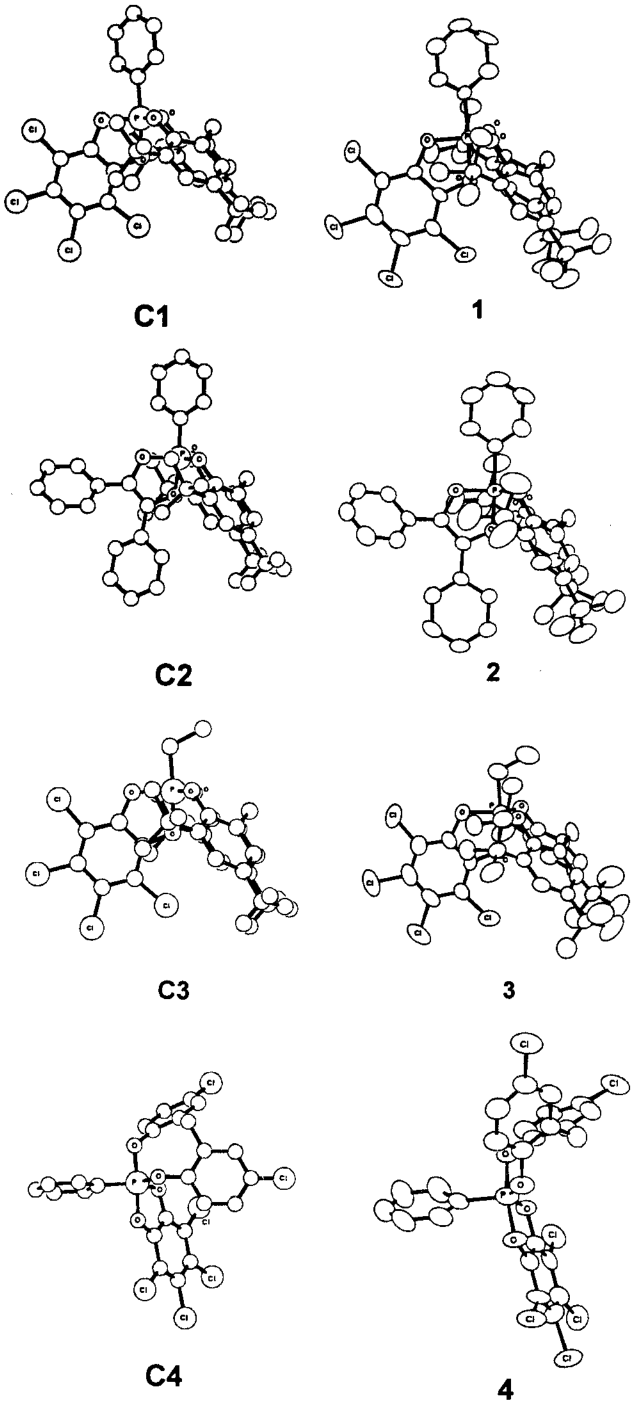

Figure 9. Comparison of calculated lowest energy geometries (left column) with X-ray geometries (right column) for **1**−**4** using HyperChem.

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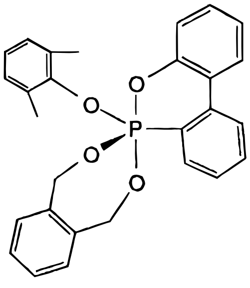
(32) Holmes, R. R. *Pentacoordinated Phosphorus*−*Reaction Mechanisms*; ACS Monograph 176; American Chemical Society: Washington, DC, 1980; Vol. II.

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



I[24]

Conclusion

A series of new bicyclic tetraoxyphosphoranes **1**−**3** were synthesized which showed trigonal bipyramidal geometries that positioned the least electronegative ligands at axial sites. This represents the first series of complexes with geometries in violation of the electronegativity rule for which ring strain was not causative. This was achieved with the use of eight-membered rings that exhibit little energy difference between the occupancy of diequatorial sites of a trigonal bipyramid compared to that of the occupancy of axial−equatorial sites.

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Supporting Information Available: Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for **1**, **2**, **3**, and **4** (16 pages). Ordering information is given on any current masthead page.

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