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Conformational Comparison of a Seven-Membered Ring in Tri- and Pentacoordinated Geometries of Oxygen-Containing Phosphorus Compounds. Solution NMR Behavior of Seven- and Eight-Membered Rings in Oxyphosphoranes[1]

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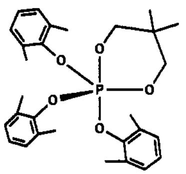
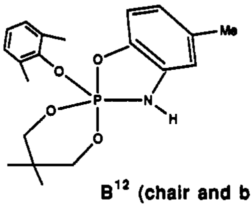
Reaction of cyclic phosphites with alcohols or a quinone in oxidative addition reactions led to the new spirocyclic oxyphosphoranes $(C_6H_4O)_2(C_8H_{12}O_2)P(O\text{-}Xyl)$ (**1**), $[(C_6H_4O)_2CH_2](C_8H_{12}O_2)P(O\text{-}Xyl)$ (**5**), and $(C_6H_4O)_2(C_{12}H_8O_2)P(S\text{-}Xyl)$ (**3**) and the monocyclic oxyphosphorane $(C_6H_4O)_2P(OC_6F_5)_3$ (**4**), containing rings varying in size from five- to eight-membered (Xyl is $C_6H_3Me_2$). In addition, the cyclic phosphite $(C_6H_4O)_2P(S\text{-}Xyl)$ (**2**) was synthesized. The X-ray structure of **1** present in a trigonal bipyramidal (TBP) geometry and that of **2** showed similar "rowboat" conformations for the common seven-membered ring system. The latter contrasts with conformational change usually found for six-membered rings from chair to boat accompanying a change of coordination from tri- to pentacoordinate at phosphorus. Variable-temperature ^1H NMR spectra of **1**, **3**, and **5** provide activation energies for intramolecular ligand-exchange processes (pseudorotation). The spectra of **1** and **5** are consistent with ground-state trigonal bipyramids (in agreement with the axial–equatorial (a–e) ring orientations found for **1** in the X-ray analysis) that undergo ligand exchange via TBP intermediates with the seven- and eight-membered rings positioned diequatorially (e–e). Activation energies of 11.5–12.9 kcal/mol are interpreted to include a steric effect and to reflect the higher energy of e–e vs a–e ring placement, which is not significantly different for seven- and eight-membered rings. In contrast, this energy difference for saturated six-membered rings in TBP geometries in the absence of steric effects has been estimated at 7 kcal/mol. Oxyphosphorane **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.497$ (2) Å, $b = 11.159$ (4) Å, $c = 13.272$ (6) Å, $\alpha = 110.50$ (3)°, $\beta = 97.19$ (3)°, $\gamma = 107.87$ (2)°, and $Z = 2$. Cyclic phosphite **2** crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.857$ (3) Å, $b = 24.200$ (5) Å, $c = 8.285$ (2) Å, $\beta = 93.27$ (3)°, and $Z = 4$. The final conventional unweighted residuals are 0.064 (**1**) and 0.053 (**2**).

Introduction

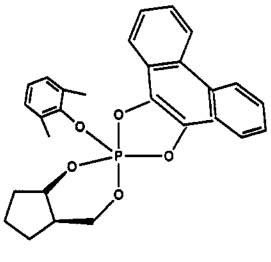
Recent work[3] on cyclic oxyphosphoranes has focused attention on six-membered ring systems. While different ring conformations were found from X-ray structural studies,[4-8] the phosphorinane rings, like five-membered rings,[9] invariably positioned themselves at axial–equatorial (a–e) sites of a trigonal bipyramid (TBP), thus dispelling the notion that six-membered rings would prefer diequatorial occupancy (e–e) of a trigonal bipyramidal geometry.[10,11] The ring conformations varied from boat,[4,6] to twist-boat,[5,6,12,13] to half-chair,[14] to twist-chair,[12] to chair,[14] and to essentially planar[5] forms. The latter was achieved with phosphorinane rings that contained ring unsaturation. The most prevalent forms were the boat and twist-boat conformations in agreement with considerations from molecular models by Trippett.[15] In the presence of hydrogen bonding,[12,14] chair forms were stabilized. Some examples are given here in A–D.[5,6,12,13,16]



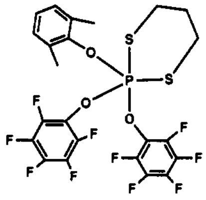
A[5] (boat)



B[12] (chair and boat)



C[6] (boat)



D[13] (boat)

As these molecules are fluxional, NMR studies of intramolecular ligand exchange led to activation energies associated with postulated TBP intermediates having diequatorial six-membered ring structures suggesting that this representation is 6–12 kcal/mol higher in energy than the phosphorane having a TBP structure with an axial–equatorial ring orientation.[3,4,12,14,15] Similar studies on oxyphosphoranes with five-membered rings have yielded activation energies in the range 17–22 kcal/mol to reach an exchange barrier state with the ring positioned diequatorially.[17]

One might expect that larger ring systems in cyclic oxyphosphoranes would lower the energy difference between the

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(1) (a) Pentacoordinated Molecules. 91. (b) Part 90: Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 725.

(2) This work represents in part a portion of the M.S. thesis of Lori Howe, University of Massachusetts, Amherst, MA, 1990.

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(13) Hans, J.; Day, R. O.; Howe, L.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3132.

(14) Hans, J.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3928.

(15) Trippett, S. *Pure Appl. Chem.* **1974**, *40*, 595.

(16) A recent study (Broeders, N. L. H. L.; Koole, L. H.; Buck, H. M. *J. Am. Chem. Soc.* **1990**, *112*, 7475) provides indirect evidence that a six-membered ring of a spirocyclic pentaoxyphosphorane occupies diequatorial positions of a TBP in equilibrium with a TBP isomer having the same ring at axial–equatorial sites. However, confirmation by an X-ray study has yet to be achieved.

(17) Holmes, R. R. *Pentacoordinated Phosphorus-Reaction Mechanisms*; ACS Monograph No. 176; American Chemical Society: Washington, DC, 1980; Vol. II, pp 41–50.

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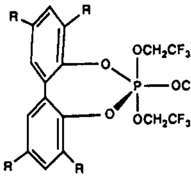
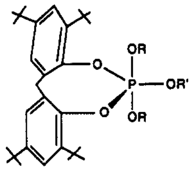
higher energy e–e ring orientation relative to the a–e arrangement even further. This represents a relatively unexplored area. Previously, Denney and co-workers[18] characterized the monocyclic pentaoxyphosphoranes E and F containing seven- and eight-membered rings, respectively, by NMR spectroscopy and reported activation energies for pseudorotational behavior. They concluded that the ground-state structures had the rings positioned diequatorially. More recently, we obtained X-ray structures[4,5] G–I, showing axial–equatorial ring formation in the mono- and bicyclic pentaoxyphosphoranes, containing these same types of ring systems. Variable-temperature NMR data support retention of this structural type in solution and show rapid intramolecular ligand-exchange behavior where the rings exchange axial–equatorial positions, a–e $\rightleftharpoons$ e–a, for the monocyclic derivatives, G and I,[5] and axial–equatorial and diequatorial positions for the seven-membered ring of the bicyclic derivative, H,[4] a–e $\rightleftharpoons$ e–e. Activation energies for these processes are indicated accompanying the representations.

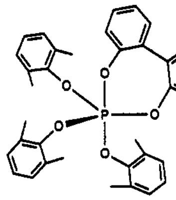


E (R = *t*-Bu ΔG‡ = 14.6,
R = H Exchange not stopped to -55°C)



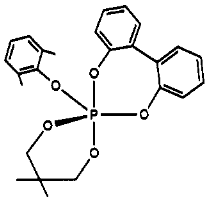
F ($R = R' = CH_2CF_3$ ΔG‡ = 15.4,
$R = CH_2CF_3$; $R' = C_2H_5$ ΔG‡ = 15.7)

Solution state structures and ligand exchange energies, ΔG‡ (kcal/mol), for ring interchanges e-e $\rightleftharpoons$ e-a, from an NMR study.[18]



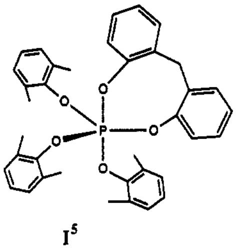
G[5]

(a-e) $\rightleftharpoons$ (e-a)
ΔG‡ = 14.2 kcal/mol



H[4]

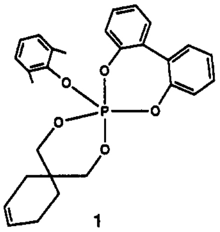
(a-e) $\rightleftharpoons$ (e-e)
ΔG‡ = 11.5 kcal/mol



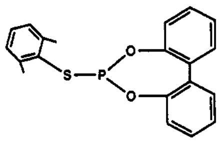
I[5]

(a-e) $\rightleftharpoons$ (e-a)
ΔG‡ = 12.1 kcal/mol

The present study was prompted by the desire to compare conformational changes occurring in a seven-membered ring system on going from tri- to pentacoordinated phosphorus. Previous work[4] suggests that differences in P–O bond lengths provide useful criteria that indicate the degree of relative ring strain present and hence may give an indication of the means to stabilize a diequatorial ring system in a TBP geometry. To this end, the synthesis, NMR study, and X-ray characterization of the pentaoxyphosphorane $(C_6H_4O)_2(C_8H_{12}O_2)P(O\text{-}Xyl)$ (**1**) and the related phosphite $(C_6H_4O)_2P(S\text{-}Xyl)$ (**2**), both containing the biphenylene seven-membered ring system, are reported here. In addition, syntheses and variable-temperature NMR data are reported for the related oxyphosphoranes **3**–**5** containing seven- and eight-membered rings and their phosphite precursors **6**–**8** in an effort to gain activation energies for ring interchanges that provide relative stabilities of diequatorial ring orientations compared to axial–equatorial ring placement.



1



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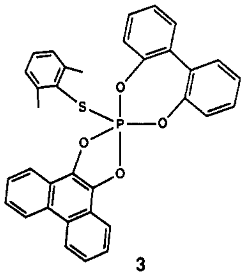

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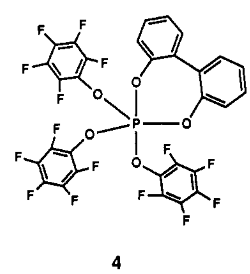

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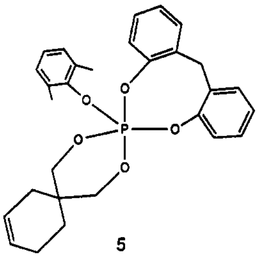

5

Experimental Section

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

^1H NMR spectra were recorded on a Varian Associates XL 300 FT-NMR or a Varian Associates XL 200 FT-NMR spectrometer. ^{19}F NMR spectra were recorded on the Varian Associates XL 300 FT-NMR spectrometer. ^{31}P NMR spectra were recorded on the latter instrumeent and also on an 80-MHz Bruker NMR spectrometer. Chemical shifts for ^{31}P NMR spectra were obtained by setting triphenyl phosphate ($CDCl_3$) at −18.0 ppm[19c] and are referenced to 85% H_3PO_4 with negative shifts upfield. ^{19}F chemical shifts were referenced relative to $CFCl_3$. All chemical shifts are reported in ppm.[19d]

Syntheses. 2-Chloro-1,3,2-dioxaphosphorinane-5-spiro-(3′-cyclohexene), $(C_8H_{12}O_2)PCl$ (6). 4,4-Bis(hydroxymethyl)-1-cyclohexene (40.74 g, 286 mmol) was slowly added with stirring to phosphorus tri-

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chloride (37.5 mL, 429 mmol). After the evolution of HCl, the solution was stirred for an additional 12 h at room temperature. Excess PCl_3 was removed by distillation and the residue distilled in vacuum (bp 125 °C, 0.5 mm). The product was obtained as a colorless liquid (46.3 g, 78.4%). Anal. Calcd for $C_8H_{12}O_2PCl$: C, 46.51; H, 5.85. Found: C, 46.51; H, 5.97. ^{31}P NMR ($CDCl_3$, 300 MHz, 18 °C): 149.28, 149.68.

2-(2,6-Dimethylphenoxy)-1,3,2-dioxaphosphorinane-5-spiro-(3′-cyclohexene), $(C_8H_{12}O_2)P(O\text{-}Xyl)$ (7). Chlorophosphonite **6** (19.1 g, 92.4 mmol) and 2,6-dimethylphenol (11.3 g, 92.4 mmol) were dissolved in diethyl ether (250 mL). Triethylamine (9.38 g, 92.4 mmol) was added slowly to the solution and the reaction mixture stirred for 2 h. After filtration, the ether was removed by distillation and the remaining oil was filtered (25.9 g, 95.9%). Anal. Calcd for $C_{16}H_{21}O_3P$: C, 65.74; H, 7.24. Found: C, 65.08; H, 6.93. ^{31}P NMR ($CDCl_3$, 300 MHz, 18 °C): 122.10, 121.64.

(Biphenyl-2,2′-diyldioxy)(3-cyclohexen-1-ylidenebis(methyleneoxo))(2,6-dimethylphenoxy)phosphorane, $(C_6H_4O)_2(C_8H_{12}O_2)P(O\text{-}Xyl)$ (1). In diethyl ether (60 mL), phosphite **7** (2.2 g, 7.52 mmol) and 2,2′-biphenol (1.4 g, 7.52 mmol) were dissolved. Freshly distilled chlorodiisopropylamine[20] (1.02 g, 7.52 mmol) was added and the solution stirred for 2 h. The precipitate that formed was filtered and the ether removed by condensing it in a trap cooled with liquid nitrogen under reduced pressure. When the total volume was 15 mL, hexane (0.5 mL) was added and the solvent removed until crystallization started to occur. Refrigeration overnight gave 2.5 g (69.8%) of colorless crystals, mp 147 °C. Anal. Calcd for $C_{28}H_{29}O_5P$: C, 70.58; H, 6.13. Found: C, 70.31; H, 6.15. ^{31}P NMR ($CDCl_3$, 80 MHz, 20 °C): −58.59. ^1H NMR (CD_2Cl_2, 300 MHz, 18.8 °C): 1.85 (br s, 4 H, cyclohexene CH_2 protons), 2.28 (s, 2 H, cyclohexene CH_2 protons), 2.44 (s, 6 H, $OC_6H_3(CH_3)_2$), 3.97 (d, 4 H, $^3J_{P-H}$ = 18 Hz, OCH_2), 5.56 (m, 2 H, cyclohexene CH protons), 6.88–7.56 (m, 11 H, H(Ar)). Variable-temperature ^1H NMR spectra were recorded over the range 18.8 to −58 °C. The singlet xylyloxy methyl signal at 2.24 ppm coalesced at −6.5 °C and separated into two signals (at 1.93 and 2.72 ppm) at reduced temperatures. The phosphorinane OCH_2 multiplet signal at 3.97 ppm separated into a complex multiplet (at 3.2–4.4 ppm) on lowering the temperature. An energy of activation[21] of 12.2 kcal/mol was obtained for the process coontrolling exchange of the xylyloxy methyl groups. No activation energy was calculated using the data on the phosphorinane OCH_2 signals due to the poor resolution of the resulting multiplets at reduced temperatures. A similar lack of resolution of the cyclohexene CH protons, which appeared as two broad peaks at lower temperatures compared to a complex multiplet at 5.56 ppm near room temperature, prevented evaluation of an activation energy.

2-(2,6-Dimethylthiophenoxy)dibenzo-1,3,2-dioxaphosphepin, $(C_6H_4O)_2P(S\text{-}Xy)$ (2). 2-Chlorodibenzo-1,3,2-dioxaphosphepin (**9**) (9.06 g, 36.2 mmol), prepared as described earlier,[18] was dissolved with 2,6-dimethylthiophenol (5.0 g, 36.0 mmol) in diethyl ether (250 mL), and the solution was cooled in a water/ice bath. A solution of triethylamine (3.65 g, 36.2 mmol) in diethyl ether (20 mL) was added dropwise with stirring. The reaction mixture was stirred overnight and filtered. During the process of removing the solvent by condensing it in a trap cooled with liquid nitrogen, crystallization occurred yielding colorless crystals (12.2 g, 96%), mp 91 °C. Anal. Calcd for $C_{20}H_{17}O_2SP$: C, 68.17; H, 4.86. Found: C, 67.95; H, 4.89. ^1H NMR ($CDCl_3$, 200 MHz, 18 °C): 2.63 (s, 6 H, $OC_6H_3(CH_3)_2$), 7.20–7.53 (m, 11 H, H(Ar)). ^{31}P ($CDCl_3$, 18 °C): 144.63.

(Biphenyl-2,2′-diyldioxy)(phenanthrene-9,10-diyldioxy)(2,6-dimethylthiophenoxy)phosphorane, $(C_{14}H_8O_2)(C_6H_4O)_2P(S\text{-}Xyl)$ (3). A solution of phosphite **2** (1.3 g, 3.7 mmol) and 0.77 g phenanthrenequinone (0.77 g, 3.7 mmol) in 20 mL of toluene was heated to 95 °C for 20 min. The reaction mixture was allowed to cool to room temperature. The precipitate was filtered and dried in vacuo, giving a slightly yellow powder (1.2 g, 59%). No melting was observed up to 230 °C. Anal. Calcd for $C_{36}H_{25}O_4SP$: C, 72.84; H, 4.50. Found: C, 72.67; H, 4.70. ^1H NMR ($CDCl_3$, 300 MHz, 19 °C): 2.51 (s, broad, 6 H, $C_6H_3(CH_3)_2$), 6.97–7.89 (m, 19 H, H(Ar)). Variable-temperature ^1H NMR spectra were recorded over the range +49 to −30 °C. The thioxylyl methyl signal (at 2.5 ppm), which is sharp at 49 °C, broadens and coalesces at 0 °C and finally appears as two relatively sharp signals at −30 °C (at 2.08 and 2.90 ppm). The energy of activation was calculated to be 12.5 kcal/mol.[21]

2-(Pentafluorophenoxy)dibenzo-1,3,2-dioxaphosphepin, $(C_6H_4O)_2P(OC_6F_5)$ (8). 2-Chlorodibenzo-1,3,2-dioxaphosphepin (**9**) (6.8 g, 27.1 mmol) and triethylamine (2.74 g, 27.1 mmol) were dissolved in diethyl ether (150 mL) with stirring. A solution of pentafluorophenol (4.99 g, 27.1 mmol) in diethyl ether (20 mL) was added, and after 2 h the precipitate that formed was filtered. The residue was washed with diethyl ether (200 mL). During the process of evaporating the solvent under a stream of dry nitrogen, crystallization occurred. In total, 8.9 g (82.5%) of colorless crystals were obtained, mp 113 °C. Anal. Calcd for $C_{18}H_8F_5O_3P$: C, 54.29; H, 2.02. Found: C, 54.29; H, 2.17. ^1H NMR ($CDCl_3$, 300 MHz, 19 °C): 7.28–7.55 (m, H(Ar)). ^{31}P NMR ($CDCl_3$, 80 MHz, 20 °C): 143.0. ^{19}F NMR ($CDCl_3$, 300 MHz, 20 °C): −162.1 (m, 2 $F_{o,m}$), −160.7 (t, J = 23.1 Hz, 1 F_p), −153.6 (m, 2 $F_{m,o}$).

(Biphenyl-2,2′-diyldioxy)tris(pentafluorophenoxy)phosphorane, $(C_6H_4O)_2P(OC_6F_5)_3$ (4). The pentafluorophenoxy phosphite **8** (1.5 g, 3.8 mmol) and pentafluorophenol (1.4 g, 7.6 mmol) were dissolved in diethyl ether (150 mL). The solution was cooled with an ethanol/dry ice bath. Freshly distilled chlorodiisopropylamine (0.51 g, 3.8 mmol) in diethyl ether (20 mL) was added dropwise with stirring. The reaction mixture was allowed to reach room temperature, and stirring was continued for an additional 4 h. After filtering of the mixture, the solution was concentrated by condensing the diethyl ether in a trap cooled with liquid nitrogen. The remaining solution was placed in a refrigerator overnight. The crystalline product that formed was filtered. A total of 0.6 g (21%) of product was obtained. Due to extreme degradation with moisture satisfactory elemental analysis was prevented. ^{31}P NMR ($CDCl_3$, 300 MHz, 18 °C): −67.12. ^{19}F NMR ($CDCl_3$, 300 MHz, 19 °C): −163.0 (t, J = 21.6 Hz, 2 $F_{o,m}$), −160.7 (t, J = 21.8 Hz, 1 F_p), −154.8 (b, 2 $F_{m,o}$).

(Methylenebis(*o*-phenyleneoxy))(3-cyclohexen-1-ylidenebis(methyleneoxy))(2,6-dimethylphenoxy)phosphorane, $(C_{13}H_{10}O_2)(C_8H_{12}O_2)P(O\text{-}Xyl)$ (5). Phosphite **7** (3.1 g, 10.6 mmol) and bis(2-hydroxyphenyl)methane (2.32 g, 11.5 mmol) were dissolved in diethyl ether (80 mL). Freshly distilled chlorodiisopropylamine (1.57 g, 11.6 mmol) was added and the solution stirred for 2 days. The precipitate that formed was removed by filtration, and the clear solution was left at ambient temperature. After 1 week the crystals that formed were collected and washed with diethyl ether (5 mL). Drying under vacuum gave 4.4 g (78.9%), mp 180–187 °C. Anal. Calcd for $C_{28}H_{33}O_5P$: C, 69.98; H, 6.92. Found: C, 70.70; H, 6.69. ^{31}P ($CDCl_3$, 300 MHz, 18 °C): −71.62. ^1H NMR ($CDCl_3$, 300 MHz, 17.8 °C): 1.71 (t, 2 H, cyclohexene (CH_2 protons) 2.05 (s, 4 H, cyclohexane CH_2 protons), 2.35 (s, 6 H, $OC_6H_3(CH_3)_2$), 4.07 (m, 6 H, OCH_2, CH_2), 5.64 (m, 2 H, cyclohexene CH protons), 6.9–7.28 (m, 11 H, H(Ar)). Variable-temperature ^1H NMR spectra were recorded over the range +17.8 to −26.5 °C. The singlet xylyloxy methyl signal at 2.35 ppm coalesced at −8 °C and split into two sharp singlets at −26.5 °C (at 2.27 and 2.45 ppm). The energy of activation was calculated to be 12.9 kcal/mol.[21] The phosphorinane OCH_2 and eight-membered-ring CH_2 signals also appeared to coalesce near −8 °C, but no activation energy could be determined due to the poor resolution of the resultant multiplet at −26.5 °C (in the range 3.9–4.3 ppm). The cyclohexene CH signal as in **1** behaved in a similar fashion on cooling and prevented detailed analysis.

X-ray Experimental Section

All X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\bar{\alpha})$ = 0.71073 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental procedures have been described previously.[22] Crystals were mounted in thin-walled glass capillaries which were sealed. For **1** this measure was precautionary. For **2** it was required in order to maintain the integrity of the crystal.[23] Data was collected using the θ–2θ scan mode, with $3° \le 2\theta(\text{Mo } K\bar{\alpha}) \le 43°$. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least-squares.[24] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinements as fixed isotropic scatterers (ideal positions or regularized difference Fourier positions for the xylyl methyl groups).

All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. Crystallographic data are summarized in Table I.[25]

Results

X-ray Studies. The atom-labeling scheme for **1** is given in the ORTEP plot of Figure 1. Selected atomic coordinates and bond distances and angles are given in Tables II and III, respectively. The corresponding information for **2** is given in Figure 5 and in

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

(21) Calculated from the equation $\Delta G^{\ddagger}_c = 4.57 \times 10^{-3} T_c(10.32 + \log(T_c\sqrt{2}/\pi\Delta\nu))$ following: Kessler, H. *Angew. Chem.* **1970**, *82*, 237. See also: Buono, G.; Llinas, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 4532.

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

(23) Crystals of **1** were of poor quality with broken surfaces, internal defects, and broad diffraction peaks. Crystals of **2** are deliquescent in an open container, puddling within 24 h.

(24) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$.

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

Table I. Crystallographic Data for $(C_6H_4O)_2(C_8H_{12}O_2)P(O\text{-}Xyl)$ (**1**) and $(C_6H_4O)_2P(S\text{-}Xyl)$ (**2**)

	compd	
	1	**2**
formula	$C_{28}H_{29}O_5P$	$C_{20}H_{17}O_2SP$
fw	476.514	352.37
cryst color	colorless	colorless
cryst dimens, mm	0.19 × 0.40 × 0.60	0.30 × 0.43 × 0.45
cryst system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	9.497 (2)	8.857 (3)
b, Å	11.159 (4)	24.200 (5)
c, Å	13.272 (6)	8.285 (2)
α, deg	110.50 (3)	
β, deg	97.19 (3)	93.27 (3)
γ, deg	107.87 (2)	
V, Å^3	1210 (2)	1773 (1)
Z	2	4
D_{calc}, g/cm^3	1.307	1.321
μ, cm^{-1}	1.444	2.808
no. of indpt data	2785 ($+h,\pm k,\pm l$)	2031 ($+h,+k,\pm l$)
no. of obsd data	1795 ($\geq 3\sigma_I$)	1336 ($\geq 3\sigma_I$)
$R(F)$	0.064	0.053
$R_w(F)$	0.084	0.073

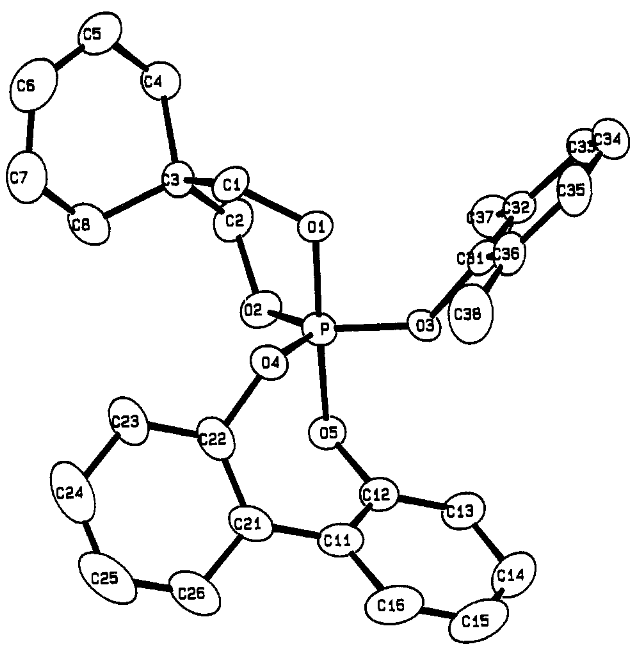


Figure 1. ORTEP plot of $(C_6H_4O)_2(C_8H_{12}O_2)P(O\text{-}Xyl)$ (**1**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

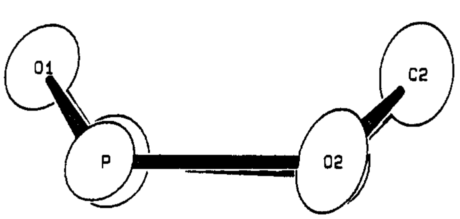


Figure 2. ORTEP plot showing the boat conformation of the phosphorinane ring in **1**.

Tables IV and V. Complete listings of atomic coordinates and bond distances and angles as well as anisotropic thermal parameters and hydrogen atom parameters for both **1** and **2** are provided as supplementary material.

NMR Studies. Analysis of variable-temperature ^1H NMR spectra yield activation energies, $\Delta G^{\ddagger}$, that are reported in Table VI. Coalescence temperatures (T_c) and line separations ($\Delta\nu$) used in the calculations are included.

Syntheses and Solid-State Structure of 1. The bicyclic pentaoxyphosphoranes **1** and **5** were prepared by the oxidative addition of a diol to the monocyclic phosphite **7** in the presence of *N*-chlorodiisopropylamine in ether solution, as illustrated for the formation of **1** in eq 1. The monocyclic pentaoxy derivative **4**

Table II. Selected Atomic Coordinates and Thermal Parameters in Crystalline $(C_6H_4O)_2(C_8H_{12}O_2)P(O\text{-}Xyl)$ (**1**)[a]

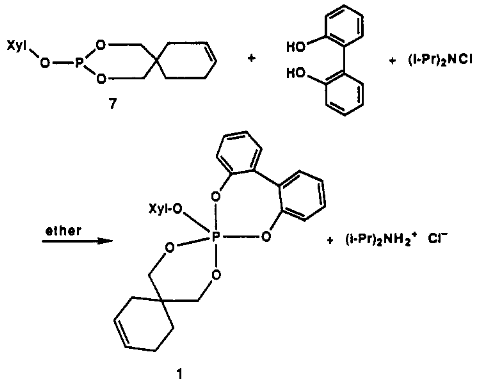
atom[b]	x	y	z	B(equiv),[c] Å^2
P	1.0240 (2)	0.4579 (2)	0.2590 (1)	3.52 (4)
O1	1.0698 (4)	0.3466 (4)	0.1633 (3)	3.6 (1)
O2	0.8710 (4)	0.3449 (4)	0.2566 (4)	4.7 (1)
O3	1.1838 (4)	0.5053 (4)	0.3437 (3)	3.7 (1)
O4	1.0126 (4)	0.5369 (4)	0.1787 (3)	3.9 (1)
O5	0.9807 (4)	0.5693 (4)	0.3614 (3)	3.9 (1)
C1	0.9611 (7)	0.2578 (6)	0.0569 (5)	4.1 (2)
C2	0.8291 (7)	0.1982 (7)	0.1913 (6)	5.0 (2)
C3	0.8130 (6)	0.1666 (6)	0.0684 (5)	3.7 (2)
C4	0.7867 (7)	0.0111 (6)	0.0078 (6)	5.4 (2)
C5	0.756 (1)	−0.0382 (8)	−0.1181 (7)	7.3 (3)
C6	0.676 (1)	0.0234 (8)	−0.1661 (7)	7.4 (3)
C7	0.6404 (9)	0.1362 (8)	−0.1074 (7)	7.4 (3)
C8	0.6734 (7)	0.1857 (6)	0.0194 (6)	5.3 (2)
C11	1.0705 (8)	0.7949 (6)	0.3639 (6)	5.1 (2)
C12	1.0818 (7)	0.7059 (6)	0.4148 (5)	4.4 (2)
C21	0.9586 (7)	0.7452 (6)	0.2620 (5)	4.8 (2)
C22	0.9251 (7)	0.6181 (6)	0.1758 (5)	4.7 (2)
C31	1.3075 (6)	0.4627 (6)	0.3316 (5)	3.7 (2)

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

Table III. Selected Distances (Å) and Angles (deg) for $(C_6H_4O)_2(C_8H_{12}O_2)P(O\text{-}Xyl)$ (**1**)[a]

	Distances		
P–O1	1.647 (4)	O5–C12	1.387 (6)
P–O2	1.593 (4)	C1–C3	1.524 (9)
P–O3	1.584 (4)	C2–C3	1.52 (1)
P–O4	1.617 (5)	C3–C4	1.558 (9)
P–O5	1.682 (4)	C3–C8	1.51 (1)
O1–C1	1.438 (6)	C4–C5	1.52 (1)
O2–C2	1.451 (7)	C5–C6	1.40 (2)
O3–C31	1.403 (8)	C6–C7	1.40 (1)
O4–C22	1.411 (9)	C7–C8	1.53 (1)
	Angles		
O1–P–O2	94.7 (2)	P–O5–C12	118.9 (4)
O1–P–O3	90.3 (2)	O1–C1–C3	111.8 (5)
O1–P–O4	89.5 (2)	O2–C2–C3	111.1 (6)
O1–P–O5	177.3 (3)	C1–C3–C2	108.2 (4)
O2–P–O3	122.9 (3)	C1–C3–C4	110.6 (5)
O2–P–O4	118.4 (2)	C1–C3–C8	112.8 (6)
O2–P–O5	84.9 (2)	C2–C3–C4	107.1 (6)
O3–P–O4	118.5 (2)	C2–C3–C8	110.7 (6)
O3–P–O5	87.7 (2)	C4–C3–C8	107.2 (4)
O4–P–O5	93.1 (2)	C3–C4–C5	112.9 (7)
P–O1–C1	119.7 (4)	C4–C5–C6	116.0 (8)
P–O2–C2	122.1 (4)	C5–C6–C7	125.4 (8)
P–O3–C31	131.2 (3)	C6–C7–C8	117.4 (9)
P–O4–C22	128.5 (4)	C3–C8–C7	112.5 (6)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shonw in Figure 1.



(1)

Table IV. Selected Atomic Coordinates and Thermal Parameters in Crystalline $(C_6H_4O)_2P(S\text{-}Xyl)$ (**2**)[a]

atom[b]	*x*	*y*	*z*	*B*(equiv),[c] Å^2
S	0.2290 (2)	0.44564 (7)	0.3755 (2)	5.84 (4)
P	0.2382 (2)	0.38435 (7)	0.1949 (2)	4.52 (4)
O1	0.0645 (4)	0.3625 (2)	0.1648 (4)	4.69 (9)
O2	0.3044 (4)	0.3375 (2)	0.3223 (5)	4.65 (9)
C1	−0.0191 (6)	0.3383 (2)	0.2844 (6)	4.2 (1)
C2	0.0161 (6)	0.2862 (2)	0.3402 (6)	4.1 (1)
C3	−0.0840 (7)	0.2618 (3)	0.4445 (8)	5.1 (2)
C4	−0.2089 (7)	0.2901 (3)	0.4909 (9)	6.5 (2)
C5	−0.2377 (7)	0.3423 (3)	0.4382 (9)	7.0 (2)
C6	−0.1424 (7)	0.3677 (3)	0.3321 (8)	5.8 (2)
C11	0.2780 (7)	0.5037 (2)	0.2574 (6)	4.1 (1)
C22	0.2881 (7)	0.2815 (2)	0.2795 (7)	4.4 (1)
C23	0.4143 (7)	0.2533 (3)	0.2338 (8)	5.7 (2)
C24	0.4065 (8)	0.1975 (3)	0.2042 (9)	6.5 (2)
C25	0.2712 (8)	0.1702 (3)	0.2150 (8)	6.0 (2)
C26	0.1457 (7)	0.1983 (3)	0.2580 (7)	5.2 (2)
C27	0.1503 (6)	0.2552 (2)	0.2908 (7)	4.1 (1)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 5. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table V. Selected Distances (Å) and Angles (deg) for $(C_6H_4O)_2P(S\text{-}Xyl)$ (**2**)[a]

Distances			
S–P	2.112 (2)	O2–C22	1.406 (7)
P–O1	1.632 (4)	C1–C2	1.374 (8)
P–O2	1.635 (4)	C2–C27	1.482 (8)
O1–C1	1.399 (7)	C22–C27	1.384 (8)
S–C11	1.779 (6)		
Angles			
S–P–O1	105.2 (2)	O1–C1–C2	120.2 (5)
S–P–O2	93.2 (2)	C1–C2–C27	122.8 (5)
O1–P–O2	100.0 (2)	O2–C22–C27	120.2 (5)
P–O1–C1	124.1 (3)	C2–C27–C22	120.8 (5)
P–O2–C22	118.5 (3)	P–S–C11	98.3 (2)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 5.

Table VI. Activation Parameters of Ligand Exchange Determined from Variable-Temperature ^{1}H NMR Spectroscopy

compd	temp range, °C	T_c, °C	$\Delta\nu$, Hz	$\Delta G^{\ddagger}{}_c$,[a] kcal/mol	exchange behavior
1	−58 to +18.8	−6.5	237	12.2	a–e ⇌ e–e
5	−26.5 to +17.8	−8.0	54	12.9	a–e ⇌ e–e
3[b]	−30 to +49	0.0	246	12.5	

[a] All $\Delta G^{\ddagger}{}_c$ values were determined from the coalescence of $C_6H_3(CH_3)_2$ signals. Values are estimated to be accurate within ±1.5 kcal/mol. See ref 21. [b] The exchange process is not established for **3** since these symmetrical ring ligands do not provide NMR discrimination.

resulted from a similar reaction of pentafluorophenol with phosphite **8** also conducted in ether solution in the presence of $(i\text{-}Pr)_2NCl$. The spirocyclic **3** was synthesized from the reaction of **2** with phenanthrenequinone in refluxing toluene solution. The synthesis of **5** represents the first example of a bicyclic pentaoxyphosphorane containing an eight-membered ring system. In general, the compounds may be handled in air for short periods of time. Hydrolysis ensues over one to a few days resulting in liquefaction of the initially formed solids. As noted earlier,[3] this action is more pronounced with the monocyclic derivatives compared to the bicyclic ones.

The molecular geometry about the phosphorus atom in the cyclic oxyphosphorane **1** can be referred to a trigonal bipyramid (TBP) with the ring systems spanning axial–equatorial sites and the xyloxy group in an equatorial position. Distortions from the ideal trigonal bipyramidal geometry are not very large and appear to be primarily occasioned by the constraints of the ring systems. It is possible to calculate an average percent displacement from the TBP toward a rectangular pyramid (RP) with O4 in the apical position. By use of the dihedral angle method with unit vectors[26] this displacement is only 8.6%. This structural form is similar to the related bicyclic pentaoxyphosphorane H depicted in the Introduction. In this case, the structural displacement toward a RP geometry was 12.0% with the equatorial oxygen atom of the seven-membered ring again in the apical position.[4] Thus, the solid-state structure of **1**, like that of the cyclic pentaoxyphosphoranes G,[5] H,[4] and I,[5] which contain either seven- or eight-membered rings, has the rings located in axial–equatorial sites of a TBP geometry.

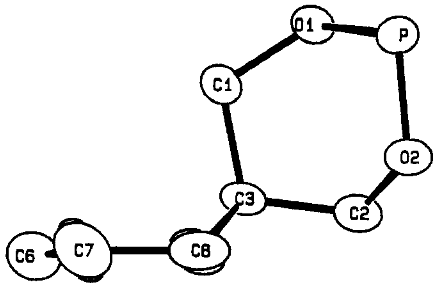


Figure 3. ORTEP plot showing the half-chair conformation of the six-membered carbocyclic ring in **1** as well as the relative orientation of the phosphorinane ring.

The packing of **1** in the solid state is apparently insensitive to the position of the double bond in the cyclohexene ring. The refined distances C5–C6 = 1.40 (2) Å and C6–C7 = 1.40 (1) Å suggest that the double bond has an equal probability of being in either position. Due to this disorder, hydrogen atoms bonded to C5, C6, and C7 were omitted from the refinement. Two positions for the double bond in the solid state do not, however, indicate the presence of two isomeric compounds. If two isomers could be isolated, these would have the potential for interconverting in solution by the "high-temperature"[27,28] Berry pseudorotation process[29] postulated to occur for **1** as described in the section on NMR behavior.

Ring Conformational Comparisons. The six-membered heterocyclic ring in the oxyphosphorane **1** (Figure 2) is in the commonly found boat conformation with the axial oxygen atom in a prow position despite the attached cyclohexene ring. For example, this same type of conformation persists in the six-membered rings of A–D shown in the Introduction.[5,6,12,13] The atoms forming the floor of the boat, P, O2, C1, and C3, are coplanar to within ±0.019 (5) Å, while prow atoms O1 and C2 are displaced from this plane in the same direction by essentially the same distance (0.632 (4) and 0.637 (7) Å). The attached cyclohexene ring is in a half-chair conformation (Figure 3). C4, C5, C6, C7, and C8 are coplanar to within ±0.036 (10) Å, while the remaining C3 is displaced from this plane by a distance of 0.676 (6) Å. The dihedral angle between this plane and the plane forming the base of the boat is 85.3 (2)°.

The seven-membered ring in **1** is in the same conformation seen previously in the X-ray structures of G[5] and H,[4] for this ligand system, namely that of a "rowboat" (Figure 4). The atoms forming the base of the boat, P, O4, C11, and C12, are coplanar to within ±0.019 (7) Å. The prow atom, O5, and the stern atoms, C21 and C22, are displaced from this plane in the same direction by distances of 0.708 (4), 0.785 (7), and 0.826 (7) Å, respectively.

The seven-membered ring in the cyclic phosphite **2** has a similar conformation. The atoms forming the base of the boat, P, O1, C22, and C27, are coplanar to within ±0.065 (6) Å, while the prow atom, O2, and the stern atoms, C1 and C2, are displaced from this plane by distances of 0.629 (4), 0.859 (5), and 0.881 (5) Å, respectively.

The conformation of this ring appears to be determined chiefly by the size of the relative rotation about the bond joining the

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

(27) Houalla, D.; Wolf, R.; Gagnaire, D.; Robert, J. B. *J. Chem. Soc., Chem. Commun.* **1969**, 443.

(28) Reference 9, pp 163–165.

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

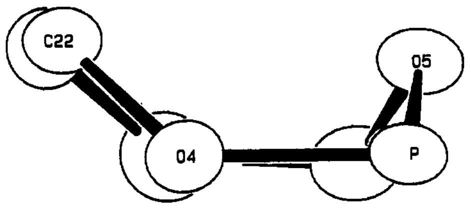


Figure 4. ORTEP plot showing the "rowboat" conformation of the seven-membered ring in **1**.

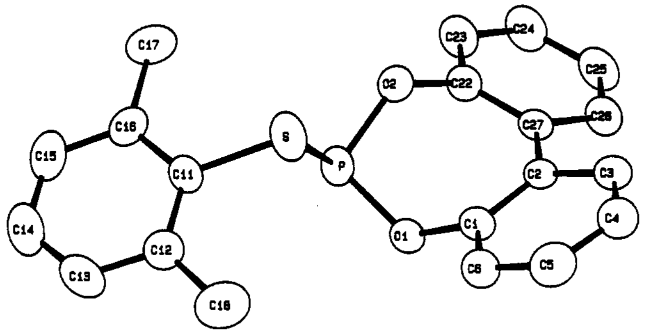


Figure 5. ORTEP plot of $(C_6H_4O)_2P(S\text{-}Xyl)$ (**2**) with thermal ellipsoids at the 30% probability level and hydrogen atoms omitted for clarity.

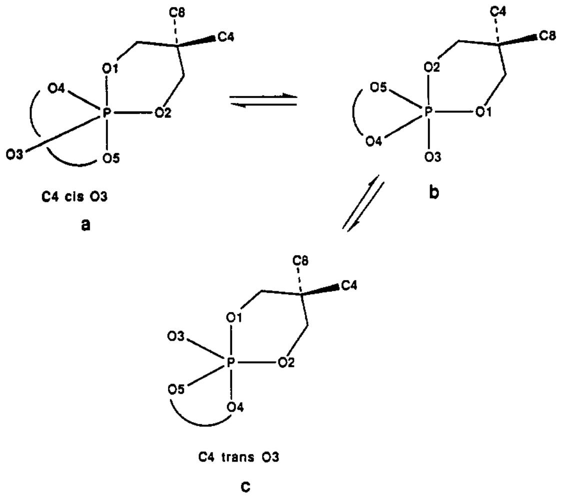
phenyl rings although the "bite" angle at phosphorus should also have an influence. For **1**, the relative rotation about the bond joining the phenyl rings is 41.3 (3)° and the O–P–O angle within the ring of 98.1 (2)° is somewhat larger than the ideal value of 90°. For **2**, the relative rotation about the bond joining the phenyl rings is very similar at 39.6 (2)°. While the corresponding O–P–O angle of 100.0 (2)° is somewhat smaller than the ideal tetrahedral angle, it is not very different from that of **1**. In **2**, the P–O bond lengths are equal (1.635 (4) and 1.632 (4) Å) while, in **1**, the $P–O_{ax}$ distance (1.682 (4) Å) (ax = axial) is longer than the $P–O_{eq}$ distance (1.617 (5) Å) (eq = equatorial) as expected for a TBP geometry.

It is therefore apparent that the seven-membered ring system can accommodate either a tetrahedral environment or the axial–equatorial environment of a trigonal bipyramid with little change in conformation. This behavior is different from that observed for the more conformationally flexible saturated six-membered rings in oxygen containing phosphorus compounds having these same two geometrical environments. Here the six-membered rings adopt different conformations in the two structural types. In a tetrahedral structure the presence of equal P–O ring bonds is usually associated with a chair conformation,[30] while the presence of unequal P–O ring bonds in a TBP structure is a factor favoring the boat conformation[3-6,12,13] for a six-membered ring in an axial–equatorial ring orientation. Although the boat form is more common, chair conformations have been induced by hydrogen bonding[12,14] and electronegativity constraints[13] for saturated six-membered rings located a–e in TBP geometries. The formation of a boat conformation for this same type of ring system in a tetrahedral geometry is not as prevalent as it is for a TBP geometry.[30]

The axial and equatorial P–O bond distances in the seven-membered ring of **1**, 1.682 and 1.617 Å, are very close to the average values of these distances for the same seven-membered ring system in G[5] and H,[4] 1.68 and 1.61 Å, respectively, and greater than the average values of 1.64 Å (ax) and 1.59 Å (eq) for these distances in six-membered ring systems in oxyphosphoranes.[5,6,12-14] The lower values for the latter rings were interpreted[4] to reflect less ring strain compared to that in seven-membered rings in TBP structures.

Solution-State NMR and Activation Energies for Ligand Exchange. The ^1H NMR spectra for the spirocyclic phosphoranes **1** and **5** containing seven- and eight-membered rings, respectively, are very similar and show similar temperature-dependent behavior. A detailed analysis of this type of spectrum has been given in connection with an analysis of related ^1H NMR spectra of H.[4] On the cooling of **1** from near room temperature, the singlet xylyloxy methyl proton signal at 2.44 ppm coalesces and splits into two signals. Similar changes are encountered in the phosphorinane OCH_2 and cyclohexene CH regions at 3.97 and 5.56 ppm, respectively, although the low-temperature spectra are less resolved as discussed in detail in the Experimental Section.

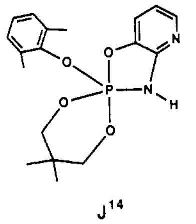
Scheme I



The fact that in both **1** and **5** the near-room-temperature spectra show a single doublet ($^3J_{P-H}$) for the phosphorinane ring OCH_2 groups implies intramolecular ligand exchange is occurring via TBP intermediates that have the seven- and eight-membered rings positioned diequatorially. This is illustrated schematically here for **1** (Scheme I) with the seven-membered ring spanning positions O4 and O5, the so-called high-energy[27,28] Berry[29] pseudorotational process. In this scheme the attachment C4 serves to indicate the orientation of the double bond in the appended cyclohexene ring. This exchange process allows the OCH_2 protons on opposite sides of the six-membered ring to achieve equivalence as well as allowing isomeric conversion with respect to the two possible orientations of the double bond in the cyclohexene ring that resulted in their disorder in the crystallographic analysis.

In addition to the exchange process in Scheme I ligand exchange resulting from simultaneous interchange of both rings between axial–equatorial positions also must be occurring, the so-called low-energy pseudorotational process.[27,28] The latter causes equivalence of the OCH_2 phosphorinane protons on the same side of the ring. The activation energies given in Table VI reflect the energy associated with the high-energy process in placing the seven- and eight-membered rings in diequatorial positions.

The low-temperature ^1H NMR spectra of **1** and **5** are consistent with the solid-state X-ray structure of **1** if it is assumed that rapid axial–equatorial ring interchange (the low-temperature exchange process) proceeds unchecked. This is reasoned to be so since the low-temperature spectra for these compounds do not show the four ABX patterns expected for four inequivalent OCH_2 ring protons associated with a static structure of the type found in the X-ray analysis. This type of pattern which should give four quartets is observed for the spirocyclic oxyphosphorane J.[14] This is the



J[14]

same conclusion that was reached on analysis of the variable-

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(30) (a) Maryanoff, B. E.; Hutchins, R. O.; Maryanoff, C. A. *Top. Stereochem.* **1979**, *11*, 187 and references cited therein. (b) Sopchik, A. E.; Beres, J.; Tomasz, J.; Bentrude, W. G. *J. Org. Chem.* **1991**, *56*, 5911 and references cited therein.

temperature ^1H and ^{13}C NMR spectra for the closely related spirocyclic derivative H[4] containing the same seven-membered ring system and xylyloxy group as present in **1**.

As found in previous work[4,5] on the function of the xylyl group rotation about the C–O bond in related compounds, it is coupled to the a–e $\rightleftharpoons$ e–e pseudorotational process for **1** and **5**. Cessation of C–O bond rotation is evidenced from the coalescence of the xylyl methyl doublet signal near the coalescence temperature of the six-membered ring OCH_2 proton singlet on cooling in each case. In fact, the energies of activation listed in Table VI were calculated from the temperature dependence of the xylyl methyl signals. In instances where the data allowed, such as with the monocyclic derivative A,[5] ΔG^* varied within experimental uncertainty from 10.6 to 10.9 kcal/mol independent of whether the coalescence of signals were from either $C_6H_3(CH_3)_2$ or $C_6H_3(CH_3)_2$ protons of the xylyl group or from OCH_2 or $OCH_2C(CH_3)_2$ signals of the phosphorinane ring.

The ΔG^* values in Table VI are the same within experimental uncertainty so that no difference due to the ring size variation from seven-membered for **1** to eight-membered for **5** is detected. These values compare with a ΔG^* value of 11.5 kcal/mol for the closely related spirocyclic H,[4] which has the same seven-membered ring system as **1**. As indicated in the Introductioin, the monocyclic derivatives G and I[5] have the same seven- and eight-membered rings as the spirocycles **1** and **5**, respectively. For the monocyclics, the exchange process is the low-temperature one which exchanges the rings between axial–equatorial positions. Here, reasoning was presented[5] suggesting appreciable steric interaction among the three xylyloxy groups encountered in reaching the transition state which would be represented by a near square pyramid with the ring occupying cis basal positions. In the spirocyclics, the transition state for exchange via a diequatorial intermediate would be a square pyramid with the ring-spanning apical–basal positions.[4] Consequently, the activation energies between the two classes of structural types are not directly comparable. However, in view of the higher energy which should accompany diequatorial ring formation encountered in the high-temperature exchange process for the spirocyclics **1**, **5**, and H,[4] compared to axial–equatorial ring positioning in the low-temperature exchange process for monocyclics[5] G and I, the previous conclusion[5] is confirmed in this study that steric effects of the three xylyloxy groups in the exchanging monocyclics must be appreciable, perhaps of the order of 5 kcal/mol greater than steric effects encountered in the spirocyclics **1**, **5**, and H.[4] Previous experimental[15] and theoretical work[31] indicated that saturated six-membered rings in diequatorial positions are ~7 kcal/mol higher than an axial–equatorial arrangement in a TBP geometry in the absence of noticeable steric effects. In the partitioning of ring strain vs steric effects suggested here due to the presence of the xylyloxy group, the ease of positioning seven- and eight-membered rings in **1**, **5**, and H[4] in diequatorial sites of a TBP relative to axial–equatorial sites may not be significantly different from that indicated for six-membered rings.

Conclusion

In contrast to saturated six-membered ring systems, seven-membered rings of the type exhibited by **1** show similar "rowboat" conformations in the tricoordinated state (compound **2**) as in the pentacoordinated state (compounds **1**, G,[5] and H[4]). Variable-temperature NMR spectra of the spirocyclic pentaoxyphosphoranes **1** and **5** indicate intramolecular ligand exchange via TBP intermediates with diequatorial placement of the seven- and eight-membered ring systems, respectively, similar to that found previously for H.[4] Activation energies which fall in the range 11.5–12.9 ± 1.5 kcal/mol indicate in combination with other data (that suggest a steric effect is associated with the presence of the xylyloxy group) that the energy accompanying the higher energy diequatorial ring placement for seven- and eight-membered rings relative to that for axial–equatorial ring placement may be comparable to the 7 kcal/mol found for this quantity in the absence of steric effects for saturated six-membered rings in TBP geometries.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, additional bond lengths and angles, and hydrogen atom parameters (Tables S1–S4 for **1** and Tables S5–S8 for **2**) (13 pages); listings of observed and calculated structure factors for **1** and **2** (14 pages). Ordering information is given on any current masthead page.

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(31) Deiters, J. A.; Holmes, R. R. Unpublished work.