Heteroatom Chemistry
Volume 2, Number 1, 1991

Conformational Properties of Cyclic Pentaalkoxy Phosphoranes: Apical–Equatorial Attachment and Nonchair Conformation of the Phosphorus-Containing Six-Membered Ring

Jaehoon Yu, Alan E. Sopchik, Atta M. Arif, and Wesley G. Bentrude*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, U.S.A.

G.-V. Roeschenthaler

Fachbereich Chemie, Universitaet Bremem, Bremen, W. Germany

Received 28 June 1990.

ABSTRACT

A series of phosphoranes with pentacovalent phosphorus contained in a 1,3,2-dioxaphosphorinane ring have been studied by ^1H NMR. One compound was investigated by low-temperature ^{13}C NMR and another by X-ray crystallography. Although the ^1H NMR parameters observed are time-averaged, the coupling constants can be accounted for if the phosphoranes have the six-membered ring attached apical–equatorial to phosphorus and occupy in solution rapidly isomerizing boat or slightly twisted boat conformations similar to that found in the X-ray study.

INTRODUCTION

Interest in pentacovalent phosphorus molecules in which P(V) is contained in a six-membered ring has recently been revived. In part this is because of a desire to understand the role of such intermediates (or transition states) in enzymic processes involving cAMP. Questions being addressed to these systems include: 1) Is the six-membered ring attached to phosphorus apical–equatorial or diequatorial? 2) If the ends of the six-membered ring are different, which end (substituent) is preferentially apical? 3) Is the ring in a chair or boat (twist) conformation?

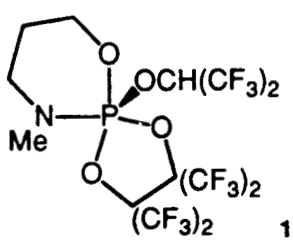
Significant findings reported recently for phosphoranes studied in solution resulted from the application of Karplus-like $^3J_{HP}$ relationships to ^1H NMR results to determine that the ring of **1** populates a twist-boat conformation [1] as do **2a** [2] and **2b** [3] (Scheme 1), as well as **3** [4] (Scheme 2). The ring of **4a** has been shown to be attached apical–equatorial to phosphorus [5]. The lack of a dominant effect of oxygen in the five-membered ring has recently been demonstrated [6] for **4b**, which also possesses an apical–equatorial ring (Scheme 2).

Important X-ray crystal structures recently reported include that of **5**, which features O5 attached apical and O3 equatorial [3,6,7]. The ring is in a twist conformation. Nonchair, apical–equatorial rings were also reported for **6** [8] and as well as for **7** and related molecules [9] in which nitrogen or sulfur is attached to phosphorus in the six-membered ring (Scheme 3).

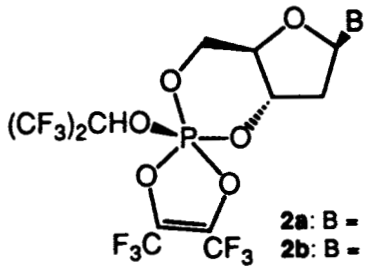
We report here NMR studies (**6**, and **8–11**) and an X-ray structure (*cis*-**11**) for a series of pentaalkoxy phosphoranes. Phosphoranes **8** and **9** feature a single six-membered ring to avoid any effects of the second spiro ring that is a structural part of **1–3**, **5**, and **6**. The series **6**, **10**, and **11** provides a systematic variation in ring substituent at C5 of the six-membered ring. ^1H NMR results of these molecules are less readily interpreted than those from 1,3,2-

*To whom correspondence should be addressed.

1042-7163/91/$3.50 + .25

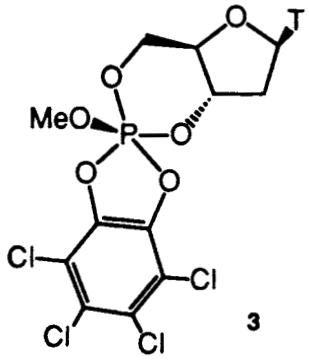


1

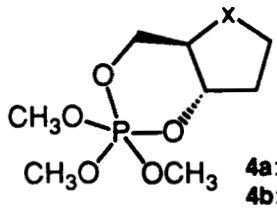


2a: B = H
2b: B = thymin-1-yl

SCHEME 1

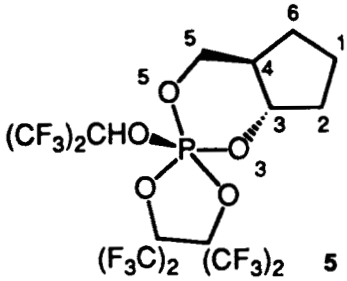


3

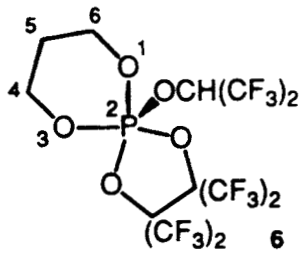


4a: X = CH_2
4b: X = O

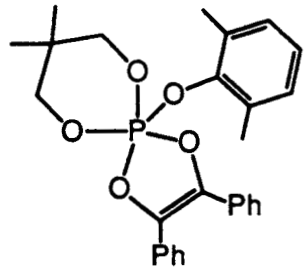
SCHEME 2



5

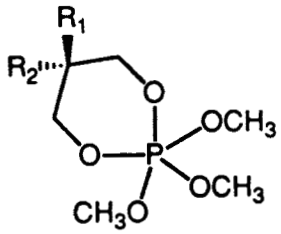


6

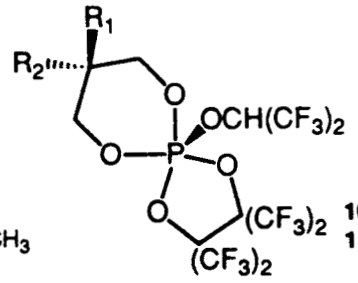


7

SCHEME 3



8: R_1 = *t*-Bu, R_2 = H
9: R_1 = CH_3, R_2 = CH_3



10: R_1 = CH_3, R_2 = CH_3
11: R_1 = *t*-Bu, R_2 = H

SCHEME 4

oxazaphosphorinane rings (**1**) or bicyclic systems (**2–5**), because the signals from the CH_2O hydrogens at carbons 4 and 6 of the six-membered rings are time averaged. However, the X-ray results for *cis*-**11**, a low-temperature investigation of the ^{13}C NMR spectrum of **8**, along with a careful comparison of the coupling constants for **6** and **8–11** with those of their 1,3,2-oxaza counterparts, lead to the conclusion that the six-membered rings of **6** and **8–11** are attached to phosphorus in apical–equatorial fashion and populate nonchair (boat or twist) conformations in solution (Scheme 7).

RESULTS AND DISCUSSION

Preparations

Phosphoranes **6** (reported previously [8]), **10**, and **11** were made by the low-temperature condensation of the phosphite precursor with 1,1,1,3,3,3-hexafluoroacetone and obtained analytically pure by vacuum distillation and/or crystallization. Crystals of *cis*-**11** for X-ray work were obtained from benzene. Methyl benzenesulfenate afforded phosphoranes **8** and **9** from the phosphites. Product **8** was obtained analytically pure, but **9** contained about 3% of phenyl disulfide byproduct. Its composition was confirmed by HRMS. All were obtained in good to excellent yields.

X-Ray Structure of cis-**11**

A PLUTO drawing of the essential features of the structure of *cis*-**11**, obtained by single-crystal X-ray crystallography, is shown in Figure 1 [10]. Its formation proceeded from the cis phosphite precursor with evident *retention of configuration about phosphorus*. The geometry about phosphorus is near trigonal bipyramidal. The bond angle O5–P–O1 is 175.7°. The apical–equatorial bond angles O1–P–O2, O1–P–O4, etc., are close to 90° (86.5(1) to 92.6(1)°) except for O1–P–O3, 97.6°. Equatorial bond angles O–P–O range from 116.3(1) to 122.8(2)°. The *t*-butyl and $OCH(CF_3)_2$ groups are clearly cis to one another.

The apical–equatorial attachment of the six-membered ring and its nonchair conformation are the most important features of the structure. The torsional angles for the 1,3,2-dioxaphosphorinane ring of *cis*-**11** are given in structure **12** (Scheme 5). As inspection of the PLUTO drawing shows, the 1,3,2-dioxaphosphorinane ring is close to being a boat structure. This also is indicated by the torsional angle C4–O3–P–O1 of 1.5°. However, distortion from the true boat geometry is seen in the O1–C6–C5–C4 angle of 19°.

The small O1–P–O3–C4 angle places the *p*-orbital lone pair of O3 in the plane of the equatorial ligands where its back-bonding with phosphorus *d*-orbitals is maximized. This stabilization has been proposed [11] as a driving force for the formation of nonchair conformations in such systems and most certainly is responsible for the population of the specific nonchair form, identified by X-ray crystallography, among the several available to the flexible 1,3,2-dioxaphosphorinane ring. The small torsional angle C11–O2–P–O1 (−13.2°) similarly maximizes backbonding [12] involving O2. Nota-

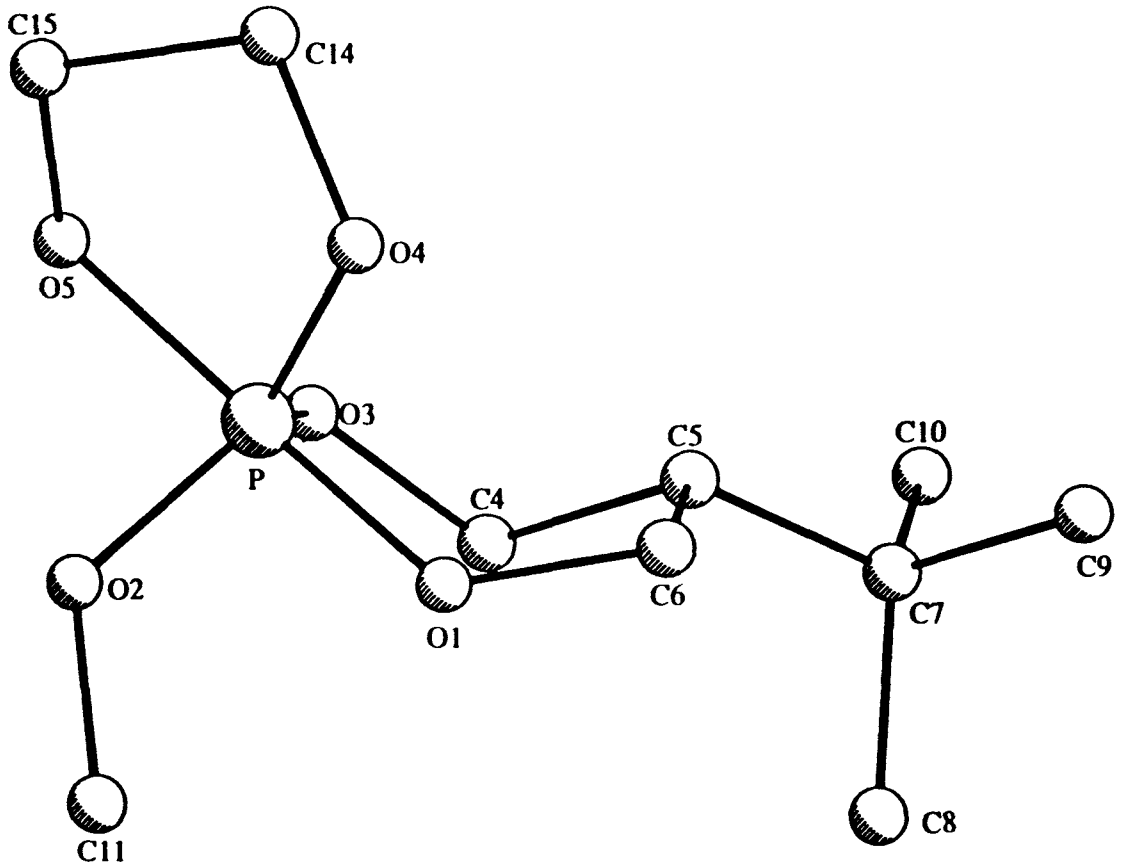
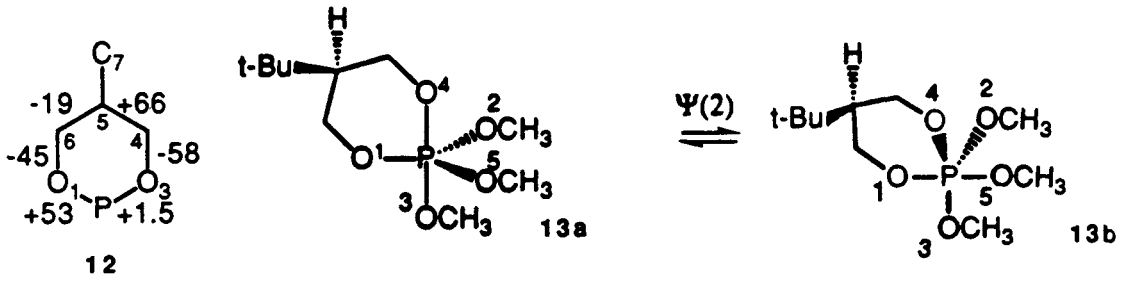


FIGURE 1



SCHEME 5

bly, the *t*-butyl group is pseudoequatorially attached to minimize steric repulsions although an axial *t*-butyl orientation requires less energy when it is 1,3 to ring oxygens than when 1,3-synaxial repulsions with axial hydrogens would be involved.

Low-temperature ^{13}C NMR Spectrum of 8

The position of the six-membered ring of **8** is expected to be totally unbiased by the other substituents on phosphorus and presents a unique opportunity to determine its position of attachment on presumably trigonal bipyramidal P(V) in the absence of bicyclic ring fusion or a second spiro ring attached to phosphorus. In Figure 2 are shown the room temperature and low temperature ^{13}C NMR spectra for the ring CH_2 and MeO carbons. The ring CH_2 resonance changes from a time-averaged single doublet at ambient temperature (J_{CP} = 8.6 Hz), spectrum *a*, to two broad singlets (J_{CP} within the linewidths) at −118°C, spectrum *c*. This is only consistent with the presence at −118°C of a structure, **13**, in which the ring CH_2 carbons are nonequivalent and totally inconsistent with the alternative diequatorial ring structure, **14** (Scheme 6). The low-temperature spectrum also shows total nonequivalence of all three MeO resonances, spectrum *f*. The two equatorial peaks are close together and, as expected [5], downfield of the lone apical MeO. These results all point to the equilibration of the CH_2 groups in **13** via apical–equatorial exchange (**13a** ⇌ **13b**).

In addition it is easy to show (Sequence 1) that only extensive Mode 1 (presumably Berry mechanism), pseudorotation processes via intermediates

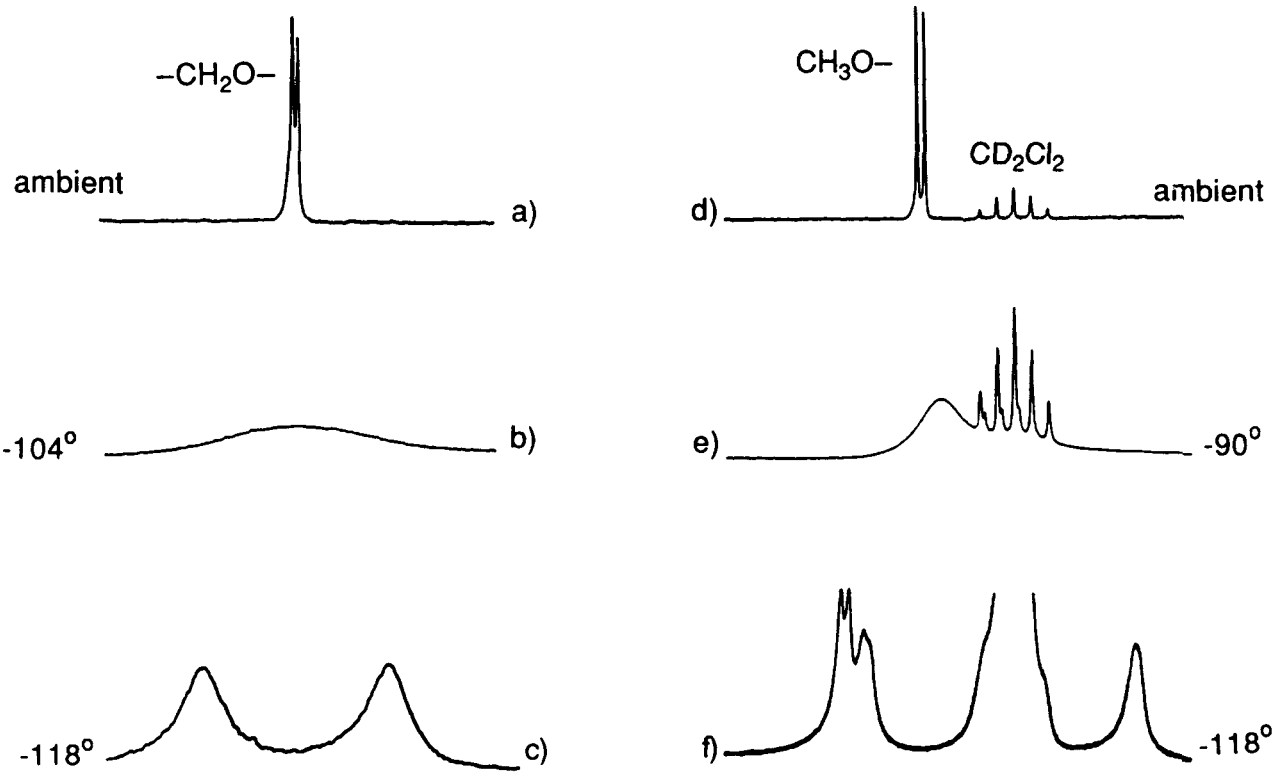
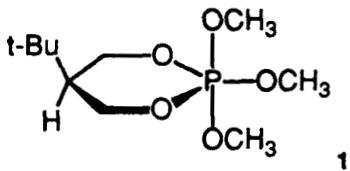


FIGURE 2



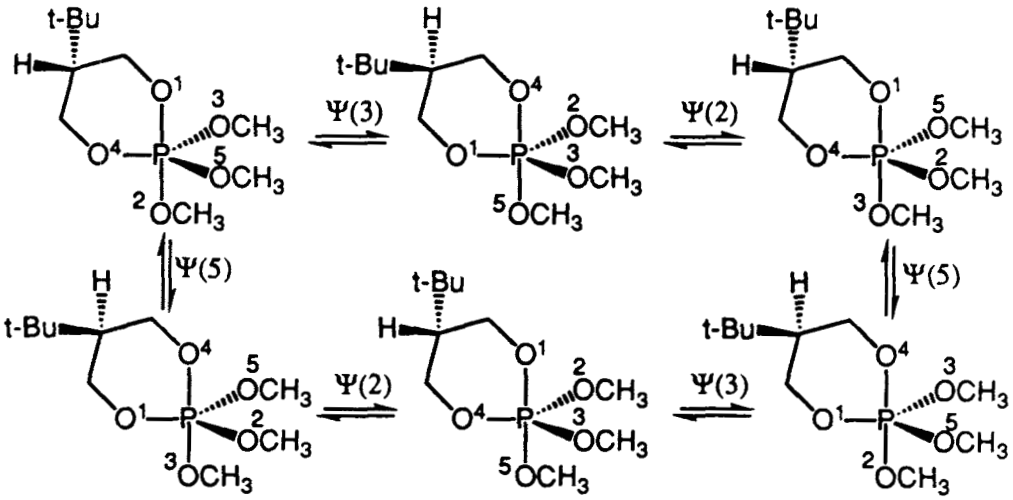
14

SCHEME 6

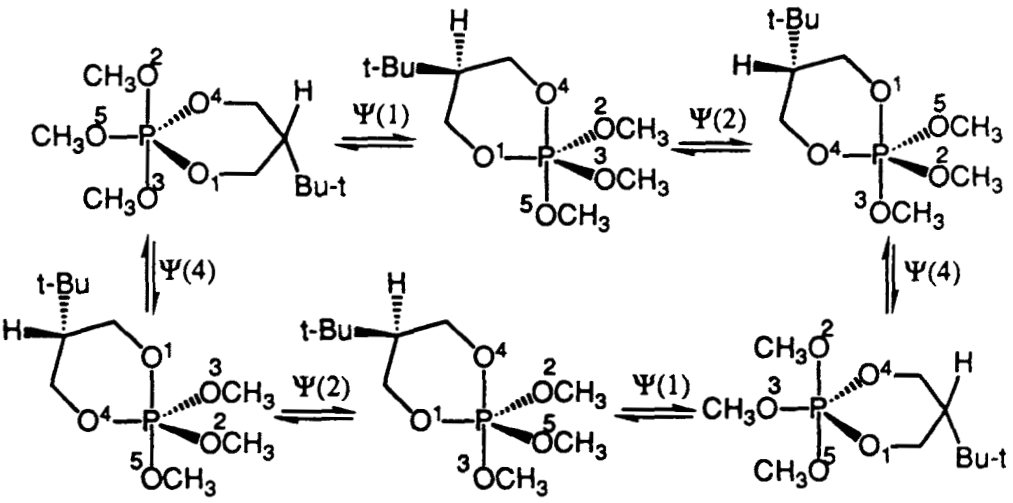
with apical-equatorial ring attachment can account for the equilibration of the MeO groups between apical and equatorial positions *and* between geometries cis and trans to the ring *t*-butyl group. The latter is not accomplished via intermediates like **14** (Sequence 2). The determination of the activation free energy for the equilibrations noted for **8** will be the subject of a subsequent publication once we have determined not only the value based on coalescence of the CH_2 signals but also, via total line shape analysis, that from the MeO coalescence to be certain that the two processes are concerted.

Proton NMR Studies of **6** *and* **8–11**

Pertinent ^1H NMR parameters for the 1,3,2-dioxaphosphorinane rings of **6** and **8–11** are recorded in Table 1. Since these phosphoranes undergo rapid pseudorotation on the NMR time scale at ambient temperatures, all coupling constants recorded are averaged values. (See structures **15** and **16** (Scheme 7) for assignments of the ^1H signals.) For **9** the CH_2O hydrogens not only are averaged between apical and equatorial positions but also become completely equivalent by conformational motions of the six-membered ring itself, i.e. chair–chair, chair–twist, or twist–twist interconversions. For **8**, however, the *t*-butyl substituent differentiates the CH_2O hydrogens that are cis (2H) or trans (2H) to



SEQUENCE 1

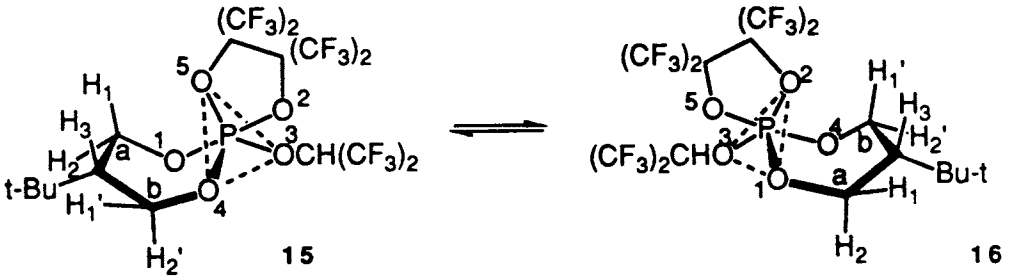


SEQUENCE 2

TABLE 1 Time-Average Coupling Constants J_{HH} and J_{HP} (Hz) and Proton Chemical Shifts for **6, 8–11** in Benzene at Ambient Temperatures[a]

Comp.	$J_{1P}(J_{1'P})$	$J_{2P}(J_{2'P})$	$J_{13}(J_{1'3})$	$J_{23}(J_{2'3})$	δ1	δ2	δ3	Ref.
6[d,e]	17.2	17.4	6.5	10.5	3.55	3.42	1.53	b,c
8[d]	17.3	16.6	6.7	9.2	3.82	3.97	1.83	c
9	17.6	17.6			3.69	3.69		c
10[e]	19.7	17.8			3.40	3.34		c
cis-**11**	19.0	16.6	6.3	10.9	3.75	3.48	1.81	c

[a] 300 MHz unless otherwise noted.
[b] See Ref. 8 for earlier values determined at 300 MHz.
[c] This work.
[d] At 500 MHz.
[e] Parameters simulated and iteratively refined using the LAOCN5 program.



SCHEME 7

it. These then have different chemical shifts and different J_{HP} values. Similarly, the CH_2O resonances on the two sides of the ring are differentiated by the stereocenter at phosphorus in **6** and **10**. Interestingly, for **8** and *cis*-**11** the $^3J_{HP}$ value for the two CH_2O hydrogens cis to the *t*-butyl group (larger J_{HP} to methine hydrogen at C5) is *smaller* than that for the two that are trans to the *t*-butyl.

Reference to the PLUTO drawing for *cis*-**11** (Figure 1) and consideration of the pseudorotation processes available to such intermediates allows an analysis of the conformation of the 1,3,2-dioxaphosphorinane ring of *cis*-**11**, which can be extended to the others in the series. First, the reasonable assumption is made that the conformation for *cis*-**11** in the crystal is close to that in solution. Second, pseudorotation is assumed to rapidly equilibrate apical and equatorial CH_2O groups, but with the conformation of the 1,3,2-dioxaphosphorinane ring energetically biased by the 5-*t*-butyl group and the substituents about phosphorus such that the only forms that need to be considered are **15** and **16**. In this equilibrium, carbon atoms a and b are exchanged. The same is true of H1 and H1', as well as H2 and H2'.

In Table 2 the observed, time-averaged J_{HH} values for the CH_2O (C4 and C6) and CH_2 or CHBu-*t* (C5) hydrogens of **6**, **8**, and *cis*-**11** are given. Alongside them are averages of J_{HH} values taken from the experimentally determined numbers for $J_{15}, J_{25}, J_{35}, J_{45}$, etc. of the similarly substituted 1,3,2-oxazaphosphorinane analogs **17–19** (Scheme 8). These rings are known both from ^1H NMR [1] and X-ray crystallography [11] to have geometries close to those shown. In using specific, measured J_{HH} values from **17–19** to simulate the time-averaged numbers for **6**, **8**, and **11**, it is assumed that the value of J_{HH} is unaffected by whether the atom bonded to CH_2 is N or O. For example, in treating **11** it is assumed that: J_{13}(**15**) = J_{15}(**17**); J_{23}(**15**) = J_{25}(**17**); $J_{1'3}$(**15**) = J_{45}(**17**); $J_{2'3}$(**15**) = J_{35}(**17**), etc. Indeed, the numbers calculated in this way from **17** fit those determined for *cis*-**11** very well. The same can be said for those for **6** vs **18** and **8** vs **19**. These results, along with the solid state conformation for *cis*-**11** [13], give strong evidence for the population of nonchair conformations by **6**, **8**, and *cis*-**11**, which are in rapid equilibrium on the NMR time scale (e.g. **15** ⇌ **16** for *cis*-**11**). In these equilibria one or the other of the 1,3,2-dioxaphosphorinane ring oxygens is in the equatorial position with its *p*-orbital lone pair stabilized [12] in the equatorial plane.

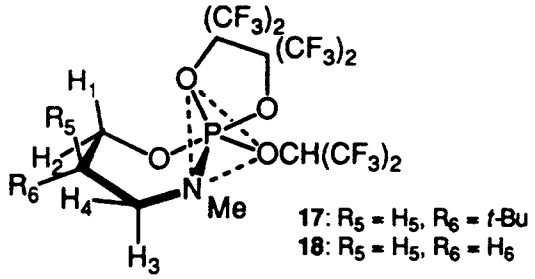
CONCLUSIONS

Evidence continues to be found for the preferential apical–equatorial attachment of the 1,3,2-dioxaphosphorinane ring to trigonal bipyramidal, pentacovalent phosphorus. Moreover, the ring has a strong preference for a boat or twist rather than a chair conformation. These features were found again in the present study with phosphoranes **6**, **8**, and

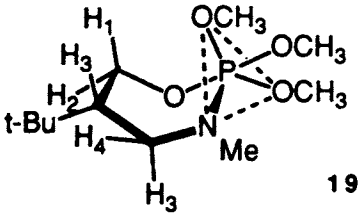
TABLE 2 Time-Average Proton–Proton Coupling Constants in Hz vs Average of Coupling Constants for **17–19**

Comp.	$J_{13}(J_{1'3})$	$1/2(J_{15} + J_{45})$	$J_{23}(J_{2'3})$	$1/2(J_{25} + J_{35})$	$J_{14}(J_{1'4})$	$1/2(J_{16} + J_{46})$	$J_{24}(J_{2'4})$	$1/2(J_{26} + J_{36})$	*Ref.*
6	6.5		10.5		3.1		5.4		*a*
18		6.4		11.1		3.2		5.5	*b*
8	6.7		9.2						*a*
19		7.0		8.5					*b*
cis-**11**	6.3		10.9						*a*
17		6.1		10.7					*c*

[a] This work. See Ref. 8 for earlier values for **6** determined at 300 MHz.
[b] J. Yu and A. E. Sopchik, unpublished results from this laboratory.
[c] Ref. 1.



17: $R_5 = H_5$, $R_6 = t$-Bu
18: $R_5 = H_5$, $R_6 = H_6$



19

SCHEME 8

cis-**11**, even with **8** containing no bicyclic structures or spiro functionality. These conclusions concerning these permutational mobile molecules were made with the guidance of the X-ray crystal structure for *cis*-**11**, the measured low-temperature ^{13}C NMR spectrum for **8**, and the application of J_{HH} and J_{HP} values from related P(V) 1,3,2-oxazaphosphorinanes for which specific coupling constants and defined geometries have been assigned.

EXPERIMENTAL

Materials and Spectroscopy

Ethyl ether was dried over sodium and freshly distilled before use. Triethylamine was dried over potassium hydroxide and distilled. ^1H NMR spectra were recorded in the Fourier transformed mode on Varian XL-300 and VXR-500 spectrometers. Coupling constants were measured with 3.75 s acquisition times and approximately 0.3 Hz precision at 300 MHz and 8.00 s acquisition times with approximately 0.1 Hz precision at 500 MHz. ^{13}C NMR spectra were taken at 75 MHz on a Varian XL-300 spectrometer operated with full proton decoupling, acquisition time >1.87 s. ^1H and ^{13}C chemical shifts are recorded in ppm downfield from TMS. Proton-decoupled ^{31}P NMR spectra were obtained at 121 MHz on a Varian XL-300 spectrometer with chemical shifts referenced to external 85% H_3PO_4 (positive downfield shifts). ^{13}C signals for the 1,3,2-dioxaphospholane rings were characteristically weak. The precise multiplicity are assigned to sufficiently strong ^{13}C signals. Weaker, poorly resolved signals are designated as multiplets.

IR spectra were taken on a Perkin-Elmer 298-A spectrometer, calibrated at 1602 cm^{-1} by polystyrene. A VG Micro Mass 7050E double-focusing high resolution mass spectrometer (VG Data System 200, EI mode, direct sample inlet) gave the mass spectral data. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points are uncorrected.

Low Temperature ^{13}C NMR Study of 5-t-Butyl-2,2,2-trimethoxy-1,3,2-dioxaphosphorinane, **8**

The ^{13}C spectrum of a 30% solution of **8** in CD_2Cl_2 was measured in the temperature range 26° to −118° at 100 MHz with full proton decoupling. The temperature of the probe had been carefully calibrated by the methanol chemical shift method.

5-t-Butyl-2-(1,1,1,3,3,3-hexafluoroisopropoxy)-1,3,2-dioxaphosphorinane

To a solution of 5-*t*-butyl-2-chloro-1,3,2-dioxaphosphorinane [14] (7.00 g, 35.6 mmol) in 50 mL of dry ether, a solution of 1,1,1,3,3,3-hexafluoropropan-2-ol (5.98 g, 3.75 mL, 35.6 mmol) and triethylamine (3.60 g, 4.96 mL, 35.6 mmol) in 50 mL of dry ether

was added dropwise at 0°C under argon. The addition took 1 h. The resulting solution was then stirred for an addtional hour. The salts were removed by filtration under argon. The solvent was removed from the filtrate by rotary evaporation. The residue was short-path distilled to give a colorless liquid (10.5 g, 32.0 mmol, 90%; bp 46–47°C/0.3 mmHg); ^{31}P NMR (121 MHz, C_6D_6) major isomer (cis) δ 127.1 (septet, J_{PF} = 7.8 Hz), minor isomer (trans) 134.3 (septet, J = 7.9 Hz), cis/trans = 93/7; ^{13}C NMR (75 MHz, C_6D_6) major isomer (cis) δ 121.9 (q, $(CF_3)_2CH$, J = 282.0 Hz), 70.0 (septet of d, $(CF_3)_2CH$, J_{FC} = 33.5 Hz, J_{PC} = 20.5 Hz), 62.7 (d, CH_2O, J = 1.7 Hz), 45.9 (d, *t*-BuCH, J = 5.5 Hz), 31.1 (s, $(CH_3)_3C$), 26.9 (s, $(CH_3)_3C$); ^{1}H NMR (300 MHz, C_6D_6) major isomer (cis) δ 4.24 (septet of d, 1H, $(CF_3)_2CH$, J_{FH} = 5.9 Hz, J_{PH} = 8.0 Hz), 4.10 (m, 2H, H_1, $H_{1'}$, $J_{11'}$ = 1.5 Hz, J_{1P} = 2.9 Hz, J_{12} = −11.2 Hz, J_{13} = 11.8 Hz), 3.66 (m, 2H, H_2, $H_{2'}$, $J_{22'}$ = 1.3 Hz, J_{23} = 4.0 Hz, J_{2P} = 11.4 Hz, J_{12} = −11.2 Hz), 1.74 (tt, 1H, H_3, J_{13} = 11.8 Hz, J_{23} = 4.0 Hz); IR (CCl_4) 2990, 2970, 2950, 2910, 2880, 2850, 1415, 1468, 1450, 1403, 1370, 1290, 1265, 1228, 1198, 1165, 1140, 1120, 1105, 1045, 1005, 965, 950, 925, 898, 870, 845, 685, 618 cm^{-1}. Anal. Calcd. for $C_{10}H_{15}O_3F_6P$: C, 36.60; H, 4.61; F, 34.73; P, 9.44. Found: C, 36.59; H, 4.47; F, 34.87; P, 9.49.

5,5-Dimethyl-2-(1,1,1,3,3,3-hexafluoroisopropoxy)-1,3,2-dioxaphosphorinane

To a solution of 5,5-dimethyl-2-chloro-1,3,2-dioxaphosphorinane [15] (19.1 g, 113 mmol) in 200 mL of dry ether, a solution of 1,1,1,3,3,3-hexafluoropropan-2-ol (19.0 g, 11.9 mL, 113 mmol) and triethylamine (11.4 g, 15.8 mL, 113 mmol) in 200 mL of dry ether was added dropwise at 0°C under argon. The addition took 2 h. The resulting solution was warmed to room temperature and stirred for 3 h. The salts were then filtered off under argon. The solvent was removed from the filtrate by a rotary evaporator. The residue was distilled to give a colorless liquid (32.1 g, 107 mmol, 95%, bp 71–71.5°C/1.5 mmHg); ^{31}P NMR (121 MHz, C_6D_6) δ 126.0 (septet, J_{PF} = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.1 (q of m, $(CF_3)_2CH$, J = 283.0 Hz), 69.9 (d, CH_2O, J = 2.3 Hz), 69.8 (septet of d, $(CF_3)_2CH$, J_{FC} = 33.9 Hz, J_{CP} = 21.6 Hz), 32.6 (d, $(CH_3)_2C$, J = 5.2 Hz), 22.5, 22.2 (two s, $(CH_3)_2C$); ^{1}H NMR (300 MHz, C_6D_6) δ 4.08 (septet of d, 1H, $(CF_3)_2CH$, J_{FH} = 5.9 Hz, J_{PH} = 7.9 Hz), 3.91 (m, 2H, $H_1H_{1'}$, $J_{11'}$ = 0.7 Hz, J_{1P} = 2.2 Hz, J_{12} = −10.9 Hz), 2.99 (m, 2H, H_2, $H_{2'}$, $J_{22'}$ = 1.4 Hz, J_{12} = −10.9 Hz, J_{2P} = 11.2 Hz), 0.92, 0.05 (two s, 6H, $(CH_3)_2C$); IR (neat) 2970, 2940, 2915, 2895, 2810, 1475, 1470, 1400, 1373, 1290, 1263, 1225, 1195, 1160, 1125, 1105, 1153, 1008, 965, 943, 910, 898, 870, 793, 780, 763, 715, 685, 630 cm^{-1}. Anal. Calcd. for $C_8H_{11}O_3F_6P$: C, 32.01; H, 3.69; P, 10.32 Found: C, 32.35; H, 3.77; P, 9.96.

8-t-Butyl-5-(1,1,1,3,3,3-hexafluoroisopropoxy)-2,2,3,3-tetrakistrifluoromethyl-1,4,6,10-tetraoxa-5-phosphaspiro(4,5)decane (**11**)

Hexafluoroacetone (10 mL) was added to 5-*t*-butyl-2-(1,1,1,3,3,3-hexafluoroisopropoxy)-1,3,2-dioxaphosphorinane (1.78 g, 5.43 mmol) at −78°C under an argon atmosphere. The resulting mixture was then warmed to −26°C and allowed to reflux for 6 h. Excess hexafluoroacetone was removed by warming the reaction mixture to room temperature to leave a white solid which was short path distilled to give 3.31 g of a crystalline solid. The solid was recrystallized from benzene affording platelike crystals (5.01 mmol, 92%, bp 86–87°C/0.4 mmHg, mp 98–99°C); ^{31}P NMR (121 MHz, C_6D_6) major isomer (cis) δ −51.0 (s), minor isomer (trans) −48.6 (s), cis/trans = 95/5; ^{13}C NMR (75 MHz, $CDCl_3/C_6D_6$) major isomer (cis) δ 121.0 (q, $(CF_3)_2CH$, J = 294.5 Hz), 120.9 (q, $(CF_3)_2C$, J = 287.1 Hz), 74.2 (septet of d, $(CF_3)_2CH$, J_{FC} = 34.7 Hz, J_{PC} = 11.0 Hz), 68.0 (d, CH_2O, J = 8.5 Hz), 44.8 (d, *t*-Bu*C*, J = 6.6 Hz), 31.1 (d, $(CH_3)_3C$, J = 0.6 Hz), 26.5 (s, $(CH_3)_3C$). The $(CF_3)_2C$ resonance was too weak to be observed. ^{1}H NMR (300 MHz, C_6D_6) major isomer (cis) δ 5.35 (septet of d, $(CF_3)_2CH$, J_{FH} = 5.8 Hz, J_{PH} = 13.2 Hz), 3.75 (ddd, 2H, H_1), 3.48 (ddd, 2H, H_2), 1.81 (tt, 1H, H_3), 0.35 (s, 9H, $(CH_3)_3C$); IR (CCl_4) 3000, 2970, 2950, 2915, 2875, 1380, 1372, 1348, 1300, 1270, 1245, 1218, 1203, 1185, 1175, 1125, 1100, 1028, 1008, 1000, 975, 965, 903, 885, 878, 860, 715, 700, 688, 635, 605 cm^{-1}; HRMS calcd. for $C_{16}H_{15}O_5F_{17}P$ (M^+ − F) 641.0385, found 641.0382. Anal. Calcd. for $C_{16}H_{15}O_5F_{18}P$: C, 29.11; H, 2.29; P, 4.69. Found: C, 29.42; H, 2.34; P, 4.73.

8,8-Dimethyl-5-(1,1,1,3,3,3-hexafluoroisopropoxy)-2,2,3,3-tetrakistrifluoromethyl-1,4,6,10-tetraoxa-5-phosphaspiro(4,5)decane (**10**)

In analogous fashion the reaction of hexafluoroacetone (10 mL) 5,5-dimethyl-2-(1,1,1,3,3,3-hexafluoroisopropoxy)-1,3,2-dioxaphosphorinane (1.74 g, 5.81 mmol) gave a white crystalline solid that was recrystallized from benzene (3.53 g, 5.60 mmol, 96%, mp 72–73°C); ^{31}P NMR (121 MHz, C_6D_6) δ −50.4 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 120.3 (q of m, CF_3 s, J = 288.0 Hz), 77.0 (d, CH_2O, J = 8.3 Hz), 73.9 (septet of d, $(CF_3)_2CH$, J_{FC} = 34.8 Hz, J_{PC} = 11.1 Hz), 32.5 (d, $(CH_3)_2C$, J = 3.2 Hz), 24.6, 23.9 (two s, $(CH_3)_2C$). The $(CF_3)_2C$ resonance was too weak to observe. ^{1}H NMR (300 MHz, C_6D_6) δ 5.35 (septet of d, 1H, $(CF_3)_2CH$, J_{HF} = 5.8 Hz, J_{HP} = 13.3 Hz), 3.41 (dd, 2H, H_1), 0.48, 0.26 (two s, 6H, $(CH_3)_2C$); IR(CCl_4) 3005, 2975, 2940, 2880, 1472, 1382, 1375, 1350, 1300, 1265, 1255, 1245, 1220, 1203, 1188, 1175, 1150, 1120, 1060, 1043, 1018, 1000, 968, 840, 903, 885, 880, 860, 718, 700, 690, 648, 615 cm^{-1}; HRMS calcd. for $C_{14}H_{12}O_5F_{18}P$ (M^+ + 1) 633.0135, found 633.0130.

Anal. Calcd. for $C_{14}H_{11}O_5F_{18}P$: C, 26.60; H, 1.75; P, 4.90. Found: C, 26.60; H, 1.73; P, 4.81.

5-t-Butyl-2,2,2-trimethoxy-1,3,2-dioxaphosphorinane (**8**)

To a solution of methyl benzenesulfenate [16] (16.0 g, 114 mmol) in 200 mL of dry methylene chloride, 5-*t*-butyl-2-methoxy-1,3,2-dioxaphosphorinane (10.0 g, 52.0 mmol) was added dropwise over a 30 min period at −78°C under an argon atmosphere with continuous stirring. The resulting solution was stirred for an additional one hour at −78°C and allowed to warm to room temperature. The solvent was removed in vacuo. To the resulting residue, 100 mL of dried *n*-pentane was added. The resulting solution was cooled to −78°C. Diphenyl disulfide, a white solid, was precipitated and filtered off under an argon atmosphere. *n*-Pentane was removed from the filtrate at reduced pressure. The residue was short-path distilled to give 13.0 g of an oil (50.0 mmol, 98%, bp 84°C/0.8 mmHg). After several precipitations of diphenyl disulfide from *n*-pentane, redistillation of the oil gave an analytically pure sample; ^{31}P NMR (121 MHz, C_6D_6) δ −65.7 (s); ^{13}C NMR (75 MHz, C_6D_6) δ 64.5 (d, OCH_2, J = 9.0 Hz), 55.11 (d, $P(OCH_3)_3$, J = 12.1 Hz), 46.4 (d, *t*-Bu*C*H, J = 4.8 Hz), 31.3 (s, $(CH_3)_3C$), 26.9 (s, $(CH_3)_3C$); ^{1}H NMR (500 MHz, C_6D_6) δ 3.97 (ddd, 2H, H_2), 3.82 (ddd, 2H, H^1), 3.67 (d, 9H, $P(OCH_3)_3$, J = 12.2 Hz), 1.83 (tt, 1H, H_3), 0.65 (s, 9H, $(CH_3)_3$); IR (neat) 2990, 2950, 2900, 2875, 2845, 2835, 1478, 1468, 1398, 1368, 1360, 1313, 1240, 1175, 1120, 1085, 1065, 1038, 1010, 983, 910, 810, 745, 658 cm^{-1}. Anal. Calcd. for $C_{10}H_{23}O_5P$: C, 47.24; H, 9.12; P, 12.18. Found: C, 47.36; H, 9.21; P, 12.63.

5,5-Dimethyl-2,2,2-trimethoxy-1,3,2-dioxaphosphorinane (**9**)

In analogous fashion methyl benzenesulfenate (9.37 g, 66.8 mmol) in 40 mL of dry methylene chloride and 5,5-dimethyl-2-methoxy-1,3,2-dioxaphosphorinane (5.58 g, 33.4 mmol) gave, after short path distillation, 7.50 g of colorless liquid (33.1 mmol, 99%, bp 33°C/0.3 mmHg). The product was >95% pure by ^{1}H NMR except for a small amount of diphenyl disulfide (<3% by ^{1}H NMR), which could not be removed from the oil after several precipitation procedures; ^{31}P NMR (121 MHz, $CDCl_3$) δ −65.6 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 74.2 (d, OCH_2, J = 8.6 Hz), 55.0 (d, $P(OCH_3)_3$, J = 11.6 Hz), 33.0 (d, $(CH_3)_2C$, J = 3.5 Hz), 24.8 (s, $(CH_3)_2C$); ^{1}H NMR (500 MHz, C_6D_6) δ 3.69 (d, 4H, OCH_2, J = 17.6 Hz), 3.58 (d, 9H, $P(OCH_3)_3$, J = 12.3 Hz), 1.00 (s, 6H, $(CH_3)_2C$); IR (neat) 2990, 2955, 2885, 2850, 2835, 1465, 1175, 1090, 1065, 1025, 930, 810, 790, 745 cm^{-1}; HRMS calcd for $C_7H_{16}O_4P$ (M^+ − OCH_3) 195.0787, found 195.0779.

ACKNOWLEDGMENT

This work was supported by a grant from the National Cancer Institute of the Public Health Service (W.G.B., grant CA11045) and by a NATO grant (W.G.B., G.V.R.).

REFERENCES

[1] J. H. Yu, W. G. Bentrude, *J. Am. Chem. Soc., 110,* 1988, 7897.
[2] J. H. Yu, W. G. Bentrude, *Tetrahedron Lett.,* 1989, 2195.
[3] J. H. Yu, A. M. Arif, W. G. Bentrude, *J. Am. Chem. Soc., 112,* 1990, 7451.
[4] N. L. H. L. Broeders, L. H. Koole, H. M. Buck, *J. Am. Chem. Soc., 112,* 1990, 7475.
[5] P. J. J. M. van Ool, H. M. Buck, *Recl. Chim. Pays-Bas, 102,* 1983, 215.
[6] J. H. Yu, A. E. Sopchik, W. G. Bentrude, *J. Org. Chem., 55,* 1990, 3444.
[7] The X-ray structure of a phosphorane containing the same bicyclic ring system as **5** has been determined: R. R. Holmes, K. C. K. Swamy, J. M. Holmes, R. O. Day, submitted.
[8] D. Schomburg, H. Hacklin, G.-V. Roeschenthaler, *Phosphorus and Sulfur, 35,* 1988, 241.
[9] Ref. 7 and K. C. K. Swamy, R. O. Day, J. M. Holmes, R. R. Holmes, *J. Am. Chem. Soc., 112,* 1990, 6095.
[10] Full details of this structure will appear elsewhere.
[11] S. Trippett, *Pure Appl. Chem., 40,* 1974, 595. J. H. Barlow, S. A. Bone, D. R. Russell, S. Trippett, P. Whittle, *J. Chem. Soc., Chem. Commun.,* 1976, 1031.
[12] R. Hoffmann, J. M. Howell, E. L. Muetterties, *J. Am. Chem. Soc. 94,* 1972, 3047.
[13] Phosphorane **10** also has a boat form 1,3,2-dioxaphosphorinane ring (unpublished X-ray results, J. H. Yu and Atta M. Arif).
[14] W. G. Bentrude, J. H. Hargis, *J. Am. Chem. Soc., 92,* 1970, 7136.
[15] D. W. White, R. D. Bentrude, G. K. McEwen, J. G. Verkade, *J. Am. Chem. Soc., 92,* 1970, 7125.
[16] The trimethoxyphosphoranes were prepared by the method of L. L. Chang, D. B. Denney, D. Z. Denney, R. J. Kazior, *J. Am. Chem. Soc., 92,* 1977, 2293.