

Conformational Preferences of Pentacoordinate Spirocyclic Phosphorus Compounds

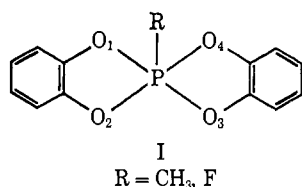
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Abstract: It is shown that existing nmr data on spirocyclic oxyphosphoranes are consistent with square pyramidal structures in agreement with X-ray data on these systems. Previously, the nmr data had been exclusively interpreted in terms of trigonal bipyramidal formulations. Structural principles are outlined for the square pyramidal model and appropriate mechanisms governing intramolecular exchange phenomena are advanced. Both reduced ring strain and enhanced electronic balance are cited as important factors stabilizing a square pyramidal conformation for spirocyclics containing highly electronegative atoms directly attached to phosphorus. Increasing distortion toward a trigonal bipyramid for these spirocyclics as the atom electronegativity is decreased is consistent with VSEPR theory.

As is well known, the structure of simple pentacoordinated phosphorus compounds is trigonal bipyramidal.¹ For more complex derivatives detailed structural parameters are available in a few cases,²⁻¹⁰ although most structural assessments have resulted from nmr interpretations on a wide variety of derivatives.¹¹

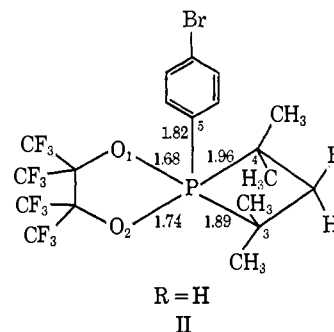
In a recent X-ray study dealing with the spiro oxyphosphoranes I, a "square" pyramidal conformation has



been reported.¹² This conformation is close to that predicted by a simple point charge model,¹³ *i.e.*, one having an axial-basal angle of approximately 105° with the basal angles near 88°. The analogous compound

with sulfur in place of oxygen (R = CH₃) is intermediate in structure between a square pyramid and a trigonal bipyramid based on an X-ray analysis.¹⁴ A summary of pertinent parameters on these derivatives is found in Table I.¹⁵

Also "square" pyramidal structures have been observed *via* X-ray diffraction for 1,3,2-dioxaphospholans



	Angle (deg)
C ₃ PC ₄	105.6
C ₃ PC ₃	110.7
C ₃ PO ₄	101.6
C ₃ PO ₃	100.0
C ₄ PC ₃	78.1
O ₁ PO ₂	85.0
C ₄ PO ₂	154.2
C ₃ PO ₁	147.7

II (R = H, CH₃) containing both a five- and a four-membered ring.¹⁶

In view of the many spirocyclic phosphorus systems whose structures have been inferred as trigonal bipyramidal by nmr spectroscopy,¹¹ it becomes necessary to reassess the structural conclusions and establish whether the nmr data are effective in discriminating be-

(1) (a) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (b) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); (c) R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson, *ibid.*, **3**, 1748 (1964); (d) J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964); (e) K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965); (f) L. S. Bartell and K. W. Hansen, *ibid.*, **4**, 1777 (1965); (g) S. B. Pierce and C. D. Cornwell, *J. Chem. Phys.*, **48**, 2118 (1968); (h) W. J. Adams and L. S. Bartell, *J. Mol. Struct.*, **8**, 23 (1971); (i) H. Yow and L. S. Bartell, *ibid.*, **15**, 209 (1973).

(2) M. J. C. Hewson, R. Schmutzler, and W. S. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 190 (1973).

(3) G. Chioccola and J. J. Daly, *J. Chem. Soc. A*, 568 (1968).

(4) P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964).

(5) (a) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 2268 (1967); (b) R. D. Spratley, W. C. Hamilton, and J. Ladell, *ibid.*, **89**, 2272 (1967).

(6) (a) M.-Ul.-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, *J. Amer. Chem. Soc.*, **93**, 5229 (1971); (b) D. D. Swank, C. N. Caughlan, F. Ramirez, and J. F. Pilot, *ibid.*, **93**, 5236 (1971).

(7) J. W. Cox and E. R. Corey, *Chem. Commun.*, 123 (1967).

(8) A. Almennigen, B. Anderson, and E. E. Astrup, *Acta Chem. Scand.*, **23**, 2179 (1969).

(9) L. G. Hoard and R. A. Jacobson, *J. Chem. Soc. A*, 1203 (1966).

(10) H. Hess and D. Frost, *Z. Anorg. Allg. Chem.*, **342**, 240 (1966).

(11) Extensive reviews of the nmr data are found in the following sources: R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements," Georg Thieme Publishing Co., Stuttgart, 1973; D. Hellwinkel, "Organo Phosphorus Compounds," Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N. Y., 1972, p 185.

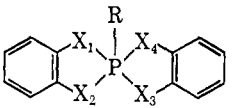
(12) H. Wunderlich, D. Mootz, R. Schmutzler, and M. Wieber, *Z. Naturforsch.*, in press, and personal communication.

(13) J. Zemann, *Z. Anorg. Allg. Chem.*, **324**, 241 (1963).

(14) M. Eisenhut, R. Schmutzler, and W. S. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 144 (1973), and personal communication.

(15) To place structural distortions on a quantitative basis, at least as observed in the solid, an acceptable criterion appears to be to take the sum of the angle differences between the idealized trigonal pyramid (90 and 120°) and that found in a given structure (angles O₁PO₂ and O₂PO₁ in I) compared to the respective sum calculated to exist between the two idealized five-coordinate forms. For the latter purpose, the idealized square pyramid is taken as the one referred to above which has trans basal angles of 150°. Thus, on a scale of 60, structure I (R = CH₃) is nine from the idealized square pyramid, while the corresponding number for structure I (R = F) is 20 and for the sulfur derivative, 26. The percentages of square pyramid then are respectively 85, 67, and 57.

(16) J. A. Howard, D. R. Russell, and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 856 (1973).

Table I.^a Selected Bond Parameters for Spirocyclic Phosphoranes


	R = F, X = O (ref 12)	R = CH ₃ , X = O ^b (ref 12)	R = CH ₃ , X = S (ref 14)
Bond Distances, Å			
P-X ₁	1.629	1.652	2.153
P-X ₂	1.659	1.668	2.206
P-X ₃	1.625	1.654	2.131
P-X ₄	1.658	1.673	2.202
P-R	1.546	1.776	1.817
Bond Angles, deg			
X ₁ PX ₂	91.2	90.1	90.6
X ₃ PX ₄	91.7	90.2	91.5
X ₂ PX ₃	85.7	82.9	
X ₄ PX ₁	84.5	83.9	
X ₁ PX ₃	146.1	147.9	132.0
X ₂ PX ₄	168.2	156.6	158.1
X ₁ PR	107.3	106.0	107.5
X ₂ PR	96.0	102.2	101.4
X ₃ PR	106.6	106.0	109.1
X ₄ PR	95.8	101.3	100.5

^a On the basis of electron pair repulsions (R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); *J. Chem. Educ.*, **40**, 295 (1963)), the presence of strongly electronegative ligands leads to decreased repulsion between bond pairs and reduces the slight preference in stability accorded the trigonal bipyramid relative to the idealized square pyramid. This effect may be invoked to rationalize the data in this table. Replacement of the unique fluorine atom by the more electropositive methyl groups produces a general lengthening of PO distances. Introduction of less electronegative sulfur atoms into the spiro system results in enhanced electron pair repulsions, in line with the observed lengthening of the P-C bond of the methyl groups and the increased structural deformation toward a trigonal bipyramid. ^b Two kinds of molecules with slightly different parameters appear in the unit cell for this derivative.¹² The ones given here are average values for the two structures.

tween the two basic pentacoordinate conformations. It is important to determine the consequences of any structural reassignment, especially if the square pyramid becomes the dominant form for these spirocyclic systems.

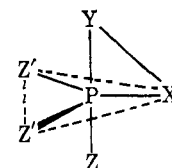
Structural Principles

Before proceeding with a proper treatment, it is worthwhile to recall two established principles of pentacoordinate behavior. These principles are particularly important in application to mechanisms involving the dynamic stereochemistry of some of the derivatives that will be discussed.

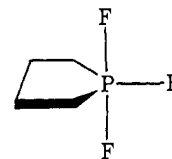
For trigonal bipyramids, it is generally observed¹ that the most electronegative ligands preferentially reside in the axial positions. The presence of cyclic systems imposes an additional constraint limiting the stereochemical possibilities. Derivatives containing four- or five-membered rings, which represent the most widely studied systems, assume a conformation with the rings spanning axial-equatorial positions.²⁻¹⁰ Only if the ring ligand atoms directly attached to the phosphorus atom are of low electronegativity is there some evidence that a ring may span an equatorial-equatorial set.^{1a} As shown by X-ray results on some ring-containing compounds,²⁻¹⁰ the typical structural arrangement will position the most electronegative ring com-

ponent in an axial position if the ring ligands differ in character. Because ring strain is minimized in the axial-equatorial compared to the equatorial-equatorial conformation, the ring arrangement will take preference in occupying an axial position, even at the expense of displacing a more electronegative atom of an acyclic substituent from this location.

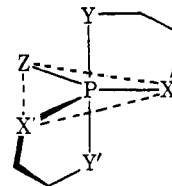
Accordingly, most published data¹¹ on monocyclic containing pentacoordinate phosphorus compounds agree with the general structural representation where X[~]Y refers to either a four- or five-membered ring and the electronegativities of the five-coordinated atoms, which may be the same or different, follow the order Z ≧ Z', Y ≧ X, and X and Y may take on any



value relative to Z and Z'. Only in the case of (CH₂)₄-PF₃ does ¹⁹F nmr data suggest^{1a} that the cyclic system is in the equatorial plane.



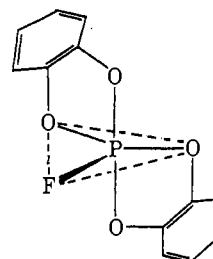
Extension of these principles to spirocyclic systems containing rings of the same size suggests a structure similar to that for monocyclic derivatives which is in accord with most available nmr data.¹¹ The electronegativities of the atoms follow the order Y(Y') ≧



X(X'), and Z may take on a range of values relative to either X or Y. The atoms X, Y, X', Y', and Z may be the same or different.

Structural Correlations between Trigonal Bipyramids and Square Pyramids

In this context the trigonal bipyramidal structure originally proposed^{17,18} for the spiro dioxaphosphole I (with R = F) based on ¹⁹F chemical shift data is rea-

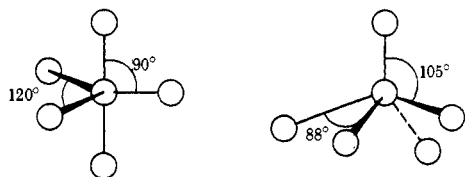


- (17) G. O. Doak and R. Schmutzler, *Chem. Commun.*, 476 (1970).
 (18) G. O. Doak and R. Schmutzler, *J. Chem. Soc. A*, 1295 (1971).

sonable and shows the rings favorably positioned, displacing the more electronegative fluorine atom from its usual position at an axial site. The value of the chemical shift, 70.4 ppm relative to CCl_3F , is close to that commonly observed for equatorially positioned fluorine atoms compared to downfield values associated with axially oriented fluorine atoms.^{17,18}

Although it is possible to argue that the square pyramidal structure found for this compound by X-ray analysis may be a result of lattice constraints, especially since energy differences between the two basic five-coordinate geometries are predictably small,^{13,19-21} structural investigations on simpler pentacoordinate phosphorus derivatives give no evidence for the occurrence of this kind of isomeric conversion with a change of state.^{1c,d} In a somewhat related example, SbPh_5 , which exists as a distorted square pyramid in the solid,²² shows evidence for retention of this structure in solution.²³

Although it is not known what chemical shift values are expected for square pyramids, electron-pair repulsion considerations, with reference to the idealized five-coordinate geometries, suggest a correspondence in



bond properties between the basal bonds of the square pyramid and the axial bonds of the trigonal bipyramid.²⁴ As a consequence, ^{19}F chemical shifts for basal fluorine atoms should appear to the low field side of ^{19}F resonances for axial fluorine atoms in the square pyramid. Hence the relatively positive chemical shift value observed^{17,18} for the fluorine derivative I is not at variance with the X-ray structure¹² showing an axial fluorine atom in a square pyramidal configuration.

Nmr Interpretations on Spirocyclic Oxyphosphoranes

If square pyramidal representations become prev-

(19) (a) R. R. Holmes, L. S. Couch, and C. J. Hora, Jr., *J. Chem. Soc., Chem. Commun.*, 175 (1974); (b) R. R. Holmes, *Accounts Chem. Res.*, 5, 296 (1972).

(20) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).

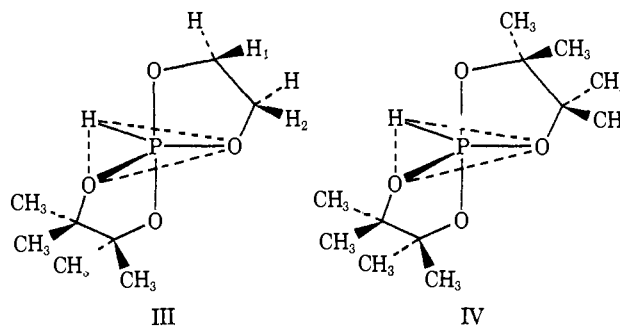
(21) (a) R. R. Holmes and R. M. Deiters, *J. Amer. Chem. Soc.*, 90, 5021 (1968); (b) *Inorg. Chem.*, 7, 2229 (1968); (c) R. R. Holmes, R. M. Deiters, and J. A. Golen, *ibid.*, 8, 2612 (1969); (d) A. Rauk, L. C. Allen, and K. Mislow, *J. Amer. Chem. Soc.*, 94, 3035 (1972); (e) R. Hoffmann, J. M. Howell, and E. Muetterties, *ibid.*, 94, 3047 (1972); (f) A. Strich and A. Veillard, *ibid.*, 95, 5574 (1973); (g) P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, 10, 687 (1971); (h) L. S. Bartell and V. Plato, *J. Amer. Chem. Soc.*, 95, 3097 (1973).

(22) (a) P. J. Wheatley, *J. Chem. Soc.*, 3718 (1964); (b) A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Amer. Chem. Soc.*, 90, 6675 (1968).

(23) (a) I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and R. Sabine, *J. Chem. Soc.*, 784 (1972); (b) G. L. Kok, *Spectrochim. Acta, Part A*, 30, 961 (1974).

(24) Bond electron pair repulsions in the case of the trigonal bipyramid should be greater for axial-equatorial pairs at 90° compared to equatorial-equatorial pairs at 120° .¹⁹ In the square pyramidal conformation, bond pair repulsions are greater for basal-basal pairs rather than axial-basal pairs based on the 88° and 105° geometry shown. Thus to equalize repulsions, the axial bonds in the trigonal bipyramid should be longer than the equatorial bonds; whereas, in the square pyramid, the basal bonds should be longer than the axial length. This hypothesis is borne out in the case of the pentachloroiodate ion InCl_5^{2-} (D. S. Brown, F. W. B. Einstein, and D. G. Tuck, *Inorg. Chem.*, 8, 14 (1969)). Presumably other bond properties will follow this comparative scheme. See also ref 19a and 21d-f.

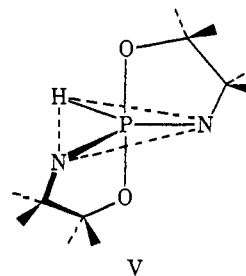
alent for spirophosphoranes, it is necessary to establish that such structures are supported by more complex spectral observations. Examination of the results of nmr studies shows that suitable interpretations are available. For example, a temperature-dependent nmr study of the spiro tetroxyhydridophosphoranes, formulated as trigonal bipyramids,²⁵ shows the presence of two types of methyl signals at reduced temperatures but one methyl peak at higher temperatures (T_c , 37° for III



and 95° for IV). Similar behavior is observed for the ring protons in the less methylated compound. Furthermore, the process is intramolecular since the doublets, corresponding to the protons directly bonded to the phosphorus atom, remain unchanged over the temperature range studied, and the coupling constant for the ring protons J_{PH} in III at high temperatures is the mean value of the J_{PH} coupling constants obtained in the lower temperature AA'BB'X system. Detailed analysis²⁵ indicates that at reduced temperatures the ring substituents that are trans to the proton atom directly bonded to phosphorus form equivalent pairs and are different from the analogous cis substituents which form equivalent pairs. In the high temperature process, all substituents of one ring become equivalent.

The process has been described²⁵ as a double intramolecular one since, in the trigonal bipyramid assumed, four types of protons in III and four kinds of methyl groups in III and IV are expected for rigid forms. A simple Berry pseudorotation²⁶ operating from the lowest temperature studied (-70°) accounts for the presence of only two types of ring protons or methyl groups, Figure 1(a), whereas a more complex multi-stage pseudorotation has been advanced²⁵ to account for the appearance of a single type of ring proton or methyl group above the coalescence temperatures, Figure 1(b).

In related amino derivatives of the type



no intramolecular exchange is evident even at room temperature.²⁷ The latter behavior is consistent with

(25) D. Houalla, R. Wolf, D. Gagnaire, and J. B. Robert, *Chem. Commun.*, 443 (1969).

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

(27) M. Sanchez, L. Beslier, and R. Wolf, *Bull. Soc. Chim. Fr.*, 2778 (1969).

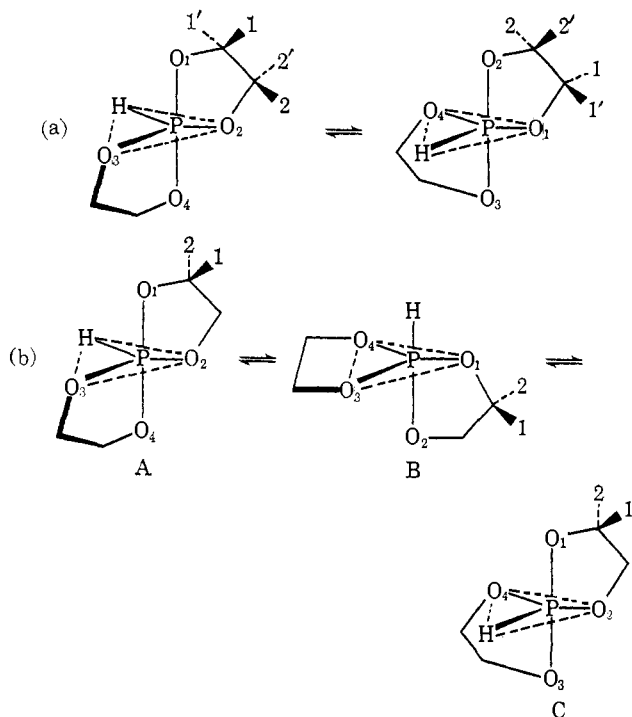


Figure 1. (a) Low temperature process, (b) high temperature process.

the proposed exchange scheme since the occurrence of exchange would imply the formation of unfavorable trigonal bipyramidal intermediates with the less electronegative nitrogen atoms situated in axial positions.

Alternatively, if a square pyramid is assumed for compounds III and IV, a "rigid" form would exhibit but two types of ring protons or methyl groups (cis and trans to the unique directly bonded proton) in agreement with the lower temperature nmr data on the tetraoxy derivatives²⁵ and, accordingly, negate the need for a double intramolecular mechanism. The higher temperature data may proceed by a multi-stage Berry process or may simply be interpreted in terms of a non-Berry single stage exchange process proceeding through a trigonal bipyramidal intermediate formed by displacing one of the basal ligands in the original square pyramid to an axial position in the trigonal bipyramid.²⁸

The process depicted in Figure 2 is applicable to a number of other kinds of spiro systems including the dioxaphospholans II which were initially interpreted in terms of trigonal bipyramidal ground state structures.²⁹ For the five- and six-membered spirocyclic oxyphosphoranes³⁰ VI and VII, interpretations in terms of intramolecular exchange among trigonal bipyramidal formulations, similar to the processes shown in Figure 1, satisfactorily account for the nmr data. For the five-membered spirocyclics, like that for the spiro hydrido derivatives, both exchange processes were involved,³⁰ the only difference being that a higher coales-

(28) In this mechanism, the isomeric trigonal bipyramids, structures III and IV, are considered lower in energy than the corresponding intermediates E of Figure 2 and most likely are intraconverting with isomers like D of Figure 2. However, this process does not allow exchange of groups labeled 1 and 2 in Figure 2; it only allows exchange of ring substituents located cis to the nonring ligand.

(29) (a) R. E. Duff, R. K. Oram, and S. Trippett, *Chem. Commun.*, 1011 (1971); (b) R. K. Oram and S. Trippett, *J. Chem. Soc. Perkin Trans. 1*, 1300 (1973).

(30) B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *J. Amer. Chem. Soc.*, **93**, 4004 (1971).

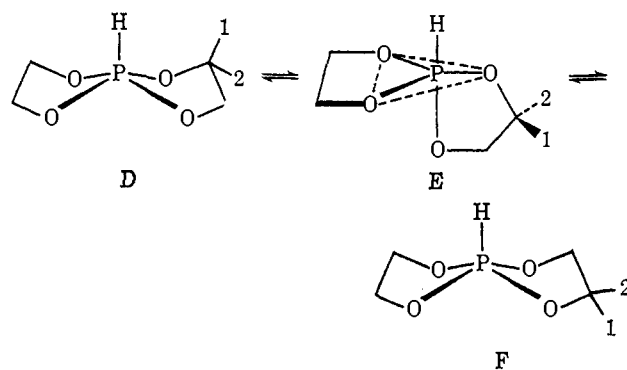
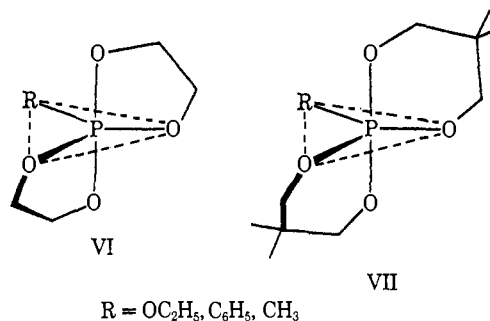


Figure 2. Non-Berry exchange based on a square pyramidal ground state for a spirocyclic derivative.



R = OC₂H₅, C₆H₅, CH₃

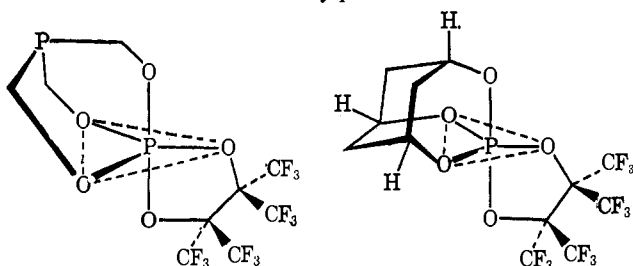
cence temperature ($T_c = 172^\circ$ for R = OC₂H₅) was observed to bring about equivalence of the ring protons compared to the hydrido derivatives. In the case of the phenyl and methyl derivatives, changes occurred in the ¹H spectra on heating, but a simple doublet (phosphorus coupling) pattern was not reached.

For the six-membered spirocyclics VII, predictably greater exchange rates are indicated by the appearance of equivalent ring methyl protons as well as equivalent ring methylene protons in their nmr spectra at room temperature.³⁰ This is because less strain should be experienced by the six-membered ring located in the diequatorial position in the postulated³⁰ exchange intermediate B for the higher temperature process in Figure 1. Furthermore, on cooling to -65° , no change was observed for the ¹H spectrum associated with the ethoxy compound whereas, in the case of the phenyl derivative, the single absorption for the hydrogens of the ring methyl groups splits into two absorptions of equal intensity, and the methylene doublet became two poorly resolved multiplets. The spectrum of the methyl derivative showed similar but less-resolved spectral changes. Consequently, both processes of Figure 1 are indicated to be occurring for all three derivatives of VII at room temperature and the higher temperature process is "stopped" for the phenyl and methyl derivatives only at -65° . The greater exchange rate observed when using the ethoxy groups is again expected in that less energy is needed in reaching intermediate B of Figure 1 (higher temperature process), since the alkoxy group should orient axially more easily because of its higher electronegativity compared to the phenyl or methyl groups.

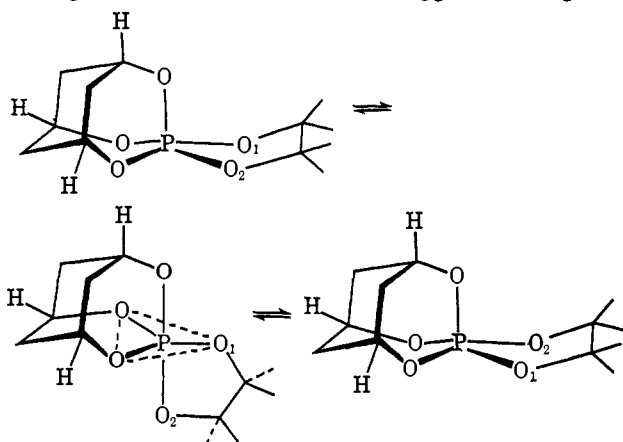
It is apparent that the nmr behavior of these compounds VI and VII may also be interpreted by the exchange process (Figure 2) involving an assumed square pyramidal ground state, since the critical intermediate in determining comparative rates is the same in each

mechanism (B in Figure 1). In terms of the square pyramidal geometry, again there is no need for postulating a double intramolecular process.

Nmr data indicating exchange of oxyphosphoranes containing both a five-membered ring and a bicyclic moiety have been cited³¹ as support for a turnstile mechanism instead of a Berry pseudorotation.²⁶

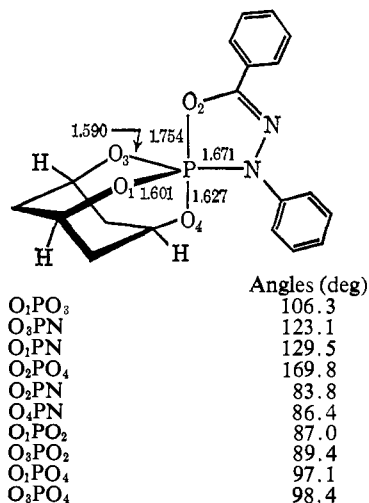


The same data may be interpreted by starting with a distorted square pyramidal ground state and following an exchange mechanism similar to that suggested in Figure 2.



However, the special geometric constraints imposed by the adamantyl moiety should significantly distort the structure from an idealized representation and render decisions regarding the likelihood of specific exchange mechanisms less useful.

An X-ray structure recently available on a related derivative $(\text{PO}_4\text{N})(\text{C}_6\text{H}_5\text{CN})(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_9)$ shows a distorted trigonal bipyramidal form.³²



(31) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, **4**, 288 (1971), and references cited therein.

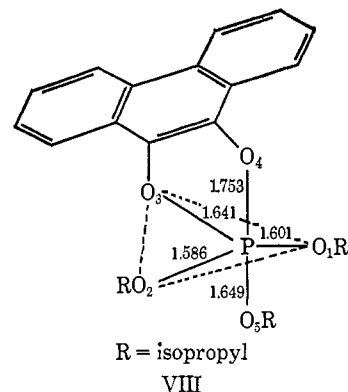
(32) W. C. Hamilton, J. S. Ricci, Jr., F. Ramirez, L. Kramer, and P. Stern, *J. Amer. Chem. Soc.*, **95**, 6335 (1973).

Compared to the pentaoxy cage compound just discussed, distortion toward a trigonal bipyramid is in accord with the presence of the less electronegative nitrogen atom directly bonded to phosphorus, similar to the observation of structural distortion of the thio derivative of the spiro phosphole I (with $\text{R} = \text{CH}_3$) when compared to the corresponding tetraoxy derivative.

Discussion

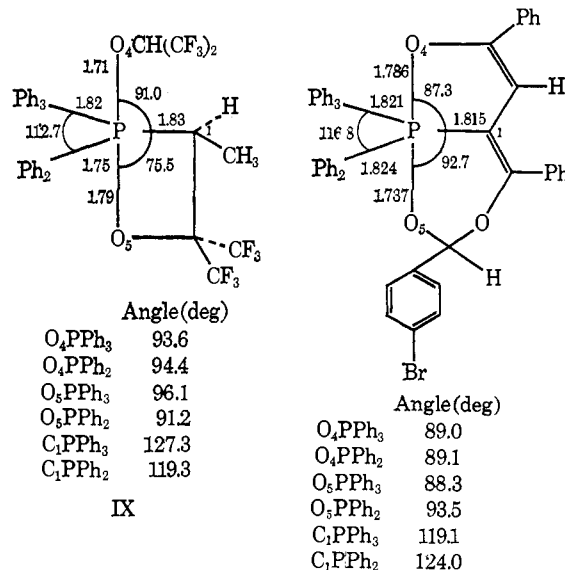
From what has been presented, it is apparent that existing nmr data on spirocyclic oxyphosphoranes support equally well either ground state trigonal bipyramidal or square pyramidal representations, depending on the type of exchange mechanism chosen, all within the framework of established structural principles for these two basic pentacoordinate conformations. Since available X-ray data^{12,14,16} on this class of compounds support the square pyramid, it appears advantageous to view these oxy spirocyclics on the latter basis and attempt to discern intrinsic structural behavior which by contrast allows monocyclic oxyphosphoranes or pentaorganyl spirocyclic phosphoranes to exist as trigonal bipyramids.

Structural determinations by X-ray diffraction on the monocyclic oxyphosphorane VIII⁵ and mixed oxy-



	Angles (deg)
O_4PO_3	89.3
O_5PO_3	88.6
O_1PO_2	117.2

organyl ring containing compounds IX^{6a} and X^{6b} show

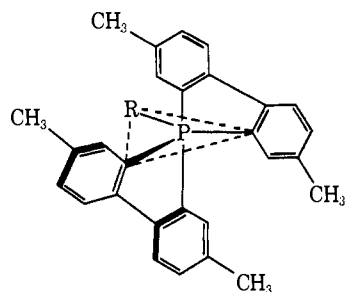


IX

X

trigonal bipyramidal conformations only moderately distorted from the idealized geometry.

While similar X-ray studies on pentaorganyl derivatives appear to be lacking, the structural inferences from nmr data³³⁻³⁵ are convincing. The fact that spirocyclic phosphorus carbon compounds derived from XI exhibit a single ¹H nmr methyl signal at 35°



XI

R = Me, Et, Bz, Ph, and β -Naphthyl

and two methyl group signals at -60° is consistent with a trigonal bipyramidal ground state undergoing rapid ligand exchange at higher temperatures and is not consistent with interpretation in terms of a square pyramidal ground state of C_{4v} symmetry. The latter symmetry qualification implies that rotation of R groups about the unique P-C bond must be rapid in the absence of positional exchange. It follows that this rotation must be rapid during positional exchange as well. The presence of rotational hindrance manifests itself in the related derivative XI containing a less symmetric group R = *o*-isopropylphenyl. Here four bitolyl methyl signals are observed³³ at room temperature indicating a static structure. These signals collapse to a single line on warming to 130° . In the more simply substituted derivatives of XI, R = Me and Et, only one methyl signal is expected for a square pyramidal conformation, whether ligand exchange is occurring rapidly or not.

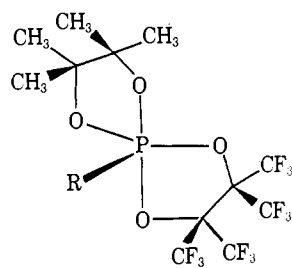
An effective structural correlation may be presented based on two observations. First, the structural data suggest, in line with decreasing electronegativity in the order $O > S > C$, that spirocyclic systems go from square pyramidal toward trigonal bipyramidal. Second, spirocyclic oxyphosphoranes, in contrast to mono- or bicyclic oxyphosphoranes like X, reside in a square pyramidal configuration and suggest the operation of some cooperative effect brought about by the formation of a set of four like bonds compared to two pairs that are possible in the trigonal bipyramidal form.

Electron delocalization, reinforced by the presence of a more extensive basal bonding system present in the square pyramid, is expected to enhance the structural stability of this conformation compared to the trigonal bipyramid. Evidence for the operation of electron delocalization is seen from an examination of P-O bond distance values in the various structures I and VIII-X. The equatorial P-O distance in the ring system of the trigonal bipyramid VIII is similar to the P-O distances in the square pyramid I (R = CH₃, F,

Table I) centered around 1.65 Å whereas the axial P-O distances in the cyclic components of the trigonal bipyramidal structures VIII-X are considerably longer, centered around 1.76 Å, even though these axial bonds are at similar angles to neighboring bonds as are found in the square pyramid, each approximating 90° to other P-O linkages (cf. VIII and I). Estimates of single bond distances³⁶ for P-O linkages range from 1.76 to 1.83 Å and support the presence of appreciable multiple bonding as discussed here.

In the argument just presented, there appears to be no reason why monocyclic oxyphosphoranes like VIII should not achieve a similar degree of electron delocalization, with the ring and two OR ligands occupying the four basal positions of the square pyramid. This suggests that the observance of square pyramidal structures for spirocyclic oxyphosphoranes must be dependent on the presence of the spirocyclic system itself, most likely associated with constraints due to ring "strain" effects.

The square pyramid allows both PO linkages of each ring to assume more or less equal character, depending on the requirements of the attached substituents, in contrast to the substantially different nature of apical and equatorial linkages found for a ring system in a trigonal bipyramid. As a result, residual ring strain should be less in the square pyramid. Thus, the energy balance may be tipped in favor of the square pyramidal configuration compared to the normally more stable trigonal bipyramid when two small-membered rings are present. Introduction of substituents which are different from each other and hence have unequal electronic requirements, whether they be part of the ring system as in V or attached thereto, should be less effective in stabilizing the square pyramidal form. This may be the reason for the appearance of trigonal bipyramidal structures for the spiro oxyphosphoranes XII,¹⁶ which



XII

R = SPh, *p*-OC₆H₄Br

somewhat resemble I in substituent composition but have unequal P-O bond character due to the rather wide difference in electronegativity between the methyl and perfluoromethyl groups.

In the spiro system II containing a four-membered ring, the consequent increase in ring strain effects, if the trigonal bipyramidal structure were adopted, coupled with the presence of a methylene group in an axial site in that configuration apparently provides a sufficient structural advantage to allow the appearance of the square pyramid in this instance.

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Obviously, the magnitude of the effects causing preference for one structure over the other need not be large, in view of previous data^{13,19-21} on simple derivatives suggesting that in many cases the two pentacoordinate conformations differ by only a few kilocalories. In the case of the relatively nonrigid trigonal

bipyramidal VF₅, an estimate of 1.8 kcal/mol has been given.¹⁹

Acknowledgment. Grateful appreciation is expressed to Professor R. Schmutzler, Dr. W. Sheldrick, and Dr. M. Fild of Braunschweig University for valuable discussions.

Calculated and Observed Field Gradients in [M(CO)_{5-x}P_x]ⁿ Complexes¹

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Abstract: Using nqr or Mössbauer spectroscopy the field gradient at the metal nucleus, eq_{zz} , has been determined in isoelectronic pentacoordinate complexes, [M(CO)_{5-x}P_x]ⁿ, where P is P(C₆H₅)₃ or P(OCH₃)₃ and M is Mn ($n = -1$), Fe ($n = 0$), or Co ($n = +1$). Values of $eq_{d_{z^2}}$ and eq_{p_z} were calculated for the metal ions Mn(-1), Fe(0), and Co(+1) in different electron configurations, using SCF atomic functions. The one-electron 4p orbital contribution to the field gradient is comparable in magnitude with the 3d term. Theoretical estimates of eq_{zz} for Fe(CO)₅ based on eigenvectors from molecular orbital studies are in reasonable agreement with the experimental field gradient. Relative values of $eq_{d_{z^2}}$ for the three metal ions are compared with relative values of eq_{zz} observed for [Mn(CO)₅]⁻ and Fe(CO)₅ and estimated for the hypothetical [Co(CO)₅]⁺. It is concluded that the populations of the planar d orbitals increase relative to the axial, in the order Mn < Fe < Co. The effect of phosphorus ligand substitution on eq_{zz} is difficult to interpret, since a simple trend is not observed. It is deduced that [Mn(CO)_{5-x}P_x]⁻ and [Co(CO)_{5-x}P_x]⁺ complexes have positive values of eq_{zz} and e^2Qq .

The electric field gradient at the metal nucleus in compounds of the transition metals in low valence states can be expressed to a good approximation as

$$eq_{zz} = eq_{d_{z^2}}[N_{d_{z^2}} + \frac{1}{2}(N_{d_{zz}} + N_{d_{yz}}) - (N_{d_{xy}} + N_{d_{x^2-y^2}})] + eq_{p_z}[N_{p_z} - \frac{1}{2}(N_{p_x} + N_{p_y})] \quad (1)$$

where $eq_{d_{z^2}}$ and eq_{p_z} are the expectation values for the field gradient operator for a single electron in a valence d_{z^2} or p_z orbital, respectively. The N 's are electron populations of the various orbitals. In evaluating field gradient data for different transition metals in similar chemical environments, or for the same element in different chemical situations, it is essential to have some idea of how $eq_{d_{z^2}}$ and eq_{p_z} vary with changing effective nuclear charge or electronic configuration at the metal. We have chosen to investigate this question by study of isoelectronic species of the form [M(CO)_{5-x}P_x]ⁿ, where M is Mn ($n = -1$), Fe ($n = 0$), or Co ($n = +1$) and P is a phosphine or phosphite. ⁵⁵Mn ($I = 5/2$) and ⁵⁹Co ($I = 7/2$) are 100% abundant in nature, so that field gradient information is obtainable by nuclear quadrupole resonance (nqr) spectroscopy. From Mössbauer spectroscopy of ⁵⁷Fe (⁵⁷Fe^m has $I = 3/2$), it is possible to obtain information regarding the field gradient at iron. By utilizing the best available values for the nuclear quadrupole moments, eQ , the quadrupole coupling

constants, $e^2q_{zz}Q/h$, may be converted to estimates of field gradients, eq_{zz} . Previous nqr³ and Mössbauer⁴⁻⁶ spectral work on five-coordinate species in these series has shown the presence of fairly large field gradients at the central metal. Since the metals in these diamagnetic systems obey the 18-electron "krypton rule," *i.e.*, have all their valence orbitals occupied, the field gradients must arise from differential levels of occupancy of these orbitals. In this contribution we examine from both theoretical and experimental viewpoints the effect on eq_{zz} of changing the central metal nuclear charge and electronic configurations. In addition, we have measured experimentally the effects of substitutions on the parent [M(CO)₅]ⁿ species by triphenylphosphine and trimethyl phosphite.

Experimental Section

Materials. Dimanganese decacarbonyl, Mn₂(CO)₁₀, was obtained from Pressure Chemical Co. or prepared according to a standard procedure⁷ and stored under argon. Dicobalt octacarbonyl, Co₂(CO)₈, (Pressure Chemical Co.) was stored at 0° under argon or nitrogen. Triiron dodecacarbonyl, Fe₃(CO)₁₂ was obtained from Strem Chemicals, Inc., or prepared by a standard method.⁸ It was purified by extraction with pentane.

Triphenylphosphine, PPh₃, and trimethyl phosphite, P(OCH₃)₃, were purchased from Aldrich Chemical Co.

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(1) This research was carried out through support by The National Science Foundation via Contract GH-33634 with The Materials Research Laboratory, University of Illinois, and Research Grants GP 6396X and GP 30256X. The Wilks NQR spectrometer was purchased through support from the Advanced Research Projects Agency, Contract ARPA-HC-15-57-C-0221 with The Materials Research Laboratory.

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