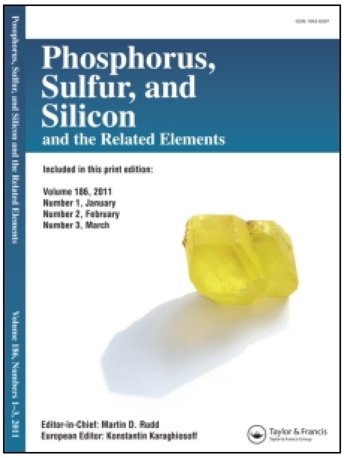


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STRUCTURE OF CYCLIC PENTACOORDINATED MOLECULES OF MAIN GROUP ELEMENTS

Robert R. Holmes[a]
[a] Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

To cite this Article Holmes, Robert R.(1995) 'STRUCTURE OF CYCLIC PENTACOORDINATED MOLECULES OF MAIN GROUP ELEMENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 98: 1, 205 — 221
To link to this Article: DOI: 10.1080/10426509508036949
URL: http://dx.doi.org/10.1080/10426509508036949

Phosphorus, Sulfur, and Silicon, 1995, Vol. 98, pp. 205–221
Reprints available directly from the publisher
Photocopying permitted by license only

STRUCTURE OF CYCLIC PENTACOORDINATED MOLECULES OF MAIN GROUP ELEMENTS

ROBERT R. HOLMES
Department of Chemistry, University of Massachusetts,
Amherst, Massachusetts 01003

(Received January 16, 1979)

Ten years ago, only one structure of a cyclic phosphorane was known, the 1:1 adduct of phenanthrenequinone and triisopropyl phosphite, characterized as trigonal bipyramidal.[1] At that time, the trigonal bipyramid was the prevailing structural form for main group elements.[2]

Since then, more than 50 structural studies on cyclic phosphoranes have appeared.[3,4] It is particularly interesting that these compounds form a continuous range of conformations extending from the ideal trigonal bipyramid to the square or rectangular pyramid.[3,4] In this respect, pentacoordinated phosphorus is unique.

It is now apparent that the square pyramid, once regarded as a transition state in interpreting fluxional behavior of pentacoordinate phosphoranes,[5] may also be regarded as a ground-state conformation for certain cyclic species.[6] This raises the possibility that the trigonal bipyramid may, on occasion, assume the role of an activated state. Presumably, this reversal in the roles of ground state-transition state represents a possibility for pentacoordinated molecules of other less investigated main group elements containing cyclic components. Since an understanding of reaction mechanisms of many cyclic phosphorus derivatives depends on an intimate knowledge of postulated pentacoordinated states in rate-controlling steps,[7] it is essential to know when one or the other structure is favored for isolatable cyclic phosphoranes.

This Account is constructed to explore factors responsible for the observed structural preferences of individual pentacoordinated members and to point to the applicability of the resulting principles to mechanistic schemes involving cyclic derivatives. We shall first examine the range of cyclic structures observed for main group elements and then consider their relative fluxional character before outlining the proposed role of pentacoordination in reaction mechanisms.

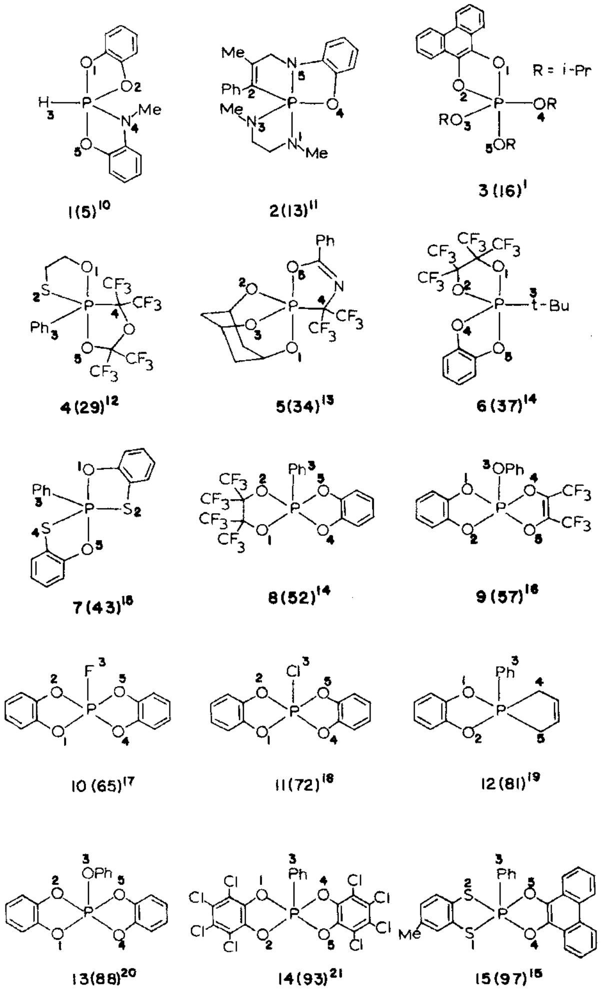
Pentacoordination is widespread, but if we confine our attention to main group elements in monomeric species which have been structurally characterized by diffraction techniques or microwave spectroscopy, a more limited number of elements comes under consideration.[8] Further, characterization of five-coordinated species

2B	**3A**	**4A**	**5A**	**6A**
	Al	**Si**	**P**	**S**
Zn			**As**	
	In	**Sn**	**Sb**	

Reprinted with permission from *Acc. Chem. Res.*, **12**, 257 (1979). Copyright 1979 American Chemical Society.

containing cyclic substituents is lacking for Al, In, Sn, and Sb. However, if we allow pseudopentacoordination, i.e., pentacoordination in which one of the coordination sites is occupied by a lone electron pair, then a number of cyclic sulfuranes and cyclic selenuranes are included.[9] Also, some acyclic selenuranes and telluranes have been characterized by X-ray diffraction.[8] Of the cyclic derivatives, those containing phosphorus as the central element comprise the vast majority.

Representative structural formulas for cyclic phosphorus-containing derivatives are given in Figure 1.[1,4,10–21] The phosphoranes are arranged so that successive members are more displaced in structural form from the ideal trigonal bipyramid (TP) and increasingly resemble an idealized square (SP) or rectangular pyramid (RP). The form of the distortion coordinate (Figure 2) connecting the two idealized geometries is identified as involving a simultaneous bending of "axial" and "equa-



1(5)[10] 2(13)[11] 3(16)[1]

4(29)[12] 5(34)[13] 6(37)[14]

7(43)[15] 8(52)[14] 9(57)[16]

10(65)[17] 11(72)[18] 12(81)[19]

13(88)[20] 14(93)[21] 15(97)[15]

FIGURE 1 Structures of cyclic phosphoranes with percent displacement along the Berry coordinate from the TP toward the RP shown in parentheses. References shown as superscripts.

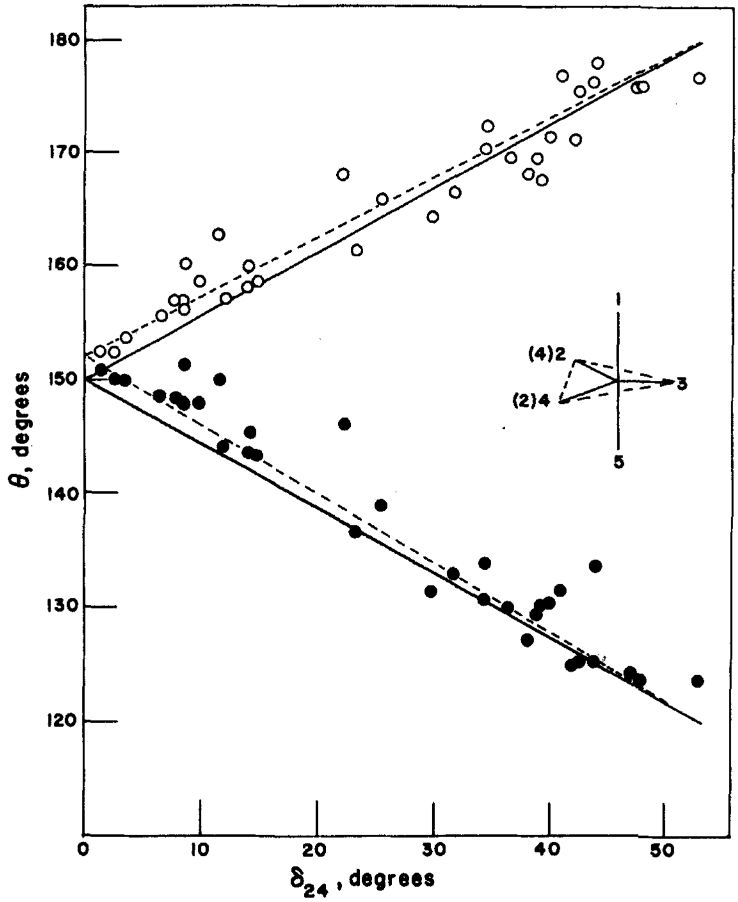
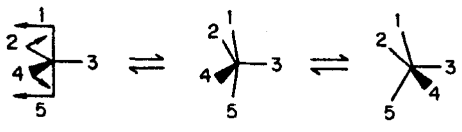


FIGURE 2 Variation of the "axial" angle, θ_{15} (open circles), and "equatorial" angle, θ_{24} (filled circles), from X-ray data vs. the dihedral angle δ_{24} as structural distortion of cyclic phosphoranes proceeds along the Berry coordinate (solid lines) from the idealized square or rectangular pyramid (RP) toward a trigonal bipyramid (TP). The dihedral angle δ_{24} which is formed from the normals to the two triangular faces, 1-2-4 and 5-2-4, goes from 0° for the RP to 53.1° for the TP. Slightly less scatter of experimental points is obtained if the Berry coordinate traversed (dashed line) leads to a square (or rectangular) pyramid having trans basal angles of 152° instead of 150°.

torial angles." This is the well-known Berry coordinate[22] depicted below. Equal



$\theta_{15} = 180°$ $\theta_{24} = 120°$ | $\theta_{15} = \theta_{24} = 150°$ | $\theta_{24} = 180°$ $\theta_{15} = 120°$

but opposite bending of the angles indicated by the arrows results in the formation of an isomeric square pyramid. Continuation of the bending motion gives a permuted conformation in which the axial and equatorial ligands have exchanged sites. The Berry motion has been invoked to rationalize intramolecular ligand-and-exchange phenomena obtained from temperature-dependent NMR studies on a wide assortment of pentacoordinated derivatives.[4,5] The construction of Figure 2 is based on 34 X-ray studies including the structures given in Figure 1.

A better representation of the close adherence to the Berry coordinate for these phosphoranes is obtained by summing up dihedral angle changes from polytopal faces formed from the five ligands attached to phosphorus relative to those for each of the idealized five-coordinate structures for each derivative. In the idealized TP there are six faces and nine edges between faces. The dihedral angle, δ_i, is defined as the angle formed by the normals to the faces which share a common edge. The dihedral angles in an idealized RP may be similarly defined and compared to the angle of the corresponding edge in a TP. The sum of the changes in the dihedral angles in moving from an idealized TP to an idealized RP structure is 217.7°.[3] Thus, $\Sigma_i|\delta_i(\mathrm{TP}) - \delta_i(\mathrm{RP})| = 217.7°$, where the sum is over all edges. From known structural parameters for a compound, C, the dihedral angles can be calculated and compared to dihedral angles for similar edges in idealized TP and RP structures, i.e., by way of the summations $\Sigma_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{TP})|$ and $\Sigma_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{RP})|$, respectively. Since the sum of the dihedral angle changes between the idealized geometries is 217.7° (= R), then $\Sigma_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{TP})|$ and $R - \Sigma_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{RP})|$ should have the same value if the Berry coordinate is adhered to. The appearance of most of the points on the Berry line in Figure 3 shows that indeed this is the case. Here again many more examples than listed in Figure 1 are included.[3,4]

Application of the dihedral angle method to the solid-state data clearly distinguishes between the Berry coordinate and other intramolecular ligand exchange coordinates, notably the turnstile coordinate.[23] Temperature-dependent NMR studies, even those involving detailed line-shape studies,[24] have not differentiated between these two exchange mechanisms simply because they are permutationally equivalent.[4] If one considers the geometry of a 30° turnstile structure (30° TR), a purported barrier structure[23] for ligand exchange by this process, the sum of the dihedral angles relative to that for a trigonal bipyramid is 223.8°.[3] The sum of the dihedral angle changes between the 30° TR and the ideal rectangular pyramid is 47.5°. The difference, 223.8° − 47.5°, is 176.3° which, when compared to the sum $\Sigma_i|\delta_i(\mathrm{TP}) - \delta_i(\mathrm{RP})| = 217.7°$, is 41.4° off. Thus, the upper end of the Berry line in Figure 3, i.e., structures near the ideal rectangular pyramid on the Berry line, will be about 41° (in terms of dihedral angles) away from a turnstile coordinate.[3] Structures progressively closer to the trigonal bipyramid along the Berry coordinate will naturally deviate less from the turnstile barrier state.

That the structures of cyclic phosphoranes can form a continuous series along the trigonal-bipyramidal-rectangular-pyramidal (TR-RP) coordinate suggests that this coordinate is one of low energy. The same conclusion is reached from NRM studies of dynamic exchange behavior or nonrigid derivatives. The exchange mechanism commonly adopted in the interpretation of these data involves the axial-equatorial bending process associated with the Berry coordinate.[22]

Data from several lines of evidence are in accord in supporting a low energy for the latter bending coordinate. Chief among them are electron-diffraction amplitude data[25] and force-constant analyses[26] on the gas-phase molecules PF_5, $(CH_3)_nP_{5-n}$ ($n = 1$–3), PCl_5, and AsF_5, indicating high in-plane vibrational amplitudes for

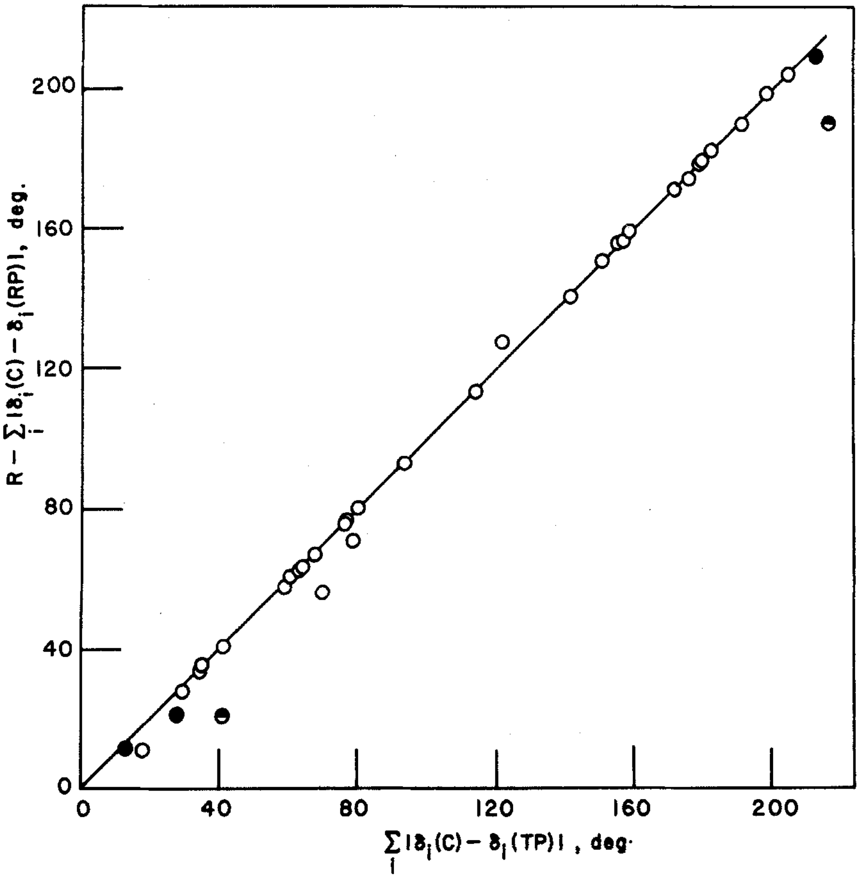


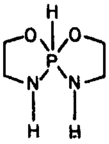
FIGURE 3 The sum of dihedral angles for cyclic phosphoranes from either a square or rectangular pyramidal idealized geometry vs. that from a trigonal pyramid on a common reference scale (see text). The solid line is along the Berry exchange coordinate. The structure corresponding to the point below the solid line (half-filled circle, upper right) is disordered. The most poorly refined structure, R = 0.135, lies below the solid line (half-filled circle, lower left). Open circles refer to calculations based on actual bond lengths and filled circles reflect use of unit bond lengths.

equatorial atoms; spectroscopic analysis establishing a normal mode, indicative of the Berry motion,[2,26,27] in the range 110 to 190 cm^{-1}; an associated study of the hot band structure of these e' bands for PF_5, AsF_5, and VF_5 leading to respective intramolecular exchange barriers of 2.8–3.3, 2.2–2.5, and 1.2–1.5 kcal/mol, and showing that upper vibrational states have an increasingly greater degree of axial motion[28,29]; and theoretical calculations[30] providing low barriers for passage through a square-pyramidal state for PF_5 (1.4–4.8 kcal/mol) and the hypothetical PH_5 molecule (2.0–4.2 kcal/mol) with d-orbital functions included. While fluorine atom exchange has not been slowed on the NMR time scale for PF_5[31,32] down to −190°C), NMR analysis has provided an exchange barrier for $PClF_4$ of 4.2 kcal/mol.

The higher exchange barriers commonly obtained from NMR data (10–30 kcal/mol) on highly structured cyclic phosphoranes are attributable to variations in electronic, steric, and ring strain terms encountered as various pseudorotations take place.[3–7,33] Above the onset temperature for the process with the highest activational free energy, several pseudorotational processes may in fact be occurring through different square-pyramidal isomers. For these phosphoranes, topological graphs are invaluable in showing allowed isomeric conversions.[4,5,7b] In the context of the above discussion, cyclic phosphoranes seek a structural minimum by balancing their inherent "strain" terms (by angular "slippage" along the low-energy Berry coordinate) against the energy required to bring them toward the inherently higher energy square or rectangular pyramid.[3,33,34]

It could be argued that the solid-state structures are sufficiently influenced by lattice interactions, i.e., intermolecular effects, that extension to solution phase studies is inappropriate. Several kinds of information may be cited to refute the latter hypothesis. The structural preferences for individual members listed in Figure 1 and others in the literature (a total of over 55) appear to correlate with substituent effects.[3,15,35] For near-TP structures, the electronegativity[32] and ringstrain[7,32,33] "rules" are in general followed. These rules summarize observations on site preferences in a TP. The former rule states that the most electronegative ligands preferentially occupy axial positions; the latter, that small-membered rings preferentially span an axial-equatorial set of positions. Infrared and Raman spectra for solid and solution states are very similar.[35a] In most cases, no short intermolecular contacts are present. Those cases where short contacts are apparent owe their presence to either intermolecular hydrogen bonding[36] or steric interactions caused by bulky substituents.[14]

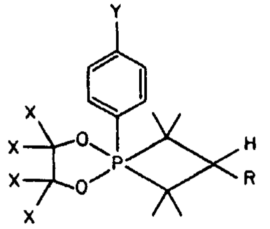
For some of these situations, molecular mechanics has been used to probe the extent of such interactions by simulating the isolated molecule structure[37] and the molecular structure perturbed by neighboring molecules in the unit cell.[14,38] For example, it is found that strong intermolecular interactions between CF_3 groups and the *tert*-butyl group account for the lesser displacement from the TP for phosphorane **6** of Figure 1 compared to the analogous phenyl derivative (8 of Figure 1).[14] For phosphorane **16**, which is about 25% displaced from the TP, computer simulation[38] shows that N—H···O hydrogen bonding caused by neighboring molecules in the unit cell is contributory in accounting for the larger N—P—N equatorial angle of 130.8 (1)° compared to a value averaging 124.0° for this angle in a number of related derivatives.



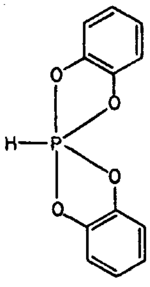
16

FACTORS STABILIZING A RECTANGULAR PYRAMID

The following factors appear conducive in favoring the formation of a rectangular pyramid: (1) increasing unsaturation in five-membered cyclic systems; (2) the presence of two such rings compared to the presence of one; (3) the presence of like atoms bonded to phosphorus in any one ring; (4) introduction of a more strained four-membered ring; and (5) the presence of an acyclic ligand in a spirocyclic derivative which is bulky and has low electronegativity.[14] Some of these trends may be seen to operate in the limited series included in Figure 1. It is noteworthy that no acyclic or monocyclic phosphorane has been found that is displaced more than 30% from the ideal TP[39] as measured by the dihedral angle method,[3,4] or that spirocyclics containing four-membered rings are near square pyramidal even when both rings are saturated,[39] as in derivatives **17**[40] and **18**.[35a] The fact that the phospholane **19**, containing a unique proton ligand, is very close to trigonal bipyramidal[41] suggests the importance of the existence of some steric effect before factor 5 becomes operative. The above preferences for the formation of a rectangular pyramid (1–4) have been related to the relief of ring strain energy expected for a ring located in cis basal positions of a RP having like bond properties compared to occupancy of an axial-equatorial pair of sites of unlike bond character in the TP.[33] This effect should be more pronounced for rings containing greater rigidity due to attachment of unsaturated components.

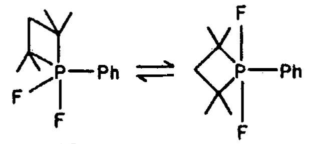


17, $X = CF_3$; $Y = Br$; $R = H$
18, $X = H$; $Y = H$; $R = CH_3$

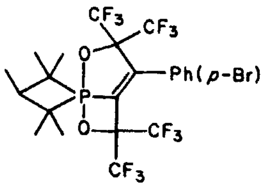


19

NMR interpretations[42] lead to structures like **20** (in equilibrium with **21**) showing the carbon atom in the less preferred apical site.[32,43] So far no X-ray structural confirmation exists. Derivatives like **12** of Figure 1 are more RP, whereas an X-ray study[44] of the highly constrained polycyclic **22** has the ring carbon atoms in



20 **21**



22

equatorial sites, analogous to **21**. The latter structure is located on an anti-Berry coordinate,[4] i.e., on an extension of the line in Figure 3 away from both the TP and RP. In terms of the dihedral angle sum, its location is −73%.

VSEPR CONSIDERATIONS

The geometry of acyclic phosphoranes, like the $(CH_3)_nPF_{5-n}$ series[25b-d] (Table I), is qualitatively in accord with the valence-shell electric-pair repulsion (VSEPR) model.[45] In terms of this model, a group of low electronegativity, e.g., the CH_3 group in the $(CH_3)_nPF_{5-n}$ series, centers the bonding electron pair in the P—C linkage closer to the phosphorus atom than that in the P—F bond. Considering the greater importance of bond-pair–bond-pair repulsions oriented at 90° to each other over electron-pair repulsions between bonds at 120°, the elongation and bending of the P—F bonds away from the equatorially positioned methyl groups, as methyl substitution increases in the above series, are rationalized. These effects are presumably masked for the most part in cyclic derivatives owing to the presence of greater structural determinants,[3,39] e.g., ring strain effects,[33] steric interactions,[14] etc., although the trend to greater displacement toward the RP with decreasing electronegativity of the acyclic substituent (derivatives **10** (F), **11** (Cl), and the corresponding methyl derivative[46]) provides some indication of its operation.

The VSEPR model takes on increasing applicability if we turn our attention to sulfuranes. The geometry of SOF_4[47a] (Table I) is accounted for in terms of the greater EPR effect of the S—O σ bond possibly aided by S—O π bonding concentrated in the equatorial plane. The effect is amplified in SF_4, wherein both the axial and equatorial angles[47b,c] are considerably more compressed away from the lone electron pair situated at the fifth coordination site. In fact, recent X-ray studies on a number of cyclic sulfuranes[9,48] show retention of this same structural form (Table II). Qualitatively then, EPR effects appear to assume a controlling influence even for cyclic sulfuranes, in contrast to the situation with phosphoranes.

The ease with which the equatorial angle compresses is seen in the diequatorial ring placement for the monocyclic sulfurane **9** of Table II. The latter structural type is unknown for monocyclic phosphoranes. Comparison of the cyclic structures

TABLE I

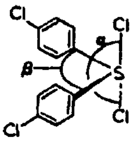
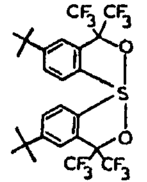
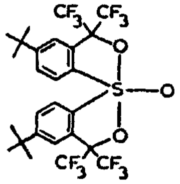
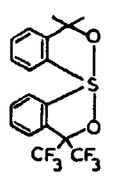
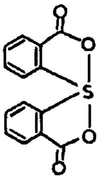
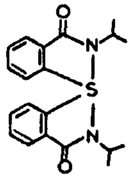
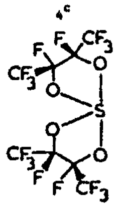
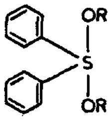
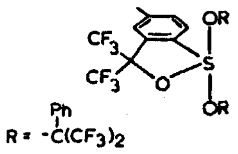
Bond Parameters[a] for Some Acyclic Pentacoordinate Molecules (Trigonal Bipyramid)

			bond angles,[b] deg			
	r_{eq}, A	r_{ax}, A	e_2–e_3	e_1–a	method[c]	ref
PF_5	1.534 ± 0.004	1.577 ± 0.005			E	25b
CH_3PF_4	1.543 ± 0.004, P-F 1.780 ± 0.005, P-C	1.612 ± 0.004	115.6 ± 0.9	91.8 ± 0.4	E	25c
$(CH_3)_2PF_3$	1.553 ± 0.006, P-F 1.798 ± 0.004, P-C	1.643 ± 0.003	124 ± 0.8	88.9 ± 0.3	E	25c
$(CH_3)_3PF_2$	1.813 (1)	1.685 (1)			E	25d
SOF_4	1.552 (4) S-F 1.403 (3) S-O	1.575 (4)	110.2 (1.8)	90.6 (0.4)	E	47a
SF_4	1.545 ± 0.003	1.646 ± 0.003	101.55 ± 0.50	93.47 ± 0.25[d]	M	47b
	1.542 ± 0.005	1.643 ± 0.005	103.8 ± 0.6	91.6 ± 1.3[d]	E	47c

[a] The standard deviations (in parentheses) and unparenthesized uncertainty limits in bond parameters refer to the least significant digits. [b] *Where it matters, the subscripts 2 and 3 on the equatorial atoms refer to the pair of identical atoms* while the subscript 1 refers to the unique atom. [c] E, electron diffraction; M, microwave spectroscopy. [d] These angles for SF_4 are one-half the reported F_{ax}–S–F_{ax} angles and refer to the angle between the axial fluorine atoms and the electron pair located along the molecular C_2 axis. The uncertainty listed is one-half the reported uncertainty for the F_{ax}–S–F_{ax} angle.

TABLE II

Bond Angles (deg) at Sulfur for Some Sulfuranes[a,b]

 185.5, 108.6 (−52)[c] **1**[a]	 177.1, 108.1[d] (−35) 178.2, 107.6 (40) **2**[b]	 172.3, 117.7 (12) **3**[b]
 177.3, 107.9 **4**[c]	 178.5, 107.8 (−40) **5**[d]	 179.8, 104.8 (−56) **6**[e]
 171.5, 104.6 **7**[f]	 175.1, 104.4 (−44) **8**[g]	 172.0, 95.0 (−77) **9**[h]

---

[a] Reference 48a–h. The specific reference is shown as a superscript to the sequentially numbered entries. [b] The axial angle α and equatorial angle β are given below each structure. [c] The parenthesized numbers are the sum of dihedral angles from the TP on the C_{2v} coordinate based on unit bond distances.[3] See Figure 4. The lone pair is taken along the bisector of the equatorial angle. [d] Two independent molecules are in each unit cell for entry 2.

2 and 3 of Table II, which differ in composition by only an S—O linkage, shows that, like the situation on going from SOF_4 to SF_4, the equatorial angle decreases on going from 3 to 2, but unlike that in the acyclic derivatives, the axial angle increases. It may be that the attached unsaturated ring component introduces a measure of rigidity holding the axial angle near 180° at the expense of the decrease in the equatorial angle. In any event, the axial angle stays relatively constant in the related sulfuranes **4**–**6** while this angle drops to 171.5° in the saturated derivative **7**. For an interpretation of structural differences in this interesting series, the reader is referred to the original papers.[9,48]

C_{2v} DISTORTION COORDINATE FOR PENTACOORDINATE S, As, AND Si

Plotting dihedral angle sums for sulfuranes (Figure 4) shows that their structures follow the C_{2v} constraint of the Berry coordinate. However, unlike the Berry

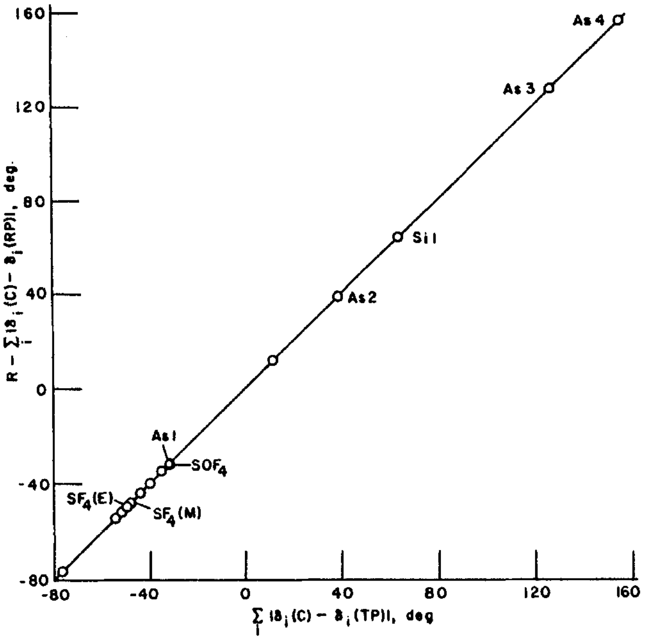
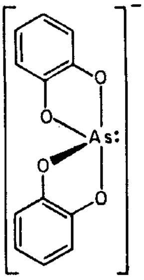
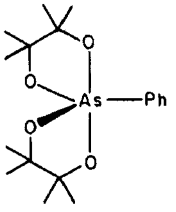


FIGURE 4 The sum of the dihedral angles for pentacoordinated structures of S, As, and Si relative to that for an idealized rectangular pyramid vs. the dihedral angle sum from a trigonal bipyramid. The solid line is due to a local C_{2v} constraint.

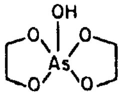
process, both apical and equatorial bonds are progressively bent away from the equatorial lone pair as one proceeds toward the lower left from what is the origin in Figure 3. In addition, points for cyclic arsoranes (**1–4**)[49] and a silicon[50] analogue



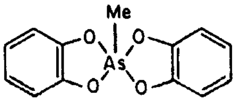
1 (−15)[49a]



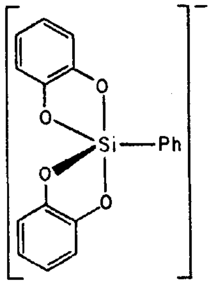
2 (18)[49b]



3 (59)[49b]



4 (72)[49c]



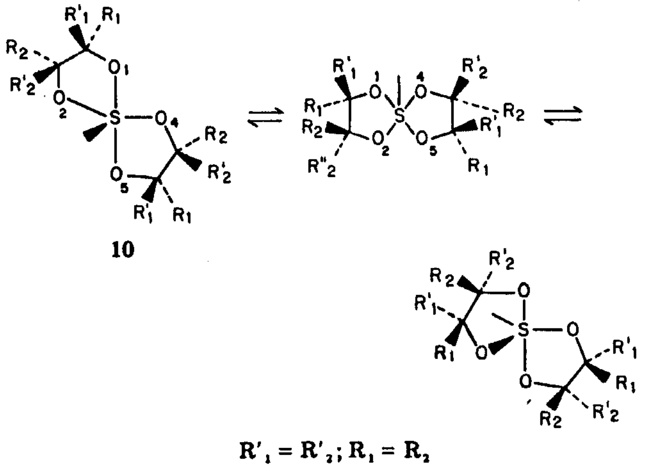
1 (30)[50]

(parenthesized values are % displacement along the TP–RP bending coordinate; references are shown as superscripts)

(Figure 4) are seen to follow the C_{2v} constraint associated with the orthogonal equatorial-apical bending coordinate. The direction of bending, except for arsorane **1**, is that for the Berry process. Again the lone-pair effect dominates for the latter arsorane like that for the related cyclic sulfuranes. It is expected that future studies of main-group pentacoordinated derivatives will yield additional structures which, in general, will be found to deform along the C_{2v} coordinate shown in Figures 3 and 4.

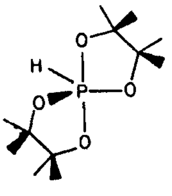
RELATIVE FLUXIONAL CHARACTER OF PENTACOORDINATE P, S, As, AND Sb

Regarding ligand-exchange behavior, the less studied sulfuranes give some evidence of having higher barrier energies than that observed for related phosphoranes. Observation and analysis of hot band structure in the gas-phase infrared spectrum, analogous to that discussed for PF_5, AsF_5, and VF_5, led to a value of 10.0 ± 0.5 kcal/mol for the exchange barrier for SF_4.[51] For the spirocyclic sulfurane **10**, low-temperature ligand exchange is consistent with the Berry pseudorotation process shown below (four nonequivalent CF_3 groups go to two on warming from −150°).[9,52] An activation energy ($\Delta G^{\ddagger}_{-100}$) of 7.5 kcal/mol was obtained.

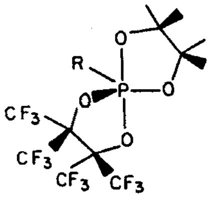


$R'_1 = R'_2; R_1 = R_2$

This type of process for tetraoxyphosphoranes, which involves equilibration among isomers of identical energies, is generally rapid on an NMR time scale even at low temperatures.[53] The lack of change in the NMR spectrum of the sulfurane **10** up to 200° indicated a barrier greater than 25 kcal/mol for higher energy exchange processes.[9,52] For corresponding cyclic phosphoranes, like **23** and **24** (R = H), the



23

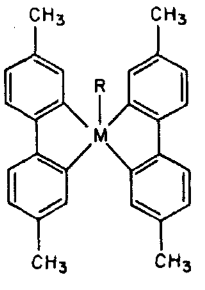


24

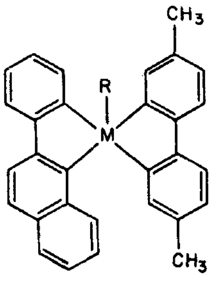
spectral transformation of two to one methyl and perfluoromethyl NMR signals, respectively, near 100°, supports more rapid pseudorotations.[54] To bring about the latter equivalency passage through a trigonal bipyramid with diequatorial ring placement is required. Activation energies of 18.4 kcal/mol for **23**[54a] and 18.8 kcal/mol for **24** (R = H)[54b] have been obtained. To achieve this ligand exchange, at least two Berry pseudorotations take place. In the first, one ring oxygen atom acts as the pivotal ligand, i.e., occupies the apical position of the rectangular pyramidal transition state, and in the second the other oxygen atom of the same ring acts as the pivotal ligand. In the case of the cyclic sulfuranes proceeding by this proces,[55] the highly electropositive lone pair would have to occupy an apical position of the intermediate trigonal bipyramid. The additional energy is estimated to be at least 7 kcal/mol relative to the placement of a proton in this position for the phosphoranes.[56]

On the other hand, cyclic arsoranes appear to undergo ligand exchange at least as facile as cyclic phosphoranes. Arsorane **2**, for example, has a $\Delta G^\ddagger$ value of 22.2 kcal/mol[57a] corresponding to exchange through a TP with diequatorial ring placement (T_c = 178°C), whereas phosphorane **24** (R = PhS) has a $\Delta G^\ddagger$ value of 22.4 kcal/mol[54b] for exchange involving the same type of process (T_c = 180°C). Similar values for exchange for a number of related arsoranes have been reported.[57] In these arsorane compounds, as in the tetraoxyphosphoranes, exchange corresponding to the simple type of Berry process shown above for sulfurane **10** is not slowed at the lowest temperatures studied.

The nonrigid character of the group 5A elements follows the order Sb > As > P in the spirocyclic bis(biarylene) series **25** and **26**. NMR exchange energies (kcal/mol)



R = biphenyl,
series 25



R = phenyl,
series 26

for a simple Berry process (cf. that for sulfurane **10**) for series **25** are 15.7 (P),[58a] 15.4 (As),[58b] and 11.5 (Sb),[58c] and for series **26**, pseudorotation through a TP exchange intermediate having a ring in a diequatorial position gives $\Delta G^\ddagger$ values[58d] of 18.2 (P), 17.2 (As), and 15.4 (Sb).[59] The decreased rigidity on going to the heavier elements is consistent with a reduction in both electron-pair repulsion effects and steric requirements. The same order of nonrigidity is obtained in the acyclic fluorides, AsF_5 > PF_5.[2,28] The use of less electronegative central atoms reduces the energy difference which favors the TP over the SP according to VSEPR theory.[45b]

APPLICATION TO RIBONUCLEASE ACTION

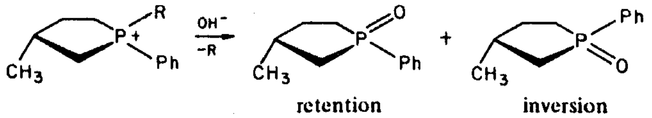
Knowledge of structural parameters on cyclic-containing pentacoordinated phosphorus compounds enables a detailed interpretation of ribonuclease action on uridylyl-(3′–5′)-adenosine.[60] The enzyme mechanism was outlined via a molecular mechanics approach and found to be consistent with the main features summarized by Roberts *et al.*[61] As found for other phosphoryl and nucleotidyl transfer enzyme reactions,[62] phosphorus is poised for incipient nucleophilic attack, leading to a pentacoordinate transition state. In the RNase action, the structure of the transition state is intermediate between a TP and SP along the Berry coordinate.[60]

ISOMER MODEL AND REACTION MECHANISMS

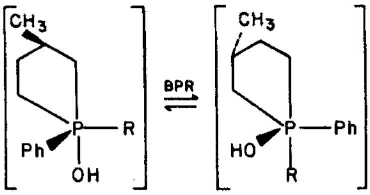
Given the wide accumulation of information on dynamic and static structures of pentacoordinated molecules, it would appear desirable to place this information in a readily available form for systematic application to new problems. As a first attempt in this direction, we have constructed a quasi-quantitative model which estimates the relative energies of all possible trigonal-bipyramidal and square-pyramidal isomers for a given phosphorane.[6] Numerical values are assigned to specific steric, ring strain, and π-bonding terms as well as to element effects appropriate to each of the positions in the TP and SP structures. The model gives relative isomer energies in excellent agreement with those obtained from ab initio calculations[30d] on acyclic phosphoranes and reproduces measured $\Delta G^{\ddagger}$ values for intramolecular ligand exchange processes on cyclic and acyclic derivatives to within ± 1.5 kcal/mol.[6]

A model of this sort is potentially applicable in the area of reaction mechanisms, i.e., to those which are postulated to be controlled by the formation of five-coordinate intermediates. The possibility of pseudorotational processes occurring during the lifetime of any intermediates in the case of phosphorus reactions must be taken into consideration. By estimating the relative energies of the various isomers encountered in these processes, one should be able to determine the most likely mechanistic pathway.

Although the amount of data available to calibrate such a model is as yet slight, qualitative applications are possible. To cite one of many examples, alkaline cleavage of chiral phosphonium salts of varying ring size shows retention and inversion of configuration directly related to the relative stability of five-coordinate intermediates.[63] A five-membered ring will experience less strain when spanning apical-equatorial positions than when located diequatorially in a trigonal bipyramid. When the leaving group (R) is benzyl, 100% retention is observed in the phosphine oxide formed. Pseudorotation of the initial intermediate is required to bring the leaving group to an apical position (groups are postulated to enter and depart from the



more weakly bonding apical sites). When R is methoxy, a more apicophilic group, about 50% inversion is detected in the oxide product.[64a] The five-coordinate intermediate would involve direct displacement of R with diequatorial ring placement. The same trend is observed with the corresponding chiral six-membered ring



salts,[64] but 100% inversion occurs with methoxide as the departing group since less strain is encountered for diequatorial placement of the larger ring. In the related chiral seven-membered ring derivative, even with R as benzyl 100% inversion is obtained.[65] These results are consistent with pentacoordinate principles.

Reactions of derivatives of some of the other main group elements proceeding through postulated five-coordinated states are not as well defined,[7b] particularly those of cyclic derivatives, although significant application of the principles discussed herein have been made in the case of reaction mechanisms involving silicon[7b,66] chemistry.

In silicon chemistry, the observance of inversion of configuration in displacement mechanisms involving good departing groups but a retention mechanism for poorer departing groups[66] has a general parallel in phosphorus chemistry. The determination of a cyclic pentacoordinate silicon structure[50] (displaced 30% from the TP on the Berry coordinate, Figure 4) and NMR exchange behavior of SiF_4^-, $RSiF_5^-$, and $R_2SiF_3^-$[67] analogous to the phosphorus series suggests that pseudorotational schemes, which have on occasion been advanced[66e–h] (some involving cyclic components), will receive increasing attention in the future. However, the structural basis for pentacoordinated silicon must be strengthened considerably before meaningful comparisons may be realized.

Although mechanisms for silicon and phosphorus reactions, featuring isostructural pentacoordinated intermediates, are expected to resemble one another, this is not the case with reactions of sulfur. In view of the observations mentioned above on structural and fluxional aspects of cyclic sulfuranes, it would appear that pseudorotations will be a less common occurrence. Also the ease of placing a five-membered ring in a diequatorial position of a TP (sulfurane **9**) suggests enhancement of an inversion mechanism for chiral cyclic derivatives.[68] For reactions of substitution at sulfur,[7b,69] one has yet to establish the need for invoking a pentacoordinated intermediate with any degree of certainty. In large measure, the same may be said for reactions of arsenic and antimony derivatives. In these cases competing processes,[5] dissociation and fission mechanisms, formation of hexacoordinated species, and polymerization processes, take over to a large extent in determining product formation.

Future studies in this area are expected to provide greater definition of similarities and differences in structural preferences among pentacoordinated main-group elements. It should then be possible to decide the role of postulated pentacoordinated species in reaction mechanisms with increased certainty, regarding both their existence and relative nonrigidity.

ACKNOWLEDGEMENT

Grateful appreciation is expressed to the National Institutes of Health and the National Science Foundation for support of much of the work of the author and his collaborators presented here. I am also deeply indebted to the valuable contributions of my colleagues, past and present, in these studies, particularly those of Professors Roberta O. Day and Joan A. Deiters.

Robert R. Holmes received his Ph.D. in 1953 with H. C. Brown at Purdue University. He taught at the Carnegie Institute of Technology for 9 years and then joined the technical staff at Bell Laboratories. Murray Hill, N. J. In 1966 he assumed his present position at the University of Massachusetts, Amherst, as Professor of Inorganic Chemistry.

REFERENCES AND NOTES

1. (a) W. C. Hamilton, S. J. LaPlaca, F. Ramirez and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 2268 (1967). (b) R. D. Spratley, W. C. Hamilton and J. Ladell, *ibid.* **89**, 2272 (1967).
2. R. R. Holmes, *Acc. Chem. Res.*, **5**, 296 (1972).
3. R. R. Holmes and J. A. Deiters, *J. Am. Chem. Soc.*, **99**, 3318 (1977); and references cited therein.
4. R. R. Holmes, "Spectroscopy and Structure of Pentacoordinated Phosphorus Compounds—With Application to Reaction Mechanisms"; ACS Monograph Series No. 175, in press; and references cited therein.
5. R. Luckenbach, "Dynamic Stereochemistry of Pentaco-ordinated Phosphorus and Related Elements"; Georg Thieme Verlag: Stuttgart, 1973; and references cited therein.
6. R. R. Holmes, *J. Am. Chem. Soc.*, **100**, 433 (1978).
7. (a) F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968). (b) K. Mislow, *ibid.* **3**, 321 (1970). (c) F. Ramirez, *ibid.* **1**, 168 (1968).
8. E. L. Muetterties and R. A. Schunn, *Q. Rev. Chem. Soc.*, **20**, 245 (1966); and references cited therein.
9. (a) J. C. Martin and E. F. Perozzi, *Science*, **191**, 154 (1976); and references cited therein. (b) B. Dahlen and B. Lindgren, *Acta Chem. Scand.*, **27**, 2218 (1973); and references cited therein. (c) R. R. Holmes and R. O. Day, 178th National Meeting of the American Chemical Society, Washington, D.C., Sept. 1979, INOR.
10. T. E. Clark, R. O. Day and R. R. Holmes, *Inorg. Chem.*, **18**, 1653 (1979).
11. W. S. Sheldrick, personal communication. A. Schmidpeter, D. Schomburg, W. S. Sheldrick and J. H. Weinmaier, *Angew. Chem.*, **88**, 851 (1976).
12. E. Duff, D. R. Russell and S. Trippett, *Phosphorus*, **4**, 203 (1974).
13. H. L. Carrell, H. M. Berman, J. S. Ricci, Jr., W. C. Hamilton, F. Ramirez, J. F. Marecek, L. Kramer and I. Ugi, *J. Am. Chem. Soc.*, **97**, 38 (1975),
14. R. K. Brown, R. O. Day, S. Husebye and R. R. Holmes, *Inorg. Chem.*, **17**, 3276 (1978).
15. R. O. Day, A. C. Sau and R. R. Holmes, *J. Am. Chem. Soc.*, **101**, (1979) in press.
16. P. Narayanan, H. M. Berman, F. Ramirez, J. F. Marecek, Y.-F. Chaw and V. A. Prased, *J. Am. Chem. Soc.*, **99**, 3336 (1977).
17. H. Wunderlich and D. Mootz, *Acta Crystallogr., Sect. B.*, **30**, 935 (1974).
18. R. K. Brown and R. R. Holmes, *Inorg. Chem.*, **16**, 2294 (1977).
19. T. E. Clark, R. O. Day and R. R. Holmes, *Inorg. Chem.*, **18**, 1660 (1979).
20. R. Sarma, F. Ramirez and J. F. Maracek, *J. Org. Chem.*, **41**, 473 (1976).
21. T. E. Clark, R. O. Day and R. R. Holmes, *Inorg. Chem.*, **18**, 1668 (1979).
22. R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
23. I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie and F. Ramirez, *Acc. Chem. Res.*, **4**, 288 (1971); F. Ramirez and I. Ugi, *Bull. Soc. Chim. Fr.*, 453 (1974).
24. (a) M. Eisenhut, H. L. Mitchell, D. D. Traficante, R. J. Kaufman, J. M. Deutch and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 5385 (1974). (b) G. M. Whitesides and H. L. Mitchell, *ibid.* **91**, 5384 (1969). (c) G. M. Whitesides and W. M. Bunting, *ibid.* **89**, 6801 (1967).
25. (a) L. S. Bartell, *Inorg. Chem.*, **9**, 1594 (1970). (b) K. W. Hansen and L. S. Bartell, *ibid.* **4**, 1775 (1965). (c) L. S. Bartell and K. W. Hansen, *ibid.* **4**, 1777 (1965). (d) H. Yow and L. S. Bartell, *J. Mol. Structure*, **15**, 209 (1973).
26. (a) R. R. Holmes and J. A. Golen, *Inorg. Chem.*, **9**, 1596 (1970). (b) P. Lockett, W. Fowler and

P. M. Wilt, *J. Chem. Phys.*, **53**, 452 (1970). (c) L. S. Bartell and V. Plato, *J. Am. Chem. Soc.*, **95**, 3097 (1973). (d) R. R. Holmes, R. M. Deiters and J. A. Golen, *Inorg. Chem.*, **8**, 2612, Field B (1969). (e) Ref 4, Chapter 4.

27. R. R. Holmes, L. S. Couch and C. J. Hora, Jr., *J. Chem. Soc., Chem. Commun.*, 175 (1974).
28. L. S. Bernstein, S. A. Abramowitz and I. W. Levin, *J. Chem. Phys.*, **64**, 3228 (1976); L. S. Bernstein, J. J. Kim, K. S. Pitzer, S. Abramowitz and I. W. Levin, *J. Chem. Phys.*, **62**, 3671 (1975).
29. Thus, the information of a square-pyramidal exchange barrier having trans basal angles of about 150° implied by the Berry coordinate is in agreement with the vibrational interpretation. See ref 2, p. 300.
30. (a) R. Hoffmann, J. M. Howell and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 3047 (1972). (b) A. Strich and A. Veillard, *ibid.* **95**, 5574 (1973). (c) J. A. Altmann, K. Yates and I. G. Csizmadia, *ibid.* **98**, 1450 (1976). (d) A. Rauk, L. C. Allen and K. Mislow, *ibid.* **94**, 3035 (1972).
31. R. P. Carter, Jr. and R. R. Holmes, *Inorg. Chem.*, **4**, 738 (1965).
32. E. L. Muetterties, *Acc. Chem. Res.*, **3**, 266 (1970).
33. R. R. Holmes, *J. Am. Chem. Soc.*, **97**, 5379 (1975).
34. In view of the existence of spirocyclic phosphorane structures closely approaching the rectangular pyramid (Figure 1), reconsideration of their solution-phase NMR data is in order. The data have in general been interpreted in terms of ground-state TP structures.[6]
35. (a) W. Althoff, R. O. Day, R. K. Brown and R. R. Holmes, *Inorg. Chem.*, **17**, 3265 (1978). (b) J. S. Szobota and R. R. Holmes, *Inorg. Chem.*, **16**, 2299 (1977). (c) J. R. Devillers and R. R. Holmes, *J. Am. Chem. Soc.*, **99**, 3332 (1977). (d) R. K. Brown and R. R. Holmes, *ibid.* **99**, 3326 (1977).
36. P. F. Meunier, R. O. Day, J. R. Devillers and R. R. Holmes, *Inorg. Chem.*, **17**, 3270 (1978).
37. J. A. Deiters, J. C. Gallucci, T. E. Clark and R. R. Holmes, *J. Am. Chem. Soc.*, **99**, 5461 (1977).
38. P. F. Meunier, J. A. Deiters and R. R. Holmes, *Inorg. Chem.*, **15**, 2572 (1976).
39. R. R. Holmes, *J. Am. Chem. Soc.*, **96**, 4143 (1974).
40. J. A. Howard, D. R. Russell and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 856 (1973).
41. H. Wunderlich, personal communication.
42. (a) N. J. De'Ath, D. Z. Denney and D. B. Denney, *J. Chem. Soc., Chem. Commun.*, 272 (1972). (b) N. J. De'Ath, D. B. Denney, D. Z. Denney and Y. F. Hsu, *J. Am. Chem. Soc.*, **98**, 768 (1976).
43. E. L. Muetterties, W. Mahler and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).
44. H. A. E. Aly, J. H. Barlow, D. R. Russell, J. H. Smith, M. Swindles and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 449 (1976).
45. (a) R. J. Gillespie, *Inorg. Chem.*, **5**, 1634 (1966). (b) R. J. Gillespie, "Molecular Geometry"; Van Nostrand-Reinhold: New York, 1972; and references cited therein.
46. H. Wunderlich, *Acta Crystallogr., Sect. B.*, **30**, 939 (1974).
47. (a) G. Gunderson and K. Hedberg, *J. Chem. Phys.*, **51**, 2500 (1969). (b) W. M. Tolles and W. G. Gwinn, *ibid.* **36**, 1119 (1962). (c) K. Kimura and S. H. Bauer, *ibid.* **39**, 3172 (1963).
48. (a) N. C. Baenziger, R. E. Buckles, R. J. Maner and T. D. Simpson, *J. Am. Chem. Soc.*, **91**, 5749 (1969). (b) E. F. Perozzi, J. C. Martin and I. C. Paul, *ibid.* **96**, 6735 (1974). (c) L. J. Adzima, E. N. Duesler and J. C. Martin, *J. Org. Chem.*, **42**, 4001 (1977). (d) A. Kálmán, K. Sasvári and I. Kapovits, *Acta Crystallogr., Sect B*, **29**, 355 (1973). (e) L. J. Adzima, C. C. Chiang, I. C. Paul and J. C. Martin, *J. Am. Chem. Soc.*, **100**, 953 (1978). (f) K. C. Hodges, D. Schomburg, J.-V. Weiss and R. Schmutzler, *ibid.* **99**, 6096 (1977). (g) I. C. Paul, J. C. Martin and E. F. Perozzi, *ibid.* **93**, 6674 (1971). (h) E. F. Perozzi and J. C. Martin, personal communication.
49. (a) A. C. Skapski, *Chem. Commun.*, 10 (1966). (b) H. Goldwhite and R. G. Teller, *J. Am. Chem. Soc.*, **100**, 5357 (1978). (c) H. Wunderlich. Third European Crystallographic Meeting, Zurich, Switzerland, 1976, 054D.
50. Boer, F. P., J. J. Flynn and J. W. Turley, *J. Am. Chem. Soc.*, **90**, 6973 (1968).
51. I. W. Levin and W. C. Harris, *J. Chem. Phys.*, **55**, 3048 (1971).
52. G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, **98**, 2895 (1976). See also Belkind *et al.* [B. A. Belkind, D. B. Denney, D. Z. Denney, Y. F. Hsu and G. E. Wilson, Jr., *J. Am. Chem. Soc.*, **100**, 6327 (1978)] for a related study.
53. A known exception involves the slow ligand reorganization observed between room temperature and −65°C the sterically hindered methyltetrakis(2,6-dimethylphenoxy)phosphorane. I. Szele, S. J. Kubisen, Jr. and F. H. Westheimer, *J. Am. Chem. Soc.*, **98**, 3533 (1976).
54. (a) D. Houalla, R. Wolf, D. Gagnaire and J. B. Robert, *Chem. Commun.*, 443 (1969). (b) S. Bone, S. Trippett and P. J. Whittle, *J. Chem. Soc., Perkin Trans.* **1**, 2125 (1974).
55. Martin and Perozzi also consider other high-energy exchange processes: the possibility of a direct inversion process through a planar intermediate, analogous to pyramidal inversion, and the formation of a zwitterion intermediate.[9,52]
56. Using the model discussed in the last part of this Account and taking into consideration the electronegativity difference between P and S, a 7 kcal/mol estimate is obtained.

57. (a) J. P. Casey and K. Mislow, *Chem. Commun.*, 1410 (1970). (b) A. J. Daly and P. Frøyen, *Acta Chem. Scand.*, **B29**, 741 (1975).
58. (a) D. Hellwinkel, *Chimia*, **22**, 488 (1968). (b) D. Hellwinkel and B. Knabe, *Phosphorus*, **2**, 129 (1972). (c) D. Hellwinkel and M. Bach, *Naturwissenschaften*, **56**, 214 (1969). (d) D. Hellwinkel, W. Lindner and W. Schmidt, Personal communication.
59. Although no structural details appear to be available for bis(biarylene)stiboranes (however, see Hellwinkel, D. [*Chem. Ber.*, **99**, 3628 (1966)], which mentions a TP structure for a derivative analogous to 25), we recently completed X-ray studies on samples (kindly supplied by D. Hellwinkel) of several phosphorane derivatives of the series 25 (R = methyl, phenyl, α-naphthyl, and 8-dimethylamino-1-naphthyl) and found near-TP structures. The low-temperature ^{1}H NMR pattern showing four methyl signals is also consistent with TP structures.
60. R. R. Holmes, J. A. Deiters and J. C. Gallucci, *J. Am. Chem. Soc.*, **100**, 7393 (1978). See also R. R. Holmes, *Int. J. Peptide Protein Res.*, **8**, 445 (1976).
61. G. C. K. Roberts, E. A. Dennis, D. H. Meadows, J. S. Cohen and O. Jardetzky, *Proc. Natl. Acad. Sci. U.S.A.*, **62**, 1151 (1969).
62. A. S. Mildvan, *Acc. Chem. Res.*, **10**, 246 (1977).
63. (a) W. Egan, G. Chauviere, K. Mislow, R. T. Clark and K. L. Marsi, *Chem. Commun.*, 733 (1970). (b) K. L. Marsi, F. B. Burns and R. T. Clark, *Org. Chem.*, **37**, 238 (1972). (c) K. L. Marsi and J. E. Oberlander, *J. Am. Chem. Soc.*, **95**, 200 (1973).
64. (a) K. L. Marsi, *J. Org. Chem.*, **40**, 1779 (1975). (b) K. L. Marsi and R. T. Clark, *J. Am. Chem. Soc.*, **92**, 3791 (1970).
65. K. L. Marsi, *ibid.* **93**, 6341 (1971).
66. (a) O. W. Steward, *J. Organomet. Chem.*, **109**, 179 (1976). (b) R. L. Hilderbrandt, G. D. Homer and P. Boudjouk, *J. Am. Chem. Soc.*, **98**, 7476 (1976). (c) R. J. P. Corriu and M. Henner, *J. Organomet. Chem.*, **74**, 1 (1974). (d) D. S. Matteson, "Organometallic Reaction Mechanisms of the Nontransition Elements"; Academic Press: New York, 1974. (e) L. H. Sommer, *Intra-Sci. Chem. Rept.*, **7**, 1 (1973). (f) R. H. Prince. In "Reaction Mechanisms in Inorganic Chemistry," M. L. Tobe, Ed.; Inorganic Chemistry Series One, Vol. 9; Butterworths: London, 1972, p. 353. (g) K. Tamao, M. Ishikawa and M. Kumada, *Chem. Commun.*, 73 (1969). (h) L. H. Sommer and D. L. Bauman, *J. Am. Chem. Soc.*, **91**, 7045 (1969). (i) L. H. Sommer, "Stereochemistry, Mechanism and Silicon"; McGraw-Hill: New York, 1965.
67. F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **7**, 155 (1968).
68. A case in point involves the inversion of configuration obtained for base hydrolysis of *cis*- and *trans*-1-ethoxy-3-methylthietanium ions: R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **91**, 5644 (1969). This is analogous to inversion of configuration of $\overline{C(CH_3)_2C(CH_3)C(CH_3)_2P}Cl$ (D. J. H. Smith and S. Trippett, *Chem. Commun.*, 855 (1969)), which also may proceed via a diequatorially placed ring system.[4]
69. (a) B. M. Trost, *Top. Curr. Chem.*, **41**, 1 (1973). (b) E. T. Kaiser and O. R. Zaborsky, *J. Am. Chem. Soc.*, **90**, 462 (1968). (c) K. F. Purcell and J. C. Kotz, "Inorganic Chemistry"; W. B. Saunders Co.: Philadelphia, 1977, p. 441.