

A Model for Calculating Conformational Energies in Pentacoordinate Phosphorus Compounds^{1,2}

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Abstract: A model is developed which allows the estimation of the relative stability of all trigonal bipyramidal (TP) and square pyramidal (SP) isomers of a given pentacoordinate phosphorus compound. It is based on the widely used pseudorotational hypothesis. The model makes use of activation energies governing fluxional behavior for simple acyclic derivatives of known structure and results of theoretical and spectroscopic studies defining TP-SP energy differences. Based on these criteria, apico-philarity scales are constructed for the TP and SP with the additional constraints that they have the same range and correlate linearly with each other as a function of ligand electronegativity. The resultant model which incorporates ring strain and steric terms has general applicability and should prove of considerable predictive value in quantifying pentacoordinate intermediates and transition states postulated in phosphorus reaction mechanisms. The model gives relative isomer energies in excellent agreement with those obtained from ab initio calculations and reproduces measured ΔG^\ddagger for intramolecular ligand exchange on cyclic and acyclic derivatives to within ± 1.5 kcal/mol.

Introduction

In order to evaluate possible mechanistic alternatives in phosphorus reactions proceeding via postulated pentacoordinate intermediates,³ it would be highly desirable to have the means of comparing the relative energies of the various isomers that may be involved. Not only is the structure of the intermediate or transition state of concern but also whether the entity postulated undergoes intramolecular reorientation during its lifetime.

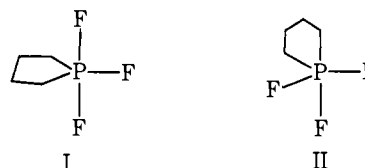
It appears that sufficient information is at hand to construct a suitable model which would have predictive value in ascertaining the course of a chemical reaction in phosphorus chemistry. There are three principal sources of information. These are (1) structural and spectroscopic studies which establish the ground state configuration of isolatable pentacoordinate phosphorus compounds,^{4,5} (2) theoretical studies⁶⁻¹³ defining trigonal bipyramidal (TP)-square pyramidal (SP) energy differences for simple acyclic derivatives, and (3) temperature-dependent NMR studies¹⁴⁻²⁸ yielding energies of activation governing fluxional behavior of both acyclic and cyclic derivatives.

Structurally, the trigonal bipyramid is the most stable conformer for acyclic and monocyclic five-coordinate phosphorus compounds.^{4,5} However, in derivatives²⁹⁻³¹ containing multiple small-membered rings coupled with the presence of electronegative ligands and ring unsaturation, the square or rectangular pyramid (RP) may become the most stable conformer. In all derivatives, two generalizations regarding positioning of ligands prevail, the "element effect", which states that the most electronegative groups prefer to locate at apical positions,³² and the "ring strain" rule, which suggests that less strain results if four- and five-membered rings locate preferentially in apical-equatorial positions rather than in diequatorial positions of a trigonal bipyramid.^{3a,20-24,27,32-35}

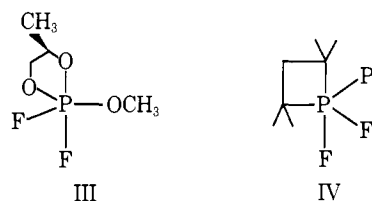
In comparing the TP with the SP, similar rules may be invoked for these two effects in the SP. The most electronegative ligands prefer basal positions and small-membered rings preferentially occupy dibasal positions. These "rules" are based on considerations⁵ for an idealized SP having an apical-basal angle of 105° . This geometry is thought to represent the most stable conformer⁷ and is the one postulated in a Berry pseudorotation for PF_5 .³⁶

With the dominant importance of these two effects in each of the two basic pentacoordinate structures, one has little difficulty in representing the lowest energy TP or lowest energy SP isomer, even for derivatives containing a variety of sub-

stituents. Difficulty arises when the two rules set up a competition for ligand sites. Thus, $(\text{CH}_2)_4\text{PF}_3$ is assigned the structure³² I based on low-temperature NMR data rather than

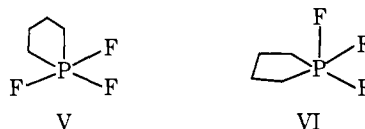


II, whereas, when the electronegativity of the ligands does not differ as widely as C and F, as in III, the strain rule becomes dominant.³⁷ If one goes to a four-membered ring, however, e.g., IV, even with ligands differing widely in electronegativity, the



fluorine atom appears to be displaced from its usual location at an apical site.³⁸ Although it is understandably more difficult to locate a four-membered ring in diequatorial positions of a TP, it would be advantageous to quantify substituent effects to resolve possible ambiguities.

Furthermore, one can argue that the NMR information which supported the structural conclusions in these examples also does not rule out the possibility of a SP representation. As an example, for $(\text{CH}_2)_4\text{PF}_3$, the SP isomers V and VI each

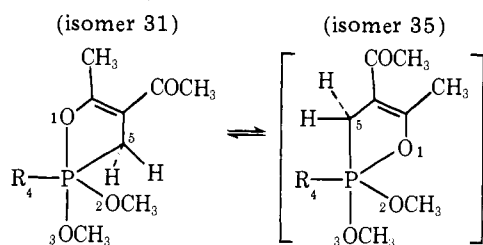


have two fluorine atom environments consistent with the ^{19}F NMR data at -80°C , and presumably would have less ring strain than I since the angle distortion from the 90° "strain-free" ring angle at phosphorus to the phosphorus angles existing in the idealized TP is more than the corresponding angle distortions necessary to reach the idealized SP (90° C-P-C angle $\rightarrow 105^\circ$ in V and essentially no change in forming VI). Hence, it appears necessary to sequence not only TP isomers in terms of relative energy but also both TP and SP isomers in one self-contained series.

We shall attempt the construction of a model of this sort, embodying the concepts outlined above. This will be done in terms of a numerical scale which will allocate a different value for each ligand, the value being a function of the position occupied in the TP or SP structure. In addition the presence of a ring strain term and a steric factor will be incorporated. In a more limited sense, π -bonding effects will be considered.

General Considerations

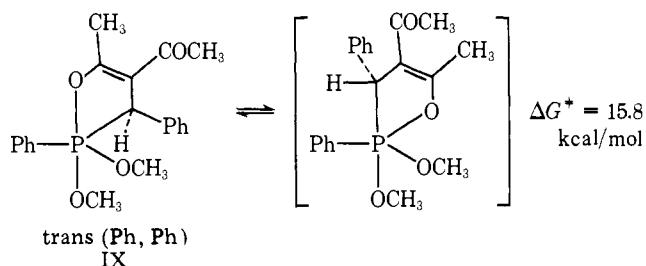
In order to see how a scale might be formulated in a qualitative manner, consider the following observations. Gorenstein²⁰ found that the free energy of activation for pseudorotation of the adduct of trimethyl phosphite and methyl vinyl ketone (VII) in methylene chloride-*d*₂ solution obtained from



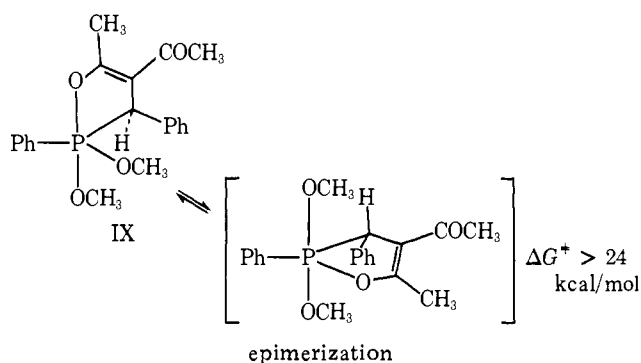
VII, R = OCH₃
VIII, R = Ph

analysis of ¹H NMR spectra run at 100 MHz is 9.6 ± 0.2 kcal/mol. He reported a²⁰ similar value, $\Delta G^\ddagger = 9.5 (9.9) \pm 1$ kcal/mol, from line shape analysis of the adduct of dimethyl phenylphosphonite with methyleneacetylacetone (VIII) in methylene chloride-*d*₂ at 100 MHz. The pseudorotation, assuming the Berry mechanism, is conventionally reported to proceed via the least stable TP, shown in brackets. The similar values are not surprising since, in each case, a difference in apicophilicity between an oxygen and a carbon atom appears to be the major factor involved in reaching the transition state.

For a more highly substituted ring derivative, additional NMR exchange processes may be observed. For example, the addition product of dimethyl phenylphosphonite and benzylideneacetylacetone, IX, undergoes isomerization and, at higher temperature, epimerization.



isomerization



epimerization

The respective activation energies, ΔG^\ddagger , are 15.8 and >24 kcal/mol,²⁰ presumably associated with the transition states.

Comparison of ground and transition states for the isomerization for IX with these states for the exchange process for VIII suggests that the near 6 kcal/mol difference in ΔG^\ddagger between the two processes is associated with a steric affect²⁰ due to the presence of the ring phenyl substituent in IX. For the epimerization of IX, the ΔG^\ddagger value appears to approximate the increase in strain energy associated with orienting the five-membered ring in diequatorial positions of a TP compared to the relatively strain-free apical-equatorial arrangement, since the ligand electronegativities are comparable in the ground and postulated transition states.

Proceeding in this manner, using ΔG^\ddagger data for other non-rigid phosphorus derivatives, our resultant model would be limited to the estimations of relative energies for TP isomers. In fact, for the processes associated with derivatives VII-IX above, the transition states may be better represented by SP rather than TP isomers.

The Berry mechanism,³⁶ which serves as a model for the postulated pseudorotations, involves the simultaneous bending of a pair of equatorial and a pair of apical bonds, causing the formation of an intermediate SP on the way to the interconverted trigonal bipyramid.

These interconversions have been summarized most conveniently in terms of topological representations³⁹ such as the one shown in Figure 1. The edges represent square pyramidal states under the Berry hypothesis. Equally well, topological maps represent the turnstile process⁴⁰ since this process is permutationally indistinguishable from the Berry process. If turnstile rotation is invoked, then the edges represent the transition state peculiar to that mechanism.⁴⁰ However, since most of the literature of interest here has been interpreted in terms of the Berry pseudorotational process, and both theoretical estimates^{7-10,13,41} and solid-state structural distortions^{5a} favor the Berry process, we will not consider the turnstile process further.

The relationship between a postulated SP and TP transition state may be seen more clearly by examination of the complete interconversions accompanying the isomerization (Figure 2) and epimerization (Figure 3) of the addition product of IX. With reference to the topological diagram³⁹ in Figure 1, the highest energy TP conformations that must be traversed for the isomerization process are the 35 and 52 isomers while the highest energy SPs are 2 and 3. For the epimerization of 31 to occur, a higher energy TP containing a diequatorial ring must be reached. This is the 23 isomer connecting the isomerization routes. The latter are shown by heavy solid lines in Figure 1. The high-energy SP isomer for this process is 1. As a result, if effective comparisons are to be made, it becomes necessary to devise complementary scales which will establish an order of isomer energies involving both trigonal bipyramidal and square pyramidal conformations. The best place to begin is with the simpler acyclic phosphoranes so that ring strain and steric factors do not unnecessarily complicate the problem.

Model Construction

Both experimentally and theoretically, the most studied pentacoordinate molecule is PF₅ whose ligands are presumed to exchange rapidly on the NMR time scale even down to -200 °C.^{42,43} Various estimates⁹⁻¹² put the energy difference between the SP and TP around 4 kcal/mol. A recent two-dimensional potential function applied to spectroscopic data has led to an estimate¹³ near 3 kcal/mol while an ab initio calculation gave 4.8 kcal/mol.⁷ Furthermore, interpretation of the spectroscopic data indicates that indeed the Berry process is operating in PF₅.¹³ For both PCIF₄ and PCl₂F₃, temperature-dependent NMR studies gave exchange barriers of 4.2¹⁴ and 7.2 kcal/mol,¹⁶ respectively. For H₂PF₃¹⁷ and (CH₃)₂PF₃,¹⁹ similar studies gave values of 10.2 and 17.8 kcal/mol,

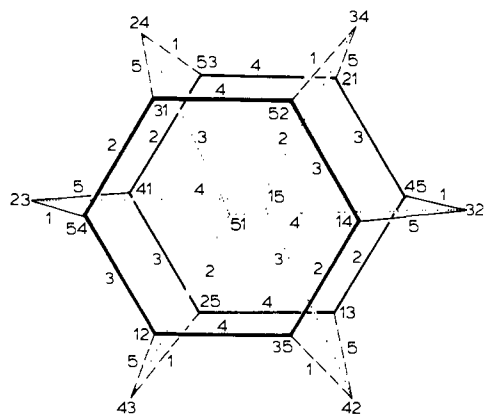


Figure 1. Topological diagram³⁹ for pseudorotations summarizing isomerization (heavy solid lines) and epimerization processes (light solid lines) for compound IX (see Figures 2 and 3). Higher energy epimerizations are shown by dashed lines and forbidden isomerizations for IX are indicated by dotted lines. The numbers refer to the axial positions in the TP or apex position in the SP as shown in Figures 2 and 3. The placement of basal ligands in the SP is established by the pairs of numbers identifying the two connecting TPs. These will be trans pairs in the SP.

respectively, for ligand exchange in these fluxional molecules.

Although it is probable that the exchange barrier cited for PClF_4 represents an energy difference between the ground state TP and transition state SP, since one ligand acts as a pivot in the favored Berry process,⁴⁴ the exchange barriers for PCl_2F_3 , $(\text{CH}_3)_2\text{PF}_3$, and H_2PF_3 are more ill defined. Under the Berry pseudorotational hypothesis, one or two pseudorotations are needed to account for the exchange (Figure 4), depending on which process represents the lower energy path. Rauk et al.⁶ performed nonempirical molecular orbital calculations on a model system applicable here, PH_2X_3 (where X is approximately 0.8 unit more electronegative than the proton on the Pauling scale). According to their results, process (b) is favored for PH_2X_3 and the SP isomer of the type F in Figure 4 would represent the barrier configuration, since it is estimated to have the highest energy of the isomers in process (b). Steric factors could alter the preferred exchange route. However, the derivatives PH_2F_3 , PCl_2F_3 , and $(\text{CH}_3)_2\text{PF}_3$ are minimal in that respect.

Proceeding on this basis then, we are in a position to construct an isomer sequencing scale which will be internally calibrated to reproduce the activation energies ΔG^\ddagger for this well-characterized series of acyclic phosphoranes. A numerical value of an element effect, which varies with the position occupied in the TP and SP, will be established for each ligand. This is accomplished by equating the ΔG^\ddagger value for an exchanging member to the difference in the sum of terms representing the positions occupied in the SP transition state $l_i(\text{SP})$, and the TP ground state, $l_i(\text{TP})$.

An additional term must be included to reflect the inherent instability of the acyclic SP relative to the TP. We will refer to this term as Δ . The ΔG^\ddagger value that we adopt for PF_5 places the SP 4 kcal/mol above the TP. However, the phosphorus and fluorine atoms differ in electronegativity by about 2 units. To remove the electronegativity factor which is to be incorporated in the scale itself, ΔG^\ddagger for the hypothetical PY_5 molecule must be obtained where the electronegativities of P and Y are the same. Accordingly, we have

$$\sum l_i(\text{SP}) - \sum l_i(\text{TP}) + \Delta = \Delta G^\ddagger \quad (1)$$

where l_i is the value of the element effect appropriate to the position occupied. For PF_5 ,

$$l(\text{F}_{\text{ap}}) + 4l(\text{F}_{\text{bas}}) - 2l(\text{F}_{\text{ax}}) - 3l(\text{F}_{\text{eq}}) + \Delta = \Delta G^\ddagger(\text{PF}_5) \quad (2)$$

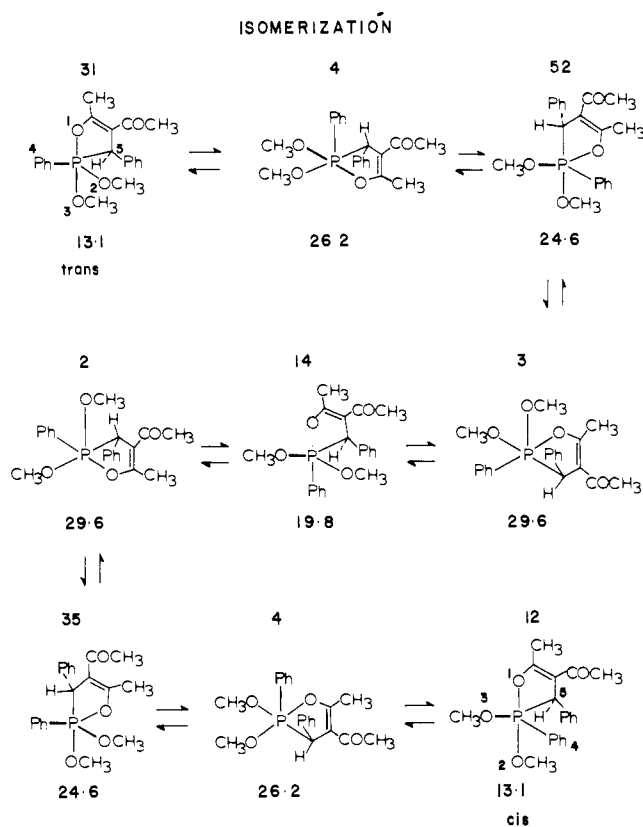


Figure 2. Intramolecular isomerization of the adduct of dimethylphenyl phosphonite and benzylideneacetylacetone IX via the low-energy pseudorotational pathway.³³ The numbers above each structure identify the isomer on the topological diagram shown in Figure 1. The numbers below each structure give the relative isomer energy in kcal/mol via the terms in Tables I, V, and VI.

where ap and bas are the two types of positions in the SP and ax and eq are the two types in the TP. Similarly for $(\text{CH}_3)_2\text{PF}_3$

$$l(\text{F}_{\text{ap}}) + 2l(\text{F}_{\text{bas}}) + 2l(\text{C}_{\text{bas}}) - 2l(\text{F}_{\text{ax}}) - l(\text{F}_{\text{eq}}) - 2l(\text{C}_{\text{eq}}) + \Delta = \Delta G^\ddagger((\text{CH}_3)_2\text{PF}_3) \quad (3)$$

Since the l_i values are relative, we choose zero values for l_C for carbon ligands (assigned an electronegativity of 2 representing one extreme of the scale) which occupies an equatorial TP or the complementary apical SP position. Correspondingly, at the other end of the scale, the element effect for fluorine (electronegativity of 4) is assigned a zero reference value when it is present in an axial TP or complementary basal SP site. This reduces 2 to

$$l(\text{F}_{\text{ap}}) - 3l(\text{F}_{\text{eq}}) + \Delta = \Delta G^\ddagger(\text{PF}_5) \quad (4)$$

and simplifies eq 3 to

$$2l(\text{C}_{\text{bas}}) + l(\text{F}_{\text{ap}}) - l(\text{F}_{\text{eq}}) + \Delta = \Delta G^\ddagger((\text{CH}_3)_2\text{PF}_3) \quad (5)$$

Subtraction of eq 5 from eq 4 gives

$$l(\text{F}_{\text{eq}}) + l(\text{C}_{\text{bas}}) = 6.9 \quad (6)$$

Considerations such as the pseudorotation process discussed for the phosphoranes VII and VIII suggest an apicophilicity difference of the order of 10 kcal between ligands having extremes in electronegativity values. Accordingly, we adopt this range as a convenient one to use for the element scales for both the TP and SP.

It remains to apportion this range in apicophilicities to the equatorial and axial sites of the ground state TP as a function of the ligand electronegativity. Fortunately, the well-studied

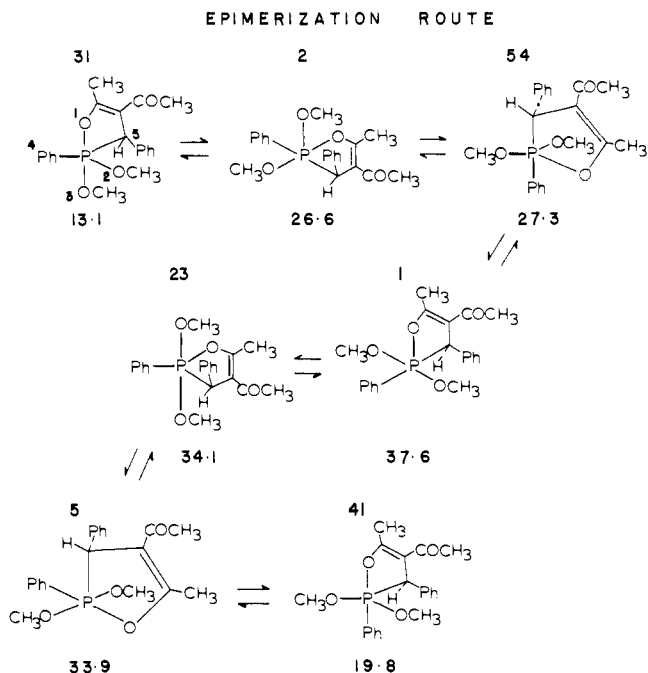


Figure 3. Part of the intramolecular epimerization route of the adduct of dimethyl phenylphosphonite and benzylideneacetylaceton IX via the low-energy pseudorotational pathway.³³ The numbers above each structure identify the isomer on the topological diagram shown in Figure 1. The numbers below each structure give the relative isomer energy in kcal/mol via the entries in Tables I, V, and VI.

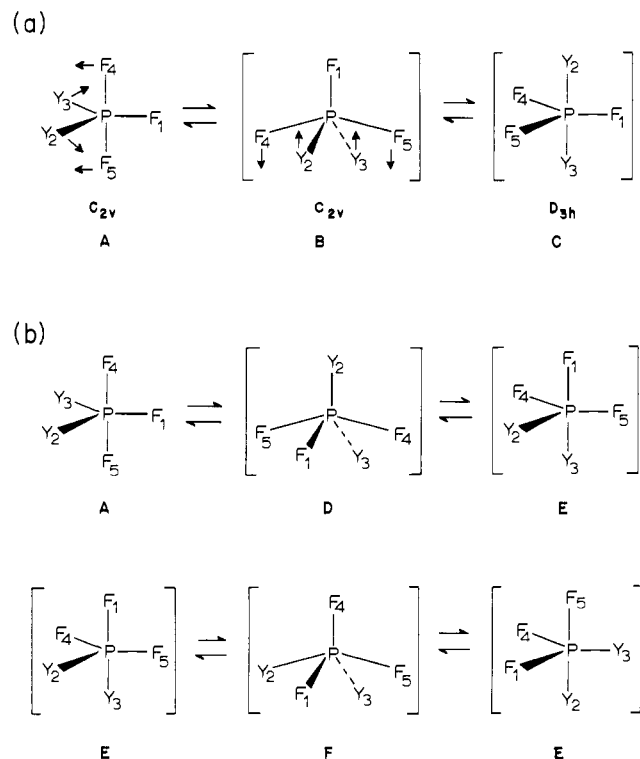


Figure 4. Pseudorotational processes for intramolecular exchange in Y_2PF_3 derivatives: (a) simple Berry process; (b) successive Berry processes. Bracketed isomers represent transition states or intermediates.

series, $(CH_3)_nPF_{5-n}$ ($n = 0-3$), whose structures have been fully characterized by electron diffraction,⁴⁵ allows insight into how the apportionment might be approximated. It is noted that the apical P-F and equatorial P-C bond distances increase nearly linearly with progressive methyl substitution and the percent increase for the axial bond is about twice that for the

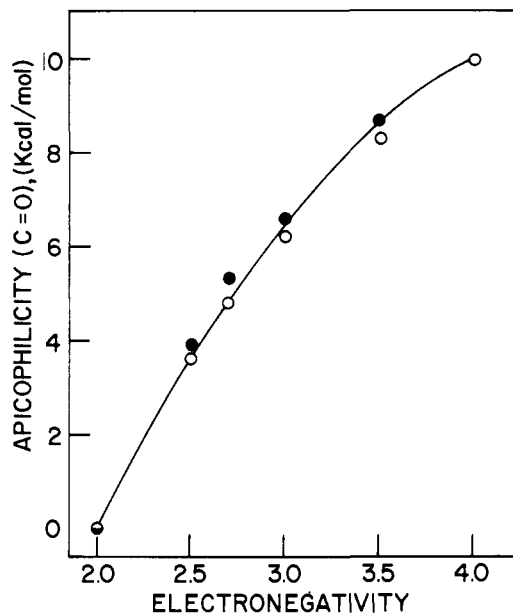


Figure 5. Apicophilicity values (from Table I) relative to the carbon atom set equal to zero (half-filled circle) for the trigonal bipyramid (open circles) and square pyramid (filled circles) as a function of electronegativity.

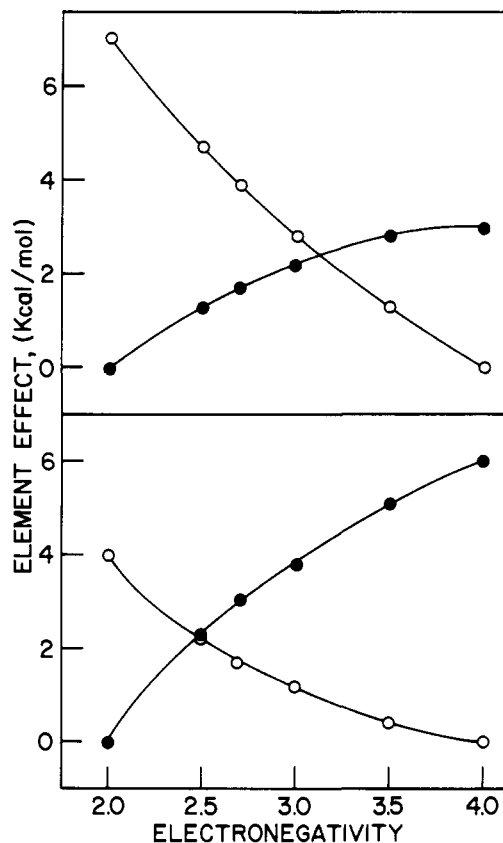


Figure 6. Element effect (from Table I) as a function of electronegativity (upper) for axial (open circles) and equatorial (filled circles) positions of a trigonal bipyramid and (lower) for basal (open circles) and apical (filled circles) positions of a square pyramid.

equatorial changes. The P-F equatorial bond changes are even a more slowly varying function. The greater variation in the axial bonds of the TP are consistent with electron pair repulsion arguments,⁴⁶ while other workers⁴⁷ have shown that axial P-F force constants successively decrease in a linear fashion in accord with the bond distance increase in this series. Conse-

Table I. Relative Values of the Element Effect (l_i) for Use in Estimating Isomer Energies (kcal/mol)^a

	TP			A^b ax-eq	$-A$ (ref C = 0)	SP		$-A^b$ bas-ap	A (ref C = 0)
	χ^c	eq	ax			ap	bas		
C	2	0.0	7.0	7.0	0.0	0.0	4.0	4.0	0.0
H	2.5	1.3	4.7	3.4	3.6	2.3	2.2	-0.1	4.1
Ph	2.7	1.7	3.9	2.2	4.8	3.0	1.7	-1.3	5.3
N, Cl	3.0	2.2	2.8	0.8	6.2	3.8	1.2	-2.6	6.6
O	3.5	2.8	1.3	-1.3	8.3	5.1	0.4	-4.7	8.7
F	4.0	3.0	0.0	-3.0	10.0	6.0	0.0	-6.0	10.0

^a To the sum of these element values for a SP, 7.0 kcal/mol must be added to obtain the energy of an acyclic SP relative to a TP isomer. If steric and/or ring strain effects are present, these terms must be included. Ring strain values are summarized in Table VI and steric effects are listed in Tables V and VII. ^b Relative values for apicophilicity A in a TP (ax-eq) or SP (ap-bas). The smaller or more negative values of A indicate a greater stabilization for a particular element in an apical position of either a TP or SP. ^c Electronegativity scale.

Table II. Comparison of Observed and Calculated Values of ΔG^\ddagger for Intramolecular Ligand Exchange (kcal/mol)

ΔG^\ddagger	PF ₅	PClF ₄	PCl ₂ F ₃	PH ₂ F ₃	P(CH ₃) ₂ F ₃
Calcd.	4.0	2.5	8.0	11.8	18.0
Obs.	4.0 ^a	4.2	7.2	10.2	17.8
Ref ^b	7, 9-13	14	16	17	19

^a As discussed in the text, this is an average value calculated from spectroscopic data and theoretical estimates. It refers to a SP which has an apical basal angle in the range of 101-105°. ^b References for observed ΔG^\ddagger values.

quently, we assign a variation in the element effect to the axial position of the TP about double that for the equatorial site over the range of the electronegativity scale. In other words, with $l(C_{eq}) = 0$, the element effect, $l(F_{eq})$, is assigned a value of 3. This leaves a value of 7 for $l(C_{ax})$.

Having fixed the value of the element effect of the axial fluorine atom in a TP, the value of $l(C_{bas})$ in a SP is obtained from eq 6 as 3.9. With this value rounded to 4, and noting that we are using the same range of apicophilicity values for the SP and the TP (namely, 10), the element effect for an apical fluorine atom in the SP results as $l(F_{ap}) = 6$. From expression 4 or 5 then, Δ of 7 is obtained.

A smooth variation in the values of the element effects as a function of electronegativity is expected. Under the constraints already defined, a linear variation was at first used, but later modified slightly to get a best fit with the ΔG^\ddagger values for the acyclic derivatives employed to calibrate the apicophilicity scales. Making the range in apicophilicities for the SP different from that for the TP did not improve the fit. The resultant values of the element effects are summarized in Table I and a plot of the apicophilicities for the TP ($-A$, column 6) and SP (A , column 10) vs. χ is shown in Figure 5.

The variation in the values of the element effect with χ for each position of the TP (upper) and SP (lower) is presented in Figure 6. The agreement between ΔG^\ddagger calculated from Table I and those determined from NMR studies is seen in Table II to be within ± 0.9 kcal/mol.

Comparison with Nonempirical Calculations

A major achievement of the use of this scale (Table I) is the close correspondence of relative isomer energies for the series PH_nF_{5-n} with those reported by Rauk et al.⁶ based on nonempirical MO methods. This agreement is shown in Table III where not only is the order of isomer energies the same with one exception, the second and third isomer for PH_4X , but the values average to within ± 0.5 kcal/mol with each other over the entire series.

The series, PH_nX_{5-n} , is for an X atom of about 0.8 electronegativity unit greater than that for the proton;⁶ whereas we obtain the best agreement between values for the fluoro series, PH_nF_{5-n} , with a somewhat higher electronegativity

Table III. Isomer Energies Relative to Ground State Trigonal Bipyramids of PH_nX_{5-n} and PH_nF_{5-n} Molecules (kcal/mol)

PHX ₄ ^a (PHF ₄) ^b					
1.4 (2.0)		6.5 (6.4)	7.0 (7.9)		
PH ₂ X ₃ (PH ₂ F ₃)					
5.5 (5.9)		6.9 (6.4)	~11 ^d (11.8)	11.7 (11.8)	13.0 (12.8)
PH ₃ X ₂ (PH ₃ F ₂)					
7.0 (6.4)		~8.5 (9.8)	9.5 (9.8)	~13.5 ^e (12.8)	15.7 (15.7)
PH ₄ X (PH ₄ F)					
6.5 (7.3)		6.9 (6.4)	13.3 (13.2)		

^a Values not in parentheses are from ref 6. It was not stated in ref 6 whether d orbitals were included or not. ^b Values in parentheses are obtained from Table I for members of the PH_nF_{5-n} series.

^c The order of isomer stabilities predicted from the EHM method of Hoffman et al.⁸ agrees with the ordering in this table except for the interchange of these square pyramidal pairs. However, trigonal bipyramid and square pyramid orders were compared as independent sets and no values were given. ^d Approximate value estimated from Figure 5 of ref 6. ^e Approximate value estimated from Figure 4 of ref 6.

difference, about 1.5 units based on our assignment of electronegativities. Other series with a reduced ligand electronegativity difference give relatively lower values but a similar order of isomer energies as that shown in Table III.

This lowering in values for comparable ligand electronegativity differences to that of Rauk et al.,⁶ i.e., ~ 0.8 , is somewhat expected since our series was internally calibrated with respect to ΔG^\ddagger values from NMR behavior of pseudorotating phosphoranes. Since these molecules are deforming intramolecularly through SP transition states along the Berry coordinate, and it has been shown from x-ray diffraction data that it is unrealistic to expect that an idealized transition state will be reached,^{5a} our element effect values (Table I) then underestimate idealized SP isomer energies compared to that resulting from the MO calculations⁶ which deal with idealized states. Further, X in the series PH_nX_{5-n} is a proton with a

nuclear charge increased to 1.1 to bring about the X difference of ~ 0.8 unit.⁶ In this regard, it should not behave precisely like any real atom.

The excellent agreement in isomer energies between the molecular orbital method⁶ and that based on ΔG^\ddagger data for fluxional behavior provides confirmation that the transitional states are those involved in the Berry exchange mechanism. Single-crystal x-ray analysis^{2b,5a,29-31,48-52} on a wide variety of cyclic phosphoranes also establishes that the Berry coordinate is the appropriate one correlating^{5a} observed structural distortions between TP and SP geometries.

Steric and Ring Strain Terms

Having established a firm basis to deal with the element effect in "sterically free" acyclic phosphoranes, the next step is to ascertain energy terms for ring and steric strains. As discussed above for derivatives VIII and IX, values for ring and steric strain terms as a function of site occupancy in a TP may be qualitatively deduced when ΔG^\ddagger data for a series of related phosphorane derivatives are available, in which these effects are systematically incorporated. Now, however, instead of entertaining only the possibility of a TP transition state, SP transition states appearing along the pseudorotational coordinate are likely candidates. For the acyclic derivatives used in developing the values for the element effect (Table I), we have shown that the SP transition state is the favored one. However, as other factors enter in more structured cyclic derivatives, with or without bulky groups, TP transition states may compete with SP transition states, especially for ligand exchange behavior requiring multiple pseudorotations.

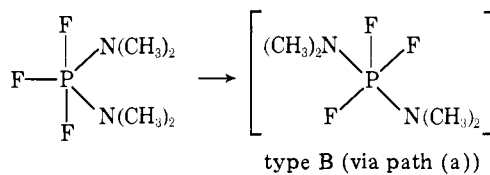
In one sense, the procedure for establishing a steric or ring strain contribution is simplified, since the wide assortment of phosphoranes, whose NMR exchange behavior has been adequately characterized, provides several examples (in many cases) where the same steric or ring strain interaction is present.

Hence, the procedure is to first sum up the element effect terms (Table I) for each isomer potentially representative of a ground or transition state in a system undergoing intramolecular exchange. Next, an estimate is made of steric or ring strain terms for both the ground state isomer (usually a TP) and a transition state in a series undergoing systematic substitutions. Finally, readjustments are made in a last recycling stage. However, none of the values in Table I are altered in this procedure.

The usefulness of the approach depends then on the ability of a simple set of terms to reproduce observed ΔG^\ddagger data. This is shown in Table IV where calculated values of ΔG^\ddagger for exchange phenomena are compared with ΔG^\ddagger values determined from NMR measurements (observed).¹⁴⁻²⁸ Steric and ring strain terms used in conjunction with element effects are summarized in Tables V and VI, respectively. A set of steric interactions between the biphenylene substituent and the R group for derivatives 43-52 of Table IV are listed separately in Table VII. The use of these tables results in an average deviation of ± 1.5 kcal/mol between measured and calculated ΔG^\ddagger values for the phosphoranes listed in Table IV. Only those elements appear in Table I for which a sufficient number of ΔG^\ddagger values have been determined to allow cross-checking. After construction of these tables, ΔG^\ddagger values for epimerization of a variety of oxaza spirocyclics were noted.⁵⁶ Application of the model here gave ΔG^\ddagger values within the 1.5 kcal/mol limit.

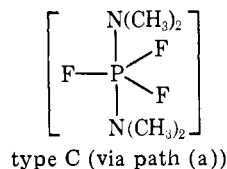
Illustrative Calculations

As an example of the calculation of a ΔG^\ddagger value from Tables I and V-VII, consider the exchange process for entry 8 in Table IV which is predicted by the model to go by way of the SP transition state of type B in Figure 4. The difference gives ΔG^\ddagger

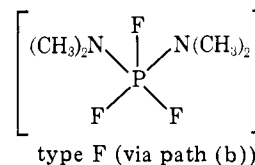


Σl_i 7.4 Table I	Σl_i 8.4 Table I
	Δ 7.0 Table I (footnote a)
	$N(CH_3)_2$ π loss 12.0 Table V (footnote d)
	27.4

= 20 kcal/mol (obsd, 19.6 kcal/mol¹⁹) for activation by path (a) of Figure 4. The other possible transition states, type C and F of Figure 4, are respectively lower in isomer energy by the same path (a) (type C) or higher in energy by a different path (path (b) of Figure 4 for F).

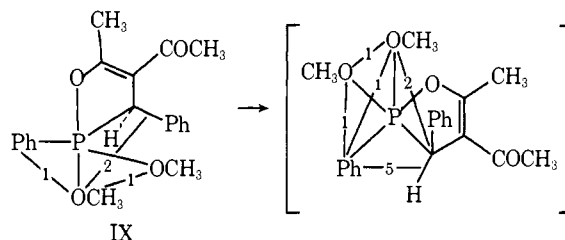


Σl_i 14.6	Table I
$N(CH_3)_2$ π loss 12.0	V (footnote d)
26.6	



Σl_i 8.4	Table I
$N(CH_3)_2$ π loss 12.0	V (footnote d)
Δ 7.0	I (footnote a)
$(CH_3)_2NPN(CH_3)_2$ steric 6.5	V
33.9	

A somewhat more complex example is illustrated by entry 16 of Table IV which is predicted by the model to isomerize



(individual steric terms are indicated)

Σl_i 7.1	Table I
Ring strain 2.0	Table VI
Steric 4.0	Table V
13.1	
Σl_i 11.6	Table I
Ring strain 1.0	Table VI
Steric 10.0	Table V
Δ 7.0	Table I (footnote a)
29.6	

(Figure 2) by way of the SP transition state. The difference gives $\Delta G^\ddagger = 16.5$ kcal/mol (obsd, 15.8 kcal/mol²⁰). Other isomers along the isomerization route (Figure 2) are of lower energy. A similar calculation for the epimerization process, encountered at higher temperatures for this phosphorane (Figure 3), suggests that the SP is likewise favored over the TP

Table IV. Calculated and Observed ΔG^\ddagger (kcal/mol) for Intramolecular Ligand Exchange for Phosphoranes

No. ^a	Ground state	Transition state	ΔG^\ddagger , kcal/mol		Ref
			SP	Obsd	
1	Y		4.0	4.0 ^b	7,9-13
2	F		2.5	4.2 ^b	14
3	N(CH ₃) ₂		8.6	8.8	14
4	N(<i>i</i> -Pr) ₂		8.6	7.5	15

Transition states						
Y	Transition states	ΔG^\ddagger , kcal/mol			Obsd	Ref
		TP C ^c	SP B ^c	SP F ^c		
5	Cl	7.2	8.0	8.0	7.2 ^b	16
6	H	12.8	11.8	11.8	10.2 ^b	17
7	NH ₂	19.2	20.0	20.0	^d	18
8	N(CH ₃) ₂	19.2	20.0	26.5	19.6	19
9	Ph	14.4	14.4	16.0	18.7	19
10	CH ₃	20.0	18.0	18.0	17.8 ^b	19

Ground state ^e					Transition states			Ref
R ₁	R ₂	X	Y	Z	TP	SP	Obsd	
								20
11	OCH ₃	OCH ₃	H	H	8.5	8.6	9.7	
12	OCH ₃	OCH ₃	CH ₃	CH ₃	12.5	13.1	14.5	
13	OCH ₃	OCH ₃	H	Ph	10.5	11.0	12	
14	Ph	OCH ₃	H	H	8.5	11.5	9.7	
15	Ph	OCH ₃	CH ₃	CH ₃	10.1	17.1	17.2	
16	Ph	OCH ₃	H	Ph	11.5	16.5	15.8	
17	OCH ₃	OPh	H	Ph	10.5	11.0	12.5	
18	OCH ₃	OPh	H	Ph	21.0	23.1	21.8	
19	Ph	OCH ₃	H	Ph	21.0	24.5	>24	
20	R ₁ CH ₃	R ₂ Ph			8.2	6.7	8.9	
21	CH ₃	OPh			16.0	16.1	14.1	

(continued)

Table IV (Continued)

No.	R ₁	R ₂	Y—X	ΔG^\ddagger , kcal/mol			Ref
				TP	SP	Obsd	
22	CH ₃	OCH ₃		21.0	14.7	21.2	
23 ^f	CH ₃	OPh } OPh }		21.0	14.7	20.5	
24	CF ₃			22.3	14.0	21.8	
25 ^f	CF ₃	OPh		17.3	14.0	17.4	
26	CF ₃	OCH(CF ₃) ₂		20.0	20.3	21.0	
27	CF ₃	OPh		17.4	19.5	20.4	
Transition states							
28				21.0	21.1	17.6	21
29				18.0	22.1	>23	21
30				3.7	8.4	11	22
31				9.5	16.7	15	23
32				14.2	11.7	20.1	23
							24
	<i>Rg, h</i>						
33	OPh			9.5	6.8	~9	
34	N(CH ₂) ₄			17.6	17.2	16.2	
35	N(CH ₃) ₂			17.6	17.2	16.2	
36	Ph(cis)			14.2	11.7	19.6	
37	Ph			14.2	11.7	>22	
38	HC=C(CH ₃) ₂			20.3	14.0	19.1	
39	<i>i</i> -Pr			20.3	14.0	17.8	
40	CH ₃			20.3	14.0	16.9	

Table IV (Continued)

No.	Rg, ^h	Transition state	TP	SP	Obsd	Ref	
41				3.0	12.4	11.6	25
42				10.0	15.4	~13.3	25
43				12.6	<11.9	26	
44	-CH ₃			12.6	12.5	26	
45	-C ₂ H ₅			12.6	13.6	26	
46				12.6	12.0	26	
47				15.9	15.7	26	
48				16.9	17.1	26	
49				17.9	17.8	27	
50				21.9	>21	28	
51				21.9	>23	28	
52				25.9 ⁱ	26.0	27	

^a Italicized number entries signify that the ground state SP structure is equal to or lower in energy than the TP. ^b ΔG^\ddagger values used in constructing Table I. ^c The favored transition state is italicized. ^d Although ΔG^\ddagger for ligand exchange has not been measured, ΔG^\ddagger for uncorrelated rotation of the amino groups was determined to be 12.3 kcal/mol.¹⁸ This value should set a lower limit to the exchange energy. ^e For these and the following entries in this table only one isomer of each configuration is shown for simplicity, e.g., cis and trans *x* and *y* to R₁ unless stated otherwise. Refer to the respective references for additional detail. ^f Related derivatives containing R₂ = SPh show similar values to R₂ = OPh, implying a similar apicophilicity.^{21b} However, this may reflect steric relief in the transition state by the SPh ligand. Further, the ground state of the analogous substance,^{2b} R₁ = CH₃, R₂ = NMe₂, and Y-X = Ph(O)C=C(O)Ph is considerably displaced toward the rectangular pyramid.^{5a} Additional ΔG^\ddagger values for other thio derivatives are needed before an element effect, steric terms, and a π bonding contribution may be ascertained. ^g The x-ray structure of a related substance (ref 29) shows a SP conformation. In agreement, the calculation shows an equal or greater stability for the SP relative to the TP ground state for derivatives 33 and 38-40. ^h All derivatives are located trans to 3-CH₃ except OPh which is reported as a mixture of cis and trans and Ph(cis) as shown. ⁱ The SP transition state formulated here for the triisopropyl derivative differs from that postulated in ref 27. See text for a discussion of this apparently unique example.

Table V. Relative Values of Steric Factors for Use in Estimating Isomer Energies^a

Steric interaction ^b (R = CH ₃ , C ₂ H ₅)	Steric factor, kcal/mol	Steric interaction ^b	Steric factor, kcal/mol	
R ₂ NPNR ₂ R ₂ NPC(CH ₃) ₂	6.5	CH ₃ NPCH ₃	2.0	
PhPPh		PhOPCHPh		
PhPC(CH ₃) ₂	ROPCHPh			
PhPCHPh	CH ₃ NPCl			
PhNPC ₂ H ₅	FPPh			
(CH ₃) ₂ NPC(CH ₃) ₂	ROPPh	1.0		
RPPh	ROPOR			
ORPC(CH ₃) ₂	ROPOPh			
CH ₃ NPPh	4.0	CH ₃ NPOCH(CF ₃) ₂		3.0
PhOPC(CH ₃) ₂		ax		
CH ₃ NPC ₂ H ₅	3.0	eq	2.0	
CH ₃ NPOPh		ax		
		NR ₂ , NH ₂ ^d	6.0	
		RNP ^e	4.0	

^aFor application to axial-equatorial orientations in the TP and both apical-basal and basal-basal cis ligand orientations in the SP. All interactions for a particular isomer should be summed up to obtain the steric destabilization. The only exception that arises is when two identical steric interactions are present which involve a single apical substituent and this substituent (not a member of a ring) has no other steric interactions. In this case, a value is taken for these two interactions which equals 1.5 times that for a single interaction. See entry 32 of Table IV, which represents this type of exception. ^bThe P-C- and P-N- bonds are part of ring systems. ^cThese represent steric terms between substituents of the ring which are applied only when these rings are oriented in axial-equatorial positions of a TP. ^dThis is not a steric term but represents a loss in π bonding and is applied in an additive sense when these groups are in locations other than the equatorial site of a TP. ^eThis is the same type of term as in (d) but refers to an NR group as part of a four- or five-membered ring. It is applied in the same manner as the term in (d). If the ring is oriented diequatorially, it might be expected that this term should also be applied since the equatorial nitrogen atom is not properly oriented for effective π bonding, at least according to extended Hückel calculations.⁹ However, the resultant loss in π bonding must not be as great as that encountered when a nitrogen atom is located in other than an equatorial site of a TP. See footnote c to Table VI. X-ray structures of phosphoranes containing Me₂N groups in equatorial sites show these groups in planes rotated 20-30° from the axial direction.^{2b} Presumably changes in π bonding effects for oxygen as a function of TP or SP site occupancy are even less important than those for nitrogen.

for the transitional state representation (see entry 19 of Table IV).

Thus, for both these exchange processes, possible TP transition states, isomers 52 or 35 of Figure 2 for the isomerization and isomer 23 of Figure 3 for the epimerization, discussed earlier under "general considerations", appear less favored as pseudorotational barriers, although isomer 23 is only 3.5 kcal/mol lower in energy than the SP transition state cited for the epimerization. The TP isomer (14 of Figure 2) along the isomerization route would appear at a trough in the potential energy surface, approximately 10 kcal/mol below the SP transition state (isomers 3 or 2), according to the model calculations. This figure is sufficiently outside the average uncertainty of the present model to suggest possible stabilization and detection as an intermediate by experimental methods.

Table VI. Relative Values of Ring Strain for Use in Estimating Isomer Energies (kcal/mol)

Ring structure	TP		SP	
	ax, eq	eq, eq ^a	bas, bas	ap, bas
	8	24	2	16
	2		1	
	2	15	1	9
	2	18 ^c	1	14
	2	21 ^c	1	14
	2	24 ^c	1	14
	2	15	1	9
	2	21	1	13
	2	23	1	15

^aValues for rings spanning apical-basal sites of a SP are approximately 0.6 times the values for strain estimates for rings positioned in diequatorial sites of a TP. ^bPresent in the bisbiphenylene derivatives, 43-52 of Table IV. ^cThe variation in the strain energy for the oxaza rings in the TP reflects a 3 kcal/mol loss in π bonding for this orientation of a nitrogen atom.

Model Predictions

In this section, the utility of the numerical scales associated with the model will be explored. In this way, the degree of confidence which should be attached to the development presented here will become apparent. This is done by considering recent x-ray structures and exchange phenomena for cyclic phosphoranes. For the latter, barrier energies have not been determined but have interesting features associated with them.

Correlation with X-Ray Data. We have recently completed the single-crystal x-ray analyses^{2b,31a-d,48,49} of the cyclic phosphoranes (a-f). The availability of these structures (a-f),

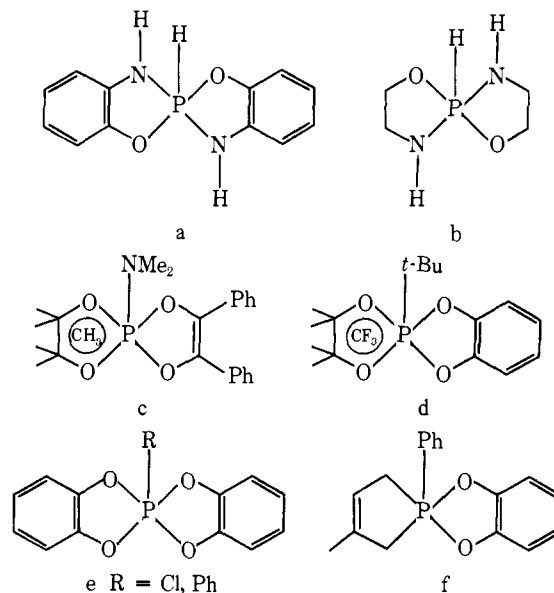
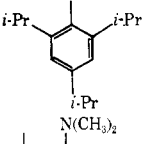
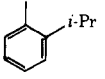



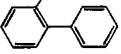
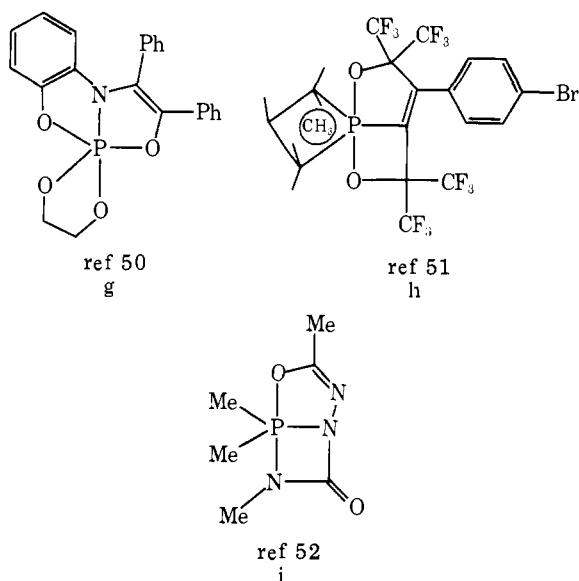


Table VII. Relative Values of Steric Effects for Substituents in Bisbiphenylene Derivatives^{a-c}

R	Steric factor, kcal/mol	R	Steric factor, kcal/mol
	10		6
	8		5.5
	8		5

^aFor application when the R group relative to a site occupied by the bisbiphenylene group is in an axial-equatorial orientation in the TP and apical-basal or cis basal-basal orientations in the SP. ^bIn addition, a steric effect between the two bisbiphenylene groups is applied when the SP transition state (shown for derivatives 43-52 in Table IV) is encountered. The value of this steric term is 4 kcal/mol. ^cThe element effect to be applied for the P-C bonds formed by the biphenylene ligands is that for the phenyl group (Table I). Also a steric term (Table V) between the unique ligand and the phenyl groups applies.

coupled with the appearance of those of the more constrained derivatives (g-i),⁵⁰⁻⁵² serves as an interesting test by comparing



possible ground state isomer energies obtained from terms in Tables I, V, and VI. Other phosphoranes of the type (e) have been studied by x-ray diffraction. Inclusion of the derivatives³⁰ (e) with R = CH₃ and F extends the range of substituent electronegativities and provides an opportunity for comparison of this systematic variation with the model estimations.

The relative energies of the two isomers predicted to be the most stable by the model calculation, a TP with the rings spanning eq-ax sites and a SP with the ring system occupying basal positions (whenever possible), are summarized in Table VIII for the phosphorane structures (a-i). We have shown^{5a,49} that distortions observed in these x-ray structures are along the Berry exchange coordinate between the idealized TP and SP. Quantitative evaluation of the degree of displacement along this coordinate was ascertained^{5a} by considering the dihedral angles calculated from polyhedral surfaces, defined by the x-ray coordinates of the five atoms attached to phosphorus, and comparing these angles with a similar set for the

Table VIII. Comparison of X-Ray Structures of Cyclic Phosphoranes with Predicted Ground State Isomer Energies

Structure	Ground state isomer energies, ^a (kcal/mol)		$\Delta(\text{SP-TP})$	% displacement ^b		Ref ^c
	TP	SP		TP → SP		
a	12.3	22.5	10.2	~23 ^d	48a	48a
b	12.3	22.5	10.2	25	48a, c	48a, c
i	14.3	19.8	5.5	(31) ^d	52	52
c	17.4	20.4	3.0	31	2b	2b
d	11.6	10.6	1.0	37	48b	48b
e (R = F)	15.2	16.6	1.4	65	30	30
e (R = Cl)	14.4	14.4	0.0	72	31c	31c
e (R = Ph)	13.9	13.6	-0.3	72	31a	31a
e (R = CH ₃)	12.2	10.6	-1.6	82	30	30
f (R = CH ₃)	22.5	20.8	-1.7	~93 ^d	31b	31b
f (R = H)				81	31d	31d
g	25.5	34.5	9.0	35	50	50
h	(32.6)	34.8	(2.2)		51	51

^a From Tables I, V, and VI. ^b From dihedral angles^{5a} of intersecting triangular faces formed by the positions of the five atoms attached to phosphorus using atom coordinates from x-ray data in each case. ^c Reference of x-ray studies used in determining the structural distortion (% displacement TP → SP). ^d These represent estimates and are probably within $\pm 5\%$. For structure (a), the proton of the P-H bond did not refine and hence its position is somewhat uncertain. For f (R = CH₃), a disorder problem introduced some uncertainty in the positions of the five-membered carbon containing ring. For (i), the geometrical constraints associated with a four-membered ring make comparison with the idealized SP less appropriate than that for the other derivatives with only five-membered rings.

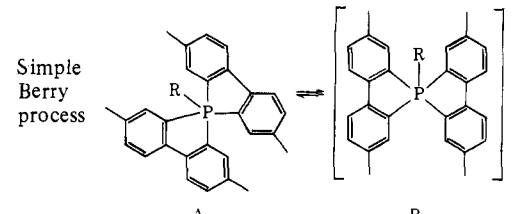
idealized structures. The resulting percent displacement from the TP is listed in Table VIII for the cyclic phosphoranes of interest here.

It is seen that in general the prediction of the ground state isomer representation correlates well with that observed from x-ray data. The trends in the relative ground state isomer stabilities from the model, $\Delta(\text{SP-TP})$, and that calculated^{5a} from x-ray data, percent displacement TP → SP, are directly comparable, except for derivatives (g) and (h). Because of the special ring requirements in the latter two phosphoranes, they would be expected to form a SP ground state isomer in which one of the rings must be positioned in apical-basal rather than cis-basal sites. Thus, $\Delta(\text{SP-TP})$ is on a different scale from that of the others.

It is not expected that agreement will be quantitative, for calculation of the relative energies of possible ground state isomers is a much more severe test of the model than dealing with the greater energy differences encountered between ground and excited state configurations upon which the model was constructed. The latter energy difference, ΔG^\ddagger , may range up to four times that of ground state isomer differences. Hence, the fact that the fluoro derivative (e) is predicted to have a TP ground state representation, but stabilized by only 1 kcal/mol, whereas that calculated^{5a} from x-ray data³⁰ shows its structure to be slightly past the crossover point between idealized TP and SP representations (65%), is within limitations of the model.

It is noted that the ground state isomer trend toward increasing SP stabilization with a decrease in substituent electronegativity for the "catechol" derivatives (e) parallels that obtained from the x-ray data. In terms of the model calculation, this is related to the relatively greater stabilization of an equatorial ligand (TP) compared to that of an apical ligand (SP) for the two competing ground state structures as electronegativity decreases. Of course, since the ranges in element effects (Table I) for the various positions in the TP and SP are in some measure referenced to electron pair repulsion argu-

Table IX. Relative Isomer Energies for Bis(4,4'-dimethyl-2,2'-biphenylene)organyl-(R)-phosphoranes as a Function of the Steric Factor of R^a

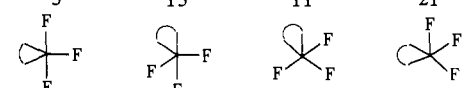


R steric factor, kcal/mol	Isomer energy, kcal/mol ^b			
	A	B	X	XI
6	28.9	46.8	47.9	48.8
7	30.9	50.8	50.9	51.8
8	32.9	54.8	53.9	54.8
10	36.9	62.8	59.9	60.8 ^c

^a See entries 43–52 of Table IV. ^b The isomer energy italicized refers to the isomer representing the transition state. Thus, until a steric factor for R of 8 kcal/mol is reached, the simple Berry process prevails, whereas at higher steric values, the pseudorotation from the ground state A via the transition state XI to the intermediate X is indicated as the exchange process. ^c Accepting this mechanism for the triisopropyl derivative means that we should increase the steric factor for this group by 2–3 kcal/mol to obtain better agreement with ΔG^\ddagger observed.

Table X. Relative Isomer Energies for Cyclic (CH₂)₄PF₃ and (CH₂)₅PF₃ (kcal/mol)

Compd	a	b	c	d
(CH ₂) ₄ PF ₃	18	15	20	22
(CH ₂) ₅ PF ₃	3	13	11	21

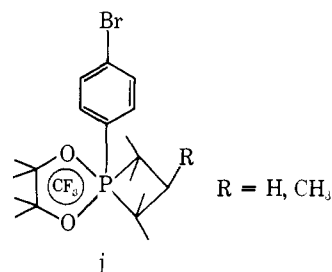


ments,^{46,53} the increasing SP character with decreasing substituent electronegativity in (e) is a function of the increased P–R axial bond pair–equatorial bond pair repulsions in the TP (idealized angle of 90°) compared with the apical–basal bond pair repulsions in the SP (idealized angle of 105°). The importance of a steric term is also indicated in this series in enhancing the formation of the SP,^{31c} particularly since the hydrido derivative is a TP.^{31d}

Similarly, one can examine the makeup of the contributing terms in other cases in Table VIII to rationalize the observed structural distortions. In (g), for example, the appearance of an axial ring nitrogen atom in a structure approximating a TP rather than at an equatorial location of a TP (as possible in derivative (h)) is associated with the large ring strain for the diequatorial five-membered ring placement that would be required. This would result in a relative isomer energy of 38 kcal/mol, even higher than that for the SP (34.5 kcal/mol, Table VIII).

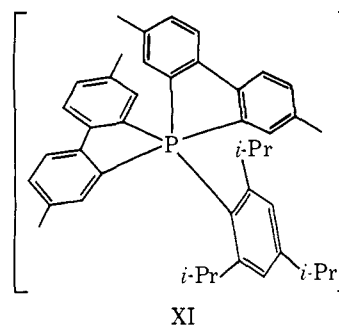
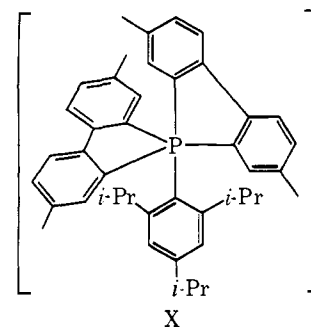
The ground state geometry suggested by the model calculations for the ligand exchange behavior of the series of diox-

aphosphoranes, entries 32–40 of Table IV, is a SP for all derivatives, except entries 34 and 35, which contain an N(CH₂)₄ or N(CH₃)₂ group in the fifth position. In agreement, the x-ray



structure²⁹ of the *p*-bromophenyl derivative (j) approximates a SP, estimated^{5a} to be 84% along the distortion coordinate from the TP to the SP.

Correlation with NMR Exchange Behavior. A study of the fluxional behavior of the bisbiphenylene derivative containing the bulky triisopropyl substituent, entry 52 of Table IV, poses a unique situation. It represents the first example of a RPY₄ derivative for which the simple Berry process (with R as the pivotal ligand) is unsupported.²⁷ Whitesides et al.²⁷ propose the exchange intermediate X consistent with their NMR data.

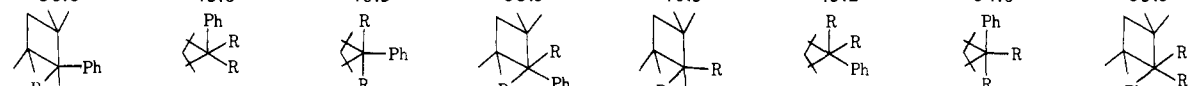


The model calculation is in accord with this result. The simple Berry process is favored until the steric factor for the substituent R (Table VII) exceeds 7 kcal/mol; then the isomeric state X becomes lower in energy.

For the triisopropyl derivative, X is estimated to be stabilized by 3 kcal/mol relative to the Berry state shown in Table IV. This difference appears just outside the limits of the model, ± 2 kcal/mol. These results are consistent with a pseudorotation which uses one of the ring carbon atoms as a pivotal ligand. The

Table XI. Relative Isomer Energies for the Cyclic Fluorophosphorane IV and the Ethoxy Analogue (kcal/mol)^a

R	a	b	c	d	e	f	g	h
F	27.7	36.0	29.7	38.7	35.9	34.7	44.9	42.7
OEt	36.8	43.8	46.3	53.5	40.5	45.2	54.0	55.5



^a Each of the four TP–SP pairs shown is related by a BR process.

SP transition state is then XI on the way to X. The relative energy of these isomers, as the steric factor of R changes, is given in Table IX.

No known monocyclic phosphorane exists with a large distortion from the TP geometry.⁵ The cyclic fluorophosphorane (CH₂)₄PF₃ mentioned in the introduction represents a limiting case in that the ligand electronegativities are most divergent and, as a consequence, sets up the possibility of the existence of a SP ground state. Even for this case the isomer sequence obtained from the model (Tables I and VI) shows that the preferred ground state is the TP isomer (b) with (a) only 3 kcal/mol higher. These isomer energies are listed in Table X. Ligand exchange by a simple Berry mechanism through SP isomer (d) suggests a ΔG^\ddagger value of 7 kcal/mol. In contrast, the much lower ring strain in the related six-membered cyclic phosphorane, (CH₂)₅PF₃, shows the same isomer distribution as (CH₃)₂PF₃ and, accordingly, should proceed by the same exchange mechanism, i.e., via path (b) of Figure 4. The activation energy indicated, 18 kcal/mol (the energy of transition state (d) minus that for ground state (a)), is over twice that indicated for exchange in (CH₂)₄PF₃. Although neither of these ΔG^\ddagger values has been measured, these results agree with the much higher exchange rate observed³² for (CH₂)₄PF₃ compared to (CH₂)₅PF₃.

Extremely interesting observations were reported by Denney and co-workers³⁸ on the cyclic fluorophosphorane IV containing a four-membered ring. The low-temperature NMR spectra revealed³⁸ the presence of two isomers in the approximate ratio of 2.3:1. Rapid exchange occurred at ambient temperatures.

In Table XI tabulation of the relative isomer energies obtained by application of the model shows that isomer (c) is more stable than (e). This is in contrast to that usually reported and, in particular, reverses the order of these isomers relative to that postulated²² in the closely related phosphorane having ethoxy groups in place of the fluorine atoms (cf. ΔG^\ddagger data for entries 30 and 31 of Table IV). The reversal, in terms of the numerical scales developed here, is due somewhat to the greater electronegativity of fluorine compared to oxygen but also due to a lower steric factor with fluorine atoms in place of ethoxy groups. Thus, the conclusions for compound IV stating³⁸ that the major isomer involves the (a-b) pair undergoing rapid exchange at -100 °C and a minor component, identified as isomer (c), containing the ring in a diequatorial orientation, are consistent with the results in Table XI. There is a substantial barrier between the (a-b) pair and isomer (c). In order to go from isomer (a) to (c), pseudorotation through the high-energy form (d) is required (cf. Figure 3).

Conclusion

Although the tabulations given in this paper for element effects, ring strains, and steric terms are a first approximation and subject to some modification as further details become available regarding specific interactions in new examples, they appear sufficiently refined at present to warrant their use in correlating exchange phenomena and giving additional insight into the structural relationships among pentacoordinate isomers of phosphorus.

The correlation of the model calculations with distortions observed in x-ray structures of cyclic phosphoranones (Table VIII and accompanying discussion) suggests the manner by which idealized representations of TP and SP ground and transition states, advanced for ligand exchange phenomena, should be modified. This structural refinement should prove of assistance in considering the relative merits of possible pentacoordinate transition states invoked in phosphorus reaction mechanisms.^{54,55}

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FC≡P, C-Fluorophosphaethyne: Preparation and Detection by Photoelectron and Microwave Spectroscopy

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Abstract: An original method of synthesizing compounds containing the C=P double bond (phosphaalkenes) and C≡P triple bond (phosphaalkynes) has been developed. This method has been used to produce the new reactive linear triatomic molecule FC≡P, C-fluorophosphaethyne, in very high yield. When trifluoromethylphosphine, CF₃PH₂, vapor is passed slowly over solid KOH at room temperature two HF units are eliminated to yield FC≡P. If the relative quantity of KOH is reduced or the flow rate increased the intermediate phosphaalkene resulting from the elimination of one HF fragment is detected. This species, CF₂=PH, had previously been characterized during pyrolysis experiments on CF₃PH₂. Both photoelectron and microwave measurements have been made on this system. There are three distinct ionization potentials which can be assigned to FC≡P, the first occurring at 10.57 ± 0.01 eV. The rotational constant B₀ has been determined from the J = 3 ← 2 transition as B₀ = 5257.78 ± 0.1 MHz.

Introduction

Until recently the only compound containing a C≡P triple bond was HC≡P, which was produced by a carbon arc discharge in phosphine by Gier in 1961.¹ Although several spectroscopic studies of this species have been reported,²⁻⁵ subsequently the chemistry of the interesting C≡P moiety (phosphaalkynes) appears to have been neglected. The absence of a satisfactory synthetic route has presumably been mainly responsible for this lack of development. As a consequence a series of experiments has been initiated to develop efficient synthetic routes to phosphaalkynes in general and also to the intermediate phosphaalkenes which contain the C=P double bond which had hitherto been unidentified. In this way it was hoped that new RC≡P species could be produced and also that the latent chemistry of these intriguing species could be explored. In this endeavor we have made full use of both microwave and photoelectron techniques to detect, characterize, and study these new molecules and in particular determine the optimum conditions for production.

Such techniques have already proven very successful in the study of various carbon-sulfur and carbon-selenium multiply bonded species such as CH₃CH=S,⁶ CH₂=C=S,⁷ and CH₃CH=Se.⁸ Multiply bonded species involving boron such as HB=S,⁹ NH₂=BF₂,¹⁰ CH₃NH=BF₂,¹¹ CH₃B=S, and ClB=S¹² have also been investigated by these methods. In

general the species have been produced in high-temperature flow reactions and the extension of these techniques to the production and study of the new class of compounds—the phosphaalkenes CF₂=PH, CH₂=PCl, and CH₂=PH—has recently been reported by us.¹³ These experiments also indicated that further elimination of HX (X ≡ halogen) from phosphaalkenes should lead to derivatives of HC≡P. In this way the first new derivative, CH₃C≡P, was made by pyrolysis of CH₃CH₂PCl₂.¹⁴

During microwave investigations of the pyrolysis products of CF₃PH₂ not only was CF₂=PH detected¹³ but also two new species, PH₂F and FC≡P. These two new molecules were produced in very low yields and it was during attempts to improve this situation that an original, simple, and effective room temperature synthesis of FC≡P was evolved which avoids the destructive conditions which obtain in high-temperature processes. The synthesis promises to have wide application and also to allow us to explore the chemistry of the phosphaalkynes (and phosphaalkenes), the avowed aim of these initial studies.

Experimental Section

During a microwave search for FC≡P among the pyrolysis products of CF₃PH₂^{13,15} a weak group of lines was detected whose Stark and vibrational satellite patterns were consistent with the J = 3 ← 2 transition of a linear molecule. The ground-state line frequency was 31 546.705 ± 0.01 MHz, which was within 450 MHz of the position predicted on the

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