The correct total energy, eq 3 of the text, is

$$E_T = \mathrm{OES} + \mathrm{CORE} - \mathrm{ER2} - \mathrm{ER1}$$

We assume (a) the one-center part of the electron repulsion energy, ER1, varies slowly with the angle and may be taken as constant, (b) the B–B distance is great enough that asymptotic form of the two-center electron interaction integral, $1/R$, may be used in ER2. With $R = R_{\mathrm{B-B}}$, the variable part of the correction to the OES is simply

$$E = (Z_B - p_B)^2/R$$

where Z_B is the core charge of atom B and p_B is its electronic population. It will differ from Z_B by some amount t, $p_B = Z_B + t$, and t may be positive for negative B as in CO_2 or negative for positive B as in Li_2O.

There are two interesting cases. In the first, noniterative model, the calculation uses the free atom population in the effective Hamiltonian, meaning that one of the p_B factors above is equal to Z_B. The correction varies as

$$E = (Z_B^2 - Z_B(Z_B + t))/R = -tZ_B/R$$

In the second case, iteration to self-consistency, both populations are $(Z_B + t)$, though t may be reduced typically by about 30–40%. Then the correction varies as

$$E = (Z_B^2 - (Z_B + t)^2)/R = -(2tZ_B + t^2)/R$$

In addition to suggesting that the neutral starting option may provide better angle estimates by OES, this analysis also suggests that the self-consistent values should be relatively worse when the ligands are negative.

It is clear that the most favorable case is that of little or no charge transfer, when the long distance corrections for angle variation disappear.

Molecular Orbital Theory of Pentacoordinate Phosphorus

Roald Hoffmann, James M. Howell, and Earl L. Muetterties

Contribution from the Department of Chemistry, Cornell University,
Ithaca, New York 14850, and the Central Research Department,
E. I. du Pont de Nemours & Co., Wilmington, Delaware 19898.
Received August 25, 1971

Abstract: The electronic structure of some idealized PH_5 geometries of D_{3h}, C_{4v}, and C_s symmetries is analyzed. Each geometry is characterized by a low-lying nodeless orbital, three singly noded orbitals close in energy, and a high-lying doubly noded nonbonding orbital. The latter orbital is the only one significantly stabilized by the inclusion of 3d orbitals in the P basis set and also determines the relative stability of substituted compounds differing in electronegativity from H. A potential surface connecting the D_{3h} and C_{4v} geometries through C_{2v} structures is constructed. It shows a small barrier for the Berry pseudorotation process. Optimum C_s structures are at higher energy than the C_{4v} geometry. An examination of substituent effects rationalizes favored apical substitution in the trigonal bipyramid and preferred basal substitution in the square pyramid by more electronegative groups. It is predicted that π acceptors will prefer axial sites in the trigonal bipyramid, π donors equatorial positions. If a substituent has a single π system and is located in the equatorial position it will prefer to have its acceptor orbital perpendicular to the equatorial plane or its donor orbital in that plane. In the square pyramid, π donors will favor the apical position, π acceptors the basal sites. The concerted fragmentation reaction $PR_5 \rightleftarrows PR_3 + R_2$ is symmetry forbidden for the least-motion axial–equatorial departure from a trigonal bipyramid, and allowed for axial–axial or equatorial–equatorial departure.

The literature is replete with theories of bonding of pentacoordinate phosphorus.[1–31] We add here a molecular orbital description which is (1) simple, (2) covers a wide range of geometries, (3) focuses on the role of substituents, and (4) gives some further insight

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(1) I. Langmuir, *J. Amer. Chem. Soc.*, **41**, 868 (1919).

(2) F. J. Garrick, *Phil. Mag.*, **14**, 914 (1932).

(3) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

(4) N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc., Ser. A*, **176**, 153 (1940).

(5) R. Daudel and A. Bucher, *J. Chim. Phys.*, **42**, 6 (1945); R. Daudel, A. Bucher, and H. Moureu, *C. R. Acad. Sci.*, **218**, 917 (1944).

(6) G. H. Duffey, *J. Chem. Phys.*, **17**, 196 (1949).

(7) A.-C. Tang and H.-K. Lee, *J. Chin. Chem. Soc. (Taipei)* **17**, 252 (1950).

(8) H. Siebert, *Z. Anorg. Allgem. Chem.*, **265**, 303 (1951).

(9) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954); D. P. Craig and E. A. Magnusson, *ibid.*, 4895 (1956).

(10) J. W. Linnett and C. F. Mellish, *Trans. Faraday Soc.*, **50**, 665 (1954); J. W. Linnett, "The Electronic Structure of Molecules," Methuen and Co., London, 1964, p 122.

(11) C. Duculot, *C. R. Acad Sci.*, **245**, 802 (1957).

(12) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 177, 178.

(13) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); **39**, 318 (1961); *J. Chem. Soc.*, 4672, 4679 (1963); *Inorg. Chem.*, **5**, 1634 (1966); *J. Chem. Educ.*, **40**, 295 (1963); *J. Amer. Chem. Soc.*, **85**, 4672 (1963).

(14) F. A. Cotton, *J. Chem. Phys.*, **35**, 228 (1961).

(15) (a) R. E. Rundle, *J. Amer. Chem. Soc.*, **85**, 112 (1963); *Rec. Chem. Progr.*, **23**, 195 (1962); *Acta Crystallogr.*, **14**, 585 (1961); (b) R. E. Rundle, *Surv. Progr. Chem.*, **1**, 81 (1963); (c) R. J. Hach and R. E. Rundle, *J. Amer. Chem. Soc.*, **73**, 4321 (1951).

(16) V. M. Volkov, A. A. Levin, and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, **152**, 359 (1963).

(17) A. Golebiewski, *Acta Phys. Polon.*, **23**, 243 (1963).

(18) (a) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (b) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); (c) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966), and references therein;

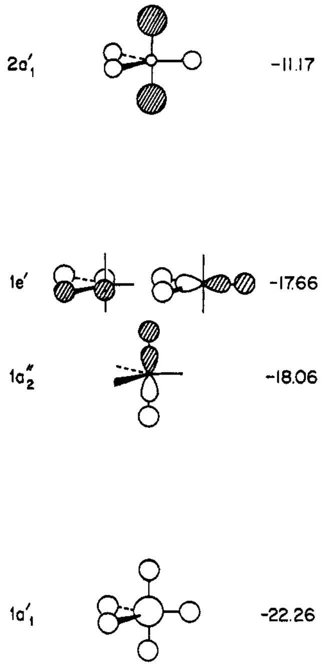


Figure 1. The occupied molecular orbitals of D_{3h} PH_5 as derived from an extended Hückel calculation without d orbitals. The circle sizes indicate schematically the magnitude of the coefficients.

into a possible concerted reaction interrelating trivalent and pentavalent phosphorus.

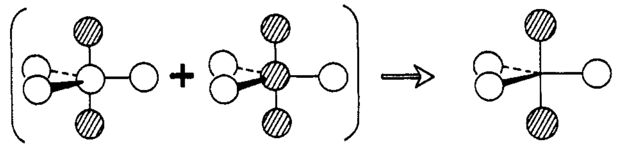
The Molecular Orbitals of Some Idealized PH_5 Geometries

We begin with the simplest and as yet unsynthesized phosphorane, PH_5. Our model is a molecular orbital calculation which uses only the valence orbitals, 3s and 3p on phosphorus, 1s on hydrogen. The effect of 3d orbitals will be subsequently examined. Since differences in bonding with geometrical orientation are one of our primary concerns we do not prejudice the results by putting in different P–H distances.[32] All the calculations reported in this paper are for P–H distances of 1.42 Å. Where energies or wave function coefficients are explicitly quoted they are derived from an extended Hückel calculation.[33]

The occupied molecular orbitals of a D_{3h} trigonal-bipyramid PH_5 are shown schematically in Figure 1.[34] The essential features of the electronic structure of the molecule are the following: (1) The ground configuration is $(1a_1')^2(1a_2'')^2(1e')^4(2a_1')^2$. There are no low-lying unoccupied orbitals. (2) The $2a_1'$ orbital has an interesting composition, one of significance in our subsequent analysis. It is essentially distributed only over the hydrogens with very little contribution from P 3s. The axial hydrogen coefficients are larger than the equatorial. Because $2a_1'$ is on the outer ligand atoms it can be classified as a nonbonding orbital. In fact, it has two nodal surfaces, and is slightly antibonding. A large energy gap segregates it from the other occupied PH_5 orbitals.

As interesting as the molecular orbitals of PH_5 are by themselves our prime concern is in *understanding* qualitatively why these orbitals came out the way they did, and their relationship to bonding schemes suggested by others.

Figure 2 contains two interaction diagrams directed toward this end. At the top we see the construction of PH_5 orbitals from the interaction of a planar PH_3 molecule with the two axial hydrogens. The lower $a_1' + e'$ set of PH_3 is the P–H σ bonds, the upper $a_1' + e'$ set the σ^* levels; a_2'' is the phosphine lone pair.[37] The axial hydrogens, assumed to interact weakly with each other, generate an a_1' and a_2'' set. The a_2'' orbitals of PH_3 and axial hydrogens interact strongly, the bonding combination of the two forming the $1a_2''$ orbital illustrated in Figure 1. The middle a_1' orbital of PH_5 is derived primarily from the a_1' axial hydrogen combination, mixing into itself the PH_3 σ and σ^* a_1' orbitals. This mixing is shown diagrammatically in **1** below—the lower a_1' is mixed in in an antibonding



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(d) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970); (e) E. L. Muetterties, *Rec. Chem. Progr.*, **31**, 51 (1970).

(19) R. Schmutzler, *Angew. Chem.*, **77**, 530 (1965); R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 1 (1965); R. Schmutzler in "Halogen Chemistry," Vol. 2, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, p 31.

(20) R. R. Holmes, R. P. Carter, Jr., and G. E. Petersen, *Inorg. Chem.*, **3**, 1748 (1964).

(21) (a) L. S. Bartell and K. W. Hansen, *ibid.*, **4**, 1777 (1965); K. W. Hansen and L. S. Bartell, *ibid.*, **4**, 1775 (1965); (b) L. S. Bartell, *ibid.*, **5**, 1635 (1966); (c) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

(22) (a) J. I. Musher, *Science*, **141**, 736 (1963); J. I. Musher, *Angew. Chem.*, **81**, 68 (1969); (b) J. I. Musher in "Conformational Analysis," G. Chiurdoglu, Ed., Academic Press, New York, N. Y., 1971, p 177.

(23) J. M. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **45**, 2916, 2927 (1966).

(24) D. Hellwinkel, *Chem. Ber.*, **99**, 3629, 3642 (1966).

(25) (a) P. C. Van der Voorn and R. Drago, *J. Amer. Chem. Soc.*, **88**, 3255 (1966); (b) P. C. Van der Voorn, K. F. Purcell, and R. S. Drago, *J. Chem. Phys.*, **43**, 3457 (1965).

(26) D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967).

(27) R. S. Berry, M. Tamres, C. J. Ballhausen, and H. Johansen, *Acta Chem. Scand.*, **22**, 231 (1968).

(28) R. D. Brown and J. B. Peel, *Austr. J. Chem.*, **21**, 2605, 2617 (1968).

(29) D. B. Boyd, *J. Amer. Chem. Soc.*, **91**, 1200 (1969).

(30) (a) I. Ugi, D. Marquarding, H. Klusacek, G. Gokel, and P. Gillespie, *Angew. Chem.*, **82**, 741 (1970); (b) F. Ramirez, S. Pfohl, E. A. Tsolis, J. F. Pilot, C. P. Smith, I. Ugi, D. Marquarding, P. Gillespie, and P. Hoffmann, *Phosphorus* **1**, 1 (1971); (c) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, **4**, 288 (1971); (d) P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem.*, **83**, 691 (1971).

(31) J. B. Florey and L. C. Cusachs, *J. Amer. Chem. Soc.*, **94**, 3040 (1972).

(32) The axial–equatorial bond length differences in some PR_5 molecules are accurately known. For instance, in pentaphenylphosphorus P–C axial is 1.99 Å, P–C equatorial is 1.85 Å (P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964)); PF_5 has P–F axial 1.58 Å, P–F equatorial 1.53 Å (K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965)). In the phosphorus series axial bond distances are consistently longer than equatorial bond distances.

(33) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179 (1962); **37**, 2872 (1962). The Slater orbitals we used had exponents of 1.3 (H), 1.6 (P); H_{ii} were −13.6 (H 1s), −18.6 (P 3s), −14.0 eV (P 3p).

(34) Similar orbitals for PH_5 were obtained in an extended Hückel calculation which used somewhat different parameters: K. Issleib and W. Gründler, *Theor. Chim. Acta*, **8**, 70 (1967). An *ab initio* calculation on PH_5 has been carried out (ref 35), yielding similar orbitals except for a reversed ordering of 1e' and $1a_2''$. A previous extended Hückel calculation in our group has been briefly discussed in ref 36.

(35) A. Rauk, Princeton University, quoted by K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970); A. Rauk, L. C. Allen, and K. Mislow, *J. Amer. Chem. Soc.*, **94**, 3035 (1972).

(36) D. Boyd, R. Hoffmann, and S. Z. Goldberg, *J. Amer. Chem. Soc.*, **92**, 3929 (1970).

(37) An excellent description of the orbitals of XH_3 species has been given by B. M. Gimarc, *J. Amer. Chem. Soc.*, **93**, 593 (1971).

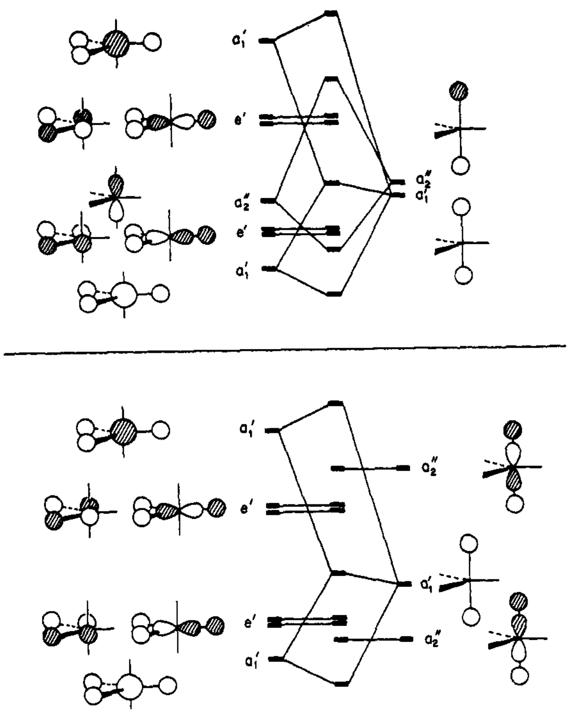


Figure 2. Two interaction diagrams for the construction of the molecular orbitals of D_{3h} PH_5. At the top the orbitals are constructed from the interaction of a planar PH_3 and two axial hydrogens. At the bottom the orbitals are formed from normal PH equatorial bonds and an electron-rich three-center bond as formulated by Rundle.

way, the upper a_1' in a bonding way.[38] Note that cancellation at P 3s follows. Moreover, since $2a_1'$ is derived primarily from the a_1' axial hydrogen combination, we can see that it should retain electron density mainly on those hydrogens.

An alternative construction of the PH_5 orbitals is based on the remarkably perceptive analysis of electron-rich three-center bonding due to Rundle.[15,21,39] Rundle viewed the equatorial PH bonding as normal, and for the axial PH bonding constructed delocalized orbitals from the P $3p_z$ and the axial hydrogen 1s functions. These three-center orbitals are shown at right in the bottom half of Figure 2. The nonbonding a_1' orbital of this three-center set is localized on the axial hydrogens. When we allow mixing of the equatorial PH σ and σ^* levels with the axial three-center system this a_1' orbital, in a manner just like that shown in **1** above, shifts a minor but significant part of its electron density to the equatorial hydrogens. Rundle's semilocalized model is very close to the completely delocalized molecular orbital picture.[40]

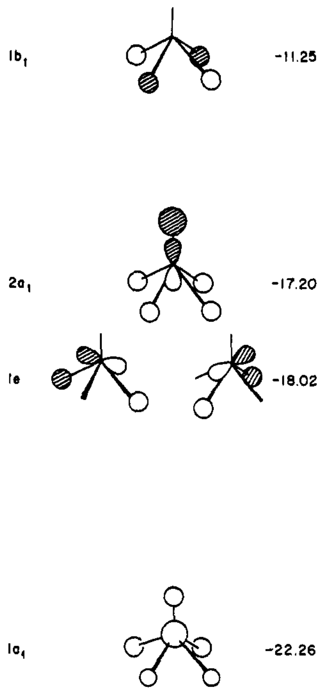
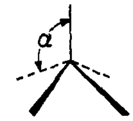
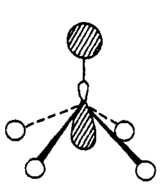


Figure 3. Occupied molecular orbtials of C_{4v} PH_5 derived from an extended Hückel calculation without d orbitals. The circle sizes indicate schematically the magnitude of the coefficients.

We turn to the C_{4v}, square pyramidal structure of PH_5. Within the C_{4v} constraint there remains a single parameter, the H_{apical}–P–H_{basal} angle α. In the absence of d orbitals, with all P–H = 1.42 Å, extended Hückel calculations yield the lowest energy for α = 99.8°. A calculation on PF_5[41] optimized α also at 99.8°. It might be noted that the simplest electrostatic model, five-point charges moving on the surface of a sphere while constrained to C_{4v} geometry, results in least repulsion for α = 104.1°.[42]



The energy levels and schematic orbital representation for this optimal α are given in Figure 3. The points to note are the following. (1) The ground configuration is $(1a_1)^2(1e)^4(2a_1)^2(1b_1)^2$. There now is an unoccupied molecular orbital not too high in energy. Its composition is indicated below. (2) As in the D_{3h} geometry there is here a very high-lying nonbonding orbital, separated by a large gap from the bonding orbitals. This is $1b_1$, by symmetry equally distributed over the four basal hydrogens only.



$3a_1$

In the square pyramid we have an essentially normal apical P–H bond and in the base electron-rich multicenter bonding. The similarity of the 1e + $1b_1$ set

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[38] The simple rules, derived from perturbation theory, which govern orbital interactions are given in R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

[39] Related to this analysis are two discussions of the electronic structure of interhalogen compounds: G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951); E. E. Havinga and E. H. Wiebenga, *Recl. Trav. Chim. Pays-Bas*, **78**, 724 (1959); E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, **3**, 133 (1961).

[40] Still another instructive construction of the PH_5 orbitals is obtained by approaching an H^- along a C_3 axis of a tetrahedral PH_4^+. See J. P. Lowe, *J. Amer. Chem. Soc.*, **93**, 301 (1971), for an analysis of the related CH_5^- problem.

[41] Where calculations involving the fluorine substituent are reported in this paper they refer to the following parameters: 2s, 2p exponents, 2.425; H_{ii}(2s), −40.0, H_{ii}(2p), −18.1 eV; P–F distance, 1.58 Å.

[42] J. Zemann, *Z. Anorg. Allgem. Chem.*, **324**, 241 (1963).

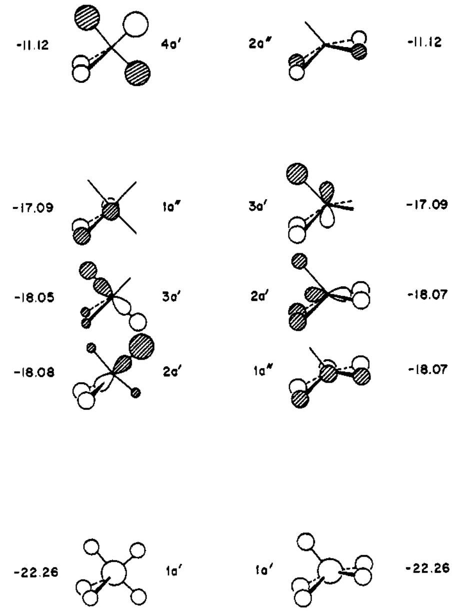
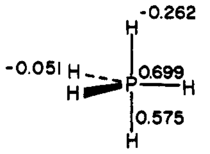
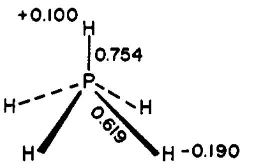


Figure 4. The occupied molecular orbitals of PH_5 with C_s geometry, as derived from an extended Hückel calculation without d orbitals. At left is the C_s structure resembling a distorted D_{3h} structure ($\delta = 0°$). At right is the C_s structure resembling a distorted C_{4v} geometry ($\delta = 30°$).

of C_{4v} PH_5 to the $1a_2'' + 2a_1'$ orbital set of the D_{3h} geometry is obvious. As noted by Rundle[15] and Bartell[21] the P–H bonds involved in this electron-rich multicenter bonding are weaker, and the corresponding hydrogens more negative. This emerges from the charges and overlap populations shown below.





There are seven degrees of freedom for the motion of five points on the surface of a sphere. The D_{3h} geometry is unique, while the C_{4v} structure is characterized by one degree of freedom. In the next section we will consider a two-dimensional surface connecting the D_{3h} and C_{4v} structures under the symmetry constraint of preserving two orthogonal planes of symmetry. However, at this point we want to consider the orbitals of a lower symmetry structure of C_s symmetry. The geometrical constraint for this structure may be easiest defined by specifying that the structure contains a PH_3 group with local C_{3v} symmetry and a PH_2' group with local C_{2v} symmetry, and moreover that the C_3 and C_2 axes coincide. Such a structure, illustrated in **2** or **3**, carries with it two

2

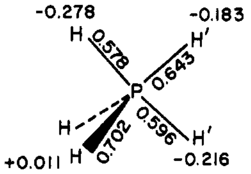
3

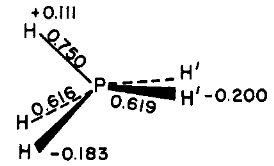
degrees of freedom: an HPH angle, β; an H'PH' angle, γ. We can define further an angle δ specifying the rotation of the threefold rotor relative to the twofold rotor. To anticipate an obvious result, the energy is expected to and does vary only very slightly with δ—we have here a sixfold barrier problem, and sixfold barriers are low in energy.

Why consider this structure? There are the following reasons: (1) such geometries, or close relations, have been suggested as possible way points in the polytopal rearrangements of phosphoranes;[43] (2) In the CH_5^+ system molecular orbital calculations make the C_s structure the global energy minimum.[44]

In our calculations the optimum energy C_s structure for PH_5 has $\beta = 91.5$, $\gamma = 87.2$, $\delta = 0°$.[45] For PF_5 these angles are 92.3, 85.6, and 0°, respectively. The energy difference between optimized **2** and **3** is only 0.07 kcal/mol. The molecular orbitals of both PH_5 C_s structures are shown in Figure 4.

The molecular orbitals of **2** are similar to those of the D_{3h} form. This is hardly a surprise since the angular distortion in going from D_{3h} to C_s (**2**) is small. Similarly the orbitals of **3** resemble those of the C_{4v} structure. Examination of structures with $0° < \delta < 30°$ shows the steady evolution of the orbitals from one extreme to the other. The results of a population analysis on the optimal C_s forms are shown below.





On comparison of the molecular orbitals of D_{3h}, C_{4v}, and C_s structures we note the following general features: (1) There is in each case a low-lying nodeless molecular orbital ($1a_1'$ in D_{3h}, $1a_1$ in C_{4v}, $1a'$ in C_s) consisting of an in-phase combination of P 3s with hydrogen 1s functions. (2) Next in energy, and not far separated from each other, is a group of three singly noded orbitals ($1a_2'' + 1e'$ in D_{3h}, $2a_1 + e$ in C_{4v}, $2a' + 3a' + 1a''$ in C_s), each composed of a single 2p orbital and an accompanying hy-

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[43] (a) *Cf.* the turnstile mechanism of I. Ugi, F. Ramirez, and coworkers, ref 30; (b) J. I. Musher in a 1969 lecture, published in ref 22b; (c) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969); (d) there is a relatively low frequency vibration of D_{3h} PX_5 molecules, $\nu_8(e'')$, which may distort the trigonal bipyramid toward this structure. ν_8 is at 514 cm^{-1} in PF_5: J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964); L. C. Hoskins and R. C. Lord, *ibid.*, **46**, 2402 (1967). The normal modes of PF_5 are shown in ref 8 and by R. R. Holmes, R. M. Deiters, and J. A. Golen, *Inorg. Chem.*, **8**, 2612 (1969).

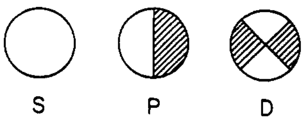
[44] (a) V. M. Volkov and A. A. Levin, *Zh. Strukt. Khim.*, **4**, 114 (1963); (b) G. Favini, G. Majorino, and M. Simonetta, *Accad. Naz. Lincei, Ser.* 8, **38**, 775 (1965); A. Gamba, G. Morosi, and M. Simonetta, *Chem. Phys. Lett.*, **3**, 20 (1969); C. R. M. Rutledge and A. F. Saturno, *J. Chem. Phys.*, **43**, 597 (1965); (d) L. C. Allen in "Quantum Theory of Atoms, Molecules and the Solid State," P.-O. Löwdin, Ed., Academic Press, New York, N. Y., 1966, p 62; (e) T. Yonezawa, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968); (f) J. L. Gole, *Chem. Phys. Lett.*, **3**, 577 (1969); **4**, 408 (1969); (g) S. Ehrenson, *ibid.*, **3**, 585 (1969); R. E. Weston and S. Ehrenson, *ibid.*, **9**, 351 (1971); (h) G. A. Olah, G. Klopman, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **91**, 3261 (1969); (i) W. Th. A. M. van der Lugt and P. Ros, *Chem. Phys. Lett.*, **4**, 389 (1969); (j) H. Kollmar and H. O. Smith, *ibid.*, **5**, 7 (1970); (k) V. Dyczmons, V. Staemmler, and W. Kutzelnigg, *ibid.*, **5**, 361 (1970); (l) J. J. C. Mulder and J. S. Wright, *ibid.*, **5**, 445 (1970); (m) N. L. Allinger, J. C. Tai, and F. T. Wu, *J. Amer. Chem. Soc.*, **92**, 579 (1970); (n) W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 808 (1971); (o) M. F. Guest, J. N. Murrell, and J. B. Pedley, *Mol. Phys.*, **20**, 81 (1971).

[45] $\delta = 0°$ refers to structure **2**. Conformation **3**, $\delta = 30°$ ($\equiv 90°$), independently optimized, has $\beta = 91.5$, $\gamma = 87.5°$. The effect of including 3d orbitals is small. For example, structure **2**, reoptimized with 3d orbitals on p, is described by $\beta = 93.3$, $\gamma = 87.4°$.

drogen combination. (3) In each case there is a high-lying nonbonding orbital, characterized by two nodal surfaces.

These features are hardly surprising when one considers a perturbed united atom model, or alternatively a system of ten electrons in a spherical box.[46a] The lowest energy level must be nodeless, S, with respect to the spherical pseudosymmetry. The next three, and only three, levels are singly noded, P, and the fifth level must be doubly noded, D.[46b]

The trivial observation of the pseudosymmetry of the PH_5 levels has some nontrivial consequences. First, we can write down qualitatively the molecular orbitals of any reasonable PH_5 geometry. Second, the interconversion of any PH_5 geometry into any other one is a reaction which conserves orbital symmetry, *i.e.*, preserves the nodal character of the orbitals.[47] Third, the pseudosymmetry observation allows us to say that no matter what the geometry of a PH_5, the participation of 3d orbitals on the central phosphorus will be effectively limited to stabilization of the doubly noded nonbonding orbital, the only one of pseudosymmetry D.[48]



The above discussion does not imply that we think the involvement of 3d orbitals in phosphorane bonding is important. The question of the role of 3d orbitals in bonding of second-row elements is an old one. Far too often have 3d orbitals been invoked as a kind of theoretical *deus ex machina* to account for facts apparently otherwise inexplicable. Our attitude toward 3d orbitals is pragmatic. We begin by working without them. We then analyze the way they would perturb the valence orbital picture *if* they were active. This allows us to span the spectrum of d orbital participation that must be present in real chemistry.

In this case, and elsewhere in the paper, whenever we wanted to probe the role of 3d orbitals, we repeated our calculations including a set of 3d orbitals with exponent 1.4, coulomb integral, −6.0 eV. The source of these parameters is traced in ref 29 and 35. We think they are reasonable, but an independent evaluation might be that they constitute only a guess, perhaps a reasonable one, for the case of moderate 3d interaction. With these parameters we confirm our supposition that only the nonbonding orbital is significantly stabilized, irrespective of geometry. In each case it is lowered by approximately 1.7 eV. This stabilization is of course accompanied by transfer of electron density, in our case approximately 0.6 of an electron, from the hydrogens to the phosphorus.

PH_5 is, of course, an unknown molecule. The most hydrogen-rich halophosphorane known is PH_2F_3.[49] The instability of PH_5 we think is likely to be a kinetic rather than a thermodynamic phenomenon. Though PH_5 is probably thermodynamically unstable relative to $PH_3 + H_2$,[50] a reaction we will discuss below, we think its instability is to be primarily attributed to the high-lying and exposed nonbonding molecular orbital. The electron density of this orbital is on the exterior of the molecule, readily available to any Lewis acid.

The Energetics of Polytopal Rearrangement in Phosphoranes

Having obtained an understanding of the electronic structure of various possible geometries of PH_5 we turn to the important problem of the pathways of interconversion of the various conformations. We must precede our considerations with several warnings to the reader concerning the reliability of our arguments. It will first be recalled that our geometries are not fully optimized, *i.e.*, all bond lengths are being kept constant. Second, the computational procedure used here, the extended Hückel method, occasionally gives misleading geometrical predictions. Third, we know that the potential surface is "soft," *i.e.*, reasonably large geometrical excursions cost little energy. This raises the possibility that, to use the language of modern collision theory, dynamic effects might be important. This means that for any specific rearrangement the height of the energy barrier need not be the only determinant and that the number, disposition, and local topography of the various reaction channels must be considered.

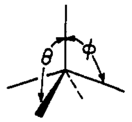
With these *caveats* in mind we show in Table I the energies of optimum C_{4v} and C_s structures, with and without d orbital participation, relative to the energy of the most stable point found by us on this surface, the trigonal bipyramid.

Table I. Calculated Conformation Energies (kcal/mol)

		D_{3h}	$C_{4v}{}^a$	$C_s{}^a$
PH_5	No 3d	[0]	2.3	9.1
	With 3d	[0]	2.1	7.4
PF_5	No 3d	[0]	0.7	9.9
	With 3d	[0]	1.4	10.0

[a] The energies given are for geometries individually optimized for PH_5 and PF_5.

We further find that neither the square pyramid nor the C_s structure is an energy minimum. From each there is a path of uniformly decreasing energy to the D_{3h} structure. A two-dimensional slice of the seven-dimensional potential surface, including one such pathway, is shown in Figure 5. The two degrees of freedom allowed in this figure are the angles shown below.



The constraint is of C_{2v} symmetry. The dashed line traces the interconversion of two trigonal bipyramids

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(46) (a) See for instance: R. Hoffmann and M. P. Gouterman, *J. Chem. Phys.*, **36,** 2189 (1962); (b) in principle a 2S orbital with a singly noded radial surface could be of a similar energy to the D orbital. In the molecular problem at hand it lies at higher energy.

(47) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81,** 797 (1969), and references therein.

(48) See also M. A. Ratner and J. R. Sabin, *J. Amer. Chem. Soc.*, **93,** 3543 (1971).

(49) (a) B. Blaser and K. H. Worms, *Angew. Chem.*, **73,** 76 (1961); (b) R. R. Holmes and R. N. Storey, *Inorg. Chem.*, **5,** 2146 (1966); (c) P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Amer. Chem. Soc.*, **89,** 2017 (1967); (d) a pentaalkylphoshorane has been reported: E. W. Turnbloom and T. J. Katz, *ibid.*, **93,** 4065 (1971).

(50) See ref 34 and W. E. Dasent, "Nonexistent Compounds," Marcel Dekker, New York, N. Y., 1965, p 153.

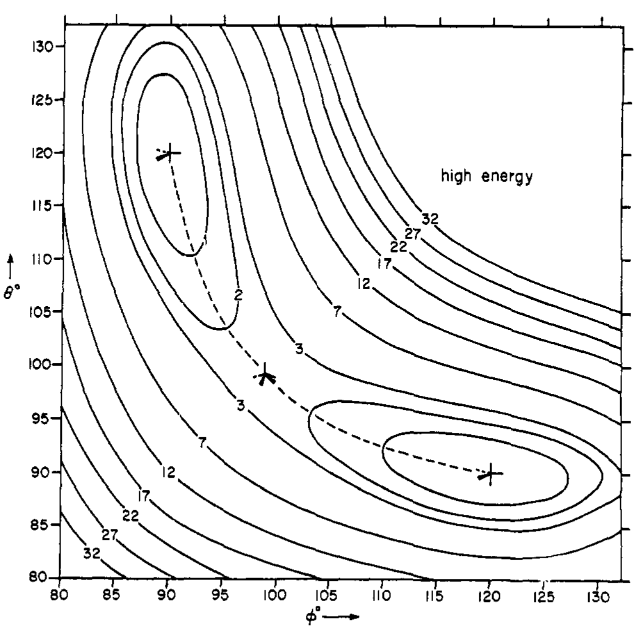

Figure 5. Potential surface for the Berry pseudorotation of PH_5. The energies were calculated by extended Hückel calculations without d orbitals. The angles are defined in the text. The pathway of minimum energy is indicated. The diagram has a mirror plane. Contours are in kcal/mol relative to the D_{3h} minima.

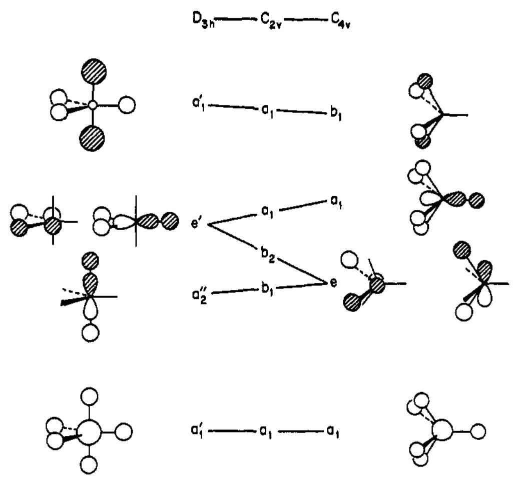

Figure 6. Correlation diagram for the $D_{3h} \rightarrow C_{2v} \rightarrow C_{4v}$ (trigonal bipyramid → square pyramid) transformation of PH_5. Only the occupied molecular orbitals are shown.

(ϕ = 120, θ = 90 and ϕ = 90, θ = 120°) through the optimal square pyramid (ϕ, θ = 99°). This C_{4v}–C_{2v}–D_{3h} pathway is the classic Berry pseudorotation.[51] In agreement with all experimental estimates[18,52,53] the barrier to this motion is small. It must be noted that the magnitude of this barrier as well as the general features of the two-dimensional surface of Figure 5 are adequately modeled by every calculation done on this system, from a classical electrostatic approach[42] to *ab initio* SCF computations.[35]

While we do not trust the absolute activation barriers calculated by us, we consider their relative magnitudes reliable.[54] It would appear therefore that in a symmetrically substituted phosphorane of the PR_5 type, interconversion of axial and equatorial positions through a C_s transition state is unlikely. This conclusion does not necessarily apply to less symmetrically substituted molecules, nor to cases where the C_{4v} structure is destabilized.

It should be emphasized that the turnstile mechanism,[30] as well as other possibilities discussed in ref 22b and 43c, are permutationally indistinguishable[55a] from the Berry mechanism; hence the importance of pursuing the question of the potential energy surface distinctions between these alternative physical realizations of a permutational process.

The evidence to date seems to us to favor the operation of the Berry mechanism for PF_5 and its derivatives. The work of Whitesides and Mitchell[56] has definitively shown that in R_2NPF_4 the character of the line changes in the nmr spectra is consistent only with the Berry mechanism or a permutationally equivalent mechanism. It should be emphasized that for this particular case the permutational group contains only two permutationally distinguishable mechanisms; thus only a few of the possible mechanisms have literally been excluded by this study. It must be kept in mind in considering mechanisms for rearrangements in five-coordinate species that if the actual bond angles in the molecule depart significantly from the idealized trigonal bipyramidal angles, it is unrealistic to consider any of the idealized mechanisms based on the trigonal bipyramid. An example of this type of situation has been found in five-coordinate transition metal hydrides of the type HML_4 where the ML_4 substructure is a regular tetrahedron or a nearly regular tetrahedron.[55b] The concept of facile *intra*molecular exchange has been questioned by Musher[22] and by Brownstein.[57] However, the studies on the rearrangement in PF_3Cl_2 and PF_3Br_2 would appear to unequivocally rule out bimolecular processes.[58]

In a molecular orbital picture one can trace the reasons for preference of D_{3h} to C_{4v} geometries one step further back. A correlation diagram for the D_{3h}–C_{2v}–C_{4v} transformation is shown in Figure 6.[59] The computed level trends show that the greatest energy changes and, within the extended Hückel method, the origin of the preference for the D_{3h} geometry, are those of the 1e' components—a_1 and b_2 in C_{2v}. These results must be considered with some skepticism since they are not fully consistent with the details of the *ab initio* calculation of PH_5.[35] But they do form the basis for a strategy to shift the stable point of the system from the trigonal bipyramid to the square pyramid—one must try to depress in energy the a_1 component of e', which favors the D_{3h} geometry.

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[51] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960); *Rev. Mod. Phys.*, **32**, 447 (1960). In these publications credit is given to F. T. Smith for the original suggestion of a pseudorotation operation. We might also note here the suggestion of pseudorotation in nuclear theory by E. Teller and J. A. Wheeler, *Phys. Rev.*, **53**, 778 (1938).

[52] L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, **46**, 2402 (1967).

[53] (a) R. R. Holmes and R. M. Deiters, *J. Amer. Chem. Soc.*, **90**, 5021 (1968); *Inorg. Chem.*, **7**, 2229 (1968); (b) R. R. Holmes, R. M. Deiters, and J. A. Golen, *Inorg. Chem.*, **8**, 2612 (1969).

[54] This statement must be viewed with the proper degree of skepticism. In ref 27 a method not very different from ours gave for PF_5 a C_{4v}–D_{3h} energy difference two orders of magnitude larger than what we obtained in Table I.

[55] (a) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971); (b) P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *ibid.*, **93**, 1797 (1971).

[56] G. M. Whitesides and H. L. Mitchell, *ibid.*, **91**, 5384 (1969).

[57] S. Brownstein, *Can. J. Chem.*, **45**, 711 (1967).

[58] W. Mahler and E. L. Muetterties, *Inorg. Chem.*, **4**, 1520 (1965).

[59] A similar correlation diagram for CH_5^+ was constructed in ref 44o.

In conclusion we note that an alternative second-order Jahn–Teller treatment of the preferred geometry of XY_5 systems has been presented by Pearson,[60] and that the molecular orbital model which predicts a close balance of D_{3h} and C_{4v} geometries for PH_5 at the same time clearly indicates a preference for the square pyramidal geometry of the equally hypothetical ClH_5. Only the C_{4v} geometry of PH_5 has a low-lying unoccupied orbital. While the halogen pentahydrides are unknown, the corresponding interhalogen XY_5 structures and $XeOF_4$ have the expected C_{4v} structures.

Substituent Effects in the Phosphorane System

We turn to a discussion of the differential effects of substituents which (1) are either more or less electronegative than hydrogen and/or (2) bear π-electron or lone-pair systems with electron donating or accepting capability. Our first steps must be in the nature of rationalizations rather than predictions—following the initial suggestion of Muetterties and coworkers[18] it is now well established that more electronegative substituents favor the axial positions of a trigonal bipyramid. The selective advantages of π-electron donors and acceptors are less well known, and provide some opportunity for a predictive analysis.

From several points of view it can be deduced that in the D_{3h} geometry more electronegative substituents will preferentially enter the axial positions.[13,15,18,21] The molecular orbital picture has as its keystone argument the relative accumulation of electron density at the axial hydrogens—the termini of the electron-rich three-center bond.[15,18] Electronegative substituents will then prefer to occupy those positions where there is most electron density—the axial positions of a trigonal bipyramid, the basal positions of a square pyramid.

To probe this effect we took *one* hydrogen in D_{3h} and C_{4v} PH_5 and made its coulomb integral more negative relative to its normal value of -13.6 eV. Figure 7 shows the resulting motion of the individual energy levels as well as the total energy. The behavior of the energy levels is entirely in accord with expectations—those levels which possess electron density at the altered hydrogen move to lower energy, and they do so in proportion to the magnitude of that electron density. For instance, the nonbonding MO of PH_5, $2a_1'$, which has a larger coefficient in its wave function at the axial hydrogens, is stabilized more by a more electronegative substituent in the axial position than it is for an equatorial substituent. It is interesting that the major part of the differential stabilization is due to the nonbonding orbital. This generalization is not upset by the introduction of 3d orbitals on phosphorus. While the energy of the nonbonding MO is altered and electron density moves to P more from the axial than the equatorial position the axial hydrogens remain more negative.

Given that the presence of the high-lying nonbonding orbital makes PH_5 susceptible to acid attack, such chemical reactivity should decrease as the energy of this orbital is lowered. While in PH_5 it is calculated to lie at -11.17 eV, in PH_4F it is at -12.83, PH_3F_2, -15.56, PH_2F_3, -15.76, PHF_4, -15.80, PF_5, -17.53.[61]

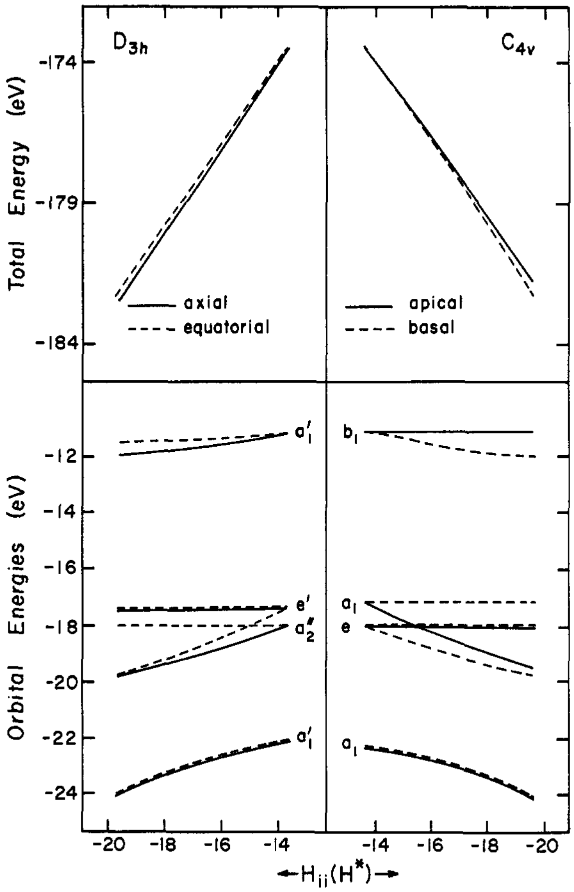

Figure 7. Effect of making a single hydrogen (H*) in PH_5 more electronegative than the others. At the right is the C_{4v} geometry while on the left is the D_{3h}. The horizontal axis is the value of the coulomb integral of H*.

The electronegativity argument was checked by a series of calculations on all substituted D_{3h} and C_{4v} fluorophosphoranes. The results are indicated pictorially in Figure 8, with A < B meaning that isomer A is at lower energy than isomer B. These stability orders remain the same whether phosphorus 3d orbitals are included or omitted. The actual energies are sensitive to the presence of 3d orbitals (*e.g.*, $E(PF_3H_aH_a) - E(PF_3H_eH_e)$ is 2.4 eV without 3d orbitals, 1.3 eV with). Geometries were not optimized for intermediate structures, and the extended Hückel method is known to poorly represent highly ionic bonding. For these reasons we do not report the computed energies, only the rough trend confirming the electronegativity argument. Similar results in the PF_xCl_{5-x} series have been reported by Van der Voorn and Drago.[25a,62] The CNDO/2 calculations of Gillespie and Ugi[30] also confirm the stability sequences, but point to a more substantial role of 3d orbitals in determining this order than is indicated by our calculations. All methods, including ours, agree on the significant effect of 3d orbitals in increasing P–X bond orders.

There is no rule that a specific molecule *must* conform to either strict D_{3h} or C_{4v} symmetry. It is perhaps worthwhile to point out in which cases distortions

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(60) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

(61) The PH_xF_{5-x} geometries are those calculated to be most stable—*i.e.*, with fluorines entering axial positions first.

(62) This work failed to predict the correct structure of PF_4Cl. In our case the correct trigonal-bipyramid geometry for PF_4H is favored only if 3d orbitals are included.

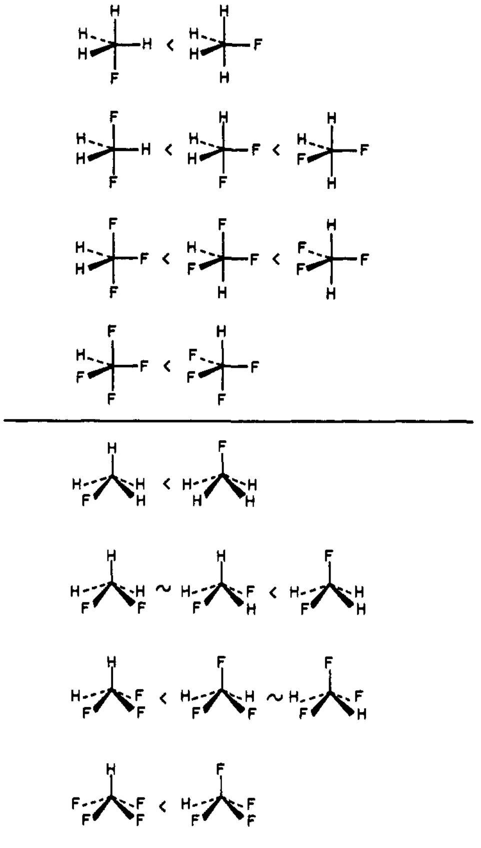
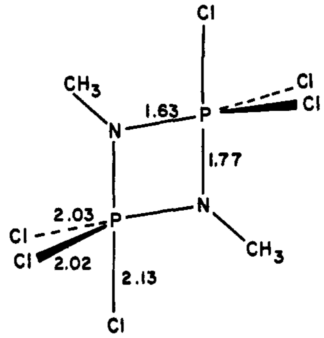


Figure 8. Relative stabilities of the various fluorophosphoranes as derived from extended Hückel calculations. At the top there are the trigonal-bipyramid structures and at the bottom the square pyramid. A < B implies A has lower energy than B.

from the favored D_{3h} skeleton are to be watched for. In the D_{3h} structure of PX_3Y_2, where X is more electronegative than Y, one X group must enter an equatorial position. In a C_s structure, on the other hand, there are three sites of high electron density. It is conceivable that the equilibrium geometry could distort from D_{3h} toward C_s, or that C_s geometries could now serve as transition states for site interchange mechanisms. Similarly in PX_4Y geometries a C_{2v} distortion away from D_{3h} and toward C_{4v} could be favored.

The available structural evidence shows little sign of such distortion in ground-state geometries. Structures are available for($CH_3)_2PF_3$,[21a] CH_3PF_4,[21a] HPF_4,[63] CF_3-PF_4,[64] and CF_2=$CFPF_4$.[65] In these cases C_s geometries for PX_3Y_2 and C_{4v} for PX_4Y do not prevail, angular departures from perfect trigonal-bipyramid symmetry are sometimes in the opposite direction, and, most importantly, there is a significant difference in bond distances for the axial and equatorial fluorine sets.

Still another striking example of the resistance of a PX_3Y_2 molecule to undergo a distortion toward a C_s ground-state geometry is shown by the structures of the dimeric *N*-methyltrichlorophosphinimine[66] and its phenyldifluoro[67a] and trifluoro[67b] analogs. In these structures, one of which is shown schematically below,[66a]



the local trigonal-bipyramid geometry at phosphorus is maintained, despite an N–P–N angle of approximately 80°.[68]

On the other hand phosphonium ylides R_3P=CR_2 apparently show no trace of a trigonal-bipyramid fragment geometry at phosphorus.[36] One way of thinking about this is that the constraint of a two-membered ring has enforced the C_s structure. The transition to C_s occurs then somewhere between the two- and four-membered ring, and the equilibrium structure of an as yet unsynthesized pentacoordinate phosphorus in a three-membered ring becomes highly interesting.

We turn to an examination of the geometrical preferences of π-electron donors and acceptors, independent of their electronegativity. The argument is twofold—a theoretical consideration of symmetry restrictions on interaction, buttressed by a computational study of model donors and acceptors.

The following concepts underlie our discussion. A π donor is defined as a substituent with one or two high-lying occupied molecular orbitals, as shown schematically in **4**. A π acceptor is defined as a substituent with one or two low-lying unoccupied molecular orbitals, *e.g.*, **5**. As shown in the interaction diagram below we have to consider three basic interactions for a donor. Interaction I, inherently destabilizing,[38,69,70]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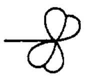
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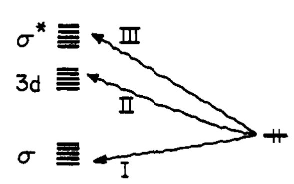

is between the donor and occupied PH_5 skeleton orbitals. Interaction II, inherently stabilizing, is between the potentially active phosphorus 3d orbitals and the donor. Interaction III, also stabilizing, is between unfilled skeletal orbitals and the donor. In

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(63) S. B. Pierce and C. D. Cornwell, *J. Chem. Phys.*, **48**, 2118 (1968).

(64) E. A. Cohen and C. D. Cornwell, *Inorg. Chem.*, **7**, 398 (1968). There is a controversy concerning the structure of this molecule. See also, J. E. Griffiths, *J. Chem. Phys.*, **49**, 1307 (1968).

(65) C. H. Chang, R. F. Porter, and S. H. Bauer, to be published.

(66) (a) L. G. Hoard and R. A. Jacobson, *J. Chem. Soc. A*, 1203 (1966); (b) H. Hess and D. Forst, *Z. Anorg. Allgem. Chem.*, **342**, 240 (1966).

(67) (a) J. W. Cox and E. R. Corey, *Chem. Commun.*, 123 (1967); (b) A. Almenningen, B. Anderson, and E. E. Astrup, *Acta Chem. Scand.*, 23, 2179 (1969).

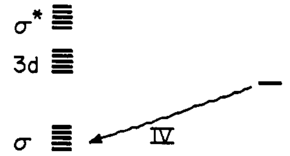
(68) A recently determined structure of a four-membered cyclic oxyphosphorane does show some distortion toward local threefold symmetry: Mazhar-Ul-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilots, and C. P. Smith, *J. Amer. Chem. Soc.*, **93**, 5229 (1971).

(69) L. Salem, *ibid.*, **90**, 543 (1968).

(70) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, and references therein.

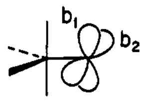
D_{3h} PH_5 there are no low-lying σ^* orbitals and we have found little trace of interaction III. In C_{4v} PH_5 there is a somewhat low-lying unfilled MO, but even here we have not found normal donors utilizing it. We can thus restrict our discussion to interactions I and II.

For an acceptor the situation is simple (see below). There is now only one chemically significant interaction, IV, between the acceptor orbital and the occupied skeletal set.



Let us begin with the group theory for the D_{3h} case. Consider axial substitution, as in **6**, and equatorial substitution, as in **7**. With the molecular symmetry lowered from D_{3h} to C_{3v} on axial substitution, or to C_{2v} on equatorial substitution, the occupied MO's of PH_5 transform as indicated below. The substituent orbitals transform as e in C_{3v}, and as $b_1 + b_2$ in C_{2v}. The immediate simplification is that for interactions I and IV only the underlined orbitals participate.

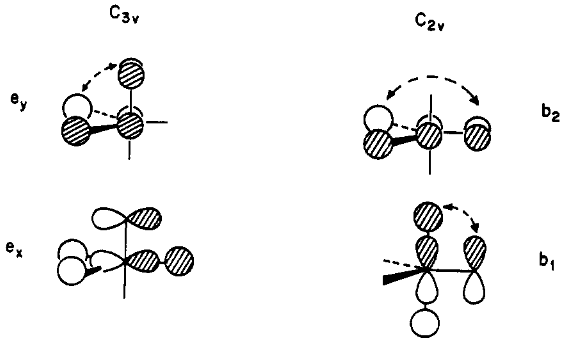
6



7

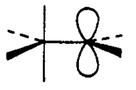
C_{3v} ⟶	D_{3h} ⟶	C_{2v}
$3a_1$	$2a_1'$	$3a_1$
$\underline{1e}$	$1e'$	$\underline{1b_2}$
$2a_1$	$1a_2''$	$2a_1$
$1a_1$	$1a_1'$	$\underline{1b_1}$
		$1a_1$

Consider interactions I and IV first. We are not as interested in the extent to which a given donor or acceptor interacts with the PH_5 skeleton as we are in whether it interacts more or less in an equatorial position compared to an axial one. For an acceptor the site with maximum interaction will be favored (IV is stabilizing). For a donor the site with maximum interaction will be destabilized (I is a repulsive term). The axial and equatorial interactions which are allowed by symmetry are shown below.



Interactions e_x and e_y, though different in appearance, are identical by symmetry. Interaction b_2 is weaker than its axial counterpart e_y since in e_y the acceptor has an increased overlap with the p-type hydrogen combination (see arrows above). Similarly we can decide that the b_1 interaction is greater than b_2. It is difficult to draw any qualitative conclusion on the relative strengths of the b_1 and e interactions. We fall back on calculations with model donors and acceptors such as CH_2^+, CH_2^-, NH_2, and a hydrogen bearing empty or filled p orbitals of variable energy. In every case the interaction b_1 was predicted to be of comparable strength to e_x and e_y, *i.e.*, stronger than b_2. Our first conclusion then is that interactions between donor or acceptor orbitals and framework σ orbitals are stronger for axial than for equatorial substitution. This immediately implies that, if 3d orbitals are not of importance, *π acceptors will prefer axial sites, π donors equatorial positions.*

An interesting further prediction can be made for a substituent bearing a single π system (*e.g.*, OR, COOR, NO_2 in contrast to Cl, CN). In an axial site there will be little preferential orientation for such a substituent—it encounters a sixfold barrier. In an equatorial site we have found that the b_1 interaction is stronger than b_2. This implies that *an equatorial single π-system acceptor will prefer to have its acceptor orbital perpendicular to the equatorial plane,* as in **8**, while *an equatorial donor will prefer to have its donor orbital in the equatorial plane,* as in **9**.



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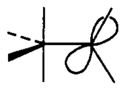


9

The differential donor-framework π-bonding effects noted here are not small. For a model equatorial amino group in PF_4NH_2 arbitrarily kept planar, conformation **9** is calculated to be 0.28 eV more stable than **8**, d orbitals not included. With 3d orbitals this difference rises to 0.78 eV. These numbers are not reliable, but they are indicative. The P–N overlap population trends also show this effect. In conformation **9**, the more stable one, the P–N overlap population is 1.02, while in **8** it is 0.91, both with 3d orbitals included.

We now turn to an analysis of interaction II, the role of 3d orbitals. It must be reemphasized that all we can produce here is an argument for a trend. We have no way of estimating the true degree of d orbital participation, which no doubt will vary with the substituent pattern. We can only include the d orbitals in the calculation with parameters which put them low in energy and with high overlap with substituent orbitals—this we call a model for extensive participation. Then we can repeat the calculation with the 3d orbitals at high energy and low overlap, and identify the result with the minimal end of the participation spectrum. We have done this and reach the following conclusions which we consider less reliable than our other results concerning substituent effects. (1) There is certainly a p–d π bonding component, with significant effects on computed bond orders over a wide range of d orbital participation. (2) The *differential* effect, *i.e.*, the increment in stability between axial and equatorial d-orbital bonding, appears to be, except for the case of maximal d-orbital participation, a *smaller* effect than the interaction of donor and framework orbitals. To put it another way, when we assign to the 3d orbitals a reasonable exponent and energy we find that any axial–equatorial energy differences are dominated by interaction I rather than II. (3) It has traditionally been assumed that axial π bonding is more efficient than equatorial π bonding. Our calculations reach the opposite conclusion.[71] The detailed rationalization may be found in the Appendix. Interaction II thus also favors equatorial donor substitution.

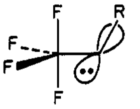
A similar analysis of donor and acceptor interactions in the square pyramid reaches the following conclusions: (1) *In a* C_{4v} *geometry* π *donors will prefer the apical position, while* π *acceptors will favor the basal sites.* (2) *If the basal substituent carries a single* π *system, it will preferentially align that system in the basal plane for an acceptor, but parallel with the apical bond for a donor.*

The conclusions derived by us apply strictly speaking to a single donor or acceptor. The arguments for multiple substitution can be similarly constructed, though they inevitably become more complicated. Our experience with substituent effects in another area, however, indicates that one can expect the effects to be approximately additive.[72]

The balance of electronegativity and π-donating or accepting capability must be judged individually in each case. Consider, for example, fluorine as a substituent. It is most electronegative and so favors the axial site. On the other hand it is also a π donor, which we predict would enter an equatorial position. Both in our calculations and in reality the electronegativity effect dominates.

We turn to the experimental evidence on preferred geometries for equatorial or basal donors or acceptors. The only information available, that for donors in an equatorial position on a trigonal bipyramid, is in excellent agreement with our predictions.

Thus, the low-temperature nmr spectra of S-substituted thiotetrafluorophosphoranes of type **10** show



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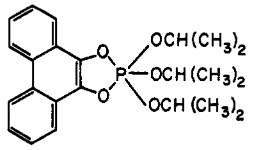
nonequivalence of the axial fluorines.[73] The donor role here is played by the highest occupied MO of the –SR group, the p-type lone pair on sulfur. Conformational preference for the sterically encumbered conformation **10** is shown. Similar observations are available for aminophosphoranes,[74–76] with activation barriers of 5–12 kcal/mol for rotation reported.[74]

In a recent nmr study of $PF_3(NH_2)_2$ we have shown that the equilibrium structure contains both amino lone pairs in the equatorial plane and that there exists a barrier of 11 kcal/mol to uncorrelated rotation about the P–N bond.[77]

In 2,2,2-triisopropoxy-4,5-(2′,2′′-biphenyleno)-1,3,2-dioxaphospholene (**11**) there are two equatorial isopropoxy groups.[78a] The crystal structure[78b] of two modifications of this molecule reveals that both isopropoxy groups assume approximately the conformation anticipated by us, namely with the oxygen p-type lone pair in the equatorial plane. However, the structure is a crowded one and the conformation found may have been forced for steric reasons.[79] It is interesting that the two equatorial isopropoxy P–O distances are on the average 0.06 Å shorter than the third equatorial distance, that involved in the phenanthrenequinone moiety.



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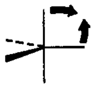
In concluding this discussion of substituent effects we would like to make explicit a connection with organic chemistry which the careful reader no doubt has noted: *every argument presented here for* PX_5 *may be carried over to* CX_5^-*, to be used for stabilizing or destabilizing the transition state for the* SN2 *reaction.*[80]

The Fragmentation of PR_5

Reaction 1 below, most commonly known with R =

$$\mathrm{PR_5} \rightleftharpoons \mathrm{PR_3} + \mathrm{R_2} \qquad (1)$$

Cl, has a venerable history dating from the middle of the 19th century to every contemporary freshman textbook of general chemistry.[81–88] What is the mechanism of this reaction? If it is truly unimolecular, and this ought to be reinvestigated with modern kinetic methods, where does the R_2 fragment come from? Given a trigonal-bipyramid geometry of PR_5, do the components of R come at random from axial and equatorial positions, or is one of the specific mechanisms **12**, **13**, or **14** operative? An analysis from the point of



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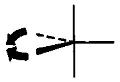

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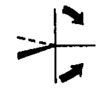

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(71) Similar conclusions were reached in ref 25a.

(72) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); R. Hoffmann and W.-D. Stohrer, *J. Amer. Chem. Soc.*, **93**, 6941 (1971).

(73) S. C. Peake and R. Schmutzler, *Chem. Commun.*, 1662 (1968); *J. Chem. Soc. A*, 1049 (1970).

(74) M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, *Zh. Strukt. Khim.*, **8**, 1097 (1967); V. V. Sheluchenko, M. A. Sokalskii, M. A. Landau, G. I. Drozd, and S. S. Dubov, *ibid.*, **10**, 142 (1969); M. A. Sokalskii, G. I. Drozd, M. A. Landau, and S. S. Dubov, *ibid.*, **10**, 1113 (1969).

(75) J. J. Harris and B. Rudner, *J. Org. Chem.*, **33**, 1392 (1968).

(76) J. S. Harman and D. W. A. Sharp, *Inorg. Chem.*, **10**, 1538 (1971).

(77) E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, in press.

(78) (a) F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *ibid.*, **86**, 4394 (1964); F. Ramirez and N. B. Desai, *ibid.*, **82**, 2652 (1960); **85**, 3252 (1963); F. Ramirez, *Bull. Soc. Chem. Fr.*, 113 (1970); (b) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Amer. Chem. Soc.*, **87**, 127 (1965); W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, **89**, 2268 (1967); R. D. Spratley, W. C. Hamilton, and J. Ladell, *ibid.*, **89**, 2272 (1967).

(79) In diphenyltriethoxyphosphorane, in which two alkoxy groups are axial and one equatorial, there appears to be no evidence for freezing in of the equatorial ethoxy group conformation: D. B. Denney, D. Z. Denney, B. C. Chang and K. L. Marsi, *ibid.*, **91**, 5243 (1969).

(80) See also P. Gillespie and I. Ugi, *Angew. Chem.*, **83**, 493 (1971).

(81) E. Mitscherlich, *Ann. Phys. Chem.*, **29**, 221 (1833).

(82) A. Cahours, *Ann. Chim. Phys.*, *Ser.* 3, **20**, 369 (1847).

(83) A. Wurtz, *C. R. Acad. Sci.*, **76**, 601, 610 (1873).

(84) W. Gibbs, *Amer. J. Sci. Arts*, [3] **18**, 381 (1919).

(85) W. Nernst, *Z. Elektrochem.*, **22**, 37 (1916); C. Holland, *ibid.*, **18**, 234 (1912).

(86) A. Smith and R. P. Calvert, *J. Amer. Chem. Soc.*, **36**, 1363 (1914); A. Smith and R. H. Lombard, *ibid.*, **37**, 2055 (1915); A. Smith, *Z. Elektrochem.*, **27**, 33 (1916).

(87) W. Fischer and O. Juberman, *Z. Anorg. Allgem. Chem.*, **235**, 337 (1938).

(88) D. P. Stevenson and D. M. Yost, *J. Chem. Phys.*, **9**, 403 (1941).

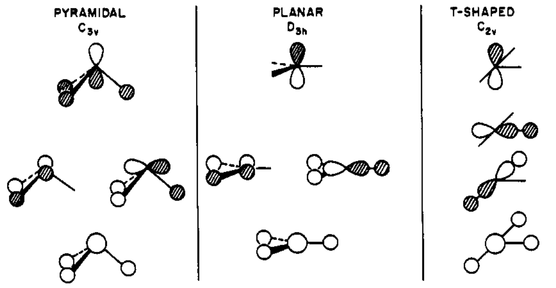

Figure 9. Occupied molecular orbitals of PH_3 with various geometries.

view of conservation of orbital symmetry[47] yields a simple and surprising answer.

Let us first analyze the least-motion process **12** for R = H. Here an axial and equatorial hydrogen atom depart. There is a temptation to draw a correlation diagram for this motion utilizing the C_s plane preserved. However, all the orbitals directly involved in this process lie in that mirror plane, and thus such a correlation diagram cannot yield the required information.[89] We must look at the evolution of the orbitals in the course of the reaction.

Consider the orbitals of the D_{3h} structure beginning the motion **12**. The initial distortion is to a C_s structure whose orbitals are given at the left side of Figure 4. The 1a′, 2a′, and 1a′′ orbitals of that C_s form have the proper shape for becoming the PH σ bonds of the PH_3 pyramid. The PH_3 orbitals in question are $1a_1$ and 1e of the left-hand side of Figure 9.[37] The 3a′ orbital becomes the PH_3 lone pair. Thus the H_2 σ_g orbital must be derived from 4a′, but 4a′ has a node between the departing hydrogens. No continuous evolution of orbitals is possible in this mode such that the PH_5 orbitals yield a ground-state configuration of PH_3 and simultaneously one of H_2. The reaction is forbidden.

We turn to the equatorial–equatorial departure **13**. Here a correlation diagram may be utilized, since it bisects the newly formed H–H σ bond. The diagram is shown in Figure 10. The orbitals at left are those of D_{3h} PH_5, reclassified in symmetry according to the two mirror planes maintained. At right are the orbitals of the product—a T-shaped PH_3 and H_2. The PH_3 orbitals were described in Figure 9.[37] The transformation of T-shaped PH_3 into the equilibrium C_{3v} structure does not change nodal patterns, *i.e.*, it is an allowed reaction. No doubt the PH_3 fragment in this allowed fragmentation would begin distorting toward a pyramid even in the early stages of the reaction. Our conclusion that this is an allowed process would be unchanged.

We finally analyze the axial–axial elimination **14**. A correlation diagram is shown in Figure 11.[59] The reaction is symmetry allowed. The process at first sight appears sterically unlikely, but in a sense it is a continuation of the Berry pseudorotation.

We have concluded that of the three possible departure modes, two, **13** and **14**, are allowed and one, the least-motion **12**, is forbidden. A similar analysis for the square pyramid indicates that the least-motion **15** is forbidden, **16** and **17** allowed.

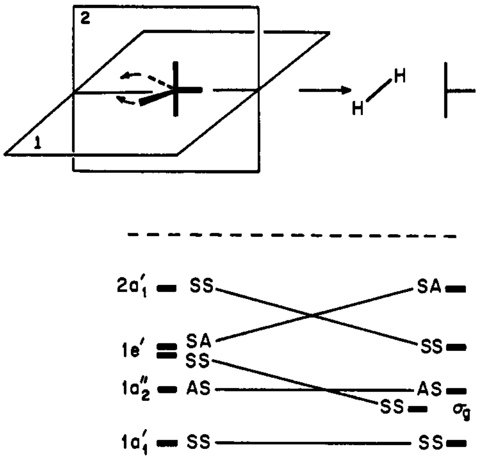

Figure 10. Correlation diagram for the departure of two equatorial hydrogens from PH_5 (left) to yield PH_3 + H_2 (right). Only occupied orbitals are shown. Symmetry classification is with respect to the indicated planes. Refer to Figure 9 for orbitals of T-shaped PH_3.

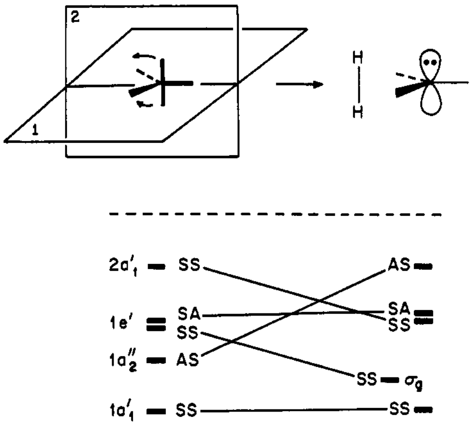

Figure 11. Correlation diagram for the departure of two axial hydrogens from PH_5 (left) to yield PH_3 + H_2 (right). Only occupied molecular orbitals are shown. Symmetry classification is with respect to the indicated planes. Refer to Figure 9 for orbitals of planar PH_3.


15


16


17

Our results for PH_5 fragmentation can be carried over directly to other PX_5 systems. Still there is no experimental evidence to test our predictions. Tracer experiments with ^{36}Cl indicated that only three chlorines are scrambled in PCl_5.[90] However, this cannot be taken as evidence for a dissociation–recombination mechanism with equatorial–equatorial elimination, since the remaining PCl_3 atoms would be scrambled. Clearly further experimental work on a carefully designed system with inhibited pseudorotation is required to test our proposal.

Acknowledgment. Our collaboration began in the course of a George F. Baker Lectureship at Cornell University by E. L. M. We are grateful to the Baker

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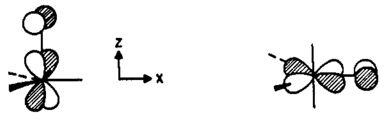
(89) See the section entitled "Precautions in the Construction of Correlation Diagrams" in ref 47.

(90) J. Downs and R. E. Johnson, *J. Chem. Phys.*, **22**, 143 (1954); *J. Amer. Chem. Soc.*, **77**, 2098 (1955). See however L. Kolditz and D. Hass, *Z. Anorg. Allgem. Chem.*, **294**, 191 (1958).

Fund for creating this circumstance. The research of R. H. and J. M. H. was generously supported by the National Science Foundation, the National Institutes of Health (GM 13468), and the Petroleum Research Fund of the American Chemical Society. The initial interest of R. H. in phosphorane chemistry was stimulated by D. A. Usher and F. H. Westheimer. We are grateful to M. Marsh, D. B. Boyd, and A. R. Rossi for discussions of this problem.

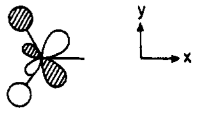
Appendix

Equatorial *vs.* Axial d–p π Bonding. The usual argument concerning this point[3,20] goes as follows: Consider a pair of donor orbitals in an axial position, e_x, e_y (**6**), and in an equatorial position, b_1, b_2 (**7**). The P 3d orbitals which can by symmetry interact with these donor orbitals are: $e_x + d_{xz}$, $e_y + d_{yz}$, $b_1 + d_{xz}$, $b_2 + d_{xy}$. The difference between axial and equatorial substitutions comes down to a weighing of the interaction $e_y + d_{yz}$ (axial) *vs.* $b_2 + d_{xy}$ (equatorial). It is assumed that the d_{xy} orbital is partially tied up in improving equatorial σ bonding. Thus the $e_y + d_{yz}$ axial interaction is said to be more stabilizing.



$e_y + d_{yz}$ $b_2 + d_{xy}$

In contrast to this we find that over a wide range of d-orbital positions there is very little interaction with the PH_5 σ orbitals. Instead we see significant mixing with PH_5 σ^* orbitals, depressing the e′ (d_{xy}, $d_{x^2-y^2}$) d orbital combination and making it more available as an acceptor orbital. The combined $d_{xy} + PH_{\sigma^*}$ orbital has the shape shown in **18**. The bonding character in its combination with the donor p orbital is enhanced, **19**.



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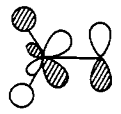

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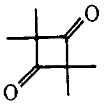
Pentacovalent Phosphorus. IV. Cyclic Pentacovalent Phosphoranes from Reaction of Trivalent Phosphorus Compounds with Dimethylketene

Wesley G. Bentrude,* W. Delmar Johnson,[1] and Wajid A. Khan

Contribution from the Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112. Received August 9, 1971

Abstract: The reaction at −70° of dimethylketene with a wide variety of PXYZ gives a series of new 2:1 adducts containing pentacovalent phosphorus in a five-membered ring (**5**). Spectroscopic and chemical evidences for structure **5** are presented. Their preferred configurations from pmr spectra are discussed on the basis of trigonal-bipyramidal structures. The relative stabilities of the series of adducts (**5**) are shown to be in accord with the expectations based on the strain and polarity rules. They are further shown to undergo clean reaction with water, methanol, CS_2, CO_2, CH_3I, and Br_2 to give structurally novel products often in high yields.

Our interests in the chemistry of pentacovalent phosphorus in general,[2] and especially in the reactions of trivalent phosphorus compounds with the dione and lactone dimers of dimethylketene (**1** and **2**),[3] led us to examine the reaction of dimethylketene itself with trivalent phosphorus nucleophiles. Reactions of **1** and **2** with various PXYZ appear to proceed[3] *via* pentacovalent species of the types **3** and **4**. It seemed quite possible that intermediates of this type might be generated independently by reactions of dimethylketene with PXYZ at low temperatures and stabilized for study under those conditions. Instead we find that near-quantitative amounts of 2:1 adducts of structure **5** are formed in reactions with general applicability to a wide variety of trivalent phosphorus derivatives, PXYZ. The phosphorane ring system containing the functionality



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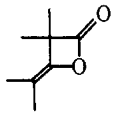

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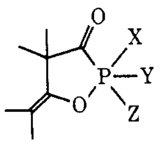

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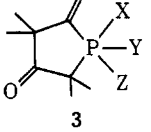

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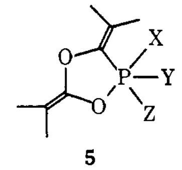

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[1] National Institutes of Health Predoctoral Fellow. Taken in part from the Ph.D. Thesis of W. D. Johnson, University of Utah, 1969; published in part in preliminary form: W. G. Bentrude and W. D. Johnson, *J. Amer. Chem. Soc.*, **90**, 5924 (1968).

[2] W. G. Bentrude and K. R. Darnall, *Chem. Commun.*, 862 (1969); W. G. Bentrude, *ibid.*, 174 (1967); W. G. Bentrude and K. R. Darnall, *Tetrahedron Lett.*, 2511 (1967); W. G. Bentrude, *J. Amer. Chem. Soc.*, **87**, 4026 (1965).

[3] W. G. Bentrude W. D. Johnson, and W. A. Khan, *ibid.*, **94**, 923 (1972); W. G. Bentrude, W. D. Johnson, W. A. Khan, and E. R. Witt, *J. Org. Chem.*, **37**, 631 (1972); W. G. Bentrude, W. D. Johnson, and W. A. Khan, *ibid.*, **37**, 642 (1972).