

Fluorine and Chlorine Apicophilicities in Five-Coordinated Phosphorus and Silicon Compounds via Molecular Orbital Calculations. A Model for Nucleophilic Substitution^{1a}

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Abstract: Comparative ab initio molecular orbital calculations on pentacoordinated phosphorus and silicon model states are used to establish apicophilicities in a series of trigonal-bipyramidal molecules composed of all combinations of the ligand atoms, hydrogen, chlorine, and fluorine. In agreement with experimental observations, it is shown that chlorine is in general more apicophilic than fluorine except when the collective electronegativity of equatorial atoms is increased sufficiently, e.g., as in the $\text{PCl}_n\text{F}_{5-n}$ series. The crossover in halogen apicophilicity for silicon has an even greater electronegativity requirement in equatorial sites than that for phosphorus. Further, as applied in nucleophilic substitution reactions, the apicophilicity of the leaving group is diminished by the composition of equatorial ligands in the order $\text{Cl} > \text{F} > \text{H}$. In contrast, the apicophilicity of the leaving group is enhanced by the opposite apical atom in this same order, $\text{Cl} > \text{F} > \text{H}$, in all cases except that in which the equatorial atoms are of very low electronegativity. Here, the order becomes $\text{Cl} > \text{H} > \text{F}$. These results allow a self-consistent interpretation of phosphorus and silicon substitution reactions that vary in the degree of inversion and retention of configuration caused by the type of leaving group and entering nucleophile. Further, it is found that when equatorial substituents are altered, the calculated apicophilicity correlates directly with ligand charges; i.e., the apicophilicity decreases as the difference of the sums of the apical and equatorial ligand atom charges, $\sum q_{\text{eq}} - \sum q_{\text{ap}}$, decreases.

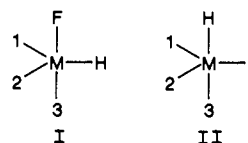
Interpretation of nucleophilic displacement reactions of phosphorus and silicon compounds proceeding by way of postulated five-coordinated intermediates is hampered by the lack of knowledge of the relative energies of isomeric trigonal bipyramids that comprise most of these states. While some progress has been made in phosphorus chemistry,^{2,3} the relevant data are almost nonexistent in silicon chemistry. It is assumed here, as in the Westheimer approach to the hydrolysis of phosphate esters,⁴ that axial entry of the nucleophile takes place in forming the intermediate trigonal bipyramid and that axial departure of the leaving group occurs in forming products. If the activated states are sufficiently long-lived, it is further assumed that ligand rearrangement, i.e., pseudorotation, may be encountered before product formation.⁴

The latter process has a strong basis in phosphorus chemistry where dynamic NMR studies have established intramolecular ligand exchange processes for many phosphorane molecules.^{2,5} More recently, in a limited way, the same type of study has been carried out^{6,7} for five-coordinated anionic siliconates that are isoelectronic with the phosphoranes. For both phosphoranes⁸⁻¹¹ and five-coordinated anionic siliconates,¹¹⁻¹⁴ X-ray studies have

mapped the distortion coordinate between trigonal bipyramids and square pyramids, showing that the coordinate followed in each case is the Berry¹⁵ pseudorotational coordinate. The latter investigations support this process as the one governing solution-state NMR ligand exchange processes.

In a theoretical approach to nucleophilic substitution, we have performed ab initio calculations^{16,17} to interpret inversion and retention processes for chiral silicon compounds proceeding by way of five-coordinated states. The results support apical entry and departure in trigonal-bipyramid intermediates (Figure 1)¹⁶ and show an order of leaving groups, in terms of relative apicophilicities,¹⁷ in agreement with experimental observations,^{18,19} i.e., $\text{H}^- < \text{OH}^- < \text{SH}^- \sim \text{F}^- < \text{Cl}^-$.

Apicophilicity is a convenient term to use in comparing relative isomer energies.^{16,17} It is defined as the change in energy when an apical and an equatorial substituent exchange positions in a trigonal bipyramid. For example, the isomer energy difference, $E_{(\text{II})} - E_{(\text{I})}$, is the apicophilicity of fluorine relative to hydrogen, $A(\text{F}_\text{H})$. The expression written this way will give a positive value for the apicophilicity when structure I with the fluorine axial is more stable than II. For acyclic derivatives having simple ligands,



apicophilicity integrates a number of factors including electronegativity, inductive effects, and π -bonding contributions. If small ring systems or sterically encumbered groups are present, then changes in strain energies as the substituents involved move between apical and equatorial positions, e.g., in pseudorotational processes, are additional factors that will contribute to isomer energy differences.^{3,20}

(1) (a) Presented in part at the Eighth International Symposium on Organosilicon Chemistry, St. Louis, MO, June 1987; Abstract B17. (b) Department of Chemistry, Vassar College, Poughkeepsie, NY 12601.

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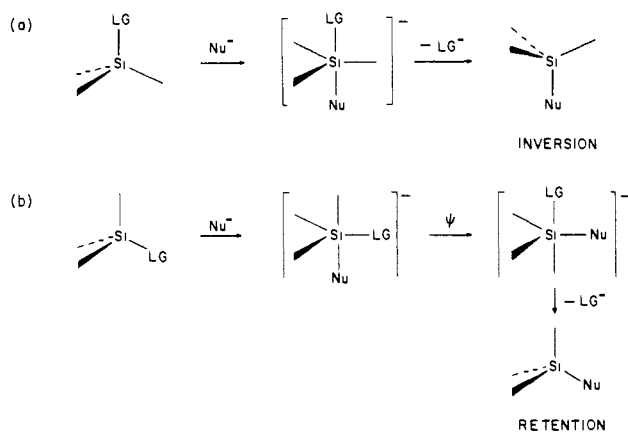


Figure 1. Mechanisms for nucleophilic substitution reactions at silicon: (a) inversion, and (b) retention involving axial attack and pseudorotation to give axial departure. ψ symbolizes a pseudorotational process.

Although apicophilicity is defined in a thermodynamic sense, most of the relevant data has its source in NMR activation energies of ligand exchange processes.^{2,3,20} These measurements yield energy differences between ground states and transition states.²¹ While it may not be unreasonable to presume that there will be a correspondence between the transition state and the trigonal-bipyramidal reaction intermediate, it would be highly desirable to have a thermodynamically established reference set to use in the analysis of reaction pathways. This set should be free of ring strain or steric effects so that a proper assessment of these terms may be made when present in a particular series subject to experimental investigation. It is the purpose of this paper to outline the construction of such a series. An important point not adequately treated before is the evaluation of the influence of the other three groups attached to either phosphorus or silicon in determining the relative apicophilicity of two groups. For example, in our previous study,¹⁷ it was established that the apicophilicity of the leaving group varied with the series of nucleophiles used and enters into the determination of the relative tendency toward a retention vs an inversion pathway.^{18,19}

An adequate knowledge of the influence of other groups on apicophilicity is required if we are to interpret nucleophilic substitution reactions with any degree of confidence. McDowell and Streitwieser^{24a} carried out an ab initio molecular orbital study of the model system PH_3X and found a ligand apicophilicity order $\text{Cl} > \text{CN} > \text{F} > \text{CCH} > \text{H} > \text{CH}_3 > \text{OH} > \text{O}^- > \text{S}^- > \text{NH}_2 > \text{BH}_2$, in general agreement with Trippett's²⁰ "experimental" scale, although it was noted^{24a} that F and Cl were in the opposite order from experimental expectations. Also, the structures of

(21) Many of these comparisons are complicated by the presence of small rings or steric effects. Rate measurements in which different groups are competitively displaced provide a relative ordering of ligands on an apicophilicity scale: Reference 2, pp 129–149. Also complicated are thermodynamic approaches where ground-state phosphorane structures are identified in competitive formation²⁵ or in equilibrium situations.²³

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(24) (a) McDowell, R. S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5849–5855. Several other ab initio calculations^{24b-d} on isomers of PHF_4 , PH_2F_3 , PH_3F_2 , and PH_4F yield apicophilicity values, but it is difficult to make comparisons within the series because the basis sets vary. (b) Keil, F.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1975**, *97*, 3623–3632. (c) Bestmann, H. J.; Chandrasekhar, J.; Downey, W. G.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1980**, 978–980. (d) Strich, A.; Veillard, A. *J. Am. Chem. Soc.* **1973**, *95*, 5574–5581. Pertinent also are gas-phase studies of halide ion affinities, which demonstrate the stability of pentacoordinated anionic silicates. These, however, mainly contain alkyl groups and do not allow a comparison here. (e) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 4992–4999. (f) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012–5015. (g) Sheldon, J. C.; Hayes, R. N.; Bowie, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 7711–7715. (h) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766–773. (i) Damrauer, R.; Yost, V. E.; Danahey, S. E.; O'Connell, B. K. *Organometallics* **1985**, *4*, 1779–1784.

members of the $\text{PCl}_n\text{F}_{5-n}$ series have the fluorine atoms in apical positions.^{25–27}

In a number of papers, Corriu²⁸ has suggested that the work of Westheimer and co-workers⁴ on phosphate ester hydrolysis is a special case applicable only to nucleophiles and leaving groups that involve the formation and cleavage of P–O bonds. In a more general experimental approach in substitution reactions, Corriu²⁸ finds analogous behavior between phosphorus and silicon, leading to the hypothesis that the change of stereochemistry, i.e., retention to inversion, and the increase in reaction rate for five-membered ring compounds are related to the symmetry of the trigonal-bipyramidal intermediate. Under this hypothesis, we expect an enhanced rate and tendency for inversion when the two apical atoms are the same, i.e., when the incoming nucleophile and leaving group are composed of the same type of ligand atom attached to the central atom in the intermediate trigonal bipyramid. When the entering and leaving groups differ in the type of atoms that are attached at the reaction center, a tendency toward a retention process is favored in that a slower reaction is expected.

It is important to define the role apicophilicity plays in bringing about the variations in interpretation noted above in both theoretical and experimental studies. In this present work, we extend the molecular orbital calculations^{16,17} to include a study of the apicophilicity of fluorine and chlorine atoms as leaving groups and how apicophilicity is affected by changes in the other ligands placed around phosphorus and silicon. This study encompasses the calculation of the energies of the permuted trigonal-bipyramidal isomers in the series composed of all combinations of the ligand atoms, hydrogen, chlorine, and fluorine, for each of these elements. The results show the factors responsible for crossovers in the ordering of apicophilicities encountered in the calculations and associate the changes in apicophilicities with electronic properties of equatorial vs apical positions of trigonal bipyramids. This analysis provides a basis for interpreting certain analogies that exist between phosphorus and silicon reaction chemistry. These are taken up in the Discussion.

Scope and Method

Optimum bond lengths and energies, $E(\text{SCF})$, were determined for every trigonal-bipyramidal isomer of each phosphorane molecule in the series $\text{PH}_x\text{Cl}_y\text{F}_z$ and for all the trigonal-bipyramidal anions of the iso-electronic silicon series $[\text{SiH}_x\text{Cl}_y\text{F}_z]^-$. All angles were constrained to those of an ideal trigonal bipyramid. The values of x , y , and z ranged from 0 to 5 with $x + y + z = 5$. Calculations were carried out with the program GAUSSIAN 82²⁹ either on line at the San Diego Supercomputer Center or via the UMass Engineering Computer Services VAX cluster. For the phosphorus molecules, the basis set was 3-21G(*) (split-level valence with polarization functions on second- and third-row atoms), and it was 6-31G* when it was evident that 3-21G(*) was not adequate for relative isomer energies. For the anionic silicon series diffuse orbitals³⁰ were added to the basis sets for all non-hydrogen atoms, as appropriate for negatively charged species. This basis set is designated 3-21+G*.

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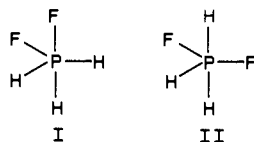
For one series of molecules (PH_2ClF_2 , PHClF_3 , PClF_4), calculations were carried out at STO-3G, 3-21G(*), 3-21+G*, 6-31G*, and 6-31+G*, and for the corresponding silicon anions, calculations were done at STO-3G, 3-21+G*, and 6-31+G* to show how the choice of basis set affects apicophilicity. For one pair of isomers of PH_2ClF_2 an optimization was done with a 6-31G** basis set. Also, a full optimization (bond angles as well as bond lengths optimized) was carried out on PHCl_2F_2 to establish that the energy differences, which determine apicophilicity, are not significantly altered by full optimization.

For selected anions in the silicon series, additional calculations were done with a 6-31+G* basis set to determine that relative isomer energies agreed within 1–2 kcal/mol with those calculated at the 3-21+G* level.

Results

Calculated energies (3-21G(*) basis set for phosphorus and 3-21+G* basis set for silicon anions) are reported in Table S1 (supplementary material). Calculated energies at optimum bond lengths for selected hydrido chlorides and for all chlorofluorides, hydrido fluorides, and hydrido chloro fluorides of the phosphorus series (6-31G* basis set) and for selected anions of the silicon series (6-31+G* basis set) are reported in Tables S2 and S3, respectively. Values of charge density (Mulliken population analysis) and bond lengths for the highest level calculation are reported for phosphorus and silicon in Tables S4 and S5, respectively. Isomer energies relative to the ground-state isomer for the phosphorus molecules are reported in Table I and for silicon anions in Table II. Calculated apicophilicities, fluorine relative to hydrogen (F_H), chlorine relative to hydrogen (Cl_H), and chlorine relative to fluorine (Cl_F), are reported for phosphorus and silicon in Tables III–V, respectively.

Apicophilicities are calculated from the relative isomer energies listed in Tables I and II. For example, in the molecule PH_3F_2 (Table I), the apicophilicity $A(F_H)$ (6-31G*), i.e., the energy difference ($E_{II} - E_I$) for the exchange of F_{ap} and H_{eq} (isomer I with F_{ap} , F_{ap} to F_{eq} and H_{ap} (isomer II with F_{ap} , H_{ap}) is 13.61 kcal/mol. This value is listed in Table III as the first entry in column 1 as the apicophilicity of F (relative to hydrogen) with a fluorine atom in the opposite apical position. One might also observe that the energy difference between the second and third isomers of PH_3F_2 (Table I) is also the apicophilicity F_H but with a different atom in the opposite apical position. This value, (6-31G*) = 21.03 – 13.61 = 7.42 kcal/mol, is reported in Table III (second entry in column 3) as $A(F_H)$ with hydrogen in the opposite apical position and hydrogen and fluorine in the remaining equatorial positions.



Discussion

Structures. In the mixed chlorofluorides of phosphorus, the entire series of molecules, $\text{PCl}_m\text{F}_{5-m}$ has been prepared²⁵ and bond lengths and angles have been determined by electron diffraction.^{26,27} Our calculations with both the 3-21G(*) and 6-31G* basis sets correctly predict the stable isomers for each member of this series and give bond lengths in good agreement with experimental values. This comparison is shown in Table VI. Figure 2 shows the comparison of experimental bond lengths with those calculated at the 6-31G* level. As seen in Figure 2, increasing substitution of fluorine by chlorine results in a lengthening of all bonds.

In this calculation, bond lengths were optimized while bond angles were held fixed at the values for the ideal trigonal bipyramid. Of the six phosphorus chlorofluorides, three have D_{3h} symmetry, one has C_{3v} symmetry, and two have the less symmetric C_{2v} structure. To test the effect of partial optimization, a full optimization was done on PClF_4 with the 3-21G(*) basis set. This is shown in Table VII along with the results of partial optimization at the 6-31G* level. Full optimization at the 3-21G(*) level results in an energy only 0.36 kcal/mol lower than the value obtained at the 3-21G(*) level with partial optimization. It was found,

Table I. Relative Energies (kcal/mol) for Trigonal Bipyramids with H, F, and Cl Substituents on Phosphorus

formula	apical atoms	relative ^a energy
	Chlorofluorides	
PClF_4	F, F	0.00 (0.00)
	Cl, F	5.64 (4.09)
PCl_2F_3	F, F	0.00 (0.00)
	Cl, F	4.45 (5.20)
	Cl, Cl	11.52 (9.17)
PCl_3F_2	F, F	0.00 (0.00)
	Cl, F	2.06 (6.25)
	Cl, Cl	8.53 (11.55)
PCl_4F	Cl, F	0.00 (0.00)
	Cl, Cl	4.94 (6.77)
	Hydrido fluorides	
PHF_4	F, F	0.00 (0.00)
	H, F	7.00 (5.82)
PH_2F_3	F, F	0.00 (0.00)
	H, F	7.84 (10.73)
PH_3F_2	H, H	10.79 (9.71)
	F, F	0.00 (0.00)
	H, F	6.84 (13.61)
PH_4F	H, H	14.05 (21.03)
	H, F	0.00 (0.00)
	H, H	11.33 (15.95)
	Hydrido chlorides	
PHCl_4	Cl, Cl	0.00
	H, Cl	0.69
PH_2Cl_3	Cl, Cl	0.00 (0.00)
	H, H	1.84 (1.69)
	H, Cl	10.42 (11.03)
PH_3Cl_2	Cl, Cl	0.00
	H, Cl	19.75
PH_4Cl	H, H	23.77
	H, Cl	0.00
	Hydrido chloro fluorides	
PHCl_3F	H, F	0.00 (0.00)
	Cl, F	2.66 (2.04)
	Cl, Cl	3.41 (5.01)
	H, Cl	6.24 (8.12)
PHCl_2F_2	H, F	0.00 (2.85)
	Cl, F	0.61 (2.60)
	Cl, Cl	2.10 (3.88)
	F, F	2.49 (0.00)
	H, Cl	8.08 (9.75)
PHClF_3	Cl, F	0.00 (1.23)
	F, F	0.34 (0.00)
	H, F	2.51 (4.23)
	H, Cl	11.43 (9.83)
	Cl, Cl	0.00 (0.00)
$\text{PH}_2\text{Cl}_2\text{F}$	F, Cl	4.40 (1.55)
	H, H	6.22 (6.28)
	H, F	11.12 (9.21)
	H, Cl	13.69 (14.24)
	Cl, F	0.00 (0.00) 0.00 ^b
	F, F	7.00 (1.98) 2.03 ^b
PH_2ClF_2	H, H	8.72 (8.56)
	H, F	9.88 (10.79)
	H, Cl	13.52 (14.33)
	Cl, F	0.00 (0.00)
	H, Cl	13.58 (18.08)
PH_3ClF	H, F	16.02 (17.15)
	H, H	19.38 (23.52)

^a Calculated with the 3-21G(*) basis set. Numbers in parentheses are relative isomer energies calculated with the 6-31G* basis set.

^b Calculated with the 6-31G** basis set.

as will be described later, that the level of the calculation had a greater effect on relative isomer energies than full optimization. In the phosphorus chlorofluorides, both basis sets, 3-21G(*) and 6-31G*, with partial optimization correctly predict the observed ground-state structures and give bond lengths with an average deviation of ± 0.14 Å (3-21G*) and ± 0.01 Å (6-31G*) from experimental values. Thus, partial optimization was used throughout the rest of the calculations.

Table II. Relative Energies (kcal/mol) for Trigonal-Bipyramidal Anions with H, F, and Cl Substituents on Silicon

formula	apical atoms	relative ^a energy
Chlorofluorides		
[SiClF ₄] ⁻	F, Cl	0.00 (0.00)
	F, F	0.44 (1.46)
[SiCl ₂ F ₃] ⁻	Cl, Cl	0.00 (0.00)
	F, F	0.01 (2.26)
[SiCl ₃ F ₂] ⁻	Cl, F	0.92 (3.10)
	F, F	0.00
	Cl, F	2.15
[SiCl ₄ F] ⁻	Cl, Cl	2.73
	Cl, F	0.00
	Cl, Cl	1.95
Hydridofluorides		
[SiHF ₄] ⁻	F, F	0.00
	H, F	4.11
[SiH ₂ F ₃] ⁻	F, F	0.00
	H, H	6.26
[SiH ₃ F ₂] ⁻	F, H	7.90
	F, F	0.00
	H, F	9.83
[SiH ₄ F] ⁻	H, H	14.76
	H, F	0.00
	H, H	12.78
Hydriochlorides		
[SiHCl ₄] ⁻	Cl, Cl	0.00
	H, Cl	0.69
[SiH ₂ Cl ₃] ⁻	Cl, Cl	0.00
	H, H	1.84
[SiH ₃ Cl ₂] ⁻	H, Cl	10.42
	Cl, Cl	0.00
	H, Cl	19.75
[SiH ₄ Cl] ⁻	H, H	23.77
	H, Cl	0.00
	H, H	18.71
Hydriochlorofluorides		
[SiHCl ₃ F] ⁻	Cl, Cl	0.00
	H, F	1.51
	Cl, F	2.03
	H, Cl	6.58
[SiHCl ₂ F ₂] ⁻	Cl, Cl	0.00
	Cl, F	3.67
	F, F	5.62
	H, F	6.04
[SiHClF ₃] ⁻	H, Cl	9.66
	Cl, F	0.00 (0.00)
	F, F	3.36 (4.66)
	H, F	5.57
[SiH ₂ Cl ₂ F] ⁻	H, Cl	7.70
	Cl, Cl	0.00
	Cl, F	6.48
	H, H	10.10
	H, F	15.75
[SiH ₂ ClF ₂] ⁻	H, Cl	16.88
	Cl, F	0.00 (0.00)
	F, F	6.72 (7.94)
	H, H	8.69 (10.19)
	H, Cl	11.94 (11.15)
[SiH ₃ ClF] ⁻	H, F	12.67 (12.67)
	Cl, F	0.00
	H, Cl	14.04
	H, F	18.58
	H, H	21.35

^a Calculated with the 3-21+G* basis set. Numbers in parentheses are relative isomer energies calculated with 6-31+G* basis set.

None of the phosphoranes of the type PH_nCl_{5-n} (hydriochlorides) or PH_nF_{5-n} (hydridofluorides) have had their structures determined experimentally, except for the phosphonium salt PH₄⁺Cl⁻.³¹ ¹⁹F NMR data³² and vibrational analysis³³ support

(31) (a) Durig, J. R.; Antion, D. J.; Pate, C. B. *J. Chem. Phys.* **1970**, *52*, 5542-5548.

(32) (a) Treichel, P. M.; Goodrich, R. A.; Pierce, S. B. *J. Am. Chem. Soc.* **1967**, *89*, 2017-2072. (b) Cowley, A. H.; Braun, R. W. *Inorg. Chem.* **1973**, *12*, 491-492.

Table III. Apicophilicity of F_H (kcal/mol)

I

II

R', R''	M = P ^a			M = Si ^b		
	R = F	R = Cl	R = H	R = F	R = Cl	R = H
H, H	13.61	18.08	15.95	9.83	14.04	12.78
H, F	10.73	14.33	7.42	7.90	11.94	4.93
F, F	5.82	8.60	-1.02	4.11	7.70	-1.64
H, Cl	8.81	12.69	6.38	5.95	10.40	2.77
Cl, Cl	2.85	6.08	-2.93	0.42	4.55	-5.65
F, Cl	4.23	7.15	-2.23	2.21	5.99	-3.98

^a Calculated with the 6-31G* basis set. ^b Calculated with the 3-21+G* basis set.

Table IV. Apicophilicity of Cl_H (kcal/mol)

I

II

R', R''	M = P ^a			M = Si ^b		
	R = F	R = Cl	R = H	R = F	R = Cl	R = H
H, H	17.15 ^c	19.75	18.71	18.58	22.01	21.42
H, F	10.79 ^c	14.24 ^c	5.44 ^c	12.67	16.88	7.31
F, F	3.00 ^c	5.87 ^c	-5.77 ^c	5.57	9.66	-3.25
H, Cl	7.66 ^c	10.42	4.02	9.27	13.83	3.68
Cl, Cl	-2.04 ^c	0.69	-8.58	-0.52	3.97	-9.63
F, Cl	0.25 ^c	3.11 ^c	-7.96 ^c	2.37	6.58	-6.78

^a Calculated with the 3-21G(*) basis set. ^b Calculated with the 3-21+G* basis set. ^c Calculated with the 6-31G* basis set.

Table V. Apicophilicity of Cl_F (kcal/mol)

I

II

R', R''	M = P ^a			M = Si ^b		
	R = F	R = Cl	R = H	R = F	R = Cl	R = H
H, H	1.98	1.55	-0.93	6.72	6.48	4.54
H, F	-1.23	-1.28	-3.54	3.36	3.67	0.73
F, F	-4.09	-3.97	-5.60	0.44	0.92	-2.13
H, Cl	-2.60	-2.97	-5.03	1.95	2.03	-1.13
Cl, Cl	-6.25	-6.77	-8.12	-2.15	-1.95	-5.07
F, Cl	-5.20	-5.30	-6.90	-0.91	-0.58	-3.62

^a Calculated with the 6-31G* basis set. ^b Calculated with the 3-21+G* basis set.

trigonal-bipyramidal structures for PHF₄, PH₂F₃, and PH₃F₂, which give preference to fluorine atoms in apical positions. Structural inferences are lacking on the remainder of the molecules considered here.

The bond length data obtained from the calculations for the PH_nCl_{5-n} series correctly predict the dissociation of PH₄Cl to ionic PH₄⁺Cl⁻. As seen in Figure 3a, the apical P-Cl bond length, which increases smoothly from PCl₅ to PH₃Cl₂, exhibits an abrupt increase of 0.12 Å from 2.19 to 2.30 Å for PH₄Cl. The P-Cl bond overlap also drops dramatically to 0.07 from 0.13 for PH₃Cl₂.³⁴

(33) (a) Holmes, R. R.; Hora, C. J., Jr. *Inorg. Chem.* **1972**, *11*, 2506-2515. (b) Seel, K.; Velleman, K. Z. *Anorg. Allg. Chem.* **1971**, *385*, 123-130.

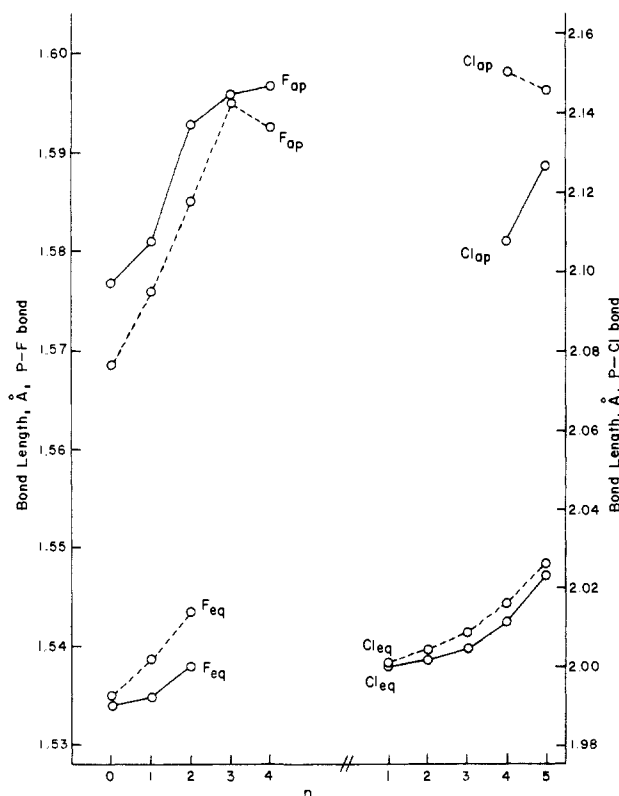
(34) Calculations done by Glaser and Streitwieser with full optimization of PH_nX (X = F, Cl) show the stable form of PH₄Cl to be an ion pair, phosphonium chloride, while, in PH₄F, the stable form is a phosphorane. Also, the order of apicophilicities calculated for these molecules agreed with our results: Glaser, R.; Streitwieser, Jr., A., personal communication.

Table VI. Experimental and Calculated Bond Lengths (Å) for the $\text{PCl}_n\text{F}_{5-n}$ Series ($n = 0-5$)

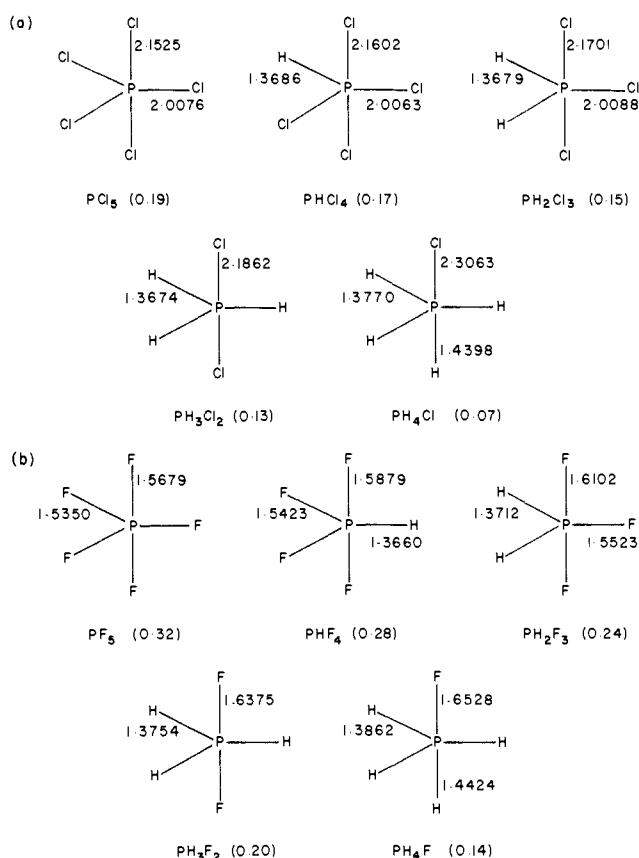
		exptl ^a	calcd ^b	calcd ^c
PF ₅	F _{ap}	1.577	1.566	1.568
	F _{eq}	1.534	1.538	1.535
PF ₄ Cl	F _{ap}	1.581	1.572	1.576
	F _{eq}	1.535	1.543	1.539
PF ₃ Cl ₂	Cl _{eq}	2.000	1.980	2.001
	F _{ap}	1.593	1.579	1.585
PF ₂ Cl ₃	F _{eq}	1.538	1.550	1.544
	Cl _{eq}	2.002	1.987	2.004
PFCl ₄	F _{ap}	1.596	1.589	1.596
	Cl _{eq}	2.005	1.995	2.008
PFC ₄	F _{ap}	1.597	1.585	1.592
	Cl _{ap}	2.107	2.151	2.151
PCl ₅	Cl _{eq}	2.011	2.002	2.017
	Cl _{ap}	2.127	2.153	2.146
	Cl _{eq}	2.023	2.008	2.026

^a Reference 26. ^b 3-21G(*) basis set. ^c 6-31G* basis set.**Table VII.** Comparison of Bond Parameters for PCIF₄ Calculated at Different Basis Sets

	3-21G(*) (partial opt ^a)	3-21G(*) (full opt)	6-31G* (partial opt ^a)	exptl ^b
Bond Lengths, Å				
P-F _{ap}	1.572	1.572	1.576	1.581
P-F _{eq}	1.543	1.545	1.539	1.535
P-Cl _{eq}	1.980	1.975	2.001	2.000
Bond Angles, deg				
Cl _{eq} PF _{ap}	90.0	90.6		90.3
F _{eq} PF _{eq}	120.0	116.5		117.8

^a Regular trigonal-bipyramidal angles. ^b Reference 26.**Figure 2.** Bond lengths in $\text{PCl}_n\text{F}_{5-n}$ molecules. A solid line indicates bond lengths determined by experiment, and a dotted line, bond lengths determined by calculation with 6-31G* basis set. The labels ap and eq refer to apical or equatorial location of the atom.

The bond length increase in the $\text{PH}_n\text{F}_{5-n}$ series (Figure 3b) shows a smooth increase across the entire series. For reasons to be discussed later, we chose to use the 6-31G* basis set for the series $\text{PH}_n\text{F}_{5-n}$ shown in Figure 3b.

**Figure 3.** Bond lengths, Å, for phosphorus hydrido-halides: (a) $\text{PH}_n\text{Cl}_{5-n}$ series, bond lengths calculated with the 3-21G(*) basis set; (b) $\text{PH}_n\text{F}_{5-n}$ series, bond lengths calculated with the 6-31G* basis set. Numbers in parentheses refer to the bond overlap in the apical bond to chlorine (or fluorine). Replacement of halogen substituents by hydrogen results in an increase in the P-Cl (or P-F) bond length and a decrease in the bond overlap in agreement with VSEPR theory.

Unlike the phosphorus chlorofluorides, no stable compound of a five-coordinated anionic silicon chlorofluoride has been synthesized nor are any members of the hydrido-halide series known. Hence, no structural data are available for comparison to the calculated structural parameters for these series.

We find, as in the $\text{PCl}_n\text{F}_{5-n}$ series, that calculations at the 3-21G(*) level (or 3-21+G* level) for all of the other series involving two kinds of ligand atoms, $\text{PH}_n\text{F}_{5-n}$, $\text{PH}_n\text{Cl}_{5-n}$, $\text{SiCl}_n\text{F}_{5-n}^-$, $\text{SiH}_n\text{F}_{5-n}^-$, and $\text{SiH}_n\text{Cl}_{5-n}^-$ ($n = 1-4$), predict, with only two exceptions, SiClF_4^- and $\text{SiCl}_2\text{F}_3^-$, that the most stable trigonal-bipyramidal isomer is the one that places the more electronegative atoms in apical positions. In SiClF_4^- , the isomer with F, Cl apical is predicted (in both the 3-21+G* and the 6-31+G* basis set) to be slightly more stable (~ 1 kcal) than the isomer with F, F apical. In $\text{SiCl}_2\text{F}_3^-$ the isomer with Cl, Cl apical is predicted in the 3-21+G* basis set to be as stable as the F, F apical isomer (Table II) and in the 6-31+G* basis set to be slightly more stable (by 2 kcal). With these two exceptions, the trend in all other cases in the series mentioned above is in agreement with what is generally known about pentacoordinated phosphorus⁸⁻¹¹ and anionic silicon compounds,¹¹⁻¹⁴ which have preferential occupancy of apical positions by the more electronegative atom. All of the X-ray structures on acyclic five-coordinated anionic fluoro- and penta-oxy-silicates that we¹²⁻¹⁴ and others¹¹ have done, covering over a dozen compounds, are in accord with this electronegativity preference.

Basis Set Comparison. It is expected that extension of the type of calculations performed here to the series containing three different kinds of ligand atoms should prove valid also. For this series, it is noted in Table I for phosphorus (3-21G(*) basis set) and Table II for silicon (3-21+G* basis set) that the lowest energy isomer in several cases no longer has the most electronegative

Table VIII. Effect of Basis Set on Apicophilicity

I

II

	$E_{(I)}$, au	$E_{(II)}$, au	$A(\text{Cl}_F)$, kcal/mol
M = P			
R' = R'' = H			
STO-3G	-988.635 181	-988.612 146	14.45
3-21G(*)	-995.527 163	-995.516 006	7.00
3-21+G*	-995.589 170	-995.593 477	-2.70
6-31G*	-1000.272 522	-1000.269 373	1.98
6-31+G*	-1000.283 654	-1000.284 902	-0.78
6-31G**	-1000.277 100	-1000.273 869	2.03
R' = H, R'' = F			
STO-3G	-1086.100 669	-1086.084 910	9.89
3-21G(*)	-1093.909 425	-1093.908 881	0.34
3-21+G*	-1093.985 273	-1093.993 187	-4.97
6-31G*	-1099.166 796	-1099.168 757	-1.23
6-31+G*	-1099.178 910	-1099.183 382	-2.81
R' = R'' = F			
STO-3G	-1183.568 969	-1183.560 607	5.25
3-21G(*)	-1192.289 025	-1192.298 015	-5.64
3-21+G*	-1192.380 955	-1192.391 267	-6.47
6-31G*	-1198.060 109	-1198.066 622	-4.09
6-31+G*	-1198.074 284	-1198.082 163	-4.94
M = Si			
R' = R'' = H			
STO-3G	-937.383 355	-937.354 497	18.11
3-21+G*	-944.163 466	-944.152 795	6.72
6-31+G*	-948.646 442	-948.633 784	7.94
R' = H, R'' = F			
STO-3G	-1034.881 340	-1034.860 998	12.76
3-21+G*	-1042.616 148	-1042.610 786	3.36
6-31+G*	-1047.588 938	-1047.581 505	4.66
R' = R'' = F			
STO-3G	-1132.381 026	-1132.368 876	7.62
3-21+G*	-1141.068 134	-1141.067 427	0.44
6-31+G*	-1146.530 333	-1146.528 011	1.46
R' = F, R'' = Cl			
STO-3G	-1488.975 626	-1488.972 629	1.88
3-21+G*	-1499.508 182	-1499.509 648	-0.92
6-31+G*	-1506.550 111	-1506.551 437	-0.83

atoms in the apical position. We determined with PHCl_2F_2 (C_{2v} symmetry with fluorines apical) that full optimization at 3-21G(*) improved the energy by only 0.07 kcal/mol while that for the isomer with hydrogen and chlorine apical (C_s symmetry) improved by only 0.52 kcal/mol. Since full optimization would not alter the relative isomer energies, we investigated the effect of a larger basis set on altering relative isomer energies.

When the isomers of PHCl_2F_2 and PH_2ClF_2 were used as a test pair, it was found, as expected, that all isomer energies were lower in 6-31G* than in 3-21G(*). More importantly, changes in the relative isomer energies occurred with the larger 6-31G* basis set with partial optimization, as compared with 3-21G(*) basis set with either full or partial optimization.

For the pair of PH_2ClF_2 isomers (Cl_{ap} , F_{ap} and F_{ap} , Cl_{ap}), which showed a large change in relative isomer energy from 3-21G(*) to 6-31G*, another test calculation was run with yet a larger basis set, 6-31G**, to see if additional orbitals on hydrogen would alter the relative isomer energies still further. However, the relative isomer energies calculated at 6-31G** differed from the results at 6-31G* by only 0.05 kcal/mol (Table VIII).

On the basis of these results, it was decided that the 3-21G(*) basis set was not large enough to represent the hydridophosphorane molecules with fluorine substituents.³⁵ Thus, energies for all

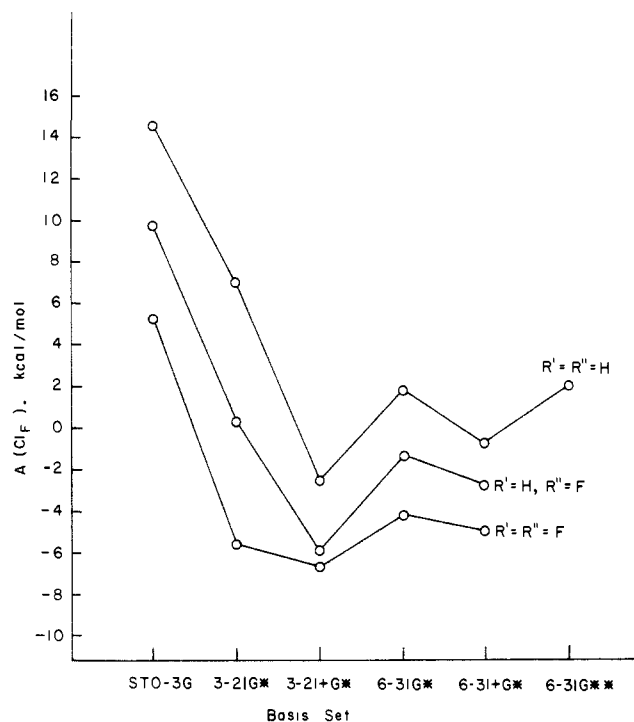


Figure 4. Effect of basis set on the apicophilicity of chlorine relative to fluorine, $A(\text{Cl}_F)$, in the molecule $\text{PCl}_{\text{ap}}\text{F}_{\text{ap}}\text{F}_{\text{eq}}\text{R}'_{\text{eq}}\text{R}''_{\text{eq}}$.

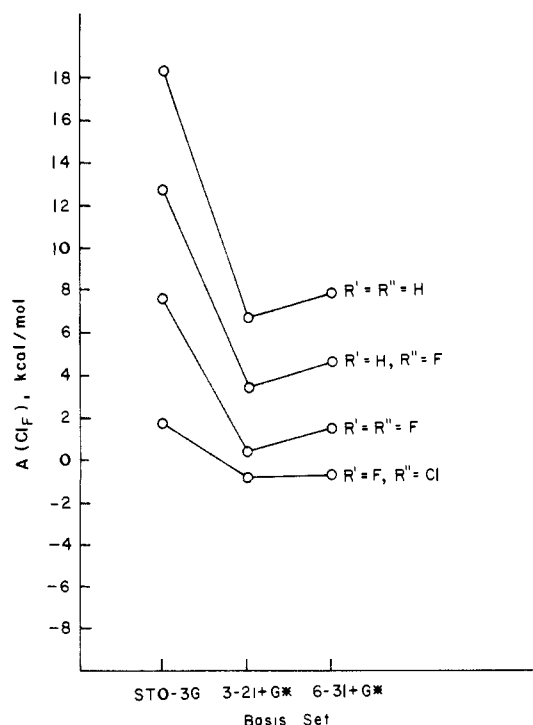


Figure 5. Effect of basis set on the apicophilicity of chlorine relative to fluorine, $A(\text{Cl}_F)$, in the anion $[\text{SiCl}_{\text{ap}}\text{F}_{\text{ap}}\text{F}_{\text{eq}}\text{R}'_{\text{eq}}\text{R}''_{\text{eq}}]^-$.

members of the phosphorus series, except the hydridochlorides, were calculated at new optimum bond lengths using a 6-31G* basis set. Relative isomer energies for PH_2Cl_3 at the 6-31G* level agreed (within 0.5 kcal/mol) with those at 3-21G(*) level (see

(35) The problem with the 3-21G(*) basis sets for compounds including fluorine and hydrogen may be that fluorine cannot "borrow" extra basis functions from hydrogen. In the phosphorus chlorofluorides, the extra basis functions on the chlorine atom help provide for a more realistic fluorine electron distribution. The problem does not occur in the silicon series 3-21+G* because of the added diffuse functions. See: Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1985; p 241.

Table IX. Change in Apicophilicity with Change in Basis Set ($A(\text{Cl}_F)$, kcal/mol)

M	R'	R''	3-21G(*)	6-31G*	Δ
P	H	H	7.00	1.98	5.02
	H	F	0.34	-1.23	1.57
	F	F	-5.64	-4.09	1.55
			3-21+G*	6-31+G*	
Si	H	H	6.72	7.94	1.22
	H	F	3.36	4.66	1.30
	F	F	0.44	1.46	1.02
	F	Cl	-0.92	-0.83	0.09

Table I). Consequently, the 3-21G(*) basis set is an adequate one for comparing relative energies in the phosphorus hydrido-chlorides.

Thus far, we have not considered what changes might take place in the silicon series. In a comparative study of both phosphorus and silicon compounds having the same ligand substitutions, we calculate isomer energies in several different basis sets. For phosphorus, the sets chosen are STO-3G, 3-21G(*), 3-21+G*, 6-31G*, and 6-31+G* and, for silicon, STO-3G, 3-21+G*, and 6-31+G*. The results, expressed in terms of apicophilicities, $E_{(II)} - E_{(I)}$, are listed in Table VIII and Figures 4 and 5 for the series $\text{R}'\text{R}''\text{MClF}_2$ where $\text{M} = \text{P}, \text{Si}$ and R', R'' comprise the pairs H, H; H, F; F, F; and F, Cl (Si only).

It is apparent that, in the isomers studied, there is no change in the relative ordering of apicophilicities with a change in basis set. With one exception, i.e., when $\text{M} = \text{P}, \text{R}' = \text{R}'' = \text{H}$, the change in apicophilicity in going from 3-21G(*) to 6-31G* is about 1–2 kcal (see Table IX). In only one case (for $\text{M} = \text{P}, \text{R}' = \text{H}, \text{R}'' = \text{F}$; Table IX) is there a change in the sign of the apicophilicity $A(\text{Cl}_F)$. This occurs on going from the 3-21G(*) to the 6-31G* basis set. Thus, a crossover in isomer energy has taken place, meaning that, at the latter level, the isomer with both fluorine atoms apical is more stable than the isomer with one fluorine and one chlorine atom in apical positions.

The analysis of the various calculations suggests that the relative isomer energies, and hence apicophilicities for $\text{PH}_n\text{Cl}_{5-n}$ (3-21G(*) level) and for all of the silicon anions (3-21+G* level), have a ± 1 –2 kcal/mol error associated with them; i.e., calculations at 6-31G* (or 6-31+G*) levels do not significantly alter the relative isomer energies that were determined at the 3-21G(*) (or 3-21+G*) level. Apicophilicities listed in Tables III–V for these series are obtained from energy differences at the 3-21G(*) or 3-21+G* level. Because calculations of the phosphorus species with fluorine substituents showed a change greater than 1–2 kcal/mol in relative isomer energies when a larger basis set was used, all apicophilicities for these molecules were determined with results from 6-31G* calculations (Tables III–V).

Apicophilicities. Examination of Tables III and IV shows a wide variation in the apicophilicities of fluorine and chlorine atoms in both the phosphorus and silicon series of pentacoordinated molecules. In each series, the apicophilicity of fluorine relative to hydrogen, $A(\text{F}_H)$, is highest when a chlorine atom is in the opposite apical position and the equatorial sites are occupied by hydrogen atoms. The apicophilicity of fluorine relative to hydrogen is lowest when a hydrogen atom occupies the opposite apical position and equatorial sites have chlorine atoms. Entirely analogous behavior is found for the apicophilicity of chlorine, $A(\text{Cl}_H)$, in that it is highest with an opposite apical chlorine atom and lowest when chlorine atoms occupy equatorial sites.

In either the phosphorus or silicon series, introduction of a chlorine or a fluorine atom in place of a hydrogen atom in an apical position raises the apicophilicity of the atom in the opposite apical position. The only exception is encountered for replacement of an apical hydrogen atom by fluorine when the equatorial positions are all occupied by hydrogen atoms. In general, the trend is

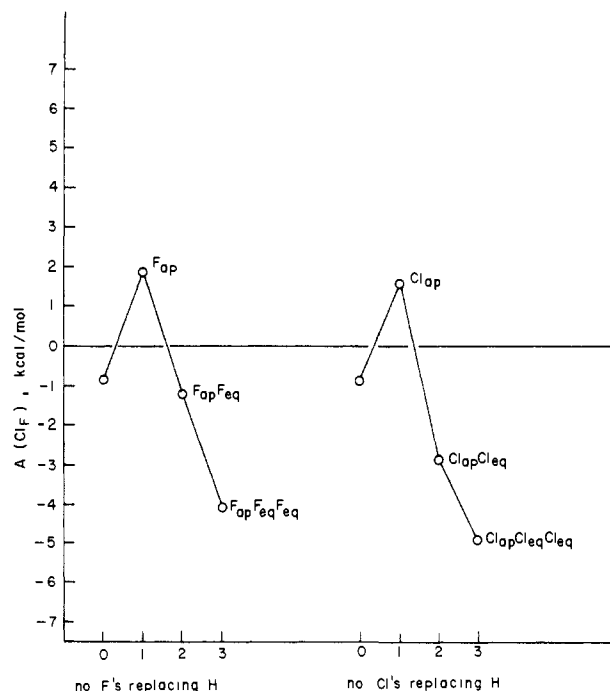


Figure 6. Effect of halogen substitution on the apicophilicity of chlorine relative to fluorine, $A(\text{Cl}_F)$, in the molecule $\text{PCl}_{1-\text{ap}}\text{F}_{\text{eq}}\text{H}_3$. The curve to the left shows replacement of hydrogen by fluorine; the curve to the right shows replacement of hydrogen by chlorine. The first halogen replaces an apical hydrogen; the second and third halogens replace equatorial hydrogens. A positive value of $A(\text{Cl}_F)$ indicates a molecule in which chlorine is more apicophilic than fluorine, while negative values indicate molecules in which chlorine is less apicophilic than fluorine.

Chart I

		a. $A(\text{F}_H)$ (kcal/mol)			
M = P:		5.82	4.23	2.85	6.08
M = Si:		4.11	2.21	0.42	4.55
		b. $A(\text{Cl}_H)$ (kcal/mol)			
M = P:		3.00	0.25	-2.04	0.69
M = Si:		5.57	2.37	-0.52	3.97

followed in both series that the effectiveness of an apical atom in increasing apicophilicity relative to hydrogen follows the order $\text{Cl} > \text{F} > \text{H}$. For equatorial atoms, the same ligand atom order holds but the effect is opposite; i.e., apicophilicity is decreased.

As an example, substitution in MHF_4 illustrates these trends, showing the magnitude of the changes in apicophilicity for the phosphorus series compared to the silicon series (Chart I).

To obtain a better perspective of the relative apicophilicities of fluorine and chlorine atoms, Table V lists apicophilicities of chlorine relative to fluorine, $A(\text{Cl}_F)$. Positive entries mean that chlorine is more apicophilic while negative values identify isomers that show fluorine more apicophilic than chlorine. Figures 6 and 7 illustrate this difference in the phosphorus and silicon series where points below zero refer to isomers that have fluorine more apicophilic than chlorine. A crossover in apicophilicity takes place in all the series depicted except for the $\text{SiH}_n\text{Cl}_{4-n}^-$ series. Here, chlorine remains more apicophilic than fluorine even at full fluorine replacement, i.e., at SiClF_4^- . In both the phosphorus and silicon series, molecules constructed of highly electronegative atoms have

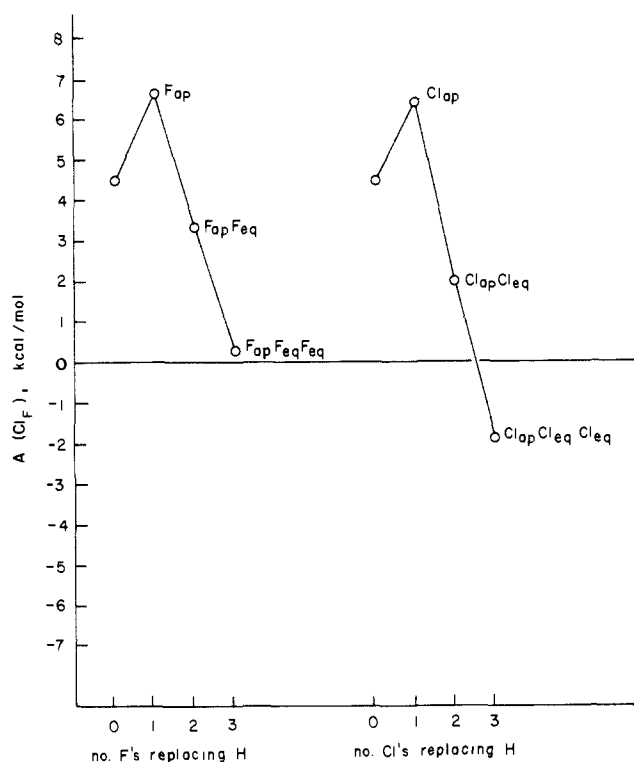


Figure 7. Effect of halogen substitution on the apicophilicity of chlorine relative to fluorine, $A(\text{Cl}_F)$, in the anion $[\text{SiH}_3\text{Cl}_{\text{ap}}\text{F}_{\text{eq}}]^-$. The curve to the left shows replacement of hydrogen by fluorine; the curve to the right shows replacement of hydrogen by chlorine. The first halogen replaces an apical hydrogen; the second and third halogens replace equatorial hydrogens. A positive value of $A(\text{Cl}_F)$ indicates an anion in which chlorine is more apicophilic than fluorine, while negative values indicate anions in which chlorine is less apicophilic than fluorine.

fluorine more apicophilic than chlorine. As the collective electronegativity of the equatorial atoms is reduced by replacement with hydrogen atoms, a crossover occurs with chlorine becoming more apicophilic than fluorine, the crossover point taking place earlier with silicon compared to that with phosphorus. Most likely, it is for this reason that McDowell and Streitwieser^{24a} were "puzzled" by the results of their calculation on PH_4X showing chlorine more apicophilic than fluorine, which was at odds with the known apical location of fluorine in PF_3Cl_2 .^{25a,26}

Ligand Charges. An underlying rationale for the variations in apicophilicity encountered above lies in an understanding of changes in electronic properties of the relative isomers involved. A significant factor giving insight into the order of isomer energies obtained in both the silicon and phosphorus series originates with the variations of ligand atom charges.³⁶ We find that a decrease in calculated apicophilicity correlates with a decrease in the difference of the sums of the apical and equatorial ligand atom charges, $\sum q_{\text{eq}} - \sum q_{\text{ap}}$. This difference becomes smaller as the sum of the equatorial negative charges approaches the sum of the apical negative charges. Figure 8 illustrates the variation in apicophilicity $A(\text{Cl}_H)$ with this charge difference for the isomer series $\text{R}'\text{R}''\text{PHClF}$, where F and Cl are in apical positions. Two lines are obtained, one for fluorine atom equatorial substitution and the other for chlorine atom equatorial substitution. Other isomer series follow analogous behavior, although, with the silicon series, the two lines are much closer together. In the case of isomer series, $\text{R}'\text{R}''\text{SiHF}_2^-$ with apical fluorine atoms, the data are best fit by a single line (Figure 9).

As electronegative atoms occupy equatorial positions, it is not necessary for the apical atoms to bear as much charge. This is seen in Figure 10 where the sum of the apical atom charges and

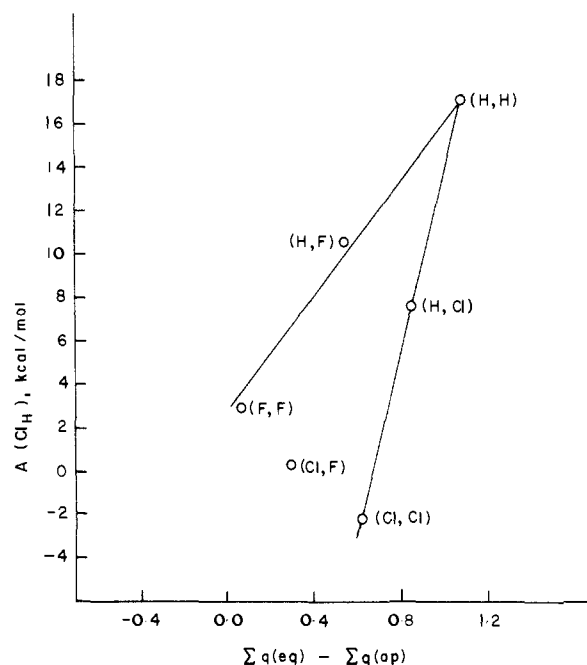


Figure 8. Apicophilicity of chlorine relative to hydrogen, $A(\text{Cl}_H)$, as a function of the apical-equatorial charge difference, $\sum q_{\text{eq}} - \sum q_{\text{ap}}$, in $\text{PCl}_{\text{ap}}\text{F}_{\text{ap}}\text{H}_{\text{eq}}\text{R}'\text{R}''$. The equatorial substituents R' and R'' are indicated in parentheses. A positive value of $(\sum q_{\text{eq}} - \sum q_{\text{ap}})$ indicates that the total charge borne by the apical atoms is greater than the total charge borne by equatorial atoms.

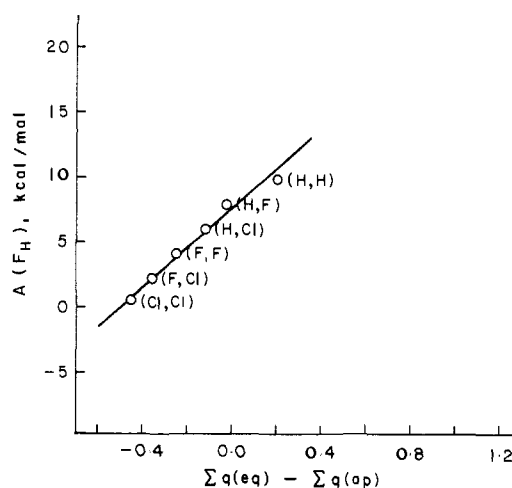


Figure 9. Apicophilicity of fluorine relative to hydrogen, $A(\text{F}_H)$, as a function of the apical-equatorial charge difference, $\sum q_{\text{eq}} - \sum q_{\text{ap}}$, in $[\text{SiF}_{\text{ap}}\text{F}_{\text{ap}}\text{H}_{\text{eq}}\text{R}'\text{R}'']^-$. The equatorial substituents R' and R'' are indicated in parentheses.

the sum of the equatorial atom charges are plotted versus equatorial atom substitution R' , R'' for the phosphorus and silicon series containing two apical fluorine atoms, $\text{R}'\text{R}''\text{MHF}_2$. In the phosphorus series, the effect of fluorine atom substitution in equatorial positions is more effective in increasing equatorial atom charges than is found for chlorine atom substitution. In the silicon series in Figure 10, the effect of chlorine atom substitution in equatorial positions is similar to the effect seen for fluorine atom substitution. However, with silicon, fluorine equatorial substitution does not affect the apical charge distribution as much as chlorine equatorial substitution affects apical charge distribution. The latter offers an explanation for the greater effect of chlorine equatorial substitution (compared to that of fluorine equatorial substitution) in reducing the apicophilicity of silicon species.

Nucleophilic Substitution. Insofar as apicophilicity can be related to the leaving ability of a group in nucleophilic substitution reactions, the calculations presented here do not support the requirement expressed by Corriu²⁸ that rate enhancements with

(36) Since charge densities based on Mulliken populations tend to be basis set dependent for one, the discussion given here should be viewed as a qualitative but useful observation.

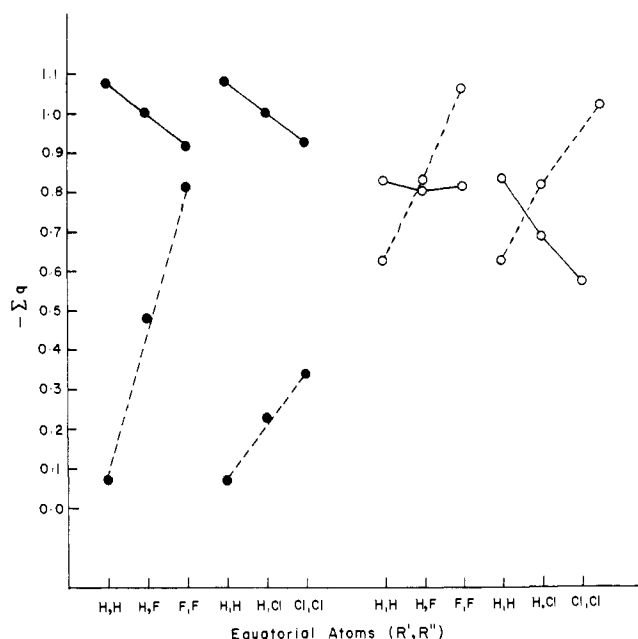


Figure 10. Influence of equatorial atoms on total apical and total equatorial charge in $MF_{ap}F_{ap}H_{eq}R'R''$. Solid circles denote molecules with $M = P$; open circles denote anions with $M = Si$. Solid lines are used to represent the total apical charge and dashed lines the total equatorial charge.

Chart II. $A(Cl_H)$ (kcal/mol)

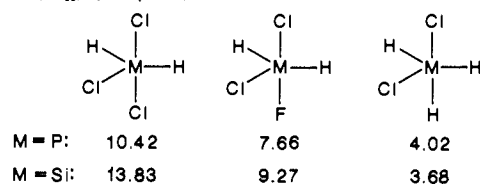
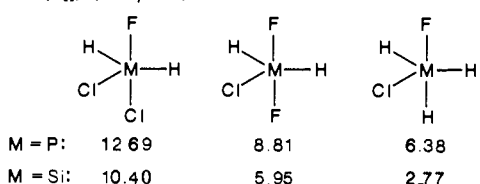


Chart III. $A(F_H)$ (kcal/mol)



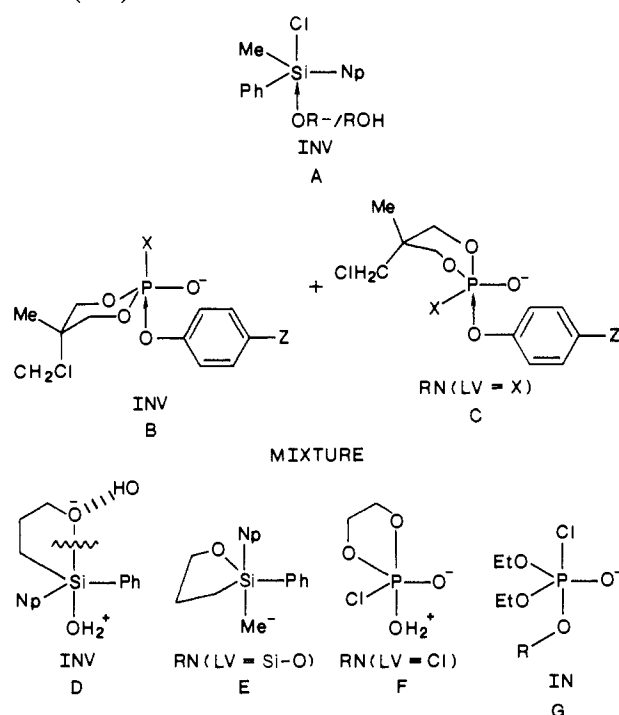
five-membered ring phosphorus or silicon compounds depend on the symmetry of the intermediate, i.e., that the entering nucleophile and leaving group involve the same atom attachment. The principal conclusion reached in the present study that might relate to the influence of an entering group in enhancing the reactivity of an electronegative leaving group is that the reactivity should be increased when the equatorial positions are occupied by ligands of low electronegativity and, of the atoms studied, the opposite apical position is occupied by an electronegative atom, where $Cl > F$ in enhancing the apicophilicity of the opposite apical group. Thus, it is seen, for example, in MH_2Cl_2X , where X is the nucleophile and Cl is the leaving group, that the apicophilicity of the leaving group is enhanced by the nucleophile in the order $Cl^- > F^- > H^-$ (Chart II).

For the species, MH_2ClFX where fluorine is the leaving group, it is also observed in this calculation that the nature of the nucleophile enhances the apicophilicity of the leaving group $A(F_H)$ in the order $Cl^- > F^- > H^-$ (Chart III). This order does not vary from that observed for $A(Cl_H)$.

However, since $Cl > F$ in leaving group ability, one would probably not be able to observe experimentally the behavior of fluorine as a leaving group with chlorine in the opposite apical position. Experimentally, one observes that, with Cl^- as a leaving group, the nucleophilic enhancement of apicophilicity is in the order $Cl^- > F^-$, whereas with fluorine as a leaving group, one

observes only that F^- enhances the apicophilicity. This could be attributed to a "like apical atom" effect, but as the calculations show, it is only a part of a more general effect, namely $Cl^- > F^- > H^-$ in enhancing the apicophilicity of the opposite apical position. Further, this apicophilicity advantage is maintained as the equatorial hydrogen atoms are substituted by the more electronegative chlorine and fluorine atoms in both the phosphorus and silicon series. For a symmetry-related enhancement, the apicophilicity should be greatest whenever the apical positions are occupied by a fluorine atom opposite a fluorine atom or whenever a chlorine atom is opposite a chlorine atom. This is not found here.

Since the series we studied are devoid of ring strain or steric effects, they provide a basis from which apicophilicities may be altered by introduction of such terms. Some representative intermediates proposed in S_N2 solvolysis, hydrolysis, and alkylation reactions²⁸ may take the following forms, if the entering nucleophile and leaving group do so at apical positions in accord with Westheimer's proposal,⁴ i.e., facial attack at tetrahedral silicon and phosphorus reactants. The predominant stereochemical course observed experimentally²⁸ is indicated as inversion (INV) or retention (RN).



To accommodate the Westheimer proposal, cleavage of the P-X bond in C,³⁷ the Si-O bond in E,³⁸ or the P-Cl bond in F³⁹ would require pseudorotation of the intermediate to bring the departing group to an apical position. In the case of the phenoxide reaction in B and C, a mixture of isomers is obtained,^{37a} showing more retention when $X = F$ as the departing group compared to when $X = Cl$. Corriu²⁸ states that since fluorine is more apicophilic than chlorine, inversion should be more favorable when $X = F$ compared to when $X = Cl$, and hence these results could not be predicted using Westheimer's concepts. On the basis of calculations, we have shown that chlorine is more apicophilic than fluorine except when highly electronegative ligands are present, i.e., in the PCl_nF_{5-n} series. In the intermediates, B and C, considerable negative charge resides on the equatorial phosphoryl oxygen making it a group of low electronegativity,⁴⁰ comparable

(37) (a) Corriu, R. J. P.; Dutheil, J. P.; Lanneau, G. F.; Ould-Kada, S. *Tetrahedron* **1979**, *35*, 2889-2894. (b) Corriu, R. J. P.; Dutheil, J. P.; Lanneau, G. *Tetrahedron* **1981**, *37*, 3681-3687.

(38) Corriu, R.; Fernandez, J. M.; Guerin, C. *Nouv. J. Chim.* **1984**, *8*, 279-284.

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(40) Reference 2, pp 89 and 98.

to that of a hydrogen atom. Thus, it may be that no "rules" are violated in interpreting the greater cleavage of P-Cl bonds by an inversion route compared to cleavage of P-F bonds.

That the two forms, B and C, might arise in competition with each other in the first place most likely rests with a balance of relief of a certain degree of ring strain for the six-membered form favoring intermediate C. As Marsi^{41,42} has shown in the alkaline cleavage of cyclic phosphonium salts varying in ring size from five to seven membered, the stereochemistry goes from 100% retention for reaction of a five-membered ring *cis*-phosphonium salt, to about 50% retention for reaction of the corresponding six-membered ring *cis*-phosphonium salt, and to 0% retention for reaction of the seven-membered ring salt, all with cleavage of the poor leaving group, benzyl.

Activated-state E may result as a kinetically favored initial intermediate if we assume that the α -naphthyl group is of sufficient size to sterically block the approach of the nucleophile opposite the endocyclic Si-O bond undergoing cleavage. Pseudorotation then brings the Si-O bond to a departing apical position. Intermediate D may gain relative stability to E with the use of a softer nucleophile. In addition to the relief of ring strain, hydrogen bonding may assist in the cleavage process as indicated in D.

(41) Reference 2, pp 153-157.

(42) Marsi, K. L. *J. Org. Chem.* **1975**, *40*, 1779-1784. Marsi, K. L. *J. Am. Chem. Soc.* **1969**, *91*, 4724-4729. Egan, W.; Chauviere, G.; Mislow, K.; Clark, R. T.; Marsi, K. L. *J. Chem. Soc. D* **1970**, 733-734. Marsi, K. L.; Burns, F. B.; Clark, R. T. *J. Org. Chem.* **1972**, *37*, 238-241. Marsi, K. L. *Chem. Commun.* **1968**, 846-847. Marsi, K. L.; Oberlander, J. E. *J. Am. Chem. Soc.* **1973**, *95*, 200-204. Marsi, K. L.; Clark, R. T. *J. Am. Chem. Soc.* **1970**, *92*, 3791-3793. Marsi, K. L. *J. Am. Chem. Soc.* **1971**, *93*, 6341-6342.

Conclusion

The results of the calculations support the main proposals that have been used in phosphorus chemistry as expressed by Westheimer⁴ and others.⁴³ It is felt that the treatment of apicophilicity presented in this paper shows variations that aid in interpreting nucleophilic displacement reactions of phosphorus and silicon. These interpretations are meant to serve as working hypotheses. The extent of their usefulness will only be known as future work in the area unfolds.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE 8504737) is gratefully acknowledged. A major portion of this work was carried out at the San Diego Supercomputer Center where we were located on leave. We thank the National Science Foundation and San Diego Supercomputer Center for generous allocation of computer time and the staff at SDSC for their advice and encouragement.

Supplementary Material Available: Total energies (au) for trigonal bipyramids with H, F, and Cl substituents for (a) phosphorus and anionic silicon species computed with the 3-21G(*) and 3-21+G* basis sets, respectively (Table S1), (b) phosphorus species computed with the 6-31G* and 6-31G** basis sets (Table S2), and (c) anionic silicon species computed with the 6-31+G* basis set (Table S3) and bond lengths and charge densities for (d) phosphorus species computed with the 3-21G(*) and 6-31G* basis sets (Table S4) and (e) anionic silicon species computed with the 3-21+G* and 6-31+G* basis sets (Table S5) (13 pages). Ordering information is given on any current masthead page.

(43) Reference 2, Chapter 2.

Ab Initio Heats of Formation of Medium-Sized Hydrocarbons. 8. On the Homoaromatic Character of Triquinacene¹

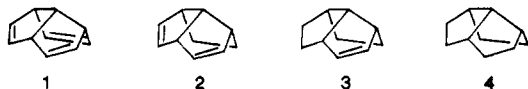
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Abstract: An ab initio molecular orbital study of the energetics of the successive hydrogenations of triquinacene provides no indication of homoaromatic stabilization of this system, a conclusion at variance with a recent thermochemical study. The absence of this effect persists even when energies are computed in the 6-31G* basis set to second order in electron correlation, and the contributions of zero-point energies and thermal corrections to enthalpies are taken into account.

I. Introduction

A recent investigation² of the heats of hydrogenation of triquinacene (**1**), dihydrotriquinacene (**2**), and tetrahydrotriquinacene (**3**) to hexahydrotriquinacene (**4**) found evidence of homoaromatic



stabilization³ in **1** to the extent of 4.5 kcal/mol. This result is

surprising, as the authors observe, because spectroscopic (IR,^{4a} UV,^{4a} CD,^{4b} PES^{4c}) and structural^{4d} data offer no evidence whatever of homoaromatic character in triquinacene. The rarity of homoaromatic character in neutral cyclic polyolefins such as **1**, together with considerations of electronic structure, leads to the observation that when three proximal π bonds interact the result is, in fact, destabilization rather than stabilization.⁵

The case for homoaromatic character in triquinacene is based solely upon thermochemical data; in view of this, we have carried

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