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Nuclear Magnetic Resonance Spectroscopic Study of the Behavior of Fluoro- and Oxyphosphorus Compounds in Fluorosulfuric Acid and Fluorosulfuric Acid–Antimony Pentafluoride Solution[1a]

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Interaction of monofluorophosphoric acid, difluorophosphoric acid, phosphorus oxyfluoride, phosphorus trifluoride, phosphonic acid, phosphinic acid, pyrophosphoric acid, and polyphosphoric acid with (primarily) fluorosulfuric acid and fluorosulfuric acid–antimony pentafluoride ("Magic Acid") superacid was studied. The ^1H, ^{19}F, and ^{31}P nmr spectra of the precursors, protonated species, and products of reaction with fluorosulfuric acid were obtained. The observations, in accordance with previously known data, indicate that monofluorophosphoric acid is nearly completely protonated in excess fluorosulfuric acid. Difluorophosphoric acid is also substantially protonated, but phosphorus oxyfluoride and phosphorus trifluoride give little indication of protonation. More complete protonation of difluorophosphoric acid and phosphorus oxyfluoride is indicated in Magic Acid solution. At 0° replacement of a hydroxy group by fluorine from fluorosulfuric acid was observed in difluorophosphoric acid, phosphonic acid, and phosphinic acid, yielding, in the last case, the new compound phosphinic fluoride (FH_2PO), as the protonated ion. Phosphonic and phosphinic acids are subject to further fluorination reactions in fluorosulfuric acid solution. Polyphosphate species are protolytically cleaved by fluorosulfuric acid to fluorophosphate and phosphoric acid. Mechanisms for the studied reactions are proposed.

Introduction

Although fluorosulfuric acid is a very useful solvent in the study of the protonation of weak phosphorus bases,[2] other reactions besides proton transfer can also take place. In particular, fluorosulfuric acid is a fluorinating agent for many substrates at ambient temperatures.[3] This paper is concerned with the chemistry of a variety of fluorophosphorus and oxyphosphorus compounds in fluorosulfuric acid solution, with attention being given to their stability, degree of protonation, and the formation of intermediates. Insofar as the nmr coupling constants observed with phosphorus directly bound to fluorine or hydrogen are distinctively large and the chemical shifts of all these nuclei are easy to obtain, following the course of the reactions in fluorosulfuric acid solution by nuclear magnetic resonance spectroscopy might especially be expected to provide information about intermediates and products resulting from these reactions.

Results and Discussion

For purposes of comparison to our earlier work on protonated phosphates,[2d] we first carried out experiments on the behavior of the fluorophosphoric acids and phosphorus oxyfluoride in fluorosulfuric acid solution. The intention was to determine the effects of successive replacement of the hydroxyl groups of orthophosphoric acid by fluorine atoms. Monofluorophosphoric acid and phosphoric oxyfluoride form stable solutions with fluorosulfuric acid without significant changes in their ^{31}P and ^{19}F nmr spectral parameters (see Table I). However, we observe that difluorophosphoric acid is almost completely converted to phosphorus oxyfluoride at room temperature in excess fluorosulfuric acid. At low temperature ($-60°$) this reaction is suppressed, so that protonated difluorophosphoric acid is the major species present.

A significant question is to what extent the fluorophosphoryl compounds are protonated by fluorosulfuric acid. Evidence indicates that phosphoric acid is fully protonated to form the tetrahydroxyphosphonium ion in fluorosulfuric acid solution.[2d] However, as more electronegative fluorine atoms successively replace hydroxy groups, the basicity of the phosphoryl compound would be expected to decrease. Indeed, phosphorus oxyfluoride is not protonated in sulfuric acid solution.[4] There are literature data which permit estimation of the extent of protonation of difluorophosphoric acid in fluorosulfuric acid solution. In sulfuric acid, difluorophosphoric acid is partially protonated,[5] with the equilibrium constant $K_b = [F_2PO_2H_2^+][HSO_4^-]/[F_2PO_2H] = 1.0 \times 10^{-2}$. The greater protonating ability of fluorosulfuric acid can usually be expressed by means of the Hammett acidity function, H_0. According to literature data,[2a] H_0 for fluorosulfuric acid is more negative by 1.8 units than for sulfuric acid. By using the equation $H_0 = pK_a + \log \{[B]/[BH^+]\}$ (K_a is the thermodynamic acidity constant of protonated difluorophosphoric acid, and B represents difluorophosphoric acid) and taking into account that in our work fluorophosphoric acids were dissolved in a tenfold molar excess of fluorosulfuric acid, one calculates that 87% of difluorophosphoric acid is protonated. If the difference in the acidity functions of sulfuric and fluorosulfuric acids is greater than 1.8, then the extent of protonation of difluorophosphoric acid is even larger. The actual degree of protonation cannot be determined from these nmr measurements alone. Proton-exchange processes are undoubtedly rapid, so that only one ^{19}F doublet absorption is observed, and the nmr spectral parameters are averages of values for the protonated and neutral species.

If difluorophosphoric acid is mostly protonated in fluorosulfuric acid solution, then monofluorophosphoric

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[1] (a) Taken in part from the Ph.D. dissertation of C. W. McFarland, Case Western Reserve University, Cleveland, Ohio, 1971. (b) National Institutes of Health Predoctoral Research Fellow, 1968–1970.

[2] (a) R. J. Gillespie, *Accounts Chem. Res.*, **1**, 202 (1968); (b) R. C. Thompson in "Inorganic Sulphur Chemistry," G. Nickless, Ed., American Elsevier, New York, N. Y., 1968, Chapter 17; (c) G. A. Olah and C. W. McFarland, *J. Org. Chem.*, **34**, 1832 (1969); (d) G. A. Olah and C. W. McFarland, *ibid.*, **36**, 1374 (1971).

[3] A. Engelbrecht, *Angew. Chem., Int. Ed. Engl.*, **4**, 641 (1965).

[4] R. J. Gillespie, R. Kapoor, and E. A. Robinson, *Can. J. Chem.*, **44**, 1203 (1966).

[5] J. Barr, R. J. Gillespie, and E. A. Robinson, *ibid.*, **39**, 1266 (1961).

TABLE I

NMR PARAMETERS OF FLUOROPHOSPHORUS COMPOUNDS IN FLUOROSULFURIC ACID SOLUTION

Compound	^{31}P chem shifts, δ_P		^{19}F chem shifts, δ_F (J, Hz)		^{1}H chem shifts, δ (J, Hz)		
	In acid	Precursor	In acid ($^1J_{PF}$)	Precursor ($^1J_{PF}$)	P–H proton	$^1J_{PH}$	$^2J_{HPF}$
$FP(O)(OH)_2$	7.3	8.3	78.6 (990)	77.3 (955)	...	...	...
$F_2P(O)OH$	22.6	21.7	85.6 (1002)	87.2 (983)	...	...	...
F_3PO	36.6	35.5[a]	91.1 (1060)	95.7 (1058)[a]	...	...	...
F_3P	−104.4	−97.0[a]	35.3 (1398)	36.5 (1405)[a]	...	...	...
$FHP(O)OH$	−15.7	−2.7[c]	71.8 (1099)	64.3 (1030)[c]	8.06[b]	899[b]	97[b]
					7.92[c]	782[c]	114[c]
FH_2PO	−39.2[d]	?	109.9 (1079)[d]	?	8.00[d]	756[d]	60[d]

[a] R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965). [b] In fluorosulfuric acid solution. [c] Precursor according to L. F. Centofanti and R. W. Parry, *Inorg. Chem.*, **7**, 1005 (1968). [d] At −60°.

acid should be nearly completely protonated under the same conditions. One indication of this is the increase in the one-bond coupling constant ($^1J_{PF}$) of 35 Hz in solution. Such increases in one-bond couplings accompany protonation of phosphorus compounds (compare phosphine and secondary phosphines,[2c] phosphonates and phosphinic acid[2d]). The ^{19}F and ^{31}P nmr chemical shifts of monofluorophosphoric acid are affected vey little by fluorosulfuric acid. It is probable that electron donation by fluorine in the fluorotrihydroxyphosphonium ion, $(HO)_3P{=}F^+$, is about the same as in the precursor acid, $^-O(HO)_2P{=}F^+$.

The presence of three fluoro substituents on a phosphorus atom (such as in phosphorus oxyfluoride) lowers the basicity of the molecule to a point where protonation is probably minimal in fluorosulfuric acid solution. Even so, hydrogen bonding between phosphorus oxyfluoride (a gas at room temperature which boils at −40°)[6] and fluorosulfuric acid is sufficiently strong to keep the former in solution.[2b] Similar results are obtained from experiments with phosphorus trifluoride, which one would expect to be comparably weakly basic. The trifluoride, which is lower boiling than the oxyfluoride by 61°,[6] can be readily dissolved in fluorosulfuric acid. Strong hydrogen bonding is assumed to keep phosphorus trifluoride in solution. However, ^{19}F and ^{31}P nmr spectra are indicative of the unprotonated trifluoride (or a rapidly exchanging system; for nmr spectral parameters see Table I) being the major species in solution. No one-bond coupling, $^1J_{PH}$, or two-bond coupling, $^2J_{HPF}$, is observed in the major resonance signals. There is also in the ^{19}F nmr spectrum a doublet of doublets characteristic of fluorine bound to phosphorus which in turn is also bound to hydrogen (δ_F 51.6, $^1J_{PF}$ = 987 Hz, $^2J_{HPF}$ = 94 Hz). These resonance signals, which are broad and very weak, possibly could be due to protonated phosphorus trifluoride (trifluorophosphonium ion, HPF_3^+), but no corroborating ^{1}H or ^{31}P spectral evidence could be obtained.

Use of 1:1 (mole:mole) fluorosulfuric acid–antimony pentafluoride (Magic Acid),[7] which is a much stronger protonating agent, gives some evidence of more extensive protonation of difluorophosphoric acid and phosphorus oxyfluoride. In particular, the larger P–F coupling constants in solution of $F_2P(O)OH$ (δ_F 83.6, $^1J_{PF}$ = 1048 Hz) and F_3PO (δ_F 88.9, $^1J_{PF}$ = 1091 Hz; also δ_P 37.8) might indicate substantial phosphoryl oxygen atom protonation. [On the other hand, solvent effects could contribute at least some of the coupling constant increases. The extent that they do so is unknown.] The ^{19}F nmr spectrum of phosphorus trifluoride in Magic Acid solution shows only phosphorus oxyfluoride (most likely as the rapidly exchanging system).

The facile conversion of difluorophosphoric acid to phosphorus oxyfluoride is in keeping with the tendency of many inorganic hydroxy compounds to be fluorinated by fluorosulfuric acid to produce volatile inorganic fluorides.[3,8] A general mechanism has been suggested for these fluorination reactions.[3] Our adaptation of this mechanism to the reaction of hydroxy phosphoryl compounds in fluorosulfuric acid is as follows (X and Y are any substituents)

$$XYP(O)OH + FSO_3H \rightleftharpoons XYP(OH)_2^+ + FSO_3^-$$

$$XYP(OH)_2^+ \rightleftharpoons XYP^+{=}O + H_2O$$

$$XYP^+{=}O + FSO_3^- \rightleftharpoons XYP(O)OSO_2F$$

$$XYP(O)OSO_2F \longrightarrow XYP(O)F + SO_3$$

A phosphoryl cation of the type $XYP^+{=}O$ is usually considered to be quite unstable,[9] but in this case it might well have a transient existence, being quickly captured by either water or fluorosulfate anion.

In our earlier work on the protonation of phosphonic and phosphinic acids,[2d] we noticed that a complex variety of fluorophosphorus compounds was formed from the protonated acids in fluorosulfuric acid solution upon warming from −60 to 0°. The formation of these compounds has now been substantially elucidated through monitoring the reactions by ^{19}F and ^{31}P nmr spectroscopy. Temperature control allows one to control reaction rates, and reactive intermediates can be stabilized by cooling to −60°.

The protonation of phosphonic and phosphinic acids in fluorosulfuric acid solution to give the first intermediates in the proposed reaction scheme (X, Y = H, OH; H, H) has been previously described.[2d] Nmr spectra conclusively demonstrate that, with both acids, the next intermediates observed at 0° are the result of replacement of one hydroxy group by fluorine. That is, phosphonic acid yields protonated phosphonic fluoride, $HFP(OH)_2^+$, and phosphinic acid yields protonated phosphinic fluoride, H_2FPOH^+. The nmr spectral parameters of these fluorides, calculated from spectra which are entirely first order, are included in Table I.

Phosphonic fluoride is a well-known compound (its nmr spectral parameters have been reported[10]), but

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(6) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965).

(7) G. A. Olah and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **90**, 2726 (1968).

(8) The word "volatile" is used by Engelbrecht.[3] Product volatility is often a driving force for reactions.

(9) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, pp 269–270.

(10) L. F. Centofanti and R. W. Parry, *Inorg. Chem.*, **7**, 1005 (1968).

phosphinic fluoride has not previously been mentioned in the literature. It now appears that, at least under special conditions, phosphinic acid does form acid halides, contrary to a generalization made 15 years ago.[11] Again, in fluorosulfuric acid solution, phosphinic fluoride is probably present as the protonated species (fluorohydroxyphosphonium ion). Comparison of the nmr spectral parameters of the (presumably) less basic phosphonic fluoride in fluorosulfuric acid with the reported nmr parameters[10] (deshielding of the phosphorus nucleus by 13.0 ppm, increase in $^1J_{PF}$ of 69 Hz, increase in $^1J_{PH}$ of 117 Hz)[12] shows that phosphonic fluoride is also protonated in acid solution (*i.e.*, it is present as the fluorodihydroxyphosphonium ion).

The expected product of further fluorination of phosphonic fluoride, phosphonic difluoride, is not observed in nmr spectra, although HF_2PO is a known compound.[10,13] The products of further reaction which are observed are phosphorus trifluoride, difluorophosphoric acid, and phosphorus oxyfluoride. It is possible that any phosphonic difluoride which is formed is fluorinated very quickly by fluorosulfuric acid, with the former compound reacting in its trivalent form (phosphorous difluoride, F_2POH).[14] Such fluorination would yield phosphorus trifluoride, which in turn might be oxidized to phosphorus oxyfluoride by the sulfur trioxide suggested as a reaction product in the fluorination reactions. Difluorophosphoric acid might result from oxidation of phosphorous difluoride or by partial hydrolysis (since water is another suggested product of the fluorination reactions) of phosphorus oxyfluoride.

The expected product of further fluorination of phosphinic fluoride (considered in its trivalent form), phosphonous difluoride, is also not observed, although HPF_2 is known.[16] The observed products are phosphorus trifluoride and phosphorus oxyfluoride. We suggest that phosphonous difluoride is oxidized by sulfur trioxide to phosphonic difluoride, which then reacts, as proposed before, to produce phosphorus trifluoride and phosphorus oxyfluoride. When phosphinic acid in fluorosulfuric acid solution is allowed to stand at room temperature for 2 days, ^{19}F nmr spectra show, besides phosphorus oxyfluoride, monofluorophosphoric and difluorophosphoric acids, which probably result from oxyfluoride hydrolysis.

Additional work involving the possible intermediacy of a phosphorus fluorosulfate has been done with pyrophosphoric acid. The ^{31}P nmr spectra of fluorosulfuric acid solutions of pyrophosphoric acid show that protonated phosphoric acid and protonated fluorophosphoric acid are obtained as products. We suggest the following protolysis mechanism (beginning with the potassium pyrophosphate which was used)

$$K_4P_2O_7 + 4H^+ \longrightarrow H_4P_2O_7 + 4K^+$$

$$H_4P_2O_7 + FSO_3H \rightleftharpoons (HO)_3\overset{+}{P}OP(O)(OH)_2 + FSO_3^-$$

$$(HO)_3\overset{+}{P}OP(O)(OH)_2 \rightleftharpoons (HO)_3PO + (O)\overset{+}{P}(OH)_2$$

$$(O)\overset{+}{P}(OH)_2 + FSO_3^- \longrightarrow FSO_3P(O)(OH)_2 \longrightarrow FP(O)(OH)_2 + SO_3$$

Nucleophilic displacement of phosphoric acid by fluorosulfate anion, rather than unimolecular fragmentation of protonated pyrophosphoric acid, cannot be ruled out. Furthermore, available evidence does not indicate the exact site of protonation of pyrophosphoric acid nor whether multiple protonation of this acid occurs. At any rate, as mentioned before, the phosphoric and fluorophosphoric acids which are formed are protonated in fluorosulfuric acid solution. The net effect of fluorosulfuric acid on pyrophosphate is as if the latter were solvolyzed by hydrogen fluoride.

In the ^{31}P spectra just discussed, besides protonated phosphoric acid (δ_P -2.3) and protonated fluorophosphoric acid (δ_P $+7.3$, $^1J_{PF} = 980$ Hz), a small peak at δ_P $+14.4$ is also observed. Since sulfur trioxide, a strong dehydrating agent, is a product in the formation of fluorophosphoric acid, it seems likely that some phosphate condensation occurs.[17] From studies on the behavior of several inorganic phosphates in strongly acidic solvents (including chlorosulfuric acid), Dillon and Waddington concluded[17] that ^{31}P nmr resonance signals at δ_P $+14$–15 indicate protonated trimetaphosphoric acid, $H_4P_3O_9^+$.

Comparable results are obtained from experiments with polyphosphoric acid (PPA), which as commercially available has a composition approximately that of tetrapolyphosphoric acid, $H_6P_4O_{13}$. A ^{31}P nmr spectrum of a 10% (w/w) solution of PPA in fluorosulfuric acid exhibits peaks due to protonated fluorophosphoric acid (δ_P $+7.5$, $^1J_{PF} = 986$ Hz), a peak at δ_P -0.7 ascribed to a rapid equilibrium between protonated phosphoric acid and a lesser amount of protonated pyrophosphoric acid,[17] and a somewhat smaller, broader peak at δ_P $+14.6$ characteristic of protonated trimetaphosphoric acid.[17] Production of sulfur trioxide by phosphate fluorination probably maintains much of the dehydrating power of the solution, so that complete solvolysis to monophosphate species is not observed. In similar hydrophilic acid solvents, protonated tripolyphosphoric acid and higher chain polyphosphoric acids are not observed—ring closure to metaphosphate species occurs instead.[17] In the fluorosulfuric acid solutions of PPA we have studied, no di- and trifluorophosphorus compounds are observed—only monofluorination of a given phosphorus atom occurs.

Experimental Section

Materials.—Commercially available monofluorophosphoric acid, difluorophosphoric acid, phosphorus oxyfluoride, phosphorus trifluoride, phosphonic acid, potassium pyrophosphate, and polyphosphoric acid were used without further purification. Anhydrous phosphinic acid was obtained from a 50% aqueous solution by means of extended water evaporation on a high-vacuum line ($\geq 25\mu$) using gentle heating ($\leq 45°$). Commercially available fluorosulfuric acid and antimony pentafluoride were twice distilled before use in the preparation of solutions.

Nmr Spectra.—Instrumentation and techniques for obtaining ^1H, ^{19}F, and ^{31}P nmr spectra have been previously described.[2d] Proton chemical shifts are reported in parts per million downfield (δ) from external (capillary) tetramethylsilane. Fluorine chemical shifts are reported in ppm relative to external trichloro-

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[11] A. I. Razumov and Sim-Do-Khen, *J. Gen. Chem. USSR*, **26**, 2497 (1956).

[12] Phosphonic acid shows very similar deshielding and coupling constant effects upon protonation.

[13] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **6**, 2204 (1967).

[14] Certain phosphinous acids with highly electronegative substituents actually prefer the trivalent hydroxy tautomeric form.[15] Although phosphonic difluoride itself prefers the tetravalent phosphoryl form,[10] there may be a sufficient concentration of the trivalent form to result in rapid reaction.

[15] (a) J. E. Griffiths and A. B. Burg, *J. Amer. Chem. Soc.*, **82**, 1507 (1960); (b) D. D. Magnelli, G. Tesi, J. U. Lowe, and W. E. McQuistion, *Inorg. Chem.*, **5**, 457 (1966).

[16] R. W. Rudolph and R. W. Parry, *ibid.*, **4**, 1339 (1965).

[17] K. B. Dillon and T. C. Waddington, *J. Chem. Soc. A*, 1146 (1970).

fluoromethane (δ_F). Phosphorus chemical shifts are reported in ppm relative to external 85% phosphoric acid (δ_P). It was noticed that monofluorophosphoric and (especially) difluorophosphoric acids reacted with glass, so 5-mm quartz nmr sample tubes were used in experiments with fluorophosphoryl compounds as precursors and in acid solutions. Direct ^{31}P nmr spectra were recorded, except that the ^{31}P chemical shift of phosphinic fluoride was obtained by the indor technique.[2d] Wide-range HR-mode direct ^{31}P spectroscopy (sweep widths 2000–13,000 Hz) was useful in monitoring the various reactions; the HA mode was used whenever possible to determine more precisely individual peak positions. All spectra could be interpreted on a first-order basis. The use of fluorosulfuric acid as a reaction medium introduced into ^{1}H spectra, besides absorption peaks due to protonated molecules and reaction products, only an extra low-field singlet absorption (δ 10–13); in ^{19}F spectra the solvent absorption singlet at δ_F *ca.* −40 was well removed from absorptions of fluorophosphorus species.

Preparation of Ions.—Most of the phosphorus compounds were dissolved in a tenfold molar excess of fluorosulfuric acid or Magic Acid solution with stirring and ice bath cooling. Ten per cent (w/w) solutions of potassium pyrophosphate and polyphosphoric acid in fluorosulfuric acid were also prepared in this manner. Dry Ice–acetone cooling was used to suppress decomposition in the cases of phosphonic and phosphinic acids. The same cooling was used to condense phosphorus oxyfluoride for use in making mixtures and to aid dissolution of phosphorus trifluoride as it was bubbled through fluorosulfuric acid.

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Phosphonitrilic Derivatives. XX.[1] The Electronic Properties of Fluorophosphonitrilic Substituents

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Three series of (fluoroaryl)fluorophosphonitriles have been prepared, of the type $N_nP_nF_{2n-1}Ar_F$ (n = 3–8; Ar_F = C_6F_5, *p*-FC_6H_4, *m*-FC_6H_4). The ^{19}F nmr spectra of the fluoroaryl groups indicate strong inductive and conjugative electron withdrawals by the fluorophosphonitrilic ring, both effects being similar to those exerted by a cyano group. For the pentafluorophenyl series, the alternation of $\delta^F{}_p - \delta^F{}_m$ as the phosphonitrilic ring size is increased is consistent with conjugation of the homomorphic π system of the pentafluorophenyl group with a homomorphic π system in the phosphonitrilic ring.

Among the many series of cyclic inorganic compounds, phosphonitrilic derivatives are distinguished by the number and variety of the substitution reactions which they undergo and by the different types of orientation pattern observed. Substituents can be broadly classified into electron withdrawing and electron releasing, but such a division, while useful, is too simple to explain all the known facts. On this basis it might be expected, for instance, that the tendency to geminal substitution of the chlorophosphonitriles by amines would decrease with increasing base strength of the amine,[3] but this is not always so; for example, the course of substitution of $N_3P_3Cl_6$ by *tert*-butylamine (pK_{BH^+} = 10.45) is exclusively geminal,[4] whereas aniline (pK_{BH^+} = 4.58), although giving predominantly geminal isomers with $N_3P_3Cl_6$, reacts nongeminally with $N_4P_4Cl_8$.[5] There is clearly a need for a more detailed study of reaction mechanisms and of the interaction of the phosphonitrilic ring with its substituents. The results can be expected to differ from those found for benzene derivatives because the atoms and their polarizabilities are different and the reaction centers are bifunctional. The π interactions, both inside and outside the ring, can also be of a different type.

Inductive effects require no net electron transfer to or from the ring, and appear to form an adequate basis for the explanation of some substitutional behavior. For instance, the predominantly geminal antipodal substitution of octafluorocyclotetraphosphonitrile by methyllithium, although unexpected in terms of purely electrostatic or σ-inductive interactions, follows naturally from a consideration of the perturbation of the π-electron density of the fluorophosphonitrile by the methyl substituent, the π-inductive effect being simulated by a reduction of the electronegativity of the substituted phosphorus atom.[6] Similarly, the variations in the lengths of the ring bonds in *gem*-$N_4P_4F_6Me_2$, which are much greater than in benzene derivatives, correlate well with polarizability calculations based on the same model.[7] By contrast, π-conjugative effects are less well established. Neither spectroscopic nor structural evidence indicates strong conjugative interaction between a phenyl group and a phosphonitrilic ring; for example, the P–C bond length is nearly the same in $N_3P_3Ph_6$ (1.804 Å[8]) as it is in $N_4P_4Me_8$ (1.80 Å[9]). The

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[1] Part XIX: T. Chivers, R. T. Oakley, and N. L. Paddock, *J. Chem. Soc. A*, 2324 (1970).

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[9] M. W. Dougill, *J. Chem. Soc.*, 5471 (1961).