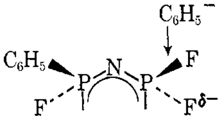
relative strong π bonds to the phosphorus atom,[9,22] whereas the phenyl group would be expected to show less tendency toward π interaction with phosphorus(V).[23a] The degree of phosphorus(V)–phenyl group π bonding is open to question, but available evidence indicates either no interaction[23a] or only a weak interaction.[23b] Inasmuch as the reaction of phenyllithium with phosphonitrilic fluorides is believed to be bimolecular,[24] the second incoming phenyl group would be repelled in this case by the fluorine atom lying *cis* to the activating fluorine atom and thus enter preferentially *cis* to the first phenyl group, as shown schematically



The "*cis* effect" can be used also to account for the observation that the nonequivalent geminal fluorine atoms have different phosphorus–fluorine coupling constants in the compound *cis*-1,3-$N_3P_3F_4(C_6H_5)_2$. The geminal fluorine atom which is *cis* to the fluorine atoms in the $\equiv PF(C_6H_5)$ centers is labilized with respect to the other geminal fluorine atom, resulting in a different distribution of electron density in the P—F bond and a different coupling constant. It is assumed, of course, that the coupling is dominated by the Fermi contact term.

The results of this investigation demonstrate that the reaction between trimeric phosphonitrilic fluoride and an aryllithium reagent is stereospecific to the extent of favoring both nongeminal disubstituted products and the *cis* molecular configuration. This reaction is the first recorded example of the synthesis of nongeminal aryl derivatives of the phosphonitrilic halides by a substitution process. Furthermore, it is the only reported reaction for the formation of nongeminal diaryl derivatives. Nongeminal triaryl derivatives can be obtained by the controlled amminolysis of phenyltetrabromo-[25] or phenyltetrachlorophosphorane,[26] but the procedure differs in that the phosphorus–phenyl bond is present in a reacting species and thus is not formed in the reaction. This investigation also suggests that in the formation of nongeminal disubstituted substitution products of the trimeric phosphonitrilic halides the observed predominance of a *cis* or *trans* isomer can be rationalized and the probable predominance predicted in terms of the relative π bonding capabilities of the exocyclic groups present. Further investigations to test the worth of this suggestion are in progress.

Acknowledgment.—The authors acknowledge, with gratitude, support of this investigation by the National Institutes of Health under Grant USPH-GM-11996.

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[22] A. C. Chapman and D. F. Carroll, *J. Chem. Soc.*, 5005 (1963).

[23] (a) J. H. Letcher and J. R. van Wazer, *J. Chem. Phys.*, **45**, 2296 (1966); (b) M. A. Whitehead, *Can. J. Chem.*, **42**, 1212 (1964).

[24] T. Moeller, A. Failli, and F. Y. Tsang, *Inorg. Nucl. Chem. Letters*, **1**, 49 (1965).

[25] T. Moeller and P. Nannelli, *Inorg. Chem.*, **1**, 721 (1962); **2**, 659, 896 (1963).

[26] B. Grushkin, M. G. Sanchez, and R. G. Rice, *ibid.*, **3**, 623 (1964).

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Aryl-Substituted Phosphonitrilic Fluorides. III. Geminally Substituted Phenylphosphonitrilic Fluoride Trimers[1]

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The syntheses of a series of geminally substituted phenylphosphonitrilic fluoride trimers have been effected by a combination of organolithium and Friedel–Crafts reactions. The phosphorus-31 and fluorine-19 nuclear magnetic resonance spectra of these compounds are in agreement with the geminal assignment. Several trends in the nuclear magnetic resonance data have been interpreted in terms of endo- and exocyclic π bonding involving the phosphorus–nitrogen ring system. The infrared spectra of these compounds have been measured and interpreted.

Introduction

The extensively investigated[2] reaction between trimeric phosphonitrilic chloride and benzene in the presence of aluminum chloride yields the three phenyl-substituted compounds 1,1-$N_3P_3Cl_4(C_6H_5)_2$, 1,1,3,3-$N_3P_3Cl_2(C_6H_5)_4$, and $N_3P_3(C_6H_5)_6$. The indicated geminal arrangement of the phenyl groups in the diphenyl[3] and the tetraphenyl[4] compounds has been confirmed by X-ray diffraction measurements. Neither a monophenyl nor a triphenyl derivative has been isolated from the Friedel–Crafts reaction. The implication of these observations is that replacement of a chlorine atom by a phenyl group so activates the other chlorine atom on this phosphorus atom that the geminally disubstituted product forms immediately.

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[1] Part II: C. W. Allen and T. Moeller, *Inorg. Chem.*, **7**, 2177 (1968).

[2] R. A. Shaw, R. Keat, and C. Hewlett in "Preparative Inorganic Reactions," Vol. 2, W. L. Jolly, Ed., Interscience Publishers Inc., New York, N. Y., 1965, pp 74–77.

[3] N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, **19**, 693 (1965).

[4] N. V. Mani, F. R. Ahmed, and W. H. Barnes, *ibid.*, **21**, 375 (1966).

Reasoning by analogy suggests that in the fluoride system the monophenyl compound, $N_3P_3F_5(C_6H_5)$, which can be prepared by a controlled reaction of phenyllithium with trimeric phosphonitrilic fluoride,[1,5] should be transformed to the geminal diphenyl derivative, 1,1-$N_3P_3F_4(C_6H_5)_2$, by means of a Friedel–Crafts reaction with benzene. Furthermore, the same type of reaction should convert the mixture of diphenyl isomers obtained by the use of phenyllithium[1,5] largely to the geminal tetraphenyl compound, 1,1,3,3-$N_3P_3F_2(C_6H_5)_4$, since this mixture contains primarily the *cis*- and *trans*-1,3 compounds. However, synthesis of the intermediate substance 1,1,3-$N_3P_3F_3(C_6H_5)_3$ should require the reaction of 1,1-$N_3P_3F_4(C_6H_5)_2$ with phenyllithium in equimolar quantities.[1]

These hypotheses have been verified by the nuclear magnetic resonance data discussed in this report and in the case of the compound 1,1-$N_3P_3F_4(C_6H_5)_2$ by an evaluation of its crystal and molecular structure by X-ray diffraction.[6] Arylation by the Friedel–Crafts route is thus shown to form geminal isomers. By a combination of the phenyllithium and Friedel–Crafts reactions, all of the compounds $N_3P_3F_{6-n}(C_6H_5)_n$ (n = 1–6) can be prepared.

Experimental Section

Materials.—Pure phosphonitrilic chloride trimer was obtained as previously described.[1] Reagent quality benzene and diethyl ether were distilled from sodium. Triethylamine was heated at reflux over potassium hydroxide for 12 hr and then distilled from fresh potassium hydroxide. Reagent quality bromobenzene, anhydrous aluminum chloride, and metallic lithium were used without additional purification.

Measurements.—All phosphorus-31 and fluorine-19 nuclear magnetic resonance spectra and all infrared spectra were obtained as previously described.[1] All microanalyses were carried out using standard techniques. Molecular weights were determined with a Mechrolab vapor-phase osmometer, using chloroform solutions. Listed melting points are uncorrected.

Preparative Procedures.—Previously reported procedures were used to prepare trimeric phosphonitrilic fluoride,[7] the compound $N_3P_3F_5(C_6H_5)$,[1] and phenyllithium.[8]

1,1-Diphenylphosphonitrilic Fluoride Trimer.—In a typical experiment, 60 g (0.225 mol) of anhydrous aluminum chloride was added to a 500-ml, three-necked, round-bottomed flask containing 7.6 g (0.075 mol) of dry triethylamine[9,10] and 200 ml of dry benzene. The flask was equipped with a mechanical stirrer, a pressure-equalizing dropping funnel containing 15.35 g (0.05 mol) of monophenylphosphonitrilic fluoride trimer dissolved in 50 ml of benzene, and a reflux condenser bearing a phosphorus(V) oxide drying tube. After the contents of the flask had been stirred for 30 min under reflux, the solution of the monophenylphosphonitrilic fluoride trimer was added slowly over a period of 30 min. The reaction mixture was then heated under reflux for 24 hr, after which it was hydrolyzed with acidified ice water. The organic layer was removed, dried over anhydrous magnesium sulfate, and decolorized with charcoal. The oil remaining after evaporation of the benzene was dissolved in a minimum quantity of *n*-pentane. The crystals that formed when this solution was cooled to Dry Ice–acetone temperature were purified by sublimation; yield, 13 g (71% of theory) of a milk-white, crystalline solid; mp 68.5–69.5°. *Anal.* Calcd for $N_3P_3F_4(C_6H_5)_2$: C, 39.45; H, 2.74; N, 11.51; mol wt, 365. Found: C, 39.85; H, 2.76; N, 11.58; mol wt, 359.

1,1,3-Triphenylphosphonitrilic Fluoride Trimer.—Typically, 50 ml of diethyl ether was distilled from sodium into a 250-ml, three-necked, round-bottomed flask containing 10 g (0.027 mol) of the compound 1,1-$N_3F_3F_4(C_6H_5)_2$. The flask was equipped with a reflux condenser attached to a mercury bubbler and a pressure equalizing dropping funnel containing 0.027 mol of phenyllithium at a concentration of *ca.* 1.0 *M* in diethyl ether. The phenyllithium solution was added to the vigorously stirred reaction mixture over a period of 30 min. The mixture was then heated under reflux for 1 hr, and the solvent was removed by evaporation. The oily residue was treated with benzene, and the insoluble lithium fluoride was removed by filtration. The filtrate was poured through a column of silica gel, and the adsorbed material was eluted with benzene. Thin layer chromatographic monitoring showed concentration of the phosphonitrilic components in the first fractions. All of these fractions which were phenol free[1] were combined, and the solvent was removed. The resulting solid was heated at 70° (0.025 mm) in a sublimation apparatus. The sublimate was a mixture of biphenyl and unreacted diphenyl trimer; the residue was the product, which was recrystallized from anhydrous methanol to a milk-white solid, mp 79.5–80.5°; yield 5.5 g (47% of theory). *Anal.* Calcd for $N_3P_3F_3(C_6H_5)_3$: C, 51.07; H, 3.57; N, 9.93; mol wt, 423. Found: C, 51.08; H, 3.61; N, 9.89; mol wt, 423.

1,1,3,3-Tetraphenylphosphonitrilic Fluoride Trimer.—This compound was prepared in an analogous fashion to the geminal diphenyl derivative, except that 18.3 g (0.05 mol) of the mixture of diphenyl-substituted isomers obtained from the phenyllithium reaction[1] was allowed to react with benzene in the presence of 120 g (0.045 mol) of aluminum chloride and 15.2 g (0.15 mol) of triethylamine. After hydrolysis, the excess benzene was removed, and hot *n*-heptane was added to the resulting oil. Crystals that formed upon cooling were removed, and the filtrate was concentrated to obtain more solid. The combined solids were heated at 70° (0.025 mm) to remove the compound 1,1-$N_3P_3F_4(C_6H_5)_2$ and then at 150° (0.025 mm) to volatilize the tetraphenyl product; yield, 9.6 g (40% of theory) of a milk-white crystalline solid; mp 137–138°. *Anal.* Calcd for $N_3P_3F_2(C_6H_5)_4$: C, 59.88; H, 4.19; N, 8.76; mol wt, 481. Found: C, 59.80; H, 4.19; N, 9.25; mol wt, 484.

Results and Discussion

The phosphorus-31 and fluorine-19 nuclear magnetic resonance spectra of the tetraphenyl compound, $N_3P_3F_2(C_6H_5)_4$, are given in Figures 1 and 2. The phosphorus spectrum can be interpreted on a first-order basis, but fine structure renders the fluorine spectrum too complicated for simple interpretation. The phosphorus spectrum contains a triplet of triplets, which is consistent only with a geminal arrangement of the two fluorine atoms. If these fluorine atoms were nongeminally arranged, a doublet of doublets should be present. The geminal arrangement was confirmed by computer synthesis of the total phosphorus and fluorine spectrum as an AB_2X_2 system, using FREQUINT IV.[11,12]

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[5] T. Moeller and F. Tsang, *Chem. Ind.* (London), 361 (1962).

[6] C. W. Allen, I. C. Paul, and T. Moeller, *J. Am. Chem. Soc.*, **89**, 6361 (1967).

[7] T. Moeller, K. John, and F. Tsang, *Chem. Ind.* (London), 347 (1961). See also R. Schmutzler, T. Moeller, and F. Tsang, *Inorg. Syn.*, **9**, 75 (1967).

[8] H. Gilman and J. W. Morton, Jr., in "Organic Reactions," Vol. 8, John Wiley and Sons, Inc., New York, N. Y., 1954, p 286.

[9] E. T. McBee, K. Okuhara, and C. J. Morton, *Inorg. Chem.*, **4**, 1672 (1965).

[10] Although the reaction takes place in the absence of triethylamine, it is then accompanied by the formation of the difficultly separable biphenyl (mp 69–71°). Biphenyl does not form in the presence of the amine.

[11] C. W. Allen, Doctoral Dissertation, University of Illinois, 1967.

[12] FREQUINT IV was altered to adapt it to a system containing two different magnetically active nuclei. The fluorine chemical shift was placed on the same scale as the phosphorus chemical shift by adding an arbitrary and large number to it and thus ensuring its behavior as an X case compared to phosphorus. The validity of this procedure was tested by varying the constant from 20,000 to 50,000 Hz. Each choice of constant gave the same result.

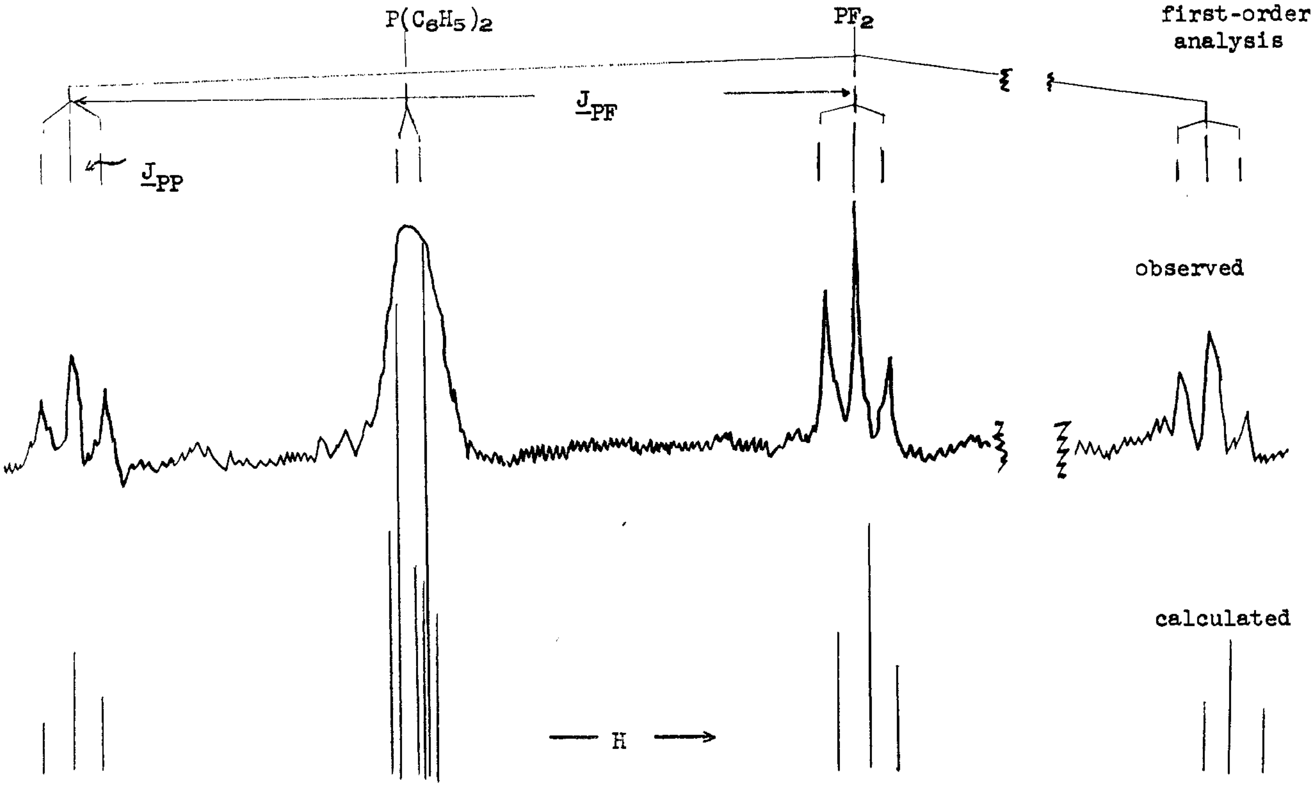

Figure 1.—Phosphorus-31 nuclear magnetic resonance spectrum of 1,1,3,3-$N_3P_3F_2(C_6H_5)_4$; scale = 66.8 Hz cm^{-1}.

The relative signs of the coupling constants obtained are the same as those reported for the compounds 1,1-$N_3P_3Cl_4F_2$[13] and $N_3P_3Cl_5F$;[14] *i.e.*, the coupling constant for directly bonded phosphorus–fluorine has a sign opposite to those for phosphorus–phosphorus and distant phosphorus–fluorine interactions. The distant value, $|J_{PF}|$, is 7 Hz. Other coupling constants and chemical shifts are summarized in Table I.

The phosphorus-31 and fluorine-19 nuclear magnetic resonance spectra of the diphenyl compound, $N_3P_3F_4(C_6H_5)_2$, are given in Figures 3 and 4. Both indicate a geminal arrangement of the phenyl groups. The phosphorus spectrum contains a triplet with complex fine structure and a singlet; the fluorine spectrum, a basic doublet with complex fine structure. For a nongeminal configuration, two well-separated doublets should characterize the fluorine spectrum. The complexity of the observed spectra is due in part to the fact that the phosphorus atoms in the $\equiv PF_2$ centers are magnetically nonequivalent—as are also the fluorine atoms. Chemical shifts and approximate coupling constants appear in Table I. The indicated geminal structure is consistent with that determined crystallographically.[6]

The phosphorus-31 and fluorine-19 nuclear magnetic resonance spectra of the triphenyl compound, $N_3P_3F_3(C_6H_5)_3$, are given in Figures 5 and 6. First-order analyses are complicated by the fact that in a 1,1,3-arrangement of phenyl groups the geminal fluorine atoms are environmentally nonequivalent, as are the geminal fluorine atoms in the compound *cis*-1,3-$N_3P_3F_4(C_6H_5)_2$.[1] The phosphorus spectrum appears, on first examination, to be less complicated than it really is, since the overlapping of peaks gives what seem to be simple triplets and doublets. However, this spectrum is interpretable on a first-order basis. As may be expected, the fluorine spectrum is very similar to that of the *cis*-1,3-diphenyl isomer.[1] The presence of two major types of doublets confirms the presence of the $\equiv PF_2$ and $\equiv PF(C_6H_5)$ groups. The presence of these functional groups and the general characteristics of the spectra indicate that the molecule in question has phenyl groups in the 1,1,3 arrangement.

Elucidation of the molecular structures of these three compounds shows clearly that the Friedel–Crafts reaction converts the exocyclic $\equiv PF(C_6H_5)$ group to the $\equiv P(C_6H_5)_2$ group and that in the reaction of 1,1-$N_3P_3F_4(C_6H_5)_2$ with phenyllithium no migration of phenyl groups occurs. The feasibility of combining the two phenylation reactions to prepare the series of geminally substituted phenylphosphonitrilic fluoride trimers is also apparent.

Comparison of the nuclear magnetic resonance data for the geminal (Table I) and nongeminal[1] compounds delineates some interesting trends. The phosphorus-31 chemical shifts for the various types of phosphorus environments (*i.e.*, $\equiv PF_2$, $\equiv PF(C_6H_5)$, $\equiv P(C_6H_5)_2$) show progressive deshielding with an increasing degree of fluorine substitution, thus reflecting the increased drain of electron density from the phosphorus atom in question by fluorine atoms on the remote phosphorus atom(s). This shift in electronic charge density could arise from inductive effects of the fluorine atoms as transmitted through the σ system or from an increase

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(13) M. L. Heffernan and R. F. M. White, *J. Chem. Soc.*, 1382 (1961).

(14) F. Heatly and S. M. Todd, *ibid.*, *A*, 1152 (1966).

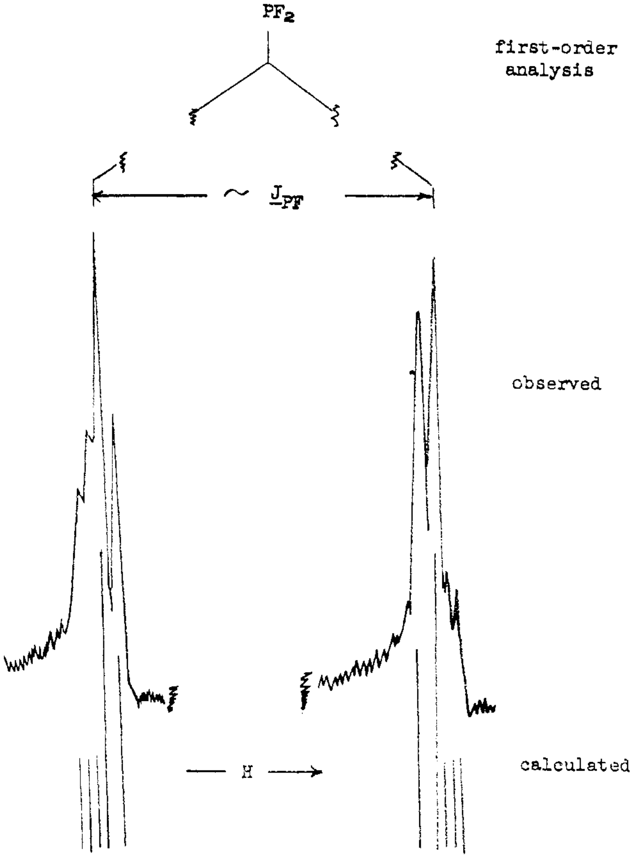

Figure 2.—Fluorine-19 nuclear magnetic resonance spectrum of 1,1,3,3-$N_3P_3F_2(C_6H_5)_4$; scale = 20 Hz cm^{-1}.

Table I

Chemical Shift and Coupling Constant Data[a]

Compound	Chemical shift, ppm: ^{31}P (from 85% H_3SO_4) ≡PF-(C_6H_5)	≡P-(C_6H_5)$_2$	≡PF_2	^{19}F (from $CFCl_3$) ≡PF-(C_6H_5)	≡PF_2
$N_3P_3F_6$			−13.9		71.3
1,1-$N_3P_3F_4(C_6H_5)_2$		−30.4	−12.1		69.7
1,1,3-$N_3P_3F_3(C_6H_5)_3$	−31.2	−27.3	−8.6	49.1	(68.6) (66.0)
1,1,3,3-$N_3P_3F_2(C_6H_5)_4$		−27.3	−6.2		

Compound	Coupling constant, Hz: J_{PF}[b] PF_2	J_{PF}[b] PF-(C_6H_5)	J_{PP} (C_6H_5)P-PF_2	J_{PP} (C_6H_5)$_2$-P-PF-(C_6H_5)	J_{PP} F_2P-PF-(C_6H_5)	J_{FF} PF_2
1,1-$N_3P_3F_4(C_6H_5)_2$	(890)		(86)			
1,1,3-$N_3P_3F_3(C_6H_5)_3$	895	958	(44)	(25)	(57)	(70)
1,1,3,3-$N_3P_3F_2(C_6H_5)_4$	896		(32.9			

[a] Values in parentheses are approximate. [b] J_{PF} measured from phosphorus-31 spectrum.

in extent of π bonding as a consequence of increased fluorine substitution.[6] The π-bonding pattern includes both the regular d_π–p_π system and the π′ system resulting from delocalization of nitrogen atom lone-pair electron density.[15] The relative order of the phosphorus-31 chemical shifts, *i.e.*, ≡PF(C_6H_5) < ≡P-(C_6H_5)$_2$ < ≡PF_2, is less easy to interpret. A possible explanation lies in the observation[16] that the bond angle between a phosphorus atom and two substituent atoms is crucial in determining the chemical shift.

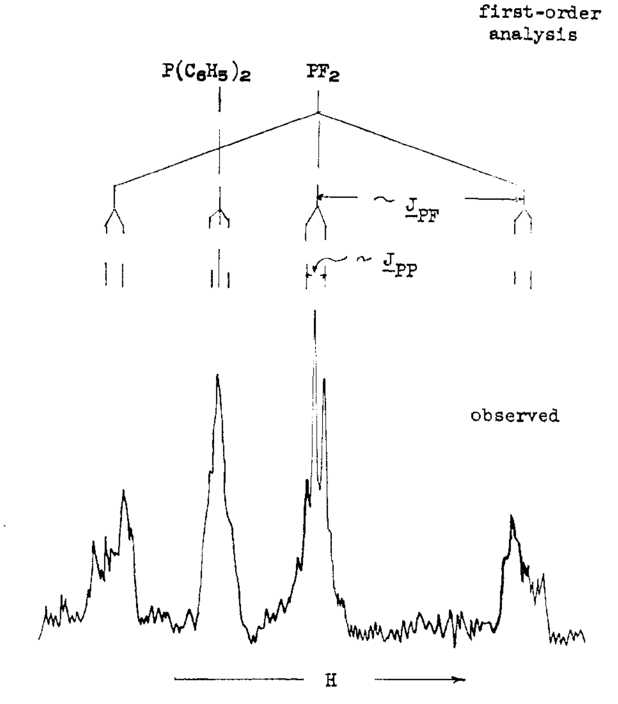

Figure 3.—Phosphorus-31 nuclear magnetic resonance spectrum of 1,1-$N_3P_3F_4(C_6H_5)_2$; scale = 233.3 Hz cm^{-1}.

The observed trend for the fluorine-19 chemical shifts characteristic of the ≡PF_2 centers is toward increased shielding with increased fluorine substitution on the ring. This effect can be ascribed to the decrease in exocyclic π bonding (*i.e.*, fluorine atom to phosphorus atom back-bonding) that accompanies an increase in endocyclic π bonding. As the degree of fluorine substitution increases, there is increased competition from the endocyclic π system for available d_π orbitals of the phosphorus atoms, thereby decreasing the exocyclic π bonding and increasing the shielding of the fluorine atoms. Force constant calculations have indicated the existence of some exocyclic π bonding in the trimeric phosphonitrilic fluoride molecule.[17] That the fluorine chemical shift for the ≡PF(C_6H_5) center is less than that for the ≡PF_2 centers is also related to exocyclic π bonding. Inasmuch as phenyl groups have little[18a] or no[18b] tendency to form π bonds with phosphorus in the pentavalent state,[18] the fluorine atom in a ≡PF(C_6H_5) center has less competition for d_π orbitals from the phosphorus atom than a fluorine atom in a ≡PF_2 center has. Hence, a greater degree of back-bonding and less shielding characterize a fluorine atom in a ≡PF(C_6H_5) center. The observation that phosphorus–fluorine exocyclic π bonding increases with decreased fluorine atom content can be used to explain the decrease in reactivity with increased degree of substitution on the trimeric phosphonitrilic fluoride ring.

The coupling constants for directly bonded phos-

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(15) D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).

(16) J. H. Letcher and H. R. Van Wazer, *J. Chem. Phys.*, **45**, 2916 (1966).

(17) A. C. Chapman and D. F. Carroll, *J. Chem. Soc.*, 5005 (1963).

(18) (a) M. A. Whitehead, *Can. J. Chem.*, **42**, 1212 (1964); (b) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **45**, 2926 (1966).

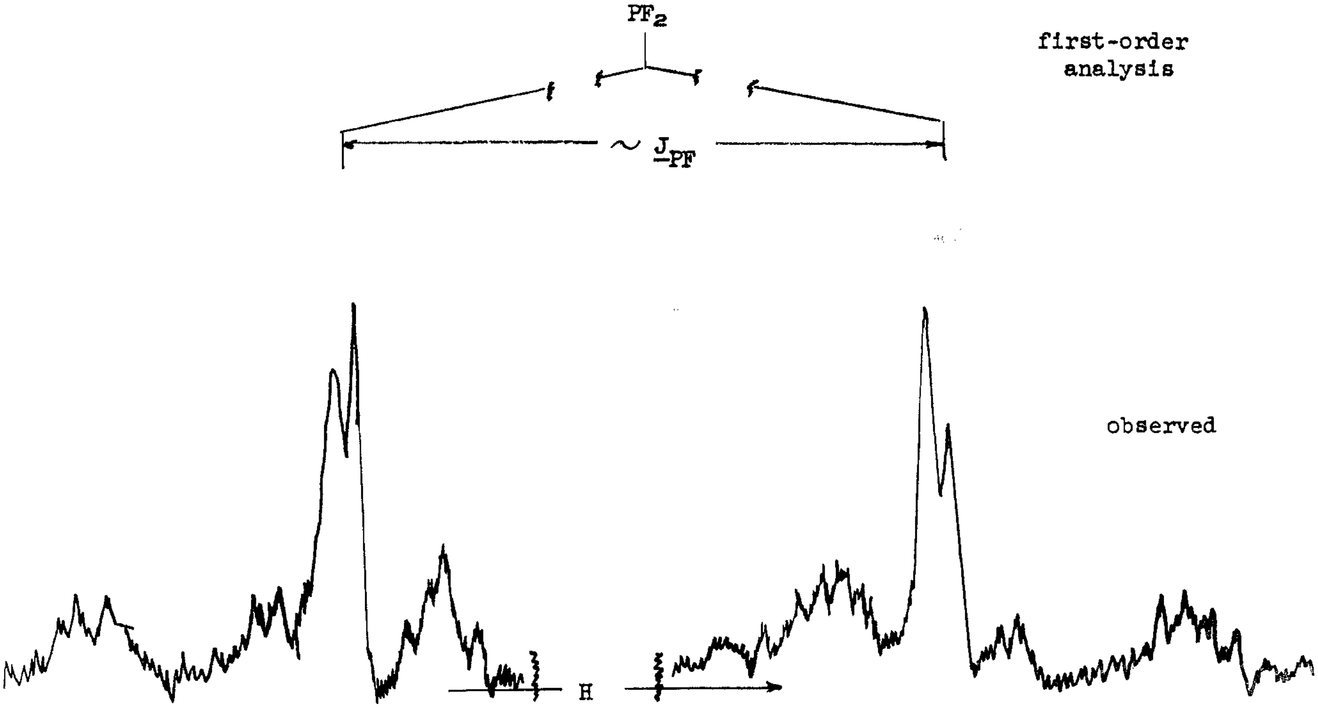

Figure 4.—Fluorine-19 nuclear magnetic resonance spectrum of 1,1-$N_3P_3F_4(C_6H_5)_2$; scale = 20 Hz cm^{-1}.

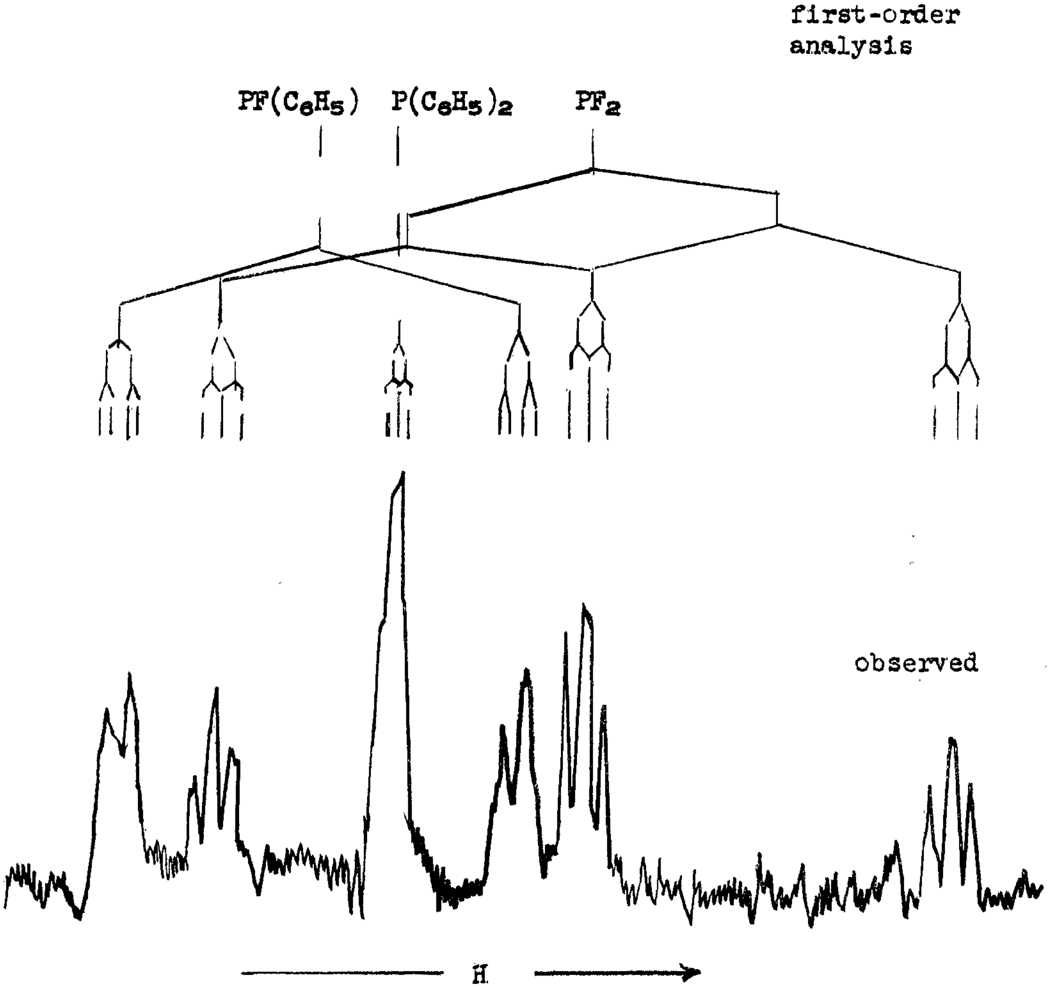

Figure 5.—Phosphorus-31 nuclear magnetic resonance spectrum of 1,1,3-$N_3P_3F_3(C_6H_5)_3$; scale = 171.4 Hz cm^{-1}.

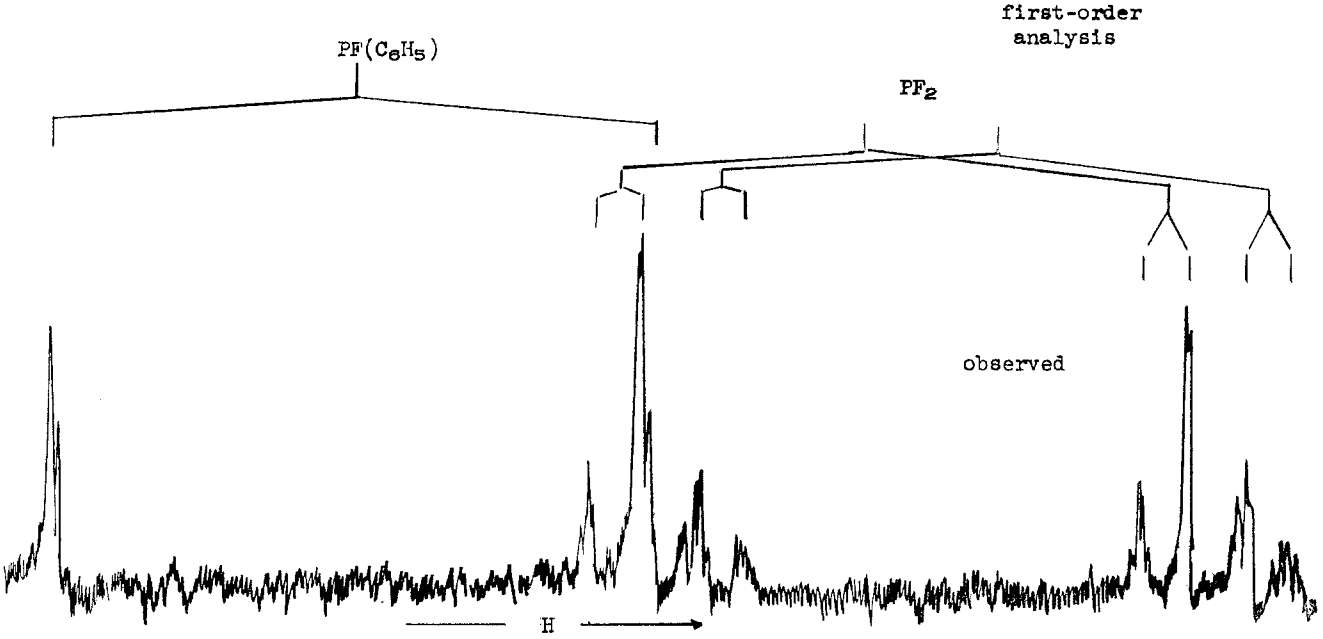

Figure 6.—Fluorine-19 nuclear magnetic resonance spectrum of 1,1,3-$N_3P_3F_3(C_6H_5)_3$; scale = 100 Hz cm^{-1}.

Table II

Infrared Data[a]

	Band position, cm^{-1}				
Compound	ν(N–P–N)		ν(P–F)$_{asym}$	ν(P–F)$_{sym}$	
1,1-$N_3P_3F_4(C_6H_5)_2$	1250 vs	950 w	920 s, 916 s, 906 ms	812 s	730 ms
	(1265 vs)	(952 mw)	(933 sh, 925 sh, 914 vs, 900 s)	(850 vw, 837 mw, 820 s)	(748 vw, 733 s)
1,1,3-$N_3P_3F_3(C_6H_5)_3$	1230 vs	962 mw	902 s, 874 m	814 s	750 m, 740 s, 706 m
	(1274 sh, 1240 vs)	(964 mw)	(915 mw, 898 s, 872 m)	(848 vw, 812 s)	(758 sh, 748 s, 713 m)
1,1,3,3-$N_3P_3F_2(C_6H_5)_4$	1218 vs	944 m	889 ms	834 m	734 ms
	(1228 vs)	(948 mw)	(930 vs, 887 s)	(840 m)	(756 w, 742 s)

[a] Values in parentheses from KBr disks; others from 10% solutions in CS_2.

phorus–fluorine atoms are larger for the $\equiv PF(C_6H_5)$ centers than for the $\equiv PF_2$ centers. If it is assumed that the Fermi contact term is of dominating importance in determining the coupling constant, this fact suggests that the P—F bond has more s character in the $\equiv PF(C_6H_5)$ center than in the $\equiv PF_2$ center. Inasmuch as the phenyl group does not polarize the d orbitals of the phosphorus atom as effectively as does a fluorine atom,[6] smaller d character and larger s character should describe the hybrid orbitals of the phosphorus atom in the $\equiv PF(C_6H_5)$ center. That certain of the values are approximate precludes discussion of additional trends in the coupling constants.

Table II summarizes infrared data for the geminal compounds. Vibrations characteristic of the phenyl group and the phosphorus–carbon bonds are not included. The listed assignments were made by comparison with data for trimeric phosphonitrilic fluoride.[19] The phosphorus–nitrogen frequency shows the expected increase with increasing electronegativity of the exocyclic substituent.

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(19) A. C. Chapman and N. L. Paddock, *J. Chem. Soc.*, 635 (1962).