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Aryl-Substituted Phosphonitrilic Fluorides. II. The Reaction of Aryllithium Reagents with Trimeric Phosphonitrilic Fluoride[1]

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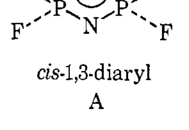
The reaction between phenyllithium and trimeric phosphonitrilic fluoride has been reinvestigated, and reliable procedures for the syntheses of several phenyl derivatives have been developed. The reaction has been shown to follow both geminal and nongeminal substitution pathways, with the nongeminal pattern predominating. Structural assignments have been made on the bases of phosphorus-31 and fluorine-19 nuclear magnetic resonance spectra and dipole moment determinations. The corresponding reaction with *o*-tolyllithium yields a larger proportion of nongeminal products, indicating the importance of steric effects. The relative isomeric yields are rationalized in terms of a directive effect operative in trimeric phosphonitrilic fluoride.

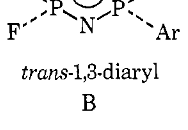
Introduction

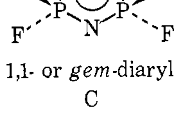
Current interest in the chemistry of the phosphonitrilic compounds centers largely in the positional pathways followed by incoming groups in substitution reactions and in the identification and structural characterization of isomeric compounds produced in these reactions. Examples of both geminal and nongeminal substitution patterns have been reported,[2,3] but lack of extensive data makes it impossible to predict with accuracy the pathway that will be followed by a given substituent reacting with a specific phosphonitrile. Definitive structural assignments for positional and geometrical isomers resulting from substitution reactions are even more limited in number.[1,4]

The aryl-substituted phosphonitrilic fluorides are of especial interest in studies of this type, in particular because of their ready preparation, the ease with which many of them can be crystallized, and their hydrolytic and thermal stabilities.[5] By way of contrast to the behavior of trimeric phosphonitrilic chloride,[6] trimeric phosphonitrilic fluoride reacts readily with aryllithium reagents by clean, stepwise replacement of halogen atoms, giving aryl-substituted products that are recoverable in good yields.[5] The degree of substitution is controlled by the mole ratio of the reactants, but in terms of preliminary phosphorus-31 and fluorine-19 nuclear magnetic resonance studies, the formation of possible geometrical and positional isomers is indicated to be a somewhat random process.

The first step in this arylation reaction can yield only the nonisomeric compound $N_3P_3F_5(Ar)$, Ar being an aryl group in general and the phenyl group in particular. The second step, however, can yield either the 1,1-diaryl compound or *cis* and *trans* forms of the 1,3-diaryl compound, depending upon whether the substitution pathway is geminal or nongeminal. The structural arrangements in these compounds, assuming the presence of an essentially coplanar N_3P_3 group, can be depicted as


cis-1,3-diaryl
A


trans-1,3-diaryl
B


1,1- or *gem*-diaryl
C

The *trans* isomer is also asymmetric and thus potentially capable of existing as a *dl* pair. Subsequent steps in the arylation process can yield additional positional and geometrical isomers.

Aryl groups can be introduced also by the Friedel–Crafts reaction[6] and, in principle, by the Grignard reaction, although recently reported data suggest that the scope of the latter reaction is severely limited.[7,8] The Friedel–Crafts and aryllithium substitution

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

[2] G. R. Feistel and T. Moeller, *J. Inorg. Nucl. Chem.*, **29**, 2731 (1967).

[3] R. A. Shaw, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **28**, 243 (1967).

[4] N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, **19**, 693 (1965); **21**, 375 (1966).

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

[6] R. A. Shaw, R. Keat, and C. Hewlett in "Preparative Inorganic Reactions," Vol. 2, W. L. Jolly, Ed., Interscience Publishers, New York, N. Y., 1967, pp 74–79.

[7] M. K. Feldt and T. Moeller, *J. Inorg. Nucl. Chem.*, in press.

[8] See also M. K. Feldt, Doctoral Dissertation, University of Illinois, 1967.

processes are mechanistically different and may be expected to follow different pathways.

It has been of interest to us to examine the trimeric phenylphosphonitrilic fluorides in particular and their tolyl analogs to a lesser degree, in terms of developing improved and reproducible methods for the syntheses of particular isomers and of making unambiguous assignments of structure to these compounds. The crystal and molecular structures have been reported for the compound 1,1-$N_3P_3F_4(C_6H_5)_2$ in the first paper of this series.[1]

The trimeric phosphonitrilic fluoride derivatives contain two nuclei of spin $^1/_2$, namely, phosphorus-31 and fluorine-19. Thus two distinct nuclear magnetic resonance spectra can be evaluated for each compound. These spectra permit one to examine a given molecule in terms of both endo- and exocyclic atoms. Nuclear magnetic resonance data have been used for the structural evaluation of the derivatives obtained by the aryllithium and Friedel–Crafts reactions. The products of the latter reaction are described in a subsequent communication.[9]

Experimental Section

Materials.—Pure phosphonitrilic chloride trimer was prepared from 95% trimer mixture obtained from the Hooker Chemical Co. by vacuum distillation at 0.05 mm and 130°. Diethyl ether was distilled over sodium. Solvents for dipole moment measurements were purified as follows: benzene, twice distilled over calcium hydride in an argon atmosphere; di-*n*-butyl ether, distilled over calcium hydride at reduced pressure. Spectroscopic grade cyclohexane was used without further purification. Other common solvents, bromobenzene, aluminum chloride, and elemental lithium were of the best grades available and were used without further purification.

Measurements.—Phosphorus-31 nuclear magnetic resonance spectra were obtained with a Varian DP-60 instrument, using a V-4311 phosphorus probe and operating at 24.3 MHz. Calibration was effected by the side-band technique. Chemical shifts were measured in terms of a phosphorus(III) oxide external standard and then converted to an 85% phosphoric acid basis in terms of the fact that the resonance of the oxide is 2812 ± 2 Hz downfield from that of the acid. Fluorine-19 nuclear magnetic resonance spectra were obtained with a Varian 56-60A spectrometer, with the probe operating at 56.4 MHz and precalibrated chart paper. Fluorotrichloromethane was used as an internal standard. Saturated solutions in chloroform were used in all cases.

Infrared spectra were obtained with a Perkin-Elmer Model 521 instrument, using both potassium bromide disks and carbon disulfide solutions.

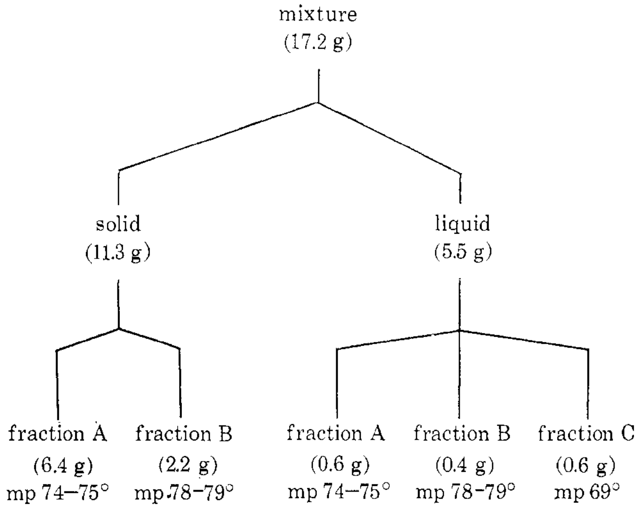
Capacitance measurements were made with a WTW dipolemeter, Type DM-01, using a DFL-2 cell. The dipolemeter was calibrated with cyclohexane, benzene, and di-*n*-butyl ether. Refractive indices were determined with an Abbé refractometer. All measurements were made with dilute solutions in benzene at 27°. Dipole moments were ultimately calculated by the procedure of Guggenheim.[10]

Reported molecular weights were determined at room temperature, using chloroform solutions and a Mechrolab vapor-phase osmometer. Reported melting points are uncorrected.

Procedures.—Previously reported procedures were used for the syntheses of trimeric phosphonitrilic fluoride[11] and phenyllithium.[12] Analysis of a phenyllithium solution was effected by hydrolyzing an aliquot with water and titrating with standard hydrochloric acid solution. Solutions of *o*-tolyllithium were prepared and analyzed similarly.

Monophenylphosphonitrilic Fluoride Trimer.—Typically, 100 ml of diethyl ether was distilled from sodium into a 500-ml, three-necked, round-bottomed flask containing 24.9 g (0.1 mol) of trimeric phosphonitrilic fluoride and a magnetic stirring bar. A pressure-equalizing dropping funnel, containing 0.1 mol of a solution of phenyllithium in diethyl ether (*ca.* 0.1 *M*), and a reflux condenser connected to a mercury bubbler were fitted to the flask. The flask was immersed in an ice–water bath and flushed with dry argon for 10 min. The flow of argon was stopped, the stirrer started, and the solution of phenyllithium added dropwise over a period of 1–2 hr. The solution was then warmed under reflux for 1 hr, after which the solvent was removed by distillation and the oily residue treated with 100 ml of low-boiling (30–60°) petroleum ether. Precipitated lithium fluoride was removed by filtration through infusorial earth. The filtrate was then adsorbed on a silica-gel column and the desired product was removed from the slower moving by-product (phenol) by elution with low-boiling petroleum ether at a rapid flow rate. The eluted material was collected in 200-ml fractions and the procedure was continued until the product was removed from the column. The combined fractions were distilled, after solvent removal, at 1 mm through a Vigreux column, and the fraction boiling at 50–52° was collected; yield 19.1 g (62.5% of theory) of a water-white liquid, bp 183–184° (1 atm). *Anal.* Calcd for $N_3P_3F_5C_6H_5$: C, 23.45; H, 1.63; N, 13.68; mol wt, 307. Found: C, 23.47; H, 1.74; N, 13.72; mol wt, 319. Complete elimination of water as a reagent contaminant is essential to the success of this procedure.

Diphenylphosphonitrilic Fluoride Trimers.—In a typical procedure, 0.22 mol of phenyllithium was allowed to react with 24.9 g (0.1 mol) of trimeric phosphonitrilic fluoride according to the procedure outlined above. The crude product was purified by short-path distillation[13] at 0.025 mm. The first fraction (32–40°) was crude monophenylphosphonitrilic fluoride trimer; the second (40–95°), biphenyl. The final fraction (115°) gave, on cooling, a mixture of crystalline and oily diphenylphosphonitrilic fluoride trimers; yield 21.8 g (60% of theory). *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, 41.58; H, 2.83. Simplification of this mixture was best effected by separate recrystallization of the crystalline and oily components from *n*-heptane, but it was complete only after many recrystallization steps. With due allowance for mechanical losses, the procedure can be summarized as



(mole ratio A:B:C = *ca.* 3:1:0.25)

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[9] C. W. Allen, F. Y. Tsang, and T. Moeller, *Inorg. Chem.*, **7**, 2183 (1968).

[10] E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

[11] 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).

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

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

Recrystallization of the solid component at 0° yielded fractions A and B. Fraction A formed within 1 hr and was obtained in the form of colorless, needlelike crystals. Fraction B was obtained as hard, milk-white, crystalline aggregates after several hours. Recrystallization of the oily component at 0° gave fractions identical with A and B, plus fraction C. Fraction C formed first. The complete separation of A, B, C from the oily component was particularly difficult.

The isomeric purity of each of these three fractions was established by mixture melting points with each other and with biphenyl and by nuclear magnetic resonance and infrared data. Fraction C was shown to be the 1,1 isomer (formula C) by comparison with a sample obtained by the Friedel–Crafts route and used for a crystal structure determination.[1] Nuclear magnetic resonance data identified fraction A as the *cis*-1,3 compound (formula A) and fraction B as the *trans*-1,3 compound (formula B). *Anal.* Found for A: C, 39.49; H, 2.79; N, 11.59; mol wt, 371. Found for B: C, 39.42; H, 2.79; N, 11.74; mol wt, 378.

Bis(*o*-tolyl)phosphonitrilic Fluoride Trimer.—In a typical synthesis, 24.9 g (0.1 mol) of trimeric phosphonitrilic fluoride was treated with 0.2 mol of *o*-tolyllithium, exactly as outlined for preparation of the diphenyl compounds. Ultimate chromatographic separation on silica gel required slower elution and collection of smaller fractions since *o*-cresol moves more rapidly than phenol. Each fraction was checked for purity by thin layer chromatography, using low-boiling petroleum ether. The *o*-cresol-free crude product was distilled at 0.025 mm, and the fraction boiling at 125° was collected; yield 18.5 g (47.3% theory) of a water-white oily liquid. Crystallization at 0° of a solution of the oil in *n*-heptane yielded a milk-white solid, mp 64–65°, which proved to be *cis*-1,3-$N_3P_3F_4(C_7H_7)_2$. Evaporation of the mother liquor yielded an oily mixture of *cis* and *trans* isomers, but no separation could be effected. Fluorine-19 and phosphorus-31 nuclear magnetic resonance spectra showed the complete absence of an observable quantity of the geminal isomer in all samples. *Anal.* Calcd for $N_3P_3F_4(C_7H_7)_2$: C, 42.74; H, 3.56; N, 10.68. Found (mixture): C, 42.72; H, 4.12; N, 10.87. Found (*cis*): C, 43.06; H, 3.57; N, 11.37.

Attempted Isomerization of *cis*-1,3-$N_3P_3F_4(C_6H_5)_2$.—To a 100-ml, single-necked, round-bottomed flask containing 50 ml of carbon disulfide, which had been distilled from anhydrous aluminum chloride, were added 2.0 g (0.0055 mol) of *cis*-1,3-$N_3P_3F_4(C_6H_5)_2$ and 4.3 g (0.016 mol) of anhydrous aluminum chloride. The mixture was heated under reflux for 12 hr and then hydrolyzed with an acidified ice–water mixture. The carbon disulfide phase was removed and evaporated to dryness. Both the melting point and the fluorine-19 nuclear magnetic resonance spectrum of the product indicated the presence of only unchanged *cis* isomer.

Results and Discussion

The reaction of phenyllithium with trimeric phosphonitrilic fluoride in a 2:1 mole ratio yields three distinctly different trimeric diphenylphosphonitrilic fluorides. The minor product has been shown to be the 1,1 or geminal compound (formula C) by comparison with the geminal isomer obtained as a sole product in the reaction of trimeric monophenylphosphonitrilic fluoride with benzene under Friedel–Crafts conditions.[1,9,13] The major components have been characterized as the *cis* (A) and *trans* (B) isomers in terms of the phosphorus-31 nuclear magnetic resonance spectra shown in Figures 1 and 2.

The basic phosphorus spectrum identifying the *trans* isomer consists of a triplet (J_{PF} in $\equiv PF_2$), further split to a triplet of triplets (J_{PP}), and a doublet (J_{PF} in $\equiv PF(C_6H_5)$), further split to a doublet of doublets (J_{PP}). The spectrum of the *cis* isomer is more complicated as a consequence of the lack of stereochemical equivalence of the geminal fluorine atoms (formula A). This nonequivalence is dramatically apparent in the fluorine-19 spectra shown in Figures 3 and 4. The basic fluorine-19 spectrum of the *trans* isomer consists of two large doublets, produced by directly bonded phosphorus–fluorine coupling (J_{PF}) in two separate environments ($\equiv PF_2$ and $\equiv PF(C_6H_5)$). The complexity of the fluorine spectrum in the $\equiv PF_2$ region is a result of nonequivalence of the geminal fluorine atoms. The complex fine structure reflects fluorine coupling with distant phosphorus atoms in the ring arrangement. Both chemical-shift and coupling-constant data are summarized in Table I. A complete discussion of the nuclear magnetic resonance parameters of these compounds appears in part III of this series,[9] where they are compared with the parameters characterizing the *gem*-phenyl derivatives.

TABLE I

CHEMICAL SHIFT AND COUPLING CONSTANT DATA[a]

	Chemical shift, ppm			
	^{31}P		^{19}F	
Compound	$\equiv PF(C_6H_5)$	$\equiv PF_2$	$\equiv PF(C_6H_5)$	$\equiv PF_2$
cis-1,3-$N_3P_3F_4(C_6H_5)_2$	−38.4	−12.4	49.3	(69.3, 65.2)
trans-1,3-$N_3P_3F_4(C_6H_5)_2$	−38.3	−10.8	51.5	67.7

	Coupling constant, Hz			
	J_{PF}[b]		J_{PP}	J_{FF}
Compound	$\equiv PF_2$	$\equiv PF(C_6H_5)$	$P(F)_2$—$PF(C_6H_5)$	F—F (geminal)
cis-1,3-$N_3P_3F_4(C_6H_5)_2$	898 879	965	58	(75)
trans-1,3-$N_3P_3F_4(C_6H_5)_2$	879	939	65	(70)

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

The phosphorus-31 and fluorine-19 spectra of the purified di-*o*-tolylphosphonitrilic fluoride trimer are virtually identical with those of the *cis*-diphenyl compound. Thus, this product is reasonably assigned a *cis* configuration. The spectra of the di-*o*-tolyl mixture obtained from the lithium reagent reaction are nearly identical with those of a mixture of *cis*- and *trans*-diphenyl isomers. There is no evidence for the presence of the *gem*-di-*o*-tolyl compound in this reaction product, whereas the presence of the *gem*-diphenyl compound is apparent from the nuclear magnetic resonance spectra of the diphenyl product mixture. This observation is reasonable in that the *o*-methyl groups could cause steric crowding in both the transition-state species and the product if the *o*-tolyl group entered geminally.

The correctness of the *cis* and *trans* assignments was confirmed by the dipole moment data summarized in Table II. A larger dipole moment can be reasonably associated with the *cis*-diphenyl isomer, in accordance with its reduced symmetry. The *cis* assignment for the di-*o*-tolyl derivative follows from a comparison of values. Added support for this argument comes from a comparison of the dipole moments for several *cis*- and *trans*-dialkylaminophosphonitrilic chloride trimers.[14]

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(14) I. Y. Kokoreva, Ya. K. Syrkin, A. A. Korpacheva, N. M. Kashnikova, and L. Mukhina, *Dokl. Akad. Nauk SSSR*, **166**, 155 (1966); *Chem. Abstr.*, **64**, 12522*h* (1966).

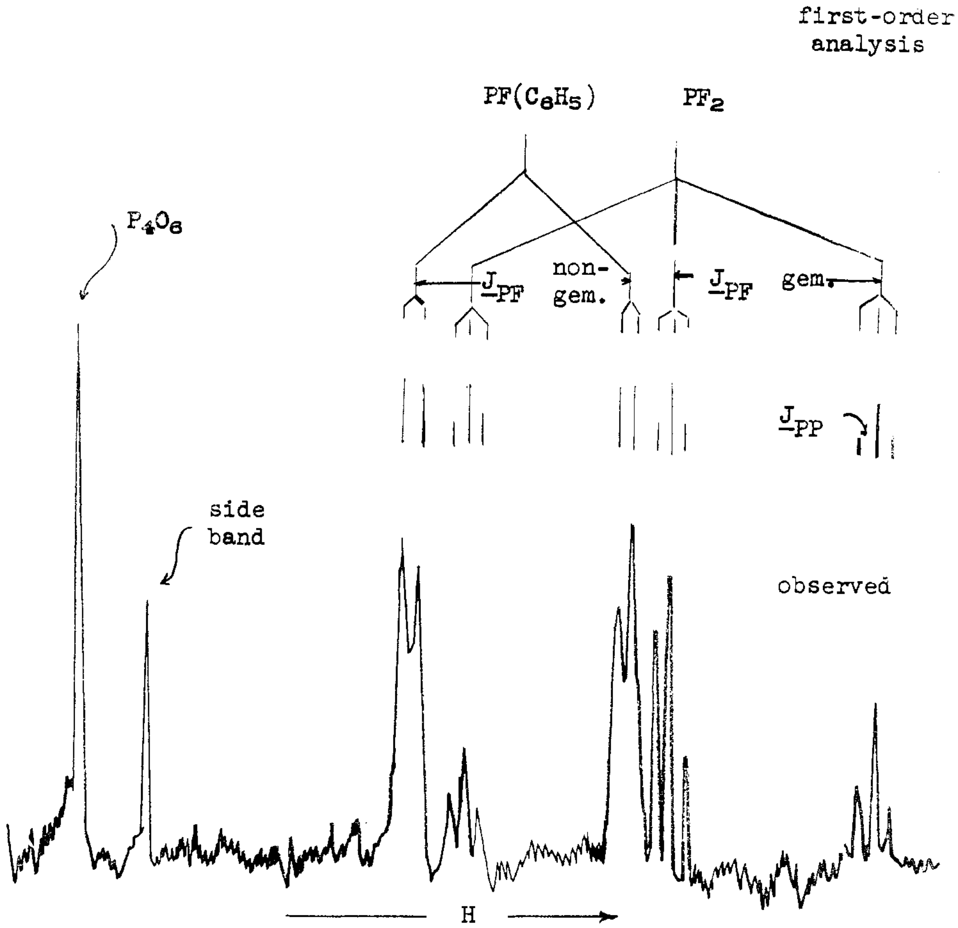

Figure 1.—Phosphorus-31 nuclear magnetic resonance spectrum of *trans*-1,3-$P_3N_3F_4(C_6H_5)_2$. Scale = 228.4 Hz cm^{-1}.

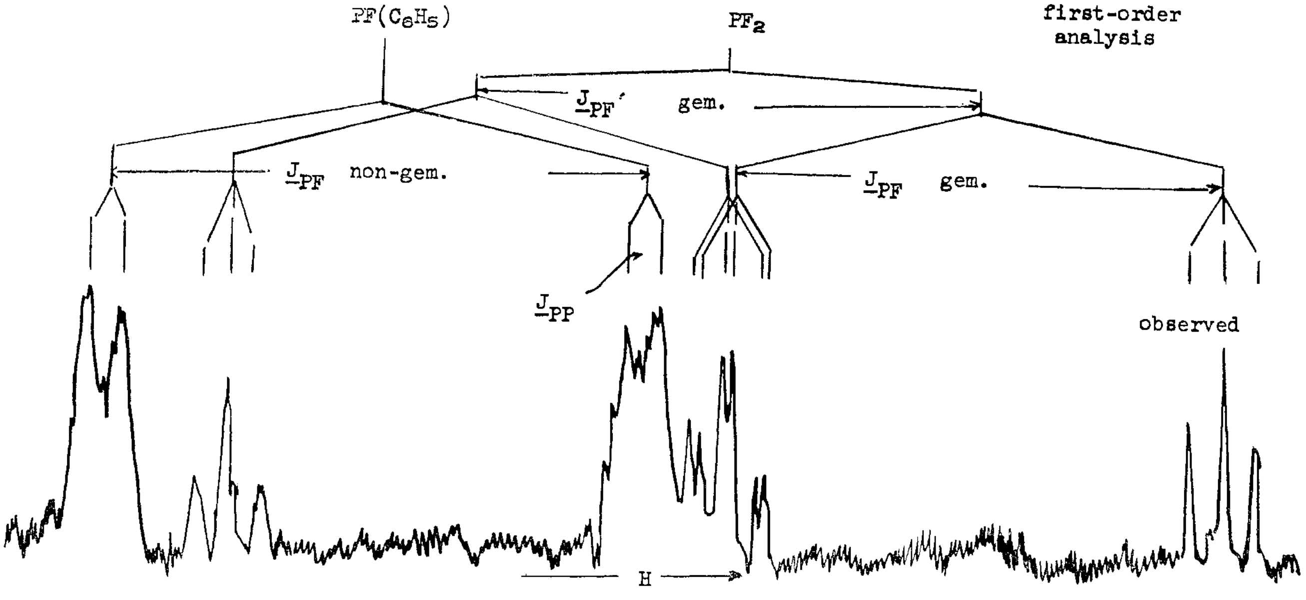

Figure 2.—Phosphorus-31 nuclear magnetic resonance spectrum of *cis*-$N_3P_3F_4(C_6H_5)_2$. Scale = 106.4 Hz cm^{-1}.

In each case, the difference in dipole moment between a *cis* and a *trans* isomer is by a factor of *ca.* 2, whereas the differences among amino derivatives having the same configuration are very small.

The phosphorus-31 and fluorine-19 nuclear magnetic resonance spectra of the monophenylphosphonitrilic fluoride, although generally indicative of both $\equiv PF_2$ and $\equiv PF(C_6H_5)$ environments, could not be adequately interpreted because of the severe overlaps of several sets of bands. Consequently, no chemical shift and coupling constant data are available for this compound.

The more significant infrared bands are summarized in Table III. Indicated assignments are based upon

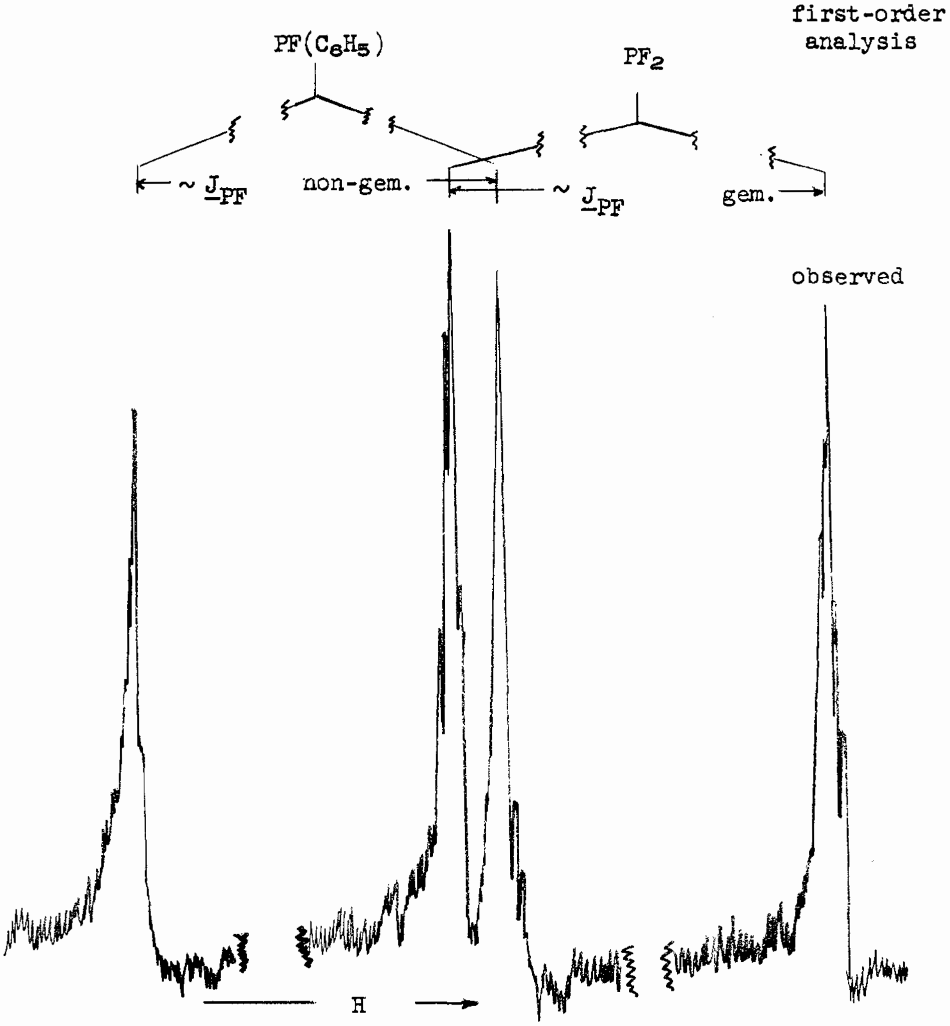

Figure 3.—Fluorine-19 nuclear magnetic resonance spectrum of *trans*-1,3-$N_3P_3F_4(C_6H_5)_2$. Scale = 100 Hz cm^{-1}.

TABLE II

DIPOLE MOMENT DATA

Compound	Weight fraction $\times 10^3$	Dielectric constant	Refractive index	Dipole moment, D	Indicated confign
1,3-$N_3P_3F_4(C_6H_5)_2$	16.815	2.5359	1.4971	4.3	*cis*
mp 74–75°	9.812	2.4925	1.4975		
	3.539	2.4868	1.4978		
	1.974	2.4528	1.4980		
1,3-$N_3P_3F_4(C_6H_5)_2$	13.275	2.4426	1.4971	2.5	*trans*
mp 78–79°	7.505	2.4331	1.4974		
	2.177	2.4248	1.4979		
1,3-$N_3P_3F_4(C_7H_7)_2$	15.145	2.4089	1.4972	4.4	*cis*
mp 64–65°	9.253	2.4631	1.4975		
	3.332	2.4307	1.4977		
	1.431	2.4268	1.4980		

those made for trimeric phosphonitrilic fluoride.[15] Bands reflecting phenyl group and phosphorus–carbon vibrations are not included. The band assigned to the P═N stretching mode falls within the 1200–1300-cm^{-1} range characteristic of the trimeric ring system.[16] The progression toward higher frequency of this vibration with increasing fluorine content is indicative of the increasing strength of the phosphorus–nitrogen bond with increase in electronegativity of the exocyclic group.[1,16] In favorable cases, the removal of degeneracy of the P═N ring stretching vibration is sufficient to permit one to distinguish between positional[17] and geometrical[18] isomers. However, in the present case only a single band is observed. The multiplicity of the P–F symmetric and asymmetric stretching vibrations may be related to the fact that two different phosphorus–fluorine bonds are present, *i.e.*, in the centers $\equiv PF_2$ and $\equiv PF(C_6H_5)$.

The yields of diphenyl isomers from the phenyllithium reaction are in the mole ratio[19] *cis*:*trans*:*geminal* = 3:1:0.25. These data are of particular interest since the reactions of trimeric phosphonitrilic chloride with dimethylamine[20] and piperidine[21] are both reported to give the 1,3-disubstituted products in the mole ratio *cis*:*trans* = 1:3, *i.e.*, the exact reverse of our observation for the diphenyl fluorides. To account for the replacement pattern observed with these amines, a "*cis* effect," in which electron density is believed to be more readily transferred between two groups on neighboring

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

[16] N. L. Paddock, *Quart. Rev.* (London), **18**, 168 (1964).

[17] A. C. Chapman, D. H. Paine, H. T. Searle, D. R. Smith, and F. R. M. White, *J. Chem. Soc.*, 1768 (1961).

[18] R. Stahlberg and E. Steger, *Spectrochim. Acta*, **23A**, 2005 (1967).

[19] The isomer distribution remained essentially the same when the reaction was carried out at 0, −30, and −78°.

[20] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 2215 (1965).

[21] R. Keat and R. A. Shaw, *ibid.*, *A*, 908 (1966).

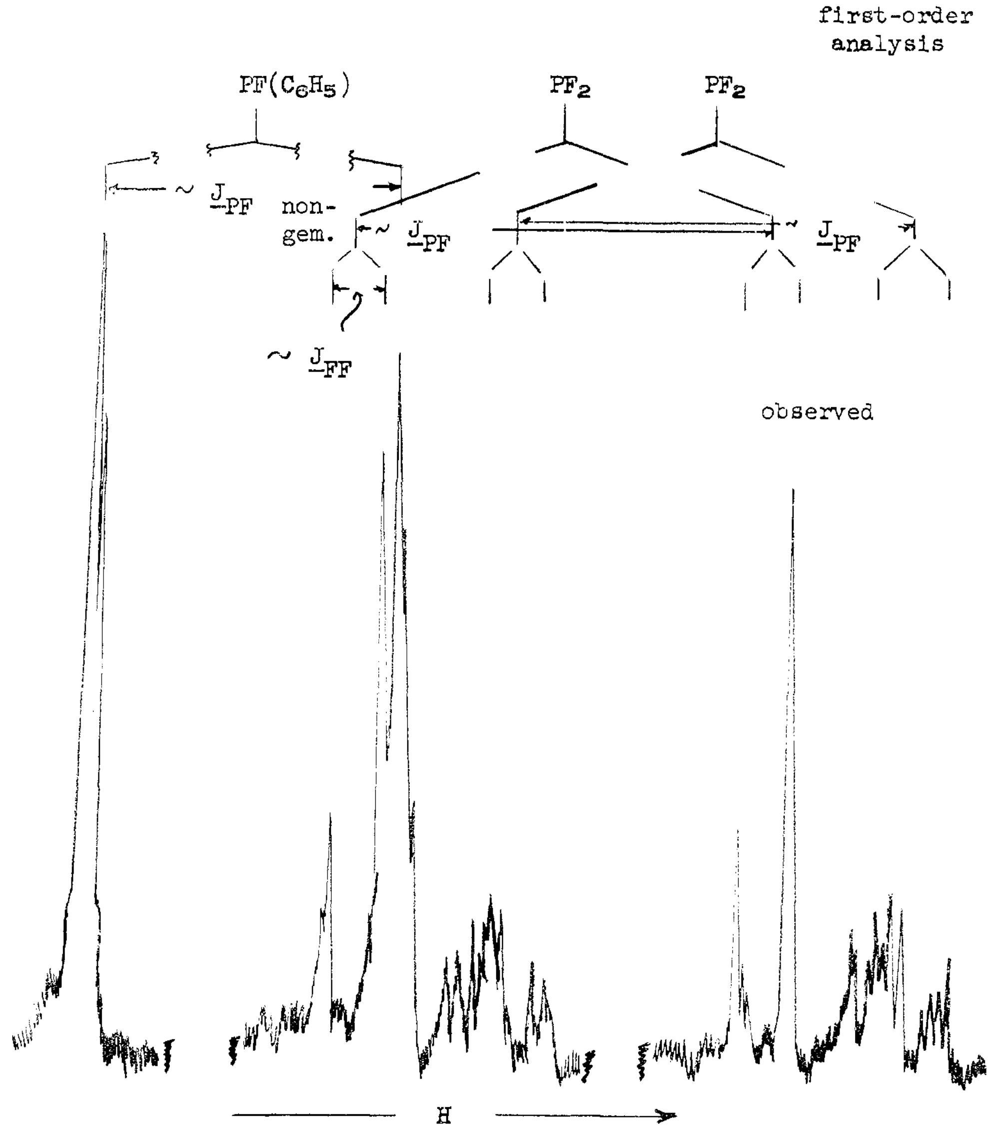


Figure 4.—Fluorine-19 nuclear magnetic resonance spectrum of *cis*-$N_3P_3F_4(C_6H_5)_2$. Scale = 100 Hz cm^{-1}.

TABLE III

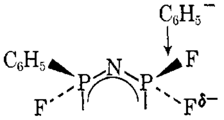
INFRARED DATA[a]

Compound	Band position, cm^{-1}				
	ν_{N-P-N}		$\nu_{P-F\ asym}$	$\nu_{P-F\ sym}$	
$N_3P_3F_5(C_6H_5)$	1270 vs	974 mw	940 vs	850 vs, 830 vs	740 s
cis-1,3-$N_3P_3F_4(C_6H_5)_2$	1240 vs	972 mw	916 s	826 s	748 s, 740 ms
	(1255 vs)	(984 m)	(937 m, 920 s)	(856 w, 834 s)	(760 s)
trans-1,3-$N_3P_3F_4(C_6N_5)_2$	1245 vs	977 mw	936 m, 916 s	844 s, 824 s	752 ms, 742 ms
	(1255 vs)	(984 mw)	(940 s, 923 s)	(850 s, 824 s)	(752 s)
cis-1,3-$N_3P_3F_4(C_7H_7)_2$	1245 vs	976 mw	936 m, 916 s	844 s, 825 s	780 vw, 753 ms, 742 ms
	(1280 sh, 1260 vs)	(982 m)	(942 mw, 932 m, 915 s)	(836 s, 812 m, 804 m)	(766 m, 753 m, 744 m)

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

phosphorus atoms when they are *cis* to each other, was proposed.[21] This effect would concentrate a partial negative charge on the chlorine atom *cis* to the first substituted amino group and cause it so to repel the second incoming nucleophilic group that preferential substitution, *via* a bimolecular pathway, would occur in the *trans* position. Data for the phenyllithium reaction suggest that this postulation be modified to *the exocyclic group which has the better ability to form* π *bonds with the phosphorus atom effects labilization of the phosphorus–halogen bond lying cis to it.*

The dimethylamino group forms stronger π bonds to the phosphorus atom than does the chlorine atom. Consequently, the chlorine atom *cis* to the first dimethylamino group bears a partial negative charge, and the second dimethylamino group enters from the opposite side of the ring and forms predominantly the *trans* product. By contrast, the fluorine atom forms 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.

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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).