appears as a doublet of triplets at −50 °C. However, cooling the sample to −100 °C results in the observation of two sets of doublets of doublets, one of which arises from each of the racemates. These couplings are assigned to the coupling of the CF_3 group with trivalent P and with the unique F on trivalent P, respectively. In this region of the spectrum it is seen that one of the two racemic mixtures is present in higher concentration (A, 65%) than the other (B, 35%) and it is this feature alone which allows assignment of the transitions in the various regions of the spectrum to one particular racemate.

At −50 °C, the spectra of the CF_3 groups on pentavalent P are well separated for the two mixtures (Figure 7b). In the major component IX (A), this group is coupled to pentavalent P resulting in a large doublet. These major peaks are further split into doublets of doublets of doublets by F on pentavalent P, by trivalent P, and by F on trivalent P. These coupling constants, although in the expected range relative to the related molecules I–VIII, must be regarded as tentative because of the problems of resolution and assignment in the spectra of the single fluorine atoms and the trivalent phosphorus nucleus. The spectrum of the minor component (IX (B)) shows a similar coupling of the trifluoromethyl groups to pentavalent P. Additional, nearly equal couplings, apparently to F on pentavalent P and to the trivalent phosphorus nucleus, give rise to a triplet structure. A very small coupling to F on trivalent P may also be present but was not resolved.

The NMR spectrum of the pentavalent phosphorus atoms (Figure 8) yields nearly equal chemical shift values for both isomers of IX but the spectra are easily analyzed because fewer couplings are involved and the magnitudes are different from those of P^{III}.

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Registry No. I, 23526-68-3; V, 67478-92-6; VI, 67478-93-7; VII, 67478-94-8; VIII, 67478-95-9; IX, 67478-96-0; $F(CF_3)P(S)SH$, 67478-97-1; $CF_3(F)PN(CH_3)_2$, 3205-95-6; $F(CF_3)P(S)N(CH_3)_2$, 18799-74-1; $(CH_3)_2NH_2^+F(CF_3)PS_2^-$, 67478-98-2; $(CF_3)_2PN(CH_3)_2$, 432-01-9; $(CH_3)_2NH$, 124-40-3; $(CF_3)_2PS_2H$, 18799-75-2; F_2PS_2H, 20773-09-5; S_8, 18808-47-4; H_2S, 7783-06-4.

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Organo-Substituted Phosphazenes. 10. Reactions of Hexafluorocyclotriphosphazene with Propenyllithium Reagents[1]

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The interactions of propenyllithium reagents with hexafluorocyclotriphosphazene ($P_3N_3F_6$) hve been investigated. The reaction of either 1-propenyl- or 2-propenyllithium with $P_3N_3F_6$ proceeds with moderate to good yields to give the appropriate monosubstituted phosphazene. The potential for use of these materials as precursors to other organophosphazenes is shown by the occurrence of facile hydrogenation and bromination reactions. Although the addition of 2 equiv of 2-propenyllithium to $P_3N_3F_6$ results in degradation products, the addition of 2 equiv of 1-propenyllithium to $P_3N_3F_6$ results in the production of the geminally substituted phosphazene. Furthermore, the reaction of phenylpentafluorocyclotriphosphazene with 1-propenyllithium also yields a geminal derivative. These results are discussed in terms of the factors which control the substitution pattern observed in the reactions of organolithium reagents with $P_3N_3F_6$. The new propenylfluorophosphazenes are characterized by infrared, NMR (proton and fluorine-19), and mass spectrometry.

Introduction

The reactions of cyclic and polymeric[2] fluorophosphazenes with organolithium reagents have proved to be a valuable method for producing a variety of organophosphazene derivatives. The reactions of alkyl-,[3-6] alkynl-,[7] and aryllithium[2,8-10] reagents have been explored in detail, but, with the exception of a brief report of the synthesis of vinylpentafluorocyclotriphosphazene,[4] the reactions of alkenyllithium reagents have not been reported. An investigation of the reactions of alkenyllithium reagents with hexafluorocyclotriphosphazene ($P_3N_3F_6$) would be of interest in order to establish the factors which are significant in the control of the substitution pathway of the organolithium–fluorophosphazene reaction. Furthermore, the alkenylphosphazenes would be valuable precursors to a wide range of organophosphazenes derived from reactions at the olefinic center. These synthetic transformations would complement those which one could accomplish through reactions of phosphazenes with ketonic functions in the exocyclic group.[11] Therefore, we wish to report the synthesis and characterization of propenyl derivatives of $P_3N_3F_6$.

Experimental Section

Hexachlorocyclotriphosphazene (Ethyl Corp.) was converted to hexafluorocyclotriphosphazene[12] which in turn was converted to

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phenylpentafluorocyclotriphosphazene[8] by previously reported procedures. Diethyl ether was distilled from sodium/benzophenone. A mixture of *cis*- and *trans*-1-bromopropene isomers (Aldrich) was distilled and stored over molecular sieves prior to use. The 2-bromopropene (Aldrich) was used without further purification. All reactions were carried out under anhydrous conditions and a nitrogen atmosphere. Lithium wire containing 1% sodium (PCR) was hammered into thin sheets and cut into small pieces. Concentrations of organolithium reagent solution were determined by quenching a 1-mL aliquot with water and titrating with 0.1 M HCl to the methyl red end point. NMR spectra in ($CDCl_3$) were obtained on a JEOL C60-HL spectrophotometer at 60 MHz (^1H) or 56.5 MHz (^{19}F). Tetramethylsilane (^1H) and fluorotrichloromethane (^{19}F) were used as internal standards. Infrared spectra were obtained on thin films using a Beckman IR-20A spectrophotometer with sodium chloride or polyethylene disks. Mass spectra were obtained on a Perkin-Elmer RMU-6D spectrometer operating at 80 eV. Samples were introduced through the liquid inlet. Analytical samples were purified by preparative VPC using a Gow Mac 69-100 chromatograph equipped with a DC 200 Chromsorb column. Elemental analyses were performed by Robertson Laboratories.

Preparation of 2-(1-Propenyl)pentafluorocyclotriphosphazene (I). In a typical experiment, 2.1 g (0.3 mol) of lithium was placed in 100 mL of diethyl ether followed by the slow addition of 17.0 g (0.14 mol) of 1-bromopropene.[13] Following the metal–halogen exchange reaction, the solution is allowed to sit for 12 h at 0 °C in order to allow the LiBr to settle. After standardization, a sufficient amount of solution to provide 0.085 mol of the propenyllithium was withdrawn by syringe and then added dropwise to a well-stirred solution of 19.0 g (0.076 mol) of $P_3N_3F_6$ in 50 mL of diethyl ether. A cold water bath was used to cool the reaction. After addition of the lithium reagent, the solution was allowed to reflux for 1 h. Pentane was then added to effect precipitation of the LiF and LiBr salts, and the remaining solution was filtered. The solvent was removed under aspiration and the resulting oil distilled (bp 41–45 °C (1.5 mm)) to give 10.5 g (52% of theory) of product. Since the initial metal–halogen exchange reaction also produces small amounts of 1-propynyllithium,[13] there is a small amount of alkyne impurity in the product. The pure alkene may be obtained by preparative vapor-phase chromatography. Anal. Calcd for $P_3N_3F_5C_3H_5$: C, 13.29; H, 1.86; N, 15.51; mol wt 271. Found: C, 13.71; H, 1.71; N, 15.64; mol wt 271 (mass spectrum).

^{19}F NMR:[14,15] $\delta(PF_2)$ 63 (4 F, $J(PF)$ = 810 Hz), $\delta(PFR)$ 52 (1 F, $J(PF)$ = 830 Hz). IR:[16] 2980 (m), 1630 (m, CC str), 1280 (s, PN str), 1070 (w), 1000 (s, PF asym), 930 (s, PF asym), 830 (s, PF sym), 790 (s, PF sym), 520 (m), 470 (m). Mass spectrum: 271 (100%, $P_3N_3F_5C_3H_5^+$), 270 (25%, $P_3N_3F_5C_3H_4^+$), 256 (5%, $P_3N_3F_5C_2H_2^+$), 252 (6%, $P_3N_3F_4C_3H_5^+$), 245 (10%, $P_3N_3F_5CH_3^+$), 242 (3%, $P_3N_3F_5C^+$), 231 (75%, $P_3N_3F_5H^+$), 230 (45%, $P_3N_3F_5^+$), 216 (23%, $P_3N_2F_5^+$), 212 (11%, $P_3N_3F_4H^+$), 211 (10%, $P_3N_3F_4^+$), 197 (18%, $P_3N_2F_4^+$), 171 (13%, $P_2NF_5^+$), 167 (7%, ?) 152 (8%, $P_2NF_4^+$), 133 (4%, $P_2NF_3^+$), 114 (14%, $P_2NF_2^+$), 107 (6%, $PN_2F_2^+$), 69 (30%, PF_2^+ and/or P_2N^+).

Preparation of 2,2-Di(1-propenyl)tetrafluorocyclotriphosphazene (II). In a typical experiment, 0.06 mol of 1-propenyllithium in 80 mL of diethyl ether was added dropwise to a well-stirred solution of 8.5 g (0.03 mol) of $P_3N_3F_6$ in 30 mL of ether at 5–10 °C. After the addition was complete, the solution was allowed to reflux for 3 h. Pentane was then added and the lithium salts were filtered. The solvent was then removed under aspiration to give an oil. The oil was distilled (bp 65–70 °C. (1.5 mm)) to give 5.0 g (48% of theory) of product. The compound was identified as geminal $P_3N_3F_4[CH{=}CHCH_3]_2$ on the basis of its mass spectrum (mol wt calcd 293, found 293 (mass spectrum)) and its ^{19}F NMR spectrum. Attempts to prepare an analytical sample by VPC resulted in compound decomposition. The material also decomposes slowly under ambiant conditions.

^{19}F NMR:[14,15] $\delta(PF_2)$ 64 (4 F, $J(PF)$ = 840 Hz). IR:[16] 2950 (m), 1630 (m, CC str), 1280 (s, PN str), 1070 (w), 1000 (s, PF asym), 930 (s, PF asym), 830 (s), 790 (s), 530 (m), 490 (m), 470 (m). Mass spectrum:[17] 293 (70%, $P_3N_3F_4C_6H_{10}^+$), 291 (19%, $P_3N_3F_4C_6H_8^+$), 278 (46%, $P_3N_3F_4C_5H_7^+$), 253 (57%, $P_3N_3F_4C_3H_6^+$), 252 (44%, $P_3N_3F_4C_3H_5^+$), 251 (24%, $P_3N_3F_4C_3H_4^+$), 212 (33%, $P_3N_3F_4H^+$), 211 (100%, $P_3N_3F_4^+$), 197 (41%, $P_3N_2F_4^+$).

Preparation of 2-(1-Propenyl)-2-phenyltetrafluorocyclotriphosphazene (III). In a typical experiment, 0.025 mol of 1-propenyllithium in 30 mL of diethyl ether was added, dropwise, to 6.0 g (0.02 mol) of $P_3N_3F_5C_6H_5$ in 30 mL of ether. After the initial exothermic reaction had subsided, the solution was allowed to reflux for 24 h. The solution was then worked up as discussed above to give 5.0 g of crude product. The crude product was shown by ^{19}F NMR to contain approximately 60% of the geminal compound, the remainder being $P_3N_3F_5C_6H_5$. The mixture was redistilled carefully at 50 °C and 1 mmHg[7] to remove the $P_3N_3F_5C_6H_5$. The purified material (mol wt calcd 329, found 329 (mass spectrum[16])) retained a trace of starting material. The ^{19}F NMR spectrum did not show any of the nongeminal derivatives to be present.

^{19}F NMR:[14,15] $\delta(PF_2)$ 62 (4 F, $J(PF)$ = 840 Hz). IR:[16] 2980 (w), 1635 (m, CC str), 1600 (m, CC str), 1270 (s, PN str), 940 (s, PF asym), 840 (s, PF sym), 580 (m), 510 (m), 490 (m), 460 (m). Mass spectrum:[18] 329 (100%, $P_3N_3F_4C_9H_{10}^+$), 314 (21%, $P_3N_3F_4C_8H_7^+$), 288 (87%, $P_3N_3F_4C_6H_5^+$), 252 (7%, $P_3N_3F_4C_3H_5^+$), 224 (17%, $P_3N_3F_4CH^+$), 212 (15%, $P_3N_3F_4H^+$), 211 (1%, $P_3N_3F_4^+$), 197 (69%, $P_3N_2F_4^+$), 167 (12%, ?), 152 (24%, $P_2NF_4^+$), 149 (18%, ?), 141 (8%, ?), 133 (1%, $P_2NF_3^+$), 114 (20%, $P_2NF_2^+$), 107 (9%, PNF_2^+), 91 (7%, $C_6H_5N^+$), 77 (57%, $C_6H_5^+$).

Preparation of 2-(Propenyl)pentafluorocyclotriphosphazene (IV). In a typical experiment, 100 mL (0.07 mol) of a previously prepared solution[19] of 2-propenyllithium in diethyl ether was added, dropwise, to a cooled, well-stirred solution containing 18.0 g (0.071 mol) of $P_3N_3F_6$ in 50 mL of diethyl ether. The solution was allowed to reflux for 1 h and worked up as before. The resulting oil was then distilled (bp 30–32 °C (1.5 mm)) to give 6.0 g (32% of theory) of product. Anal. Calcd for $P_3N_3F_5C_3H_5$: C, 13.30; H, 1.86; N, 15.51; mol wt 271. Found: C, 13.89; H, 1.76; N, 15.57; mol wt 271 (mass spectrum).

^{19}F NMR:[14] $\delta(PF_2)$ 62 (4 F, $J(PF)$ = 835 Hz), $\delta(PFR)$ 57 (1 F, $J(PF)$ = 870 Hz). ^1H NMR: $\delta(PCH$ trans) 6.2 (1 H, $J(PH)$ = 2 Hz), $\delta(PCH$ cis) 5.8 (1 H, $J(PH)$ = 55 Hz), $\delta(CH_3)$ 2.0 (3 H, $J(PH)$ = 18 Hz). IR:[16] 2980 (w), 1650 (w, CC str), 1270 (s, PN str), 1000 (w), 930 (s, PF asym), 830 (s, PF sym), 740 (m, CH bend), 540 (m), 500 (m), 450 (m). Mass spectrum: 271 (69%, $P_3N_3F_5C_3H_5^+$), 256 (4%, $P_3N_3F_5C_2H_2^+$), 252 (4%, $P_3N_3F_4C_3H_5^+$), 245 (3%, $P_3N_3F_5CH_3^+$), 231 (100%, $P_3N_3F_5H^+$), 230 (18%, $P_3N_3F_5^+$), 216 (7%, $P_3N_2F_5^+$), 212 (12%, $P_3N_3F_4H^+$), 211 (6%, $P_3N_3F_4^+$), 197 (6%, $P_3N_2F_4^+$), 171 (7%, $P_2NF_5^+$), 167 (6%, ?), 152 (4%, $P_2NF_4^+$), 133 (3%, $P_2NF_3^+$), 114 (7%, $P_2NF_2^+$), 107 (3%, $PN_2F_2^+$), 69 (14%, PF_2^+ and/or P_2N^+).

After distillation, a viscous red-brown oil, which could not be decolorized upon treatment with powdered charcoal, remained. The quantity of this material varied between preparations, but generally nearly an equal amount as the desired product was obtained.

^1H NMR: $\delta(=CH_2)$ 6.2–6.5 (complex, 2 H), $\delta(OH)$ 5.1–4.7 (broad,[1] H), δ(alkyl) 2.02–1.64 (complex, 9 H). IR:[16] 3340 (OH str), 2980 (m), 2180 (w), 1715 (w), 1605 (m, CC str), 1430 (w), 1370 (w), 1250 (vs, PN str), 1040 (w), 980 (w), 915 (s, PF asym), 810 (s, PF sym), 710 (m), 625 (w), 475 (m), 435 (m).

Reaction of $P_3N_3F_5C_3H_5$ (I) with Phenyllithium. A solution of I in diethyl ether was treated with an equimolar amount of phenyllithium in diethyl ether. The reaction was allowed to proceed as above, but only insoluble residues were obtained.

Attempted Preparation of Di(2-propenyl)pentafluorocyclotriphosphazene. The reaction of 2-propenyllithium with $P_3N_3F_6$ on a 2:1 molar basis resulted only in the formation of insoluble residues.

Bromination of I. One gram of I was treated with excess bromine in carbon tetrachloride and allowed to stir for 24 h at room temperature. The ^1H NMR spectrum of the reaction mixture indicated complete conversion to $P_3N_3F_5C_3H_5Br_2$. Similar results were obtained when carbon disulfide was employed as the solvent.

^1H NMR: $\delta(CBrH)$ 4.6 (complex, 2 H), $\delta(CH_3)$ 2.1 (doublet, 3 H), $J(HH)$ = 12 Hz). IR:[16] 2930 (w), 1445 (w), 1385 (w), 1270 (vs, PN str), 935 (s, PF asym), 860 (m), 830 (s, PF sym), 795 (m).

Hydrogenation of I. Approximately 1 g of I in methanol was combined with 100 mg of Lindlar catalyst and two drops of quinoline. Hydrogen gas was passed through the solution for 1 h at room temperature. Solvent was removed under aspiration, and the resulting oil was distilled to yield $P_3N_3F_5C_3H_7$, which was identified by its NMR spectrum, and a trace of I.

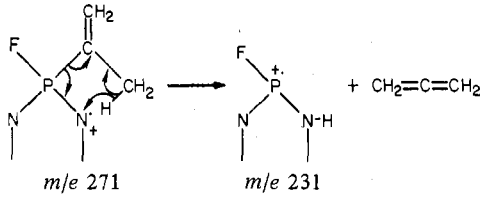
^1H NMR: $\delta(CH_2)$ 2.0 (complex, 4 H), $\delta(CH_3)$ 1.3 (broad multiplet, 3 H). IR:[16] 2975 (w), 1270 (s, PN str), 945 (s, PF asym), 870 (m), 845 (s, PF sym), 810 (s).

Results and Discussion

The reaction of 1 equiv of 1-propenyllithium with 1 equiv of $P_3N_3F_6$ results in the production of the olefinic phosphazene $P_3N_3F_5CH{=}CHCH_3$ (I). The fluorine-19 NMR data in-

dicate the presence of the $P_3N_3F_5$ moiety and the expected phosphorus–nitrogen, phosphorus–fluorine, and olefin[20] stretching frequencies are found in the infrared spectrum. The molecular ion is the most intense ion in the mass spectrum. There are low-intensity peaks which result from olefin fragmentation and loss of fluorine, but the most significant fragments are *m/e* 230 and 231 resulting from phosphorus–carbon bond cleavage. The latter peak may arise from hydrogen-atom transfer to a ring nitrogen atom concomitant with the elimination of the organic fragment. The predominance of phosphorus–carbon over phosphorus–fluorine bond cleavage and the intensities of the $P_2NF_n^+$ linear ions are comparable to the behavior of the corresponding aryl derivatives.[10,21] Whereas doubly charged ions are significant in the aryl derivatives,[20] they are not observed in the mass spectra of the propenyl derivatives.

The reaction of 1 equiv of 2-propenyllithium with $P_3N_3F_6$ proceeds, as expected, to give $P_3N_3F_5C(CH_3)=CH_2$ (IV). The identity of the product (IV) is confirmed by the NMR (fluorine-19 and proton), infrared, and mass spectra. The mass spectra of I and IV are comparable in terms of the observed fragments, but it is of interest to note that the most abundant species is now the $P_3N_3F_5H^+$ (*m/e* 231) ion, and the intensity of the $P_3N_3F_5^+$ is substantively reduced. A reasonable pathway for the formation of the $P_3N_3F_5H^+$ in the spectrum of IV involves a McLafferty rearrangement[22] of the molecular ion with the elimination of allene.



m/e 271 *m/e* 231

The yield of this compound is somewhat low, as compared to the previous reaction, and may be due to the fact that 2-propenyllithium is a more bulky nucleophile as compared to 1-propenyllithium, or it may reflect the reactivity of the olefinic center in II. The identity of the byproduct in the synthesis of IV has not been definitively established, but the spectroscopic data show the existence of hydroxyl and olefinic functions in addition to the phosphorus–fluorine and phosphorus–nitrogen components of a monosubstituted fluorocyclotriphosphazene. These observations can be rationalized by the process

$$P_3N_3F_5C(CH_3)=CH_2 + LiC(CH_3)=CH_2 \rightarrow$$

$$P_3N_3F_5C(Li)(CH_3)CH_2C(CH_3)=CH_2 \xrightarrow[2.\ H_2O]{1.\ O_2} P_3N_3F_5C(OH)(CH_3)CH_2C(CH_3)=CH_2 \quad (1)$$

Thus, the overall yield of the desired product is reduced by the fact that the organolithium reagent can attack either a phosphorus atom or the polarized olefin attached to the phosphazene ring.

The reaction of 2 equiv of 1-propenyllithium with 1 equiv of $P_3N_3F_6$ results in the production of geminal $P_3N_3F_4(C-H=CHCH_3)_2$ (II). In addition, the reaction of 1 equiv of 1-propenyllithium with 1 equiv of $P_3N_3F_5C_6H_5$ also gives the geminally substituted mixed-organo tetrafluorocyclotriphosphazene $P_3N_3F_4(C_6H_5)(CH=CH-CH_3)$ (III).

The infrared spectra of both II and III indicate the presence of olefinic (II and III) and aryl (III) groups. Note that there is no significant change in the C=C stretching frequency of II as compared to I.

The mass spectrum of II is interesting in that the high-intensity ions result from the successive cleavage of the propenyl substituents from the phosphazene ring. In fact, the 100% ion is the $P_3N_3F_4^+$ moiety which is different from the usual case where the molecular ion is the most intense. In the aryl analogues this sort of behavior is typical of a geminal disposition of substituents.[21] The mass spectrum of III is also indicative of a geminally substituted material because of the high intensity of the ions resulting from loss of the organic substituents. The large relative abundance of the $P_3N_3F_4C_6H_5^+$ ion vs. the $P_3N_3F_4C_3H_5^+$ ion is suggestive of a more facile cleavage of the propenyl–phosphorus than the phenyl–phosphorus bond. The question of the origin of this effect remains unclear. It could reflect either an inherent difference in carbon–phosphorus bond strengths or a differential in the ability of the two organic moieties to stabilize the resulting positive ion.

Table I. Substitution Pathways Observed in the Reactions of Fluorophosphazenes with Organometallic Reagents

phosphazene	organometallic reagent	positional isomer	ref
$P_3N_3F_8$	CH_3Li	geminal	5, 6
$P_3N_3F_6$	CH_3Li	geminal	5
$P_3N_3F_6$	$C_6H_5C{\equiv}CLi$	geminal	9
$P_3N_3F_6$	C_6H_5Li	nongeminal + trace geminal	8
$P_3N_3F_6$	(*o*-tol)Li	nongeminal	8
$P_3N_3F_6$	C_6H_5MgBr	geminal	23

The geminal assignments for II and III are confirmed on the basis of the ^{19}F NMR spectra which allows one to assign geminal vs. nongeminal structures unambiguously.[8] In geminal derivatives, only $\equiv PF_2$ resonances are observed, while in nongeminal derivatives, both $\equiv PF_2$ and $\equiv PFR$ resonances are observed.

From this and previous data (Table I), it appears that geminal substitution is favored over nongeminal substitution in the reactions of organolithium reagents with $P_3N_3F_6$. Intuitively, one would expect a nongeminal pathway to be favored, at least on a steric basis. Furthermore, one would predict that a phosphorous atom bearing two fluorine atoms would be more positive than one bearing one organic substituent and one fluorine atom. The more positive atom would be more prone to nucleophilic attack; hence nongeminal substitution should result. This does not appear to be the case for organophosphazenes. The phosphorus atom bearing only one fluorine atom carries a larger partial positive charge because the organic substituent can donate electron density to the phosphorus atom via an inductive mechanism. This causes the phosphorus d orbitals to expand in size. The expanded d orbitals, however, can no longer have effective overlap with the small nitrogen lone-pair orbitals; hence the phosphorus atom bears a partial positive charge while the nitrogen bears a partial negative charge. An example of this type of behavior is observed in the relative basicity of ring nitrogen atoms in $P_3N_3Cl_6$ and $P_3N_3(CH_3)_6$. While the equilibrium constant for protonation of the former is too low to be measured, the latter acts as a strong base toward a variety of Lewis acids.[24] Similarly, the $-N-P(C_6H_5)_2$ bond length in $2,2\text{-}P_3N_3F_4(C_6H_5)_2$ is significantly longer than the remaining phosphorus–nitrogen bond in the ring.[25]

If geminal substitution is electrostatically favored, why does nongeminal substitution predominate when 1 equiv of $P_3N_3F_6$ is reacted with 2 equiv of phenyllithium (5% geminal, 95% nongeminal)[8] or 2 equiv of *o*-tolyllithium (100% nongeminal)? It is believed that aryllithium reagents are in associated form in diethyl ether. One can thus rationalize nongeminal substitution as a result of the steric bulk of the attacking nucleophile. As evidence for this proposal, the reaction of 1 equiv of $P_3N_3F_6$ with 2 equiv of C_6H_5MgBr,[23] which is monomeric in THF, gives the geminal compound. Further support for this model is found in the reaction of 1 equiv of $P_3N_3F_5C_6H_5$ with 1 equiv of 1-propenyllithium, which results in the pro-

duction of the geminal compound. If the aryl group were exerting a directive effect, one would expect nongeminal substitution; hence, the stereochemistry of the reaction would be independent of the incoming nucleophile. It therefore seems reasonable to conclude that geminal substitution is the most favored process and is controlled primarily by the incoming reagent. Nongeminal substitution will predominate only in cases where the incoming organometallic reagent is excessively bulky. Stereochemical control of phosphazene substitution reactions by the incoming nucleophile has previously been demonstrated for several reactions of amines with chlorocyclophosphazenes.[26]

Several attempts were made to synthesize $P_3N_3F_4(C(CH_3)=CH_2)_2$; however, only insoluble residues could be isolated. Apparently, addition of the second equivalent of 2-propenyllithium serves to initiate anionic attack on the olefinic center in IV, which, in turn, gives rise to an olefinic phosphazene which again may undergo attack by the propenyllithium reagent.

The facile bromination of I demonstrates the potential for the transformation of olefinic phosphazenes into a variety of new organophosphazenes. The Lindlar catalyst[27] was originally chosen for the hydrogenation reaction because it has been shown to catalyze the reduction of acetylenes to olefins[28] and hence would provide a chemical method of removing the alkyne impurity from I. However, the olefinic center in I is sufficiently activated by the strongly electron-withdrawing phosphazene ring[10,29] to also undergo hydrogenation under the very mild conditions employed in the reaction.

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Registry No. I, 67488-11-3; II, 67488-12-4; III, 67488-13-5; IV, 67488-14-6; $P_3N_3F_6$, 15599-91-4; $P_3N_3F_5C_6H_5$, 2713-48-6; $LiCH=CHCH_3$, 29283-76-9; $LiC(CH_3)=CH_2$, 3052-45-7.

References and Notes

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(14) Chemical shifts in ppm; coupling constants in Hz; all $J(PF)$ values are based on a first-order approximation; R = alkenyl function.
(15) ^1H NMR of the 1-propenyl derivatives are complex due to the fact that one is dealing with a mixture of cis and trans olefins. A reasonable simulation of the spectrum was obtained by using coupling constants from the literature and from the 2-propenylphosphazene derivatives. However, due to the imprecise nature of this approach the data are not reported.
(16) In cm^{-1}. Several weak bands below 1600 cm^{-1} not reported.
(17) Several high-mass/low-intensity peaks are omitted.
(18) Several low-intensity peaks (<3%) are omitted. Peaks due to trace impurity of $P_3N_3F_5C_6H_5$ are omitted. When common fragments arise from III and $P_3N_3F_5C_6H_5$, the intensities of the fragments from III are corrected for the contributions from $P_3N_3F_5C_6H_5$.
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