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Organophosphazenes. 26. Factors Controlling the Pathways Observed in the Reactions of Ethynyl Lithium Reagents with Hexafluorocyclotriphosphazene

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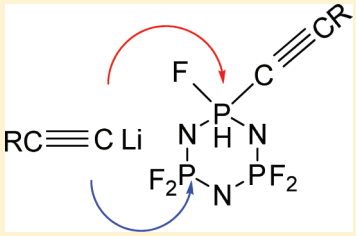
ABSTRACT: In contrast to previously studied reactions of ethynyl lithium reagents, the reactions of propynyl and hexynyl lithium with $N_3P_3F_6$ lead to predominantly nongeminal isomers. A modest cis stereo selectivity was observed. The sequential addition of a lithio acetylene reagent which follows a predominately geminal pathway (lithiophenylacetylene) and an aryl lithium reagent (p-propenylphenyl lithium) which follows a predominantly nongeminal pathway were examined. The relative order of addition of the two reagents was interchanged, resulting in a change of reaction pathway demonstrating ring substituent control of the regio and stereo chemical pathways. Hydrogenation of the ethynyl unit in the phosphazene derivatives provides a facile pathway to the difficult to prepare alkylphosphazenes. The chemical shift of the organosubstituted phosphorus center undergoes a remarkably large change (46−47 ppm) on going from the ethynyl to the alkyl derivatives, which reduces the complex ^{31}P and ^{19}F NMR spectra of the ethynyl derivatives to easily interpretable first-order spectra, thus allowing for structure assignment. The ^{13}C NMR data shows that nongeminal regio selectivity increases with the amount of s character on the ethynyl carbon atom attached to the phosphorus center. These observations allow for an understanding of the factors controlling regio and stereo chemical control in the reactions of carbanionic nucleophiles with $N_3P_3F_6$.



INTRODUCTION

Reasonable models to rationalize the factors controlling the nucleophilic substitution reactions of amines[2] and oxyanions[2−5] with cyclophosphazenes are available. By way of contrast, a general understanding of the reactions with carbanionic reagents with cyclophosphazenes is not complete. Allcock has shown that the reactions of Grignard reagents with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, proceed by a halogen abstraction pathway, leading to metalated phosphazene intermediates.[6] A similar pathway is followed in the reactions of organolithium reagents.[6,7] The corresponding reactions with hexafluorocyclotriphosphazene, $N_3P_3F_6$, are more typical of the nucleophilic substitutions referred to above.[2,6,8] A geminal pathway is preferred for certain alkyl,[2,9,10] alkenyl,[2,11] phenylethynyl,[12,13] and trimethylsilylethynyl[13] lithium reagents, while nongeminal products are obtained for a variety of aryllithium reagents[2,14] and *t*-butyl lithium.[10] With the exception of the region and stereospecific *t*-butyl lithium case,[10] the observed pathways are all regioselective with nongeminal products accompanying geminal products.[13,14] The resulting organofunctional phosphazenes have proved to be useful synthetic intermediates. The alkenylphosphazenes undergo addition polymerization at the exocyclic olefin site.[15−17] The ethynyl center in phenylethynyl phosphazenes can react with metal carbonyls to give the appropriate organometallic derivatives[11,12,18−20] or undergo cyclooligomerization reactions.[18−23] Recent detailed work by Elias and co-workers has shown how these processes may be used to create phosphazenes with structurally complex organic substituents.[21−23] In order to understand better the role of the carbanionic species in the observed reaction pathways of $N_3P_3F_6$ and to provide additional ethynylphosphazenes for reactions with organometallic reagents, we have examined the reactions of alkylethynyl lithium reagents and mixed substituent ethynyl lithium reagents and aryl lithium reagents.

EXPERIMENTAL SECTION

Materials. Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (Nippon Soda Co., Ltd.), was converted to $N_3P_3F_6$ (**1**),[24] which in turn was converted to $N_3P_3F_5C{\equiv}CPh$ (**8**)[13] and $N_3P_3F_5C_6H_5CMe{=}CH_2$ (**9**)[14] by previously reported procedures. *n*-Butyl lithium (2.5 M in hexane, Aldrich), phenylacetylene (Aldrich), propyne (Farchan Laboratories), and hexyne (Farchan Laboratories) were used without further purification. All solvents were distilled from appropriate drying agents prior to use. All organo lithium reagents were handled under an inert atmosphere.

Characterization. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer. Mass spectrometry was carried out on a Finnigan 4610 spectrometer operating at 70 eV. GC-MS studies utilized a Finnegan GC equipped with a 30 m capillary column coated with SE-30 (Restex). NMR spectra were recorded on a Bruker WM250 spectrometer operating at 250.1 MHz (^1H), 62.9 MHz (^{13}C), 235.35 MHz (^{19}F), and 101.2 MHz (^{13}P) and using $CDCl_3$ for a lock compound. Tetramethylsilane (TMS) (^1H and ^{13}C) was used as an internal reference, while 85% H_3PO_4 (^{31}P) and $CFCl_3$ (^{19}F) were used as external references. Chemical shifts upfield from the reference are negative. Broad band ^1H decoupling was used for the ^{13}C, ^{19}F, and ^{31}P spectra. Elemental analyses were performed by Robertson Laboratory Microlit Laboratories, Inc., Ledgewood, New Jersey.

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Preparation of $N_3P_3F_5C{\equiv}CMe$ (2). A 250 mL two-necked flask equipped with magnetic stirrer and a dry ice condenser was flame-dried and allowed to cool under an inert nitrogen atmosphere. The apparatus was then evacuated and backfilled with nitrogen three times. Dry ether (100 mL) was introduced into the flask via a syringe, and the whole apparatus was immersed in a liquid N_2−ethyl acetate slush bath. After allowing the temperature to drop below −50 °C, excess propyne was condensed in the reaction flask. A solution of 4.3 mL of 2.5 M *n*-butyl lithium (0.01 mol) was added dropwise via a syringe, and the reaction mixture was stirred for 3 h. The temperature was then raised to −20 °C, allowing the excess propyne to be removed. In a separate 250 mL round-bottom flask, 2.5 g (0.01 mol) of $P_3N_3F_6$ was dissolved in 75 mL of Et_2O, and the whole apparatus was cooled in an ice bath. The lithiopropyne solution was then added via a cannula into the hexafluorocyclotriphosphazene solution. The reaction mixture was allowed to stir at room temperature for 12 h, during which time it turned dark brown. The solvent was removed at room temperature, and low boiling petroleum ether was added to precipitate the lithium salts. After filtration through Celite, the crude product was sublimed, yielding 1.0 g of white solid (37.1% yield) melting at 42−43 °C. Anal. calcd. for $N_3P_3F_5C_3H_3$: C, 13.35; H, 1.12; mol wt, 269. Found: C, 13.51; H, 1.12; mol wt, 269 (mass spec). ^{1}H NMR: 2.10 (multiplet CH_3). ^{13}C NMR: 4.68 (s, CH_3); 69.5 (d of d of t, $^1J_{PC}$ = 366, $^2J_{FC}$ = 61.4, $^3J_{PC}$ = 15, $\underline{C}{\equiv}CCH_3$); 103.58 (d, $^2J_{PC}$ = 65.9, $C{\equiv}\underline{C}CH_3$). ^{31}P NMR: 4.68 (d, J_{PF} = 862, ≡PF[C≡CMe]); 9.12 (t, J_{PF} = 888, ≡PF_2). ^{19}F NMR: 73.4 (d, J_{PF} = 861, ≡ PF_2[cis]; 72.1 (d, J_{PF} = 902, ≡ PF_2[trans]): 48.9 (d, J_{PF} = 892, ≡ PF[C≡CCH_3]). IR: 2958, 2857 (w, ν_{C-H}), 2215 (s, $\nu_{C{\equiv}C}$), 1271 (vs, $\nu_{P=N}$), 942 (s, $\nu_{P-F\ (asym)}$, 852 (s, $\nu_{P-F\ (sym)}$).

Preparation of $N_3P_3F_4(C{\equiv}CMe)_2$ (3). This procedure is equivalent to that used for the preparation of **2** using the following amounts of reagents: 2.5 g (0.01 mol) of $P_3N_3F_6$, 8.6 mL (0.02 mol) of 2.5 M *n*-BuLi in hexane, and excess propyne gas. The crude reaction mixture was sublimed to remove the monosubstituted product (0.56 g, 20.9% yield). The residue was mixed with petroleum ether, filtered to remove insoluble materials, and distilled at reduced pressure to isolate the product as the fraction boiling at 71−73 °C (1.23 g, 42.5% yield). Mass spectrum: M^+ ion, 289 (calcd., 289). A gas chromatographic analysis of the mixture showed that all three isomers are present.

Preparation of $N_3P_3F_5C{\equiv}CC_4H_9$ (4). A dry 250 mL flask equipped with a magnetic stirrer was purged with nitrogen and charged with 0.83 g (0.01 mol) of hexyne in 100 mL of dry ether at 0 °C. A solution of 4.0 mL of 2.5 M (0.01 mol) *n*-BuLi was added dropwise via a syringe, and the solution was stirred for 5 h. The lithiohexyne solution was added via cannula technique to a solution of 2.5 g (0.01 mol) of $P_3N_3F_6$ in 50 mL of ether at 0 °C, and the reaction was stirred overnight at room temperature, during which time it turned brown. The solvent was removed under reduced pressure, and light petroleum ether was added to precipitate the lithium salts. The solution was filtered through Celite to remove the lithium salts. The crude product was distilled under reduced pressure (boiling point 44−45 0 °C at 0.02 mmHg) to yield 1.76 g (56% yield) of product. Anal. Calcd for $P_3N_3F_5C_6H_9$: C, 23.15; H, 2.89; mol wt, 311. Found: C, 23.18; H, 2.85, mol wt, 311 (mass spec). ^{31}P NMR: 9.0 (t, J_{PF} = 896, ≡PF_2); 4.7 (d, J_{PF} = 865.84, ≡PF[C≡CC_4H_9]). ^{19}F NMR: 49.0 (d, J_{PF} = 893, ≡PF[C≡CC_4H_9]; 72.5 (d, J_{PF} = 897, ≡PF_2[trans]), 74.0 (d, J_{PF} = 875, ≡PF_2[cis]). ^{13}C NMR: 13.03 (s, CH_3); 18.98 (s, CH_2); 21.82 (s, CH_2); 28.95 (s, CH_2); 70.1 (d of d, of t, J_{PC} = 371, $^2J_{FC}$ = 60.4, $^3J_{pc}$ = 14.7, $\underline{C}{\equiv}CC_4H_9$); 107.6 (d, J_{PC} = 65.8, $C{\equiv}\underline{C}C_4H_9$). IR: 2953, 2869 (w, ν_{C-H}), 2207 (s, $\nu_{C{\equiv}C}$), 1274 (s, $\nu_{P=N}$).

Preparation of $N_3P_3F_4(C{\equiv}CC_4H_9)_2$ (5). This procedure is equivalent to that used for the preparation of **4** using the following amounts of reagents: 1.64 g (0.02 mol) of hexyne in 100 mL of ether, 8.0 mL of 2.5 M *n*-BuLi solution (0.02 mol), and 2.5 g (0.01 mol) of $P_3N_3F_6$. After completion, the solvent was removed, and petroleum ether was added to precipitate the lithium salts, which were removed by filtration through Celite. The crude product was distilled at reduced pressure (0.02 mmHg) to remove the monosubstituted derivative (boiling point 44−45 0 °C, 0.47 g, 15.3% yield). The fraction boiling at 91 −93 °C was the desired product (1.70 g, 45.6% yield). A gas chromatographic analysis of the mixture showed that all three isomers are present.

Preparation of $N_3P_3F_4$(4-$C_6H_4CMe{=}CH_2$)$C{\equiv}CPh$, Method A (6A). A 250 mL two-necked round-bottom flask was equipped with a pressure equalizing addition funnel, magnetic stirrer, and nitrogen bubbler. The whole apparatus was flame-dried and allowed to cool to room temperature under positive pressure of nitrogen. The reaction flask was charged with 100 mL of dry ether via cannula techniques, and 1.35 mL of phenylacetylene (12.0 mmol) was added via a syringe. The whole apparatus was immersed in an ice bath, and 4.8 mL (12.0 mmol) of 2.5 M *n*-BuLi in hexane was added dropwise, during which time the reaction mixture turned yellow. The reaction mixture was stirred an additional 3 h after the addition was complete. A three-necked 500 mL round-bottom flask, equipped with an oil bubbler and magnetic stirrer, was flushed with nitrogen and charged with a solution of 4.2 g (12 mmol) of [4-(2-propenylphenyl)]-pentafluorocyclophosphazene (**9**) in 75 mL of dry ether. The flask was placed in an ice bath. The phenylethynyl lithium solution was added dropwise at 0 °C. After the addition was complete, the ice bath was removed, and the reaction mixture was allowed to stir overnight, during which time it turned turbid brown. The ether was removed, and low boiling petroleum ether was added to precipitate the lithium salts. The salts were allowed to settle and removed by filtration through diatomaceous earth. The petroleum ether was removed to yield a yellowish oil, which was subjected to flash chromatography on silica gel using petroleum ether−methylene chloride (80−20 v/v), to give 1.02 g (34.7% yield) of a mixture of isomers of [(propenyl-phenyl)][*β*-phenylethynyl]tetrafluorocyclotriphosphazene, $N_3P_3F_4$(4-$C_6H_4CMe{=}CH_2$)($C{\equiv}CPh$) (**6A**). A gas chromatographic analysis in conjunction with ^{31}P and ^{19}F NMR revealed the isomer ratio to be 1.0:0.53:<0.10 for the cis, trans, and geminal isomers, respectively. The isomers resisted further separation. Anal. calcd. for $P_3N_3F_4C_{17}H_{14}$: mol wt, 429. Found: mol wt, 429 (GC mass spectrum). ^{31}P NMR (non geminal cis and trans): 6.4 (t, J_{PF} = 906, ≡PF_2); 5.2 (d, J_{PF} = 896, ≡ PF[C≡CPh]); 33.2 (d, J_{PF} = 974, ≡PF(4-C_6H_4C(Me)=CH_2). ^{19}F NMR (non geminal cis): 69.8 (d, J_{PF} = 918, ≡PF_2[cis]; 72.8 (d, J_{PF} = 918, ≡PF_2[trans]); 54.6 (d, J_{PF} = 982, ≡PF[4-C_6H_4C(Me)=CH_2]); 44.1 (d, J_{PF} = 915, ≡PFC≡CPh). ^{19}F NMR (non geminal trans): 71.5 (d, J_{PF} = 907; ≡PF_2); 56.1 (d, J_{PF} = 982, ≡PF[p-C_6H_4C(Me)= CH_2]); 46.3 (d, J_{PF} = 915 ≡PF[C≡CPh]). ^{13}C NMR: 21.5 (CH_3); 103.3 (d, J_{PC} =46.7; $\underline{C}{\equiv}CPh$); 119.2 ($C{\equiv}\underline{C}Ph$); 115.4 ($C(CH_3){=}\underline{C}H_2$); 141.5 ($\underline{C}(CH_3){=}CH_2$), 124−133 (overlapping resonances from the two phenyl groups). IR: 2920, 2950, 3030, 3060 (m, ν_{C-H}), 2250 (s, $\nu_{C{\equiv}C}$), 1633 (m, $\nu_{C=C}$), 1280 (vs, $\nu_{P=N}$), 920 (s, $\nu_{P-F(asym)}$), 810 (s, $\nu_{P-F(sym)}$).

Preparation of $N_3P_3F_4$(4-$C_6H_4CMe{=}CH_2$)$C{\equiv}CPh$, Method B (6B). In this reaction, 2-(4-lithophenyl)propene was allowed to react with $P_3N_3F_5$[C≡CPh]. The details of the synthetic procedure are similar to the previous reaction using the following amounts of reagents: 8.0 mL (20 mmol) of 2.5 M *n*-BuLi in hexane was added dropwise to a solution of 3.8 g (20 mmol) of 4-bromophenylpropene in 100 mL of ether at 0 °C. The yellow solution was stirred for 4 h at 0 °C and then added dropwise to a solution of 6.62 (20 mmol) of $P_3N_3F_5$[C≡CPh] in 50 mL of ether at 0 °C. The reaction was monitored using TLC and required 18 h of stirring at room temperature for completion. The workup was similar to that for method A. After flash chromatography, 1.8 g (25% yield) of the disubstituted material was obtained. A gas chromatographic analysis in conjunction with ^{31}P and ^{19}F NMR revealed the geminal isomer to be the major product, and only small amounts of nongeminal products were observed. Anal. calcd. for $N_3P_3F_4C_{17}H_{14}$: mol wt, 429. Found: 429 (GC mass spectrum). ^{31}P NMR (geminal): 6.4 (t, J_{PF} = 906, ≡ PF_2); 4.68 (t, $^2J_{PP}$ = 61.7, ≡P[4-C_6H_4CMe]=CH_2][C≡CPh]). ^{19}F NMR (geminal): 71.8 (d, J_{PF} = 857, ≡PF_2). ^{13}C NMR: 21.5 (CH_3); 103.3 (d, J_{PC} = 46.7; $\underline{C}{\equiv}CPh$); 119.2 ($C{\equiv}\underline{C}Ph$); 115.4 ($C(CH_3){=}\underline{C}H_2$); 141.5 ($\underline{C}(CH_3){=}CH_2$); 124−133 (overlapping resonances from the two phenyl groups). IR: 2920, 2950, 3030, 3060 (m, ν_{C-H}), 2250 (s, $\nu_{C{\equiv}C}$), 1635 (m, $\nu_{C=C}$), 1280 (vs, ν_{P-N}), 920 (m, $\nu_{P-F(sym)}$).

Preparation of 2,4-N_3P_3(4-$C_6H_4CH(CH_3)_2$)(CH_2CH_2Ph) (7A). A solution of 0.25 g (0.58 mmol.) of the cis/trans mixture of

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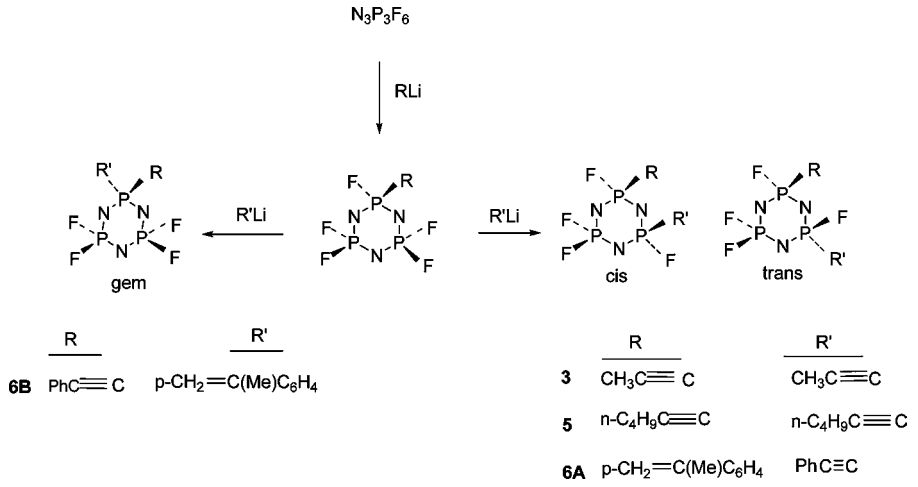
Scheme 1. Reactions of Selected Ethynyl Lithium Reagents



$N_3P_3F_4C_6H_5$ C(CH_3)=CH_2)(C≡CPh) (**6A**) in 50 mL of methanol was hydrogenated using palladium/charcoal as a catalyst. The reaction flask was connected to a balloon filled with hydrogen gas. The flask was evacuated and backfilled with hydrogen gas, and the procedure was repeated three times to ensure complete exclusion of air in the reaction flask. The reaction mixture was stirred at room temperature, and the reaction was allowed to proceed until the uptake of hydrogen gas had ceased. After completion, the reaction mixture was filtered twice from Celite to remove the catalyst, and the solvent was removed under reduced pressure. The crude product was subjected to chromatography (petroleum ether as eluant) on activated silica through a short path (~10 cm) column to isolate 0.18 g (82% yield) of the product. ^{31}P NMR: 7.7 (d of d of d of d, J_{PF} = 937, J_{PF} = 881, $^2J_{PP}$ = 59.8, $^2J_{PP}$ = 56.4, $^3J_{PF}$ = 5.6, ≡PF_2[cis]; 6.5 (t of t of t, J_{PF} = 903, $^2J_{PP}$ = 62.1, $^2J_{PP}$ = 63.5, $^3J_{PF}$ = 3.7, ≡PF_2[trans]); 32.4 (overlapping multiplets, J_{PF} = 999, ^2J = 56.5, ≡PF[4-C_6H_4CH-(CH_3)$_2$]); 47.0 (overlapping multiplets, J_{PF} = 1005, $^2J_{PP}$ = 45.1, ≡PF[CH_2CH_2Ph]). ^{19}F NMR (non geminal cis): 69.4 (d of d, J_{PF} = 917, $^2J_{FF}$ = 73.0, ≡PF_2[trans]; 73.1 (d of d, J_{PF} = 893, $^2J_{FF}$ = 73, ≡PF_2[cis]); 53.2 (d, J_{PF} = 974, ≡PF[4-C_6H_4CH(CH_3)$_2$]); 60.1 (d, J_{PF} = 1006, ≡PF[CH_2CH_2Ph]). ^{19}F (non geminal trans): 71.3 (d, J_{PF} = 909, ≡PF_2); 56.1 (d, J_{PF} = 974, ≡PF[4-C_6H_4CH(CH_3)$_2$]); 61.9 (d, J_{PF} = 1006, ≡PF[CH_2CH_2Ph]). ^{1}H NMR (mixture of isomers): 1.28 (d, J_{HH} = 3.85, CH(C<u>H</u>$_3$)$_2$); 2.3 (complex multiplets, C<u>H</u>(CH_3)$_2$); 2.8–3.1 (overlapping multiplets, C<u>H</u>$_2$C<u>H</u>$_2$Ph); 7.1–7.9 (complex multiplets, phenyl groups).

Preparation of (2,2-$N_3P_3F_4$[4-C_6H_4CH(CH_3)$_2$](CH_2CH_2Ph) (7B). A solution of 0.15 g (0.35 mmol) of geminal $N_3P_3F_4$(4-C_6H_4C-(CH_3)=CH_2)(C≡CPh)(**6B**) was hydrogenated in 50 mL of methanol using palladium/charcoal as a catalyst. The procedure for the reaction was similar to that in the previous section. After work up and chromatography, 0.11 g (73% yield) of the product was isolated. ^{31}P NMR: 9.1 (t, J_{PF} = 891, ≡PF_2); 36.7 (t, $^2J_{PP}$= 41 0.5, ≡P[4-C_6H_4CH(CH_3)$_2$][CH_2CH_2Ph]). ^{19}F NMR: 71.7 (d of d, J_{PF} = 882, ≡PF_2). ^{1}H NMR: 1.28 (d, J_{HH} = 3.85, CH(C<u>H</u>$_3$)$_2$); 2.3 (complex multiplets, C<u>H</u>(CH_3)$_2$); 2.8–3.1 (overlapping multiplets, C<u>H</u>$_2$C<u>H</u>$_2$Ph); 7.1–7.9 (complex multiplets, phenyl groups). ^{13}C NMR: 23.59 (CH(<u>C</u>H$_3$)$_2$); 27.24 and 27.28 (CH_2CH_2); 34.29 ((<u>C</u>H(CH_3)$_2$); 126–132 (phenyl groups).

Preparation of $N_3P_3F_5C_3H_7$ (8). A solution of 0.02 g of $P_3N_3F_5$[C≡CMe] (**2**) in 15 mL of methanol was hydrogenated using the same procedure as above. No further purification was required as evidenced by the TLC experiments on silica gel using petroleum ether and GC. Mol wt. calcd.: 273. Found: 273 (mass spec). ^{31}P NMR: 10.0 (t, J_{PF} = 991, ≡PF_2); 50.3 (d, J_{PF} = 899, ≡PF[C_3H_7]). ^{19}F NMR: 73.7 (d, J_{PF} = 901, ≡PF_2 [cis]); 71.2 (d, J_{PF} = 915, ≡PF_2[trans]]); 65.3 (d, J_{PF} = 977, ≡PF[C_3H_7]). ^{1}H NMR: 0.98 (broad, 3H); 1.58 (2H); 1.9 (2H). ^{13}C NMR: 32.1 (m, $^1J_{PC}$ = 145, $^2J_{PC}$ = 16.5, C_α); 25.7 (d, $^2J_{PC}$ = 6.0, C_β); 18.5 (CH_3).

Preparation of $N_3P_3F_4(C_3H_7)_2$ (9). A solution of 8.0 mg of $P_3N_3F_4$(C≡CCH_3)$_2$ (**3**) in 5 mL of methanol was hydrogenated using the same procedure as above. No further purification was done. Mol wt. calcd.: 297. Found: 297 (mass spec). ^{31}P NMR (cis): 8.0 (d of t, J_{PF} = 899, J_{PF} = 916, $^2J_{PP}$ = 49.0, ≡PF_2); 48.6 (d of d, J_{PF} = 998, J_{PP} = 49.0, ≡PF[C_3H_7]). ^{31}P NMR (trans): 6.8 (d of t, J_{PF} = 899, $^2J_{PP}$ = 57.2, ≡PF_2); 48.6 (d of d, J_{PF} = 998, $^2J_{PP}$ = 57.2, ≡PF[C_3H_7]). ^{31}P NMR (gem): 10.1 (t, J_{PF} = 891, ≡PF_2); 48.0 (t, $^2J_{PP}$ = 32.7, ≡P(C_3H_7)$_2$). ^{19}F NMR (cis): 69.6 (d of d, J_{PF} = 918, $^2J_{FF}$ = 75.0, ≡PF_2[cis]); 73.5 (d, J_{PF} = 918, ≡PF_2[trans]); 60.3 (d, J_{PF} = 1010, ≡PF[C_3H_7]). ^{19}F NMR (trans): 72.0 (d, J_{PF} = 900, ≡PF_2); 62.1 (d, J_{PF} = 992, ≡PF[C_3H_7]). ^{19}F NMR (gem): 72.6 (d, J_{PF} = 881, ≡PF_2).

Preparation of $N_3P_3F_5C_6H_{13}$ (10). The hydrogenation reaction of $P_3N_3F_5$[C≡CC_4H_9] (**4**) was performed as above. No purification was necessary. Mol wt. calcd.: 315. Found: 314 (mass spec). ^{31}P NMR: 6.8 (t, J_{PF} = 1,000, ≡PF_2); 52.3 (d, J_{PF} = 898, ≡PF[C_6H_{13}]). ^{19}F NMR: 72.3 (d, J_{PF} = 878, ≡PF_2[cis]); 71.8 (d, J_{PF} = 925, ≡PF_2[trans]; 63.7 (d, J_{PF} = 967, ≡PF[C_6H_{13}]). ^{13}C NMR: 30.1 (complex, $^1J_{PC}$ = 150.2, $^2J_{FC}$ = 18.9, C^1); 24.6 (d, $^2J_{PC}$ = 9.8, C^2); 21.6, 20.5, 18.1, 12.6.

Preparation of $N_3P_3F_4(C_6H_{13})_2$ (11). The hydrogenation of $P_3N_3F_4$(C≡CC_4H_9)$_2$ (**5**) was carried out as described in the previous sections. Mol. wt. calcd.: 381. Found: 380 (mass spec). ^{31}P NMR (cis): 5.5 (d of d of d, J_{PF} = 893, J_{PF} = 917, $^2J_{PP}$ = 48.7, ≡PF_2); 45.7 (d of d, J_{PF} = 1003, $^2J_{PP}$ = 48.7, ≡PF(C_6H_{13}). ^{31}P NMR (trans): 5.2 (d of d of t, J_{PF} = 893, $^2J_{PP}$ = 56.8, $^3J_{PP}$ = 6.5, ≡PF_2); 45.7 (d of d, J_{PF} = 1003, $^2J_{PP}$ = 56.8, ≡PF[C_6H_{13}]). ^{31}P NMR (gem): 5.7 (d, J_{PF} = 909, ≡PF_2); 45.7 (t, $^2J_{PP}$ = 34.1, ≡P[C_6H_{13}]$_2$). ^{19}F NMR: 69.6 (d, J_{PF} = 927, ≡PF_2[cis]); 73.4 (d, J_{PF} = 898, ≡PF_2[trans]; 60.5 (d, J_{PF} = 1004, ≡PF[C_6H_{13}]). ^{19}F NMR: 72.5 (d, J_{PF} = 888, ≡PF_2); 62.4 (d, J_{PF} = 994, ≡PF[C_6H_{13}]). ^{19}F NMR (gem): 71.8 (d, J_{PF} = 908, ≡PF_2).

RESULTS AND DISCUSSION

The reactions of $N_3P_3F_6$ (**1**) with various lithioacetylene reagents were carried out to produce the mono- and disubstituted derivatives. In general, it was found that the substituted ethynyl derivatives (**2**–**5**) could be synthesized in moderate yields (40–60%). In the reactions of **1** with two equivalents of the lithioacetylene reagents, significant amounts of the monosubstituted product were obtained. Additionally, the sequential addition of a lithioacetylene reagent which follows a predominately geminal pathway (lithiophenylacetylene)[13] and an aryl lithium reagent (p-propenylphenyl lithium) which follows a predominately nongeminal pathway[14] were examined. The relative order of addition of the two reagents was interchanged, resulting in a change of reaction pathway. We

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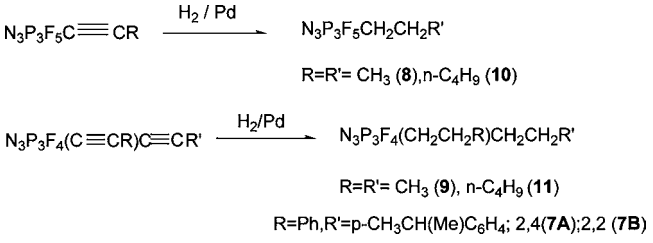
have previously shown that one of the resulting mixed substituent derivatives, **6A**, can be transformed into hybrid organic–inorganic polymers.[20] The results of all of these reactions are summarized in Scheme 1. The disubstituted ethynylphosphazenes (**3**, **5**) were mixtures of the geminal and nongeminal isomers which resisted further bulk scale separation. All of the bis derivatives showed three peaks in the GC-MS with the same parent ion peaks, indicating that all of the isomers were present. Previous work has shown that the ^{31}P and ^{19}F NMR spectra can be used for definitive structural assignment for fluorophosphazene derivatives.[1,4,10,11,14] However, in the case of the ethynylphosphazenes, the spectra were complicated by second order effects and resonance overlap due to the small difference in chemical shifts between the various phosphorus centers to such a degree that it is difficult to make more than a rough estimate of the major NMR parameters and impossible to assign the various isomers in the disubstituted derivatives. This problem was overcome by hydrogenation of the ethynyl center (and also the olefin in **6A** and **6B**) in the ethynyl phosphazenes (Scheme 2). The chemical shift of the organosubstituted phosphorus center undergoes a remarkably large change (46–47 ppm) on going from the ethynyl to the alkyl derivatives, while the PF_2 resonances only undergo minimal change. Similar changes were observed in the ^{19}F NMR spectra. The changes are sufficient to transform the complex spectra to readily interpretable ones, as demonstrated in Figure 1. There are two possibilities for the origins of the change in phosphorus chemical shifts in the organofluorocyclotriphosphazenes. The observed trend shown in Figure 2 is a linear decrease in the phosphorus chemical shift with increased s character (hence, increased orbital electronegativity) of the α carbon atom of the organic substituent. This is the direction one would predict if the shift were controlled by the local diamagnetic term (σ_d). However, σ_d control is not expected in heavier nuclei. Alternatively, the increased number of low lying excited states available with the unsaturated organic substituents allows for larger local paramagnetic term (σ_p) contributions as the cause of the trend in the phosphorus shifts. It is important to note that all evidence available argues against specific phosphorus–carbon multiple bonds,[25−27] but the global MOs of the molecules will contain contributions from the unsaturated carbon centers. A general understanding of substituent effects in phosphazene chemical shifts is lacking and would be of interest if it were to become available. In addition to ruling out rearrangement to an allene,[18] further insight into the electronic effects operative in these systems comes from a consideration of the ^{13}C NMR data (Table 1) of alknylphosphazenes. There is a progressive deshielding of the C_2 (carbon attached to the phosphazene) carbon atom on going from the alkyl to aryl substituted alkyne,

Scheme 2. Hydrogenation of Ethynyllphosphazenes



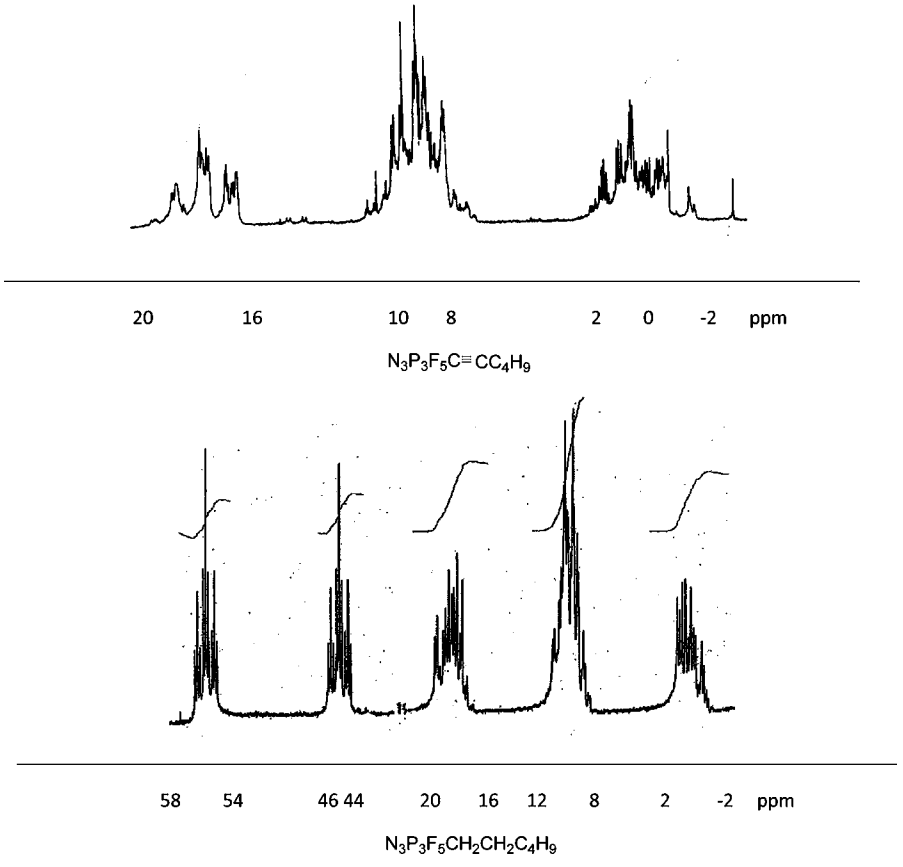


Figure 1. Effect of hydrogenation on ^{31}P NMR spectra.

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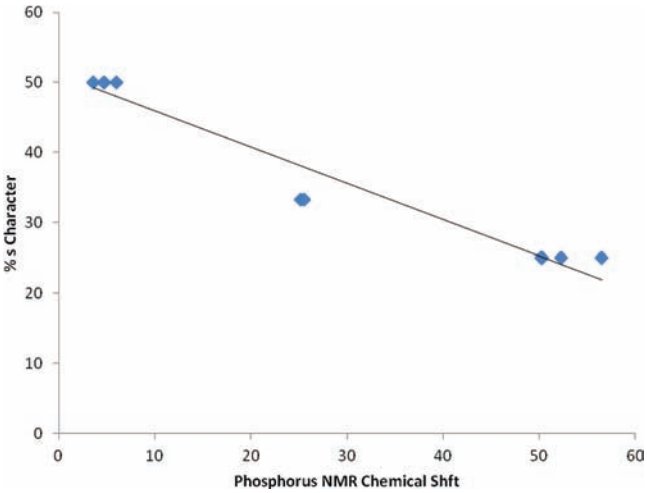

Figure 2. Plot of ^{31}P NMR chemical shifts for $N_3P_3F_5R$ (R = alkyl, alkenyl, alkynyl) vs percentage of s character of the carbon atom attached to the phosphorus center.

Table 1. Seleted ^{13}C NMR[a] and IR[b] Data for $N_3P_3F_5C{\equiv}CR$

R	δ C_2	$^1J_{PC}$	δ C_1	$^2J_{PC}$	$\nu_{C\equiv C}$
C_6H_5[c]	102.7	69.2	118.0	61	2180
$SiMe_3$[c]	92.6	332.8	112.7	51.5	2145
CH_3	69.5	366	103.6	61.4	2215
n-C_4H_9	70.1	371	107.6	60.4	2207

[a]Chemical shifts in ppm; C_2 is carbon attached to the phosphorus center, coupling constants in Hz [b]Frequencies in cm^{-1} [c]Data from ref 11.

indicating increased removal of electron density from C2.[28−30] The mechanisms involved include hyperconjugation in the trimethylsilyl derivative[31] and resonance delocalization from the alkyne to the phenyl group in the phenyl acetylene derivative.[28−30] This proposal is consistent with the parallel decrease in the carbon−carbon triple bond stretching frequency (Table 1). The remarkable decrease in $^1J_{pc}$ on going from the alkyl to the other derivatives is based on the higher percentage of s character in C_2 when the alkyne is unperturbed. The fact that the ^{13}C NMR parameters do not change significantly on going from the monosubstituted to the geminal disubstituted phenyl acetylene derivatives[11] indicates that the phosphazene does not contribute to changes in the alkyne electronic structure. This, in turn, is consistent with the proposal of absence of mesomeric interactions between unsaturated substituents and the phosphazene.[25−27]

In addition to spectral simplification, the hydrogenation reactions described above provide a high yield route to a variety of primary and secondary alkyl-substituted cyclophosphazenes which are not available, with the exception of the methyl derivatives,[9] from direct reactions with alkyl lithium reagents due to the facile formation of stabilized α anions at the α carbon atom.[10]

The ^{31}P NMR of the hydrogenated materials clearly shows the presence of all three disubstituted products. The PF_2 center in the cis-2,4 isomer appears as a doublet of doublets due to the nonequivalence of the fluorine atoms, whereas in the trans isomer the equivalent fluorine atoms give rise to a triplet in the ^{31}P NMR. The geminal isomer was identified from the PR_2 resonance without the $^1J_{PF}$ coupling. The qualitative estimation of the mixture composition available from the NMR spectra allowed for assignment of the gas chromatograms and quantification of the relative amount of each isomer. The mass spectral fragmentation patterns conform to previously observed pathways with the nongeminal isomers proceeding through ring cleavage to produce linear ions, while the geminal isomers exhibit cleavage of the phosphorus−carbon bonds, leaving the phosphazene ring intact.[32,33] Structural assignments of the mixed substituent derivatives, **6A** and **6B**, were accomplished by an analogous process from the hydrogenated derivatives **7A** and **7B**. The isomers obtained in all of the reactions are summarized in Scheme 1.

There are several intriguing observations concerning regio and stereo control in the reactions of cyclophosphazenes which have arisen from this work. The reactions leading to the mixed substituent derivatives, **6A** and **6B**, show clearly that the reaction pathway is controlled by the substituent on the phosphazene. Thus, the isomeric composition of products of the reaction of **9** with lithio phenyl acetylene is essentially the same as found in the reaction of **9** with 2-(4-lithophenyl)-propene, and the reaction of **8** with 2-(4-lithophenyl)propene gives a similar isomeric distribution to that observed in the reaction of **8** with lithio phenyl acetylene. In each case, the incoming nucleophile does not influence the reaction pathway. The reactions of *n*-alkylethynyl lithium reagents with **1** were surprisingly found to exhibit nongeminal regioselectivity, which is more pronounced for the propynyl derivatives (**3**, cis > trans > gem; **5**, (cis > trans) ~ gem). Previously reported reactions of substituted ethynyl lithium reagents with **1** follow a primary geminal pathway with greater geminal selectivity shown for the phenyl versus the trimethylsilyl substituted entity.[12,13] An examination of the ^{13}C NMR data (Table 1) shows a remarkable correlation between increasing removal of π electron density (by polarization, conjugation, or hyperconjugation) from the ethynyl center to the substituent and increased regio selectivity. The *n*-alkylethynyl derivatives also show some degree of contra steric cis stereo selectivity. These observations provide added insight into the factors which control the reaction pathways followed by carbanionic nucleophiles in reactions with cyclophosphazenes. We have previously shown that the halogen abstraction mechanism which controls the reactions of Grignard and organolithium reagents with chlorophosphazenes[6,7,18] plays, at best, a minor role in the reactions of **1**,[34] so one can assume that nucleophilic substitution is the dominant mechanism. It is a general observation in the reactions of chlorophosphazenes that geminally substituted products arise from dissociative processes.[2] If one assumes that the same fundamental mechanistic factors are operative in the corresponding fluorophosphazenes, then the geminal products observed arise via a dissociative mechanism, and the balance of geminal to nongeminal product distribution reflects the relative rates of the dissociative and associative pathways. The ethynyl lithium reagents which favor geminal substitution are those in which the terminal carbon atom has a reduced s character and hence more σ electron releasing. This in turn reduces the effective positive charge on the phosphorus atom allowing for more facile fluoride dissociation. Conversely, the alkyl substituted ethynyl lithium reagents have a higher terminal carbon s character (see above) and thus a concomitantly higher phosphorus formal charge, thereby strengthening the phosphorus fluorine bond and favoring an associative process. Steric factors, such as in the case of *t*-butyl lithium,[10] can also result in the nongeminal pathway. In the associative process, the nongeminal site has a

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higher positive formal charge[27,35] and thus is the site of nucleophilic attack. In consideration of the stereochemistry of the associative reactions, it is important to recognize that the expectation in reactions of any ring system is that the second reagent will approach from the opposite side of the ring, giving a trans product.[2,10] The cis stereo selectivity observed in the formation of **3** and **5** follows the general pattern of a reagent containing an unsaturated organic center[2,5] and has been attributed to the attraction of the positive counterion to the distributed negative charge on the ring substituent and thus directs the incoming entity to the cis position.[5] Counter ion directive effects have also been established in other cyclophosphazene substitution reactions.[36,37]

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Notes

The authors declare no competing financial interest.

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