do not allow any quantitative conclusions.

The dramatic increase of the rate of olefin substitution—more than 2 orders of magnitude—on changing of the coligand from triethylphosphine to triisopropylphosphine points to a pronounced contribution of nonbonding forces to the ground-state free energy of the molecule.

A linear free energy type plot of log k_1 vs. cone angle of the coligand L in the series $W(CO)_4L(dmf)$ is shown in Figure 1. The θ's of the mixed phosphines $P(i\text{-}Pr)_2Ph$ and $P(i\text{-}Pr)Ph_2$ have been taken as the average of the semicone angles of the substituents at phosphorus as suggested by Tolman.[12] This procedure neglects the ligand's ability to rotate about the metal–phosphorus bond until the nonbonding interactions between ligands are minimized. Therefore, the effective cone angles of the mixed phosphines should be a few degrees smaller than indicated in Figure 1, bringing the plot of log k_1 vs. θ even closer to linearity.

The reactivity of the triphenylphosphine derivative is less well understood. From steric considerations alone the rate of dissociation of the tungsten–olefin bond should be smaller by a factor of 10 than what is actually observed. It is equally difficult to invoke electronic properties since the donor ability of the ligands $P(i\text{-}Pr)_nPh_{3-n}$ decreases steadily with decreasing n. There are, however, more examples of anomalous reactivity of group 6 metal carbonyl/triphenylphosphine complexes in both thermal[13] and photochemical[14] reactions. We conclude that the observed kinetics for olefin substitution in $M(CO)_4L(olefin)$ derivatives demonstrate the possibility to tune the reactivity of the metal–olefin bond over a wide range by varying the metal M and the coligand L.

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Registry No. $Cr(CO)_4(PEt_3)(ma)$, 75248-36-1; $Mo(CO)_4(PEt_3)(ma)$, 75266-36-3; $Mo(CO)_4(P(i\text{-}Pr)_3)(ma)$, 75248-37-2; $W(CO)_4(P(i\text{-}Pr)_3)(ma)$, 75248-38-3; $W(CO)_4(PEt_3)(dmf)$, 75248-39-4; $W(CO)_4(P(i\text{-}Pr)_3)(dmf)$, 75248-40-7; $W(CO)_4(PPh(i\text{-}Pr)_2)(dmf)$, 75266-37-4; $W(CO)_4(PPh_2(i\text{-}Pr))(dmf)$, 75248-41-8; $W(CO)_4(PPh_3)(dmf)$, 75248-42-9; $W(CO)_4(P(i\text{-}Pr)_3)(btf)$, 75248-43-0; $W(CO)_4(P(i\text{-}Pr)_3)(dmm)$, 75282-34-7; $P(O(i\text{-}Pr))_3$, 116-17-6; $W(CO)_4(P(i\text{-}Pr)_3)(C_2H_4)$, 75248-44-1.

(11) Pentacarbonyl olefin complexes of the group 6 transition metals are reported to be very unstable.[3c,3j] We have not been able to isolate any derivatives $M(CO)_4L(olefin)$ with L = $P(OMe)_3$, $P(O(i\text{-}Pr))_3$, or $P(OPh)_3$.[1]

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Organophosphazenes. 13. Reactions of Hexafluorocyclotriphosphazene with *p*-(Dimethylamino)phenyl Grignard and Lithium Reagents[1]

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The reactions of *p*-(dimethylamino)phenyl Grignard and Lithium reagents with hexafluorocyclotriphosphazene ($P_3N_3F_6$) have been examined. These reactions yield the *p*-(dimethylamino)phenyl-substituted cyclophosphazenes $P_3N_3F_{6-n}[C_6H_4N(CH_3)_2]_n$ (n = 1–3) in moderate to poor yields with the Grignard reagent giving the better yields. The reaction follows a nongeminal pathway, giving an approximately equimolar mixture of cis and trans isomers at the disubstituted stage. In a 6:1 molar reaction of the Grignard reagent with $P_3N_3F_6$, ring degradation appears to be the predominant mode of reaction with the *trans*-2,4,6-$P_3N_3F_3[C_6H_4N(CH_3)_2]_3$ moiety being the only isolable cyclophosphazene. The monosubstituted derivative and the mixture of disubstituted isomers were converted to the geminally substituted mixed-aryl derivatives $P_3N_3F_4C_6H_5[C_6H_4N(CH_3)_2]$ and $P_3N_3F_2(C_6D_5)_2[C_6H_4N(CH_3)_2]_2$ by the Friedel–Crafts reaction. The structures of the new phosphazene derivatives were established by ^{19}F and ^1H NMR spectroscopy. A novel dimeric phosphazene, $[P_3N_3F_4C_6H_4N(CH_3)_2]_2$, has also been obtained from the Grignard reaction.

Introduction

The reactions of organometallic reagents with halocyclophosphazenes have proven to be valuable routes to the preparation of organophosphazenes.[2-4] These reactions are often among the most complex in phosphazene chemistry and, depending on the nature of the reactants, can lead to ring substitution or cleavage.[5-7] In substitution reactions both geminal[8-14] and nongeminal[15] reaction pathways have been observed, and the balance between these two routes can be altered by subtle changes in the nature of the reagents employed.[9] In this investigation we have chosen to examine the reactions of hexafluorocyclotriphosphazene ($P_3N_3F_6$) with *p*-(dimethylamino)phenyl Grignard and lithium reagents. A study of this type is of interest in order to examine the effect of the electronic perturbation of the aryl ring (produced by the strongly electron-donating dimethylamino moiety) on the stereochemistry of the substitution reaction.

Experimental Section

Materials and Measurements. Practical grade *p*-bromo-*N*,*N*-dimethylaniline (p-$BrC_6H_4N(CH_3)_2$) (Eastman) was purified by recrystallizing twice from ethanol. Tetrahydrofuran (THF) was dried

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by first distilling from sodium and then from lithium aluminum hydride. Benzene and benzene-d_6 (99.5% isotopic purity) were distilled over sodium. Commercially available Vitride (sodium bis(2-methoxyethoxy)aluminum hydride) 70% in benzene (Eastman), lithium aluminum hydride, aluminum chloride, magnesium turnings, *tert*-butyllithium, and lithium metal were used without further purification. NMR spectra in ($CDCl_3$) were obtained by using 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 for thin films by using a Beckman IR-20A spectrophotometer with sodium chloride or polyethylene disks. Mass spectra were obtained by using a Perkin-Elmer RMU-60 spectrometer operating at 80 eV. Elemental analyses were performed by Robertson Laboratories.

Procedures. Hexachlorocyclotriphosphazene (El Monte or Ethyl Corp.) was converted to $P_3N_3F_6$ by a previously reported procedure.[16] All organolithium and Grignard reactions were carried out under anhydrous conditions and a nitrogen atmosphere. Grignard reagents were prepared by adding a THF solution of $BrC_6H_4N(CH_3)_2$ to an equal volume of THF containing a slight stoichiometric excess of Mg turnings which had been activated with Vitride (approximately 1 drop of Vitride solution/g of Mg). The mixture was then allowed to reflux, with stirring, for 3 h. A modification of the method of Jones et al.[17] was used for the preparation of [*p*-(dimethylamino)phenyl]lithium. A pentane solution of *tert*-butyllithium was transferred from a syringe through a septum to a benzene solution containing a slight molar excess of $BrC_6H_4N(CH_3)_2$. The mixture was allowed to reflux, with stirring, for 1 h.

[*p*-(Dimethylamino)phenyl]pentafluorocyclotriphosphazene and 2,2′-Bis[*p*-(dimethylamino)phenyl]-4,4,4′,4′,6,6,6′,6′-octafluorobicyclotriphosphazene. A solution of 1.0 mol of $P_3N_3F_6$ in 250 mL of THF was added from a 250-mL pressure-equalizing dropping funnel to a 2-L, three-necked round-bottomed flask containing 1.1 mol of $(CH_3)_2NC_6H_4MgBr$ in 500 mL of THF and a magnetic stirring bar. The reaction mixture was stirred magnetically at reflux for 3 weeks. The hot mixture was filtered through Celite, the solvent removed, and the residue dissolved in 2 L of hot heptane. After decolorization with charcoal, the solution was cooled to room temperature, and a precipitate was obtained which, after recrystallization from heptane, yielded 0.8 g (0.24% of theory) of a white solid melting at 256–260 °C. Anal. Calcd for $\{P_3N_3F_4[C_6H_4N(CH_3)_2]\}_2$: C, 29.00; H, 3.02; N, 16.92; mol wt 662. Found: C, 29.01; H, 3.25; N, 16.82; mol wt 662 (mass spectrum).

^1H NMR: $\delta(H_{o,m})$ = 7.6–6.6 (overlapping multiplets); $\delta(CH_3)$ = 2.97. Mass spectrum: 662 (13.0%, $P_6N_6F_8C_{16}H_{20}N_2^+$), 451 (23.1% $P_3N_3F_4C_{16}H_{20}N_2^+$), 331 (100%, $P_3N_3F_4C_8H_{10}N^+$), 316 (2.4%, $P_3N_3F_4C_7H_7N^+$), 287 (1.2%, $P_3N_3F_4C_6H_4^+$), 116 (10.7%), 115 (13.0%), 114 (7.1%, P_2NF_2), 101 (17.8%), 100 (10.1%).

The remaining solution was evaporated to a volume of 200 mL and stored at 0 °C overnight. The resulting precipitate, after recrystallization from heptane, yielded 112.0 g (32.0% of theory) of a white solid, melting at 69–70 °C. Anal. Calcd for $P_3N_3F_5C_6H_4N(CH_3)_2$: C, 27.44; H, 2.88; mol wt 350. Found: C, 26.09; H, 2.91; mol wt 350 (mass spectrum[18]).

^{19}F NMR: $\delta(PF_2)$ = 67.0 (J(PF) = 910 Hz), 68.8 (J(PF) = 969 Hz); δ(PFR) = 50.6 (J(PF) = 997 Hz). ^1H NMR: $\delta(H_o)$ = 7.65 ($J(PH_o)$ = 14.4, $J(H_oH_n)$ = 9 Hz); $\delta(H_m)$ = 6.88 ($J(PH_m)$ = 4.5 Hz); $\delta(CH_3)$ = 3.0.

Cis and Trans Isomers of 2,4-Bis[*p*-(dimethylamino)phenyl]tetrafluorocyclotriphosphazene from Hexafluorocyclotriphosphazene via the Grignard Method. A mixture of 0.1 mol of $(CH_3)_2NC_6H_4MgBr$ in 100 mL of THF and 0.05 mol of $P_3N_3F_6$ in 100 mL of THF was allowed to react as above. After filtration and removal of the solvent, the solid was extracted for 2 days with 200 mL of heptane by using a Soxhlet extractor. The insoluble residue did not melt below 500 °C, but its infrared spectrum (ν_{PN} = 1250 cm^{-1}) indicated that it was a phosphazene (probably an ionic salt). The heptane extract, left overnight at 25 °C, formed a precipitate which was recrystallized from heptane to yield 0.5 g (2.2% of theory) of a white solid melting at 157–159 °C. Anal. Calcd for $P_3N_3F_4[C_6H_4N(CH_3)_2]_2$: C, 42.57; H, 4.43; N, 15.52; mol wt 451. Found: C, 42.48; H, 4.60; N, 15.46; mol wt 451 (mass spectrum[18]). Fluorine and proton NMR indicated that this product was approximately a 1:1 mixture of the cis and trans isomers of 2,4-$P_3N_3F_4[p\text{-}C_6H_4N(CH_3)_2]_2$.

The remaining heptane solution from the extraction was reduced to a volume of 50 mL and stored overnight at −20 °C. A precipitate formed which was purified as above to yield 3.3 g (18.9% of theory) of a white crystalline solid melting at 69–70 °C. The fluorine NMR spectra of this product indicated that it was the monosubstituted derivative $P_3N_3F_5[C_6H_4N(CH_3)_2]$. A mixture melting point with a known $P_3N_3F_5[C_6H_4N(CH_3)_2]$ sample confirmed this assignment.

Cis and Trans Isomers of 2,4-Bis[*p*-(dimethylamino)phenyl]tetrafluorocyclotriphosphazene via the Grignard Method from [*p*-(dimethylamino)phenyl]pentafluorocyclotriphosphazene. A mixture of 0.055 mol of $(CH_3)_2NC_6H_4MgBr$ and 0.05 mol of $P_3N_3F_5[C_6H_4N(CH_3)_2]$ was allowed to react as above. With the same isolation procedure, a yield of 8.2 g (35.5% of theory) of a white crystalline product melting at 157–159 °C was obtained. Infrared and ^1H and ^{19}F NMR spectra and mixture melting point of this product confirmed that it was identical with the 1:1 cis/trans isomeric mixture of 2,4-$P_3N_3F_4[C_6H_4(CH_3)_2]_2$ previously obtained. Unreacted $P_3N_3F_5C_6H_4N(CH_3)_2$ was also recovered.

***trans*-2,4,6-Tris[*p*-(dimethylamino)phenyl]trifluorocyclotriphosphazene via the Grignard Method.** A mixture of 0.44 mol of $(CH_3)_2NC_6H_4MgBr$ and 0.05 mol of $P_3N_3F_6$ was allowed to react as above. After 12 h, the solvent was removed and the residue extracted for 3 days with 500 mL of heptane in a Soxhlet extractor. Upon cooling of the solution to room temperature, a white precipitate immediately formed. This material was purified by vacuum sublimation at 210 °C and 0.01 mmHg, giving 0.62 g (2.2% of theory) of product melting at 224–226 °C. Anal. Calcd for $P_3N_3F_3[C_6H_4N(CH_3)_2]_3$: C, 52.17; H, 5.43; mol wt 552. Found: C, 52.86; H, 5.58; mol wt 552 (mass spectrum).

^{19}F NMR: $\delta(PF_2)$ = 48.1 (J(PF) = 931 Hz), 51.2 (J(PF) = 925 Hz). ^1H NMR: $\delta(H_{o,m})$ = 7.5–6.5 (overlapping multiplets): $\delta(CH_3)$ = 2.92, 2.95. Mass spectrum: 552 (100%, $P_3N_3F_3R_3^+$), 538 (11.3%, $P_3N_2F_3R_3^+$), 537 (16.5%, $P_3N_2F_3R_2C_6H_3N(CH_3)_2^+$ and/or $P_3N_3F_3R_2C_6H_4NCH_3^+$), 409 (11%), 270 (60.6%), 268 (43.7% $P_3N_3F_3C_6H_4^+$), 262 (40.1%, $P_2N_3F_2(C_6H_4NCH_3)_2^+$), 252 (11.4%), 244 (12.2%), 184 (2.1%, PNFR$^+$), 174 (10.5%, $P_3N_3F_2^+$).

The phosphazene-containing residue (ν_N = 1250 cm^{-1}) remaining in the extraction thimble was insoluble in a wide range of solvents and did not melt below 500 °C.

Preparation of Cis and Trans Isomers of 2,4-Bis[*p*-(dimethylamino)phenyl]tetrafluorocyclotriphosphazene Using the Lithium Reagent. A mixture of 0.05 mol of $(CH_3)_2NC_6H_4Li$ in 50 mL of benzene and 0.05 mol of $P_3N_3F_5C_6H_4N(CH_3)_2$ in 50 mL of THF was allowed to react for 3 days at reflux while being stirred magnetically. Product isolation, following the method used for disubstituted phosphazenes, gave a mixture which was separated on a silica gel column by using benzene as the eluant. The first fractions contained the disubstituted phosphazenes, and the remaining materials were not phosphazenes, as indicated by infrared and NMR spectra. The melting point (158–160 °C); of the desired product and its NMR spectra (^1H and ^{19}F) showed it to be an approximately 1:1 mixture of the cis and trans isomers of 2,4-$P_3N_3F_4[C_6H_4N(CH_3)_2]_2$. A yield of 1.8 g (8% of theory) was obtained.

Isolation of *cis*-2,4-Bis[*p*-(dimethylamino)phenyl]tetrafluorocyclotriphosphazene. A solution of 1.0 g of the cis/trans 2,4-$P_3N_3F_4[C_6H_4N(CH_3)_2]_2$ isomeric mixture in 10 mL of 50:50 benzene/medium boiling petroleum ether solution was placed on a silica gel column (5 × 60 cm) and eluted with the benzene/petroleum ether mixture. The first phosphazene-containing fractions yielded 0.13 g of a white solid, mp 188–190 °C, which was shown by ^{19}F and ^1H NMR spectra to be the pure cis isomer. The remaining fractions (0.82 g) were shown by the NMR spectra to be a cis/trans mixture.

NMR data for each of the isomers is given below. The data for the trans isomer was obtained by subtracting the spectrum of the cis isomer from the spectrum of the cis/trans mixture.

***cis*-2,4-$P_3N_3F_4[C_6H_4N(CH_3)_2]_2$.** ^{19}F NMR: $\delta(PF_2)$ = 65.2 (J(PF) = 879 Hz), 67.5 (J(PF) = 851 Hz); δ(PFR) = 47.6 (J(PF) = 952 Hz). ^1H NMR: $\delta(H_o)$ = 7.53 ($J(PH_o)$ = 14.4, $J(H_oH_m)$ = 9 Hz); $\delta(H_m)$ = 6.52 ($J(PH_m)$ = 3.6 Hz); $\delta(CH_3)$ = 2.92.

***trans*-2,4-$P_3N_3F_4[C_6H_4N(CH_3)_2]_2$.** ^{19}F NMR: $\delta(PF_2)$ = 67.0 (J(PF) = 875 Hz); δ(PFR) = 51.3 (J(PF) = 938 Hz). ^1H NMR:

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$\delta(H_o)$ = 7.58 ($J(PH_o)$ = 14.7, $J(H_oH_m)$ = 9 Hz); $\delta(H_m)$ = 6.60; $\delta(CH_3)$ = 2.95.

2-Phenyl-2-[*p*-(dimethylamino)phenyl]-4,4,6,6-tetrafluorocyclotriphosphazene. A mixture of 0.055 mol of anhydrous aluminum chloride and 40 mL of dry benzene was refluxed and stirred magnetically for 30 min. A solution of 0.015 mol of freshly distilled triethylamine in 10 mL of dry benzene was added slowly, and the mixture was allowed to reflux for 10 min. A solution of 0.01 mol of $P_3N_3F_5[C_6H_4N(CH_3)_2]$ in 10 mL of dry benzene was added slowly, and the reaction mixture was stirred at reflux for 3 days. The mixture was hydrolyzed over acidified ice water, and the layers were separated. The aqueous layer was extracted with benzene, and the combined benzene layers were washed sequentially with a saturated sodium bicarbonate solution and distilled water. The benzene solution was dried over anhydrous sodium sulfate and decolorized with activated carbon. The solvent was removed, leaving a yellow oil, which was then dissolved in a minimum amount of hot pentane. Upon cooling of the solution to −78 °C a white solid formed which was recrystallized a second time from pentane to yield 3.1 g (76.4% of theory) of a white solid (mp 69–71 °C). Anal. Calcd for $P_3N_3F_4(C_6H_5)[C_6H_4N(CH_3)_2]$: C, 41.18; H, 3.68; N, 13.73; mol wt 408. Found: C, 41.33; H, 3.83; N, 13.69; mol wt 408 (mass spectrum[18]).

^{19}F NMR: $\delta(PF_2)$ = 66.9 ($J(PF)$ = 853 Hz).

Preparation of 2-(Perdeuteriophenyl)-2-[*p*-(dimethylamino)-phenyl]-4,4,6,6-tetrafluorocyclotriphosphazene via the Friedel–Crafts Method. The method employed for this preparation was identical with that previously described for 2,2-$P_3N_3F_4(C_6H_5)[p\text{-}C_6H_4N(CH_3)_2]$ with the exception that deuteriobenzene (C_6D_6) was substituted for the benzene.[20] Anal. Calcd for $P_3N_4F_4(C_6D_5)[C_6H_4N(CH_3)_2]$: C, 40.68; N, 13.56; mol wt 413. Found: C, 40.70; N, 13.67; mol wt 413 (mass spectrum[18]).

^1H NMR: $\delta(H_o)$ = 7.43 ($J(PH_o)$ = 12.9, $J(H_oH_m)$ = 9 Hz); $\delta(H_m)$ = 6.48 ($J(PH_m)$ = 3.0 Hz); $\delta(CH_3)$ = 2.93.

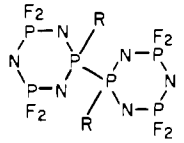
Preparation of 2,4-Bis(perdeuteriophenyl)-2,4-bis[*p*-(dimethylamino)phenyl]-6,6-difluorocyclotriphosphazene via the Friedel–Crafts Method. The method employed for this preparation was identical with that previously described with the following exceptions. Deuteriobenzene was used instead of benzene,[20] the amounts of anhydrous aluminum chloride and triethylamine were increased to 0.10 and 0.03 mol, respectively, and 0.01 mol of 2,4-$P_3N_3F_4[C_6H_4N(CH_3)_2]_2$ was substituted for the $P_3N_3F_5[C_6H_4N(CH_3)_2]$. A yield of 1.5 g (26% of theory) of a white crystalline product melting at 154–157 °C was obtained. Anal. Calcd for $P_3N_3F_2(C_6D_5)_2[C_6H_4N(CH_3)_2]_2$: C, 58.23; N, 12.13; mol wt. 577. Found: C, 58.62; N, 12.81; mol wt 577 (mass spectrum[18]).

^{19}F NMR: $\delta(PF_2)$ = 63.8 ($J(PF)$ = 871 Hz). ^1H NMR: $\delta(H_o)$ = 7.48 ($J(PH_o)$ = 12.6, $J(H_oH_m)$ = 9 Hz); $\delta(H_n)$ = 6.47; $\delta(CH_3)$ = 2.87.

Results and Discussion

The 1:1 molar reaction of $(CH_3)_2NC_6H_4MgBr$ with $P_3N_3F_6$ leads to the expected [*p*-(dimethylamino)phenyl]pentafluorocyclotriphosphazene, $P_3N_3F_5C_6H_4N(CH_3)_2$, derivative in moderate yields (comparable to those obtained in the analogous reaction with phenylmagnesium bromide[9]). However, the time required to obtain comparable yields is significantly increased on going from C_6H_5MgBr to $(CH_3)_2NC_6H_4MgBr$, thus indicating decreased reactivity of the *p*-(dimethylamino)phenyl Grignard compared to the phenyl Grignard reagent. The ^{19}F and ^1H NMR spectra along with mass spectrometry data are in accord with the proposed structure. Infrared spectroscopy was of limited value in the characterizations of [*p*-(dimethylamino)phenyl]phosphazenes since the aryl unit exhibited several strong absorptions in the regions assigned to the principal phosphazene absorptions. The chloro analogue $P_3N_3Cl_5C_6H_4N(CH_3)_2$ has been obtained as the minor product in the reaction of hexachlorocyclotriphosphazene, $P_3N_3Cl_6$, with *N*,*N*-dimethylaniline.[21]

In addition to the expected product, small amounts of a novel dimer, $[P_3N_3F_4C_6H_4N(CH_3)_2]_2$, were isolated.



Similar materials have been obtained from the reaction of diphenylmagnesium with $P_3N_3Cl_6$.[6] Although the presence of the *p*-(dimethylamino)phenyl substituent was established by ^1H NMR, further characterization by ^{19}F NMR spectroscopy was prevented by the low solubility of the dimeric species. Mass spectrometry data give a clear indication of the identity of the product. The parent ion is observed, thus establishing the molecular mass which, when combined with the analytical data, gives the molecular formula of the material. The most abundant ion $P_3N_3F_4C_6H_4N(CH_3)_2^+$ arises from the cleavage of the weak phosphorus(V)–phosphorus(V) bond. One can envision two possible routes to the dimeric material. Considerable amounts of diarylmagnesium species exist in THF solutions of aryl Grignard reagents,[22] and consequently a pathway similar to that observed in the diphenylmagnesium/$P_3N_3Cl_6$ reaction[6] may be followed. Alternatively, metalation of $P_3N_3F_5C_6H_4N(CH_3)_2$ by the Grignard species followed by coupling with an additional $P_3N_3F_5C_6H_4N(CH_3)_2$ unit may occur. Bicyclic phosphazenes have been prepared by the coupling of metalated phosphazenes with halophosphazenes.[23]

There are several points of interest in the results of the 2:1 molar reactions of *p*-(dimethylamino)phenyl Grignard and lithium reagents with $P_3N_3F_6$. The low reactivity of the organometallic reagent is reflected in the low yields of the 2:1 reactions. Moderate yields of the disubstituted derivatives could be obtained by a 1:1 molar reaction by using $P_3N_3F_5C_6H_4N(CH_3)_2$ as the phosphazene starting material. Contrary to the results obtained for the phenyl derivatives,[9,15] the yields in the Grignard reaction are significantly better than those obtained by using the lithium reagent. The disubstituted derivatives obtained from both the Grignard and lithium reagents are approximately 1:1 mixtures of the cis and trans nongeminal derivatives. The structural assignments are primarily based on the ^{19}F NMR spectra which show both $\equiv PF_2$ and $\equiv PFR$ centers with the cis derivative exhibiting nonequivalent $\equiv PF_2$ resonances. The phosphorus–ortho proton coupling constant, obtained from ^1H NMR spectra, is in the range expected for a $\equiv PFR$ center[24] and hence confirms the nongeminal structure. It is of particular interest that the $N(CH_3)_2$ resonances due to cis and trans isomers are well resolved in the ^1H NMR spectrum, thus giving a convenient measure of the relative amounts of each isomer.

The observation of a nongeminal substitution pattern for the Grignard reagent is in contrast to the results obtained by using phenylmagnesium bromide, where an exclusively geminal substitution pattern is observed.[9] The reasons for this change are not clear and certainly add to the perplexity in understanding the reactions of organometallic reagents with cyclophosphazenes. One possible explanation is a steric barrier to geminal substitution which would arise if there were an increase in the degree of association of the Grignard reagent due to intermolecular interaction of a magnesium center with an amine nitrogen atom.

One also observes a change in the isomer distribution on going from the phenyllithium reaction (cis:trans ratio 3:1[15]) the systems under consideration in this investigation (cis:trans ratio 1:1). The increase in the amount of trans isomer is predicted by the empirical cis effect[15] in that the *p*-(di-

(20) The incorporation of C_6D_5 rather than C_6H_5 allowed analysis of the ^1H NMR spectrum of the $C_6H_4N(CH_3)_2$ group in these derivatives.
(21) Cheng, C. Y.; Shaw, R. A. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1739.
(22) Evans, D. F.; Fazakerly, G. V. *J. Chem. Soc. A* **1971**, 184.
(23) Schmidpeter, A.; Hogel, J.; Ahmed, F. R. *Chem. Ber.* **1976**, *109*, 1911.
(24) Allen, C. W.; White, A. J. *Inorg. Chem.* **1974**, *13*, 1220.

methylamino)phenyl moiety is a better electron-releasing group than the phenyl group.[25] Alternatively, in a nonplanar phosphazene derivative, the ortho hydrogen atoms on the aryl ring may undergo hydrogen bonding with cis fluorine atoms, thereby blocking cis attack. This effect is expected to be more significant for the *p*-(dimethylamino)phenyl derivative, where the ring hydrogen atoms are more acidic than in the phenyl derivatives. A thorough examination of factors involved in control of isomer distribution will have to await detailed mechanistic and thermodynamic investigations.

A 6:1 molar reaction of $(CH_3)_2NC_6H_4MgBr$ with $P_3N_3F_6$ was undertaken in an attempt to obtain the hexakis[*p*-(dimethylamino)phenyl]cyclotriphosphazene. The only cyclophosphazene isolated was the trisubsituted derivative *trans*-2,4,6-$P_3N_3F_3[C_6H_4N(CH_3)_2]_3$ which is obtained in low yields. The structural assignment follows from NMR data. The ^{19}F NMR spectrum shows two sets of doublets in the $\equiv PFR$ region which is consistent with the trans disposition of fluorine atoms. The ^1H NMR spectrum shows two resolved resonances in the $N(CH_3)_2$ region in a ratio of 2:1 which can be assigned to the two different aryl environments which are the consequence of a trans structure.

The low yield and apparent reluctance of the reaction to proceed past the level of trisubstitution can be understood in terms of both the previously established low reactivity of the *p*-(dimethylamino)phenyl Grignard reagent and also decomposition reactions. Ring-opening degradation is the primary mode of reaction in the interactions of Grignard[5] and organolithium[7] reagents with hexachlorocyclotriphosphazene. At the stage of trisubstitution of $P_3N_3F_6$, the point may be reached where the barrier to additional substitution is high and the ring nitrogen atoms become sufficiently basic to allow coordination of the organometallic reagent, thus initiating ring opening[5] and giving the large amounts of insoluble residue observed. The tendency toward formation of the trans isomer is again noted in the formation of the trisubstituted derivative. Reaction of the organometallic reagent at the trans rather than the cis position may be related to the expected steric constraints favoring trans attack in bimolecular reactions and/or the factors previously discussed relating to stereochemical control in the formation of the disubstituted derivatives.

It has been shown that one may convert a $\equiv PFC_6H_5$ center, in a phosphazene derivative, to a $\equiv(C_6H_5)_2$ center via the Friedel–Crafts reaction.[26] In this investigation, the reaction of [*p*-(dimethylamino)phenyl]fluorophosphazenes with aluminum chloride in benzene (or deuteriobenzene) proved to be a successful method for the conversion of a $\equiv PFC_6H_4N(CH_3)_2$ center to a $\equiv P(C_6H_5)C_6H_4N(CH_3)_2$ center. Excess aluminum chloride was used to account for deactivation of the Lewis acid by coordination to a $N(CH_3)_2$ group. The yields ranged from excellent in the reaction of $P_3N_3F_5C_6H_4N(CH_3)_2$ to moderate in the reaction of 2,4-$P_3N_3F_4[C_6H_4N(CH_3)_2]_2$. The factors which favor nongeminal substitution in the organometallic reactions are not operative in the Friedel–Crafts reaction, where a mechanistic pathway based on phosphorus–halogen ionization is believed to prevail.[2,3] Consequently, the electron-releasing *p*-(dimethylamino)phenyl group will stabilize a phosphonium ion[18] which is created from a $\equiv PFC_6H_5N(CH_3)_2$ center and hence favors geminal substitution. The structures were established in each case by consideration of the NMR data. The ^{19}F spectra show resonances only in the $\equiv PF_2$ region, and the phosphorus–ortho hydrogen coupling constants in the ^1H spectra are in the range previously observed for a geminal arrangement of aryl groups.[24] The tetrasubstituted derivative $P_3N_3F_2(C_6H_5)_2[C_6H_4N(CH_3)_2]_2$ is expected to exhibit two isomeric forms arising from cis and trans disposition of identical aryl substituents. While there is no direct NMR evidence on this point, the $N(CH_3)_2$ resonance in the ^1H spectrum is considerably broadened, suggesting unresolved lines within the band envelope.

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Registry No. $P_3N_3F_5[p\text{-}C_6H_4N(CH_3)_2]$, 53968-86-8; $\{P_3N_3F_4[p\text{-}C_6H_4N(CH_3)_2]\}_2$, 75232-92-7; *cis*-2,4-$P_3N_3F_4[p\text{-}C_6H_4N(CH_3)_2]_2$, 75232-93-8; *trans*-2,4-$P_3N_3F_4[p\text{-}C_6H_4N(CH_3)_2]_2$, 75232-94-9; *trans*-2,4,6-$P_3N_3F_3[p\text{-}C_6H_4N(CH_3)_2]_3$, 75232-95-0; 2,2-$P_3N_3F_4(C_6H_5)[p\text{-}C_6H_4N(CH_3)_2]$, 75232-96-1; 2,2-$P_3N_3F_4(C_6D_5)[p\text{-}C_6H_4N(CH_3)_2]$, 53968-88-0; $P_3N_3F_2(C_6D_5)_2[p\text{-}C_6H_4N(CH_3)_2]_2$, 75232-97-2; *p*-$BrC_6H_4N(CH_3)_2$, 586-77-6; *p*-$LiC_6H_4N(CH_3)_2$, 13190-50-6; $P_3N_3F_6$, 15599-91-4.

(25) In the original form, the electron-releasing effect was via a π mechanism.[15] However recent work[1] has shown that there are no significant aryl–phosphazene π interactions.

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Synthesis of Alkylphosphazenes via Copper–Phosphazene Intermediates[1,2]

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A new reaction route has been developed for the synthesis of a hitherto inaccessible series of 1,1-dialkyltetrachlorocyclotriphosphazenes, $N_3P_3Cl_4RR'$ (III), where R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *i*-C_4H_9, *t*-C_4H_9, or allyl and R' = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, or allyl. The high-yield route involves the interaction of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, with alkyl Grignard reagents in the presence of $[n\text{-}Bu_3PCuI]_4$, followed by treatment with alkyl halides. The structural characterization of these compounds by NMR and mass spectrometric techniques is discussed, together with the reaction mechanism.

The synthesis of linear or cyclic alkyl-substituted phosphazene compounds has attracted considerable attention in recent years but has met with only limited success. Cyclic alkyl- or arylphosphazenes that contain side groups bound to the phosphazene skeleton through direct phosphorus–carbon bonds are useful models[3] for preliminary macromolecular reactivity studies or "monomers" for polymerization reactions.[4,5]

(1) For a previous paper in this series see: Allcock, H. R.; Evans, T. L.; Fuller, T. J. *Inorg. Chem.* **1980**, *19*, 1026.

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