carboxylation and oxidation) have been recently observed in peptide complexes containing histidine residues bound histamine-like.[54]

## Conclusions

The mode of coordination to copper(II) of histidine residues has been investigated in a series of Schiff base chelates derived from pyridoxal, salicylaldehyde, and pyruvic acid. The corresponding complexes derived from amino acids with nonpolar side chains provide appropriate references for the glycine-like coordination mode, while the derivatives of histidine methyl ester are appropriate references for the histamine-like mode. The preference for either mode is apparently ruled by the chelate ring type of the fused carbonyl residue, and histidine exhibits a striking tendency to bind copper(II) through chelate ring types complementary rather than similar to those of the carbonyl residues. Thus, copper(II) complexes derived from pyridoxal, salicylaldehyde, or (+)-(hydroxymethylene)camphor[9] contain histidine residues bound glycine-like, while in those derived from pyruvic acid or 2-pyridinecarboxaldehyde[55] the histidine residues are bound histamine-like. These results can be of some importance to infer the coordination mode of histidine residues in complexes with small peptides, where the deprotonation of amide nitrogen atoms often leads to chelate ring systems similar to those of the complexes reported here.[31d,e,56] Circular dichroism can easily distinguish the glycine-like and histamine-like binding modes in these complexes of histidine Schiff bases, since the preference for a pseudoaxial disposition of the side chain involves opposite conformation chiralities for the histidine chelate rings in the two binding modes. The investigation of solvent effects on the variations of the EPR parameters enables one to refine the stereochemical description of copper(II) complexes of amino acid Schiff bases in terms of donor sets, ligand field symmetry, and bonding character. A simple conformational model accounts for the observed trends in the circular dichroism spectra and provides a key to the interpretation of vitamin $B_6$ model reactions on a stereochemical basis. Although different theoretical approaches to the circular dichroism of chiral transition-metal complexes have been developed, particularly for copper(II) complexes,[57,58] they have not produced a model capable of widely applicable spectra-structure correlations. These largely rely upon simpler approaches applied to series of chiral complexes of closely related structures, even though they may give no account for the mechanisms leading to the CD. The intuitive conformational model employed here is particularly useful for correlating the overall CD features of the complexes to the stereochemistry of the chiral polydentate ligands.

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**Registry No.** Cu(pdx-himNCH$_3$)ClO$_4$, 80864-78-4; Cu(pdx-L-his), 80864-79-5; Cu(Hpdx-L-his)Cl, 80864-80-8; Cu(Hpdx-L-hisOCH$_3$)Cl$_2$, 80864-81-9; Cu(Hpdx-L-hisOCH$_3$)(ClO$_4$)$_2$, 80878-13-3; Cu(Hpdx-L-hisOCH$_3$')ClO$_4$, 80864-83-1; Cu(pdx-L-val), 63569-28-8; Cu(Hpdx-L-val)Cl, 80864-84-2; Cu(Hpdx-L-val)ClO$_4$, 80864-85-3; Cu(pdx-L-phe), 63569-29-9; Cu(Hpdx-L-phe)Cl, 80864-86-4; Cu(sal-L-his), 64254-72-4; Cu(sal-L-ser), 80864-87-5; Cu(sal-L-hisOCH$_3$)ClO$_4$, 80864-89-7; Cu(sal-L-hisOCH$_3$'), 80878-97-3; Cu(pyv-L-his), 80864-90-0; Cu(pyv-L-hisOCH$_3$)Cl, 80864-91-1; Cu(pyv-L-hisOCH$_3$'), 80878-96-2; Cu(pyv-L-val), 80864-92-2; Cu(pyv-L-ala), 80864-93-3; Cu(pyv-gly), 75441-94-0.

**Supplementary Material Available:** Listings of elemental analysis (Table I), electronic and CD spectra of copper(II) complexes derived from D-amino acids (Table III), and EPR data of copper(II) complexes derived from D-amino acids (Table V) (5 pages). Ordering information is given on any current masthead page.

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# Organophosphazenes. 15. Reactions of Hexafluorocyclotriphosphazene with *tert*- and *n*-Butyllithium Reagents[1]

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**Abstract:** The reactions of *tert*- and *n*-butyllithium reagents with hexafluorocyclotriphosphazene ($N_3P_3F_6$) have been examined. In contrast to the behavior of *n*-butyllithium, the reaction of *tert*-butyllithium with $N_3P_3F_6$ gives good yields of $N_3P_3F_5C_4H_9$. While the *n*-butyllithium reaction follows a geminal pathway at the stage of disubstitution, the *tert*-butyllithium reaction gives exclusively the trans nongeminal isomer for the compounds $N_3P_3F_{6-n}(t\text{-}C_4H_9)_n$ ($n$ = 2, 3). This is the first example of a regio- and stereospecific reaction in phosphazene chemistry. At the stage of trisubstitution, solvent (diethyl ether) cleavage by *tert*-butyllithium is competitive with phosphazene substitution, resulting in the concomitant formation of *trans*-2,4,6-$N_3P_3F_3(OC_2H_5)(t\text{-}C_4H_9)_2$. These results are discussed in terms of competing steric and electronic effects. The butylphosphazenes are characterized by mass spectrometry and infrared and NMR ($^1H$, $^{13}C$, $^{19}F$, $^{31}P$) spectroscopy.

One of the most active fields of investigation in cyclophosphazene chemistry is the study of substitution reactions.[2-4] Aminolysis and alcoholysis reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, have received a great deal of attention,

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and various substitution patterns have been observed.[2,3] On the other hand, reactions of organometallic reagents with $N_3P_3Cl_6$ and $N_3P_3F_6$ are less well understood.[4] One reason for this is the complexity of these reactions. Depending on the nature of the reagents, these reactions give rise to substitution of halogen atoms[4,5] and/or cleavage of the phosphazene ring.[6] Previous studies in this laboratory[7,8] and elsewhere[9-11] have shown that reactions of $N_3P_3F_6$ with organometallic reagents follow both geminal and nongeminal pathways, with the geminal pathway being more frequently observed.[4]

In any attempt to identify factors involved in the stereochemical control of phosphazene substitution reactions, studies of the reactions of alkyllithium reagents would be of value due to the electronic simplicity of the organic function. While a detailed study of the reaction of methyllithium with $N_4P_4F_8$ has appeared,[12] only brief reports of the reactions of alkyllithium reagents with $N_3P_3F_6$ are available.[9,13,14] Part of the lack of interest in these derivatives is related to the low yields obtained in their syntheses. While various proposals have been advanced to rationalize this observation, the most reasonable suggestion appears to be that facile deprotonation of the alkyl group $\alpha$ to the phosphorus atom leads to an anionic center at the exocyclic position.[15,16] These heteroatom-stabilized $\alpha$ anions[17] can lead to intramolecular ring degradation[16] or intermolecular cross-linking.[18] In this investigation we have chosen to test this model by examining the reactions of an alkyllithium reagent without $\alpha$-hydrogen atoms (*tert*-butyllithium) and to explore the effect of steric requirements of the alkyl group on the stereochemistry of the substitution reaction.

## Experimental Section

**Materials and Methods.** Hexafluorocyclotriphosphazene ($N_3P_3F_6$) was prepared from $N_3P_3Cl_6$ (Ethyl Corp.) by a previously reported procedure.[19] *tert*-Butyllithium (2.0 M solution in pentane) and *n*-butyllithium (1.55 M solution in hexane) were obtained from Aldrich. Diethyl ether was distilled from sodium benzophenone ketyl. Pentane, hexane, petroleum ether (bp 35–55 °C), and benzene (Fisher) were distilled over sodium ribbon. NMR spectra (in $CDCl_3$) were recorded on a Bruker WM250 spectrometer operating at 250.1 ($^1$H), 62.9 ($^{13}$C), 235.2 ($^{19}$F), and 101.2 ($^{31}$P) MHz. Tetramethylsilane, $Me_4Si$ (for $^1$H and $^{13}$C NMR), and fluorotrichloromethane, $CFCl_3$ (for $^{19}$F NMR), were used as internal references. For $^{31}$P NMR, 85% $H_3PO_4$ was used as an external reference. Chemical shifts upfield to the reference are assigned a negative sign. $^{13}$C, $^{19}$F, and $^{31}$P NMR spectra were recorded under conditions of broad-band decoupling. Infrared (IR) spectra were obtained as their films (NaCl disks) or KBr pellets on a Beckman IR20A spectrometer. Mass spectra were recorded on a Perkin-Elmer RMU-6D spectrometer operating at 80 eV. Elemental analyses were performed by Integral Microanalytical Laboratories.

All reactions were carried out under anhydrous conditions in a three-necked round-bottomed flask fitted with a reflux condenser and a pressure-equalizing dropping funnel. The system was stirred magnetically and flushed with nitrogen which exited through a mercury bubbler. Lithium reagents were transferred by syring techniques.

**Reaction of $N_3P_3F_6$ with 1 Equiv of $t$-$C_4H_9Li$.** *tert*-Butyllithium (15 mL, 0.03 mol) was added over a 1-h period to a solution of $N_3P_3F_6$ (7.5 g, 0.03 mol) in 200 mL of diethyl ether which was cooled in a dry ice–acetone bath. The reaction mixture was allowed to come to room temperature and stirred for 3 h. The solvent was removed under reduced pressure and 150 mL of hexane was added. The solid was removed by filtration and the solvent was removed from the filtrate. The resulting liquid was distilled at reduced pressure (0.02 mmHg) to yield 5.8 g (67.4% of theory) of a colorless liquid, bp 28 °C (0.02 mmHg). Anal. Calcd for $N_3P_3F_5C_4H_9$ (I): C, 16.72; H, 3.14; N, 14.63; mol wt 287. Found: C, 16.80; H, 3.20; N, 14.51; mol wt 287 (mass spectrum[20]).

$^1$H NMR[21] $\delta_{C(CH_3)_3}$ 1.226 (d), $^3J_{P-H}$ = 19.823. $^{13}$C NMR $\delta_{C(CH_3)_3}$ 23.187 (d), $^2J_{P-C}$ = 16.062; $\delta_{C(CH_3)_3}$ 31.968 (m), $^1J_{P-C}$ = 142.817, $^2J_{F-C}$ = 26.502. $^{31}$P NMR $\delta_{=PF_2}$ 9.088 (m, 2 P), $^1J_{P-F}$ = 935.914; $\delta_{=PF(t\text{-}C_4H_9)}$ 56.461 (m, 1 P), $^1J_{P-F}$ = 1048.306. $^{19}$F NMR $\delta_{=PF_2}$ −68.243, $^1J_{P-F}$ = 900.711; $\delta_{=PF_2}$ −69.820, $^1J_{P-F}$ = 894.433; $\delta_{=PF(t\text{-}C_4H_9)}$ 79.298, $^1J_{P-F}$ = 1033.177. IR[22] 1265 (s, $\nu_{P=N}$), 970 (m, P–F asym), 935 (m, P–F asym), 805 (m, P–F sym), 735 (s, P–F sym).

At higher distillation temperatures, 0.26 g (2.7% of theory) of a second product was obtained. The colorless liquid, bp 50 °C (0.02 mmHg), was identified as di-*tert*-butyltetrafluorocyclotriphosphazene (II). Anal. Calcd for $N_3P_3F_4C_8H_{18}$: C, 29.53; H, 5.54; N, 12.92; mol wt 325. Found: C, 29.56; H, 5.84; N, 12.80; mol wt 325 (mass spectrum[20]).

$^1$H NMR[21] $\delta_{C(CH_3)_3}$ 1.223 (d), $3J_{P-H}$ = 19.531. $^{13}$C NMR $\delta_{C(CH_3)_3}$ 23.288 (d), $^2J_{P-C}$ = 26.000; $\delta_{C(CH_3)_3}$ 32.097 (m), $^1J_{P-C}$ = 147.914, $^2J_{F-C}$ = 25.569, $^3J_{P-C}$ = 4.949. $^{19}$F NMR $\delta_{=PF_2}$ −68.964 (m, 2 F), $^1J_{P-F}$ = 902.832; $\delta_{=PF(t\text{-}C_4H_9)}$ −78.017 (m, 2 F), $^1J_{P-F}$ = 1022.909. $^{31}$P NMR $\delta_{=PF_2}$ 9.548 (m, 1 P), $^1J_{P-F}$ = 903.320, $^2J_{P-P}$ = 51.270, $^3J_{P-F}$ = 6.103; $\delta_{=PF(t\text{-}C_4H_9)}$ 56.202 (m, 2 P), $^1J_{P-F}$ = 1021.632. IR[22] 1265 (s, $\nu$P=N), 970 (m, P–F asym), 935 (s, P–F asym), 850 (s, P–F sym), 825 (s, P–F sym), 725 (s, P–F sym).

**Reaction of $N_3P_3F_6$ with $t$-$C_4H_9Li$ in Pentane.** The method employed for this reaction was identical with that previously described except that pentane was used in place of diethyl ether. After 9 h, 2.5 g (0.01 mol) of $N_3P_3F_6$ yielded (in addition to unreacted $t$-$C_{H9}Li$) 0.4 g of a mixture of I and II.

**Reaction of $N_3P_3F_6$ with 2 Equiv of $t$-$C_4H_9Li$.** The reaction of $t$-$C_4H_9Li$ (20 mL, 0.04 mol) with $N_3P_3F_6$ (5.0 g, 0.02 mol) in diethyl ether at −78 °C was conducted as previously described. Reduced-pressure fractional distillation of the colorless liquid product yielded $N_3P_3(t\text{-}C_4H_9)F_5$ (I) [bp 28 °C (0.02 mmHg), 1.2 g (20.9%)] and $N_3P_3(t\text{-}C_4H_9)_2F_4$ (II) [bp 50 °C (0.02 mmHg), 2.7 g (41.5%)]. Separation of the above products can also be achieved by column chromatography over silica gel using petroleum ether as eluent.

**Reaction of $N_3P_3F_6$ with 3 Equiv of $t$-$C_4H_9Li$.** The reaction of $t$-$C_4H_9Li$ (45 mL, 0.09 mol) with $N_3P_3F_6$ (7.5 g, 0.03 mol) in 150 mL of diethyl ether at 0 °C was conducted as previously described. The oily product mixture was separated on a silica gel column using a 1:1 benzene–hexane mixture as the eluent. The first product was identified as $N_3P_3F_4(t\text{-}C_4H_9)_2$ (II) (3.2 g, 32.8%). The second component was identified as tri-*tert*-butyltrifluorocyclotriphosphazene (III) (0.12 g, 1.1%), mp 80 °C. Anal. Calcd for $N_3P_3F_3C_{12}H_{27}$: C, 39.67; H, 7.44; mol wt 363. Found: C, 39.95; H, 7.72; mol wt 363 (mass spectrum[20]).

$^1$H NMR[21] $\delta_{C(CH_3)_3}$ 1.216 (d, 18 H), $^3J_{P-H}$ = 18.516; $\delta_{C(CH_3)_3}$ 1.201 (d, 9 H), $^3J_{P-H}$ = 18.516. $^{31}$P NMR $\delta_{=PF(t\text{-}C_4H_9)}$ 33.176 (m, 1 P), $^1J_{P-F}$ = 102.789; $\delta_{=PF(t\text{-}C_4H_9)}$ 31.122 (m, 2 P), $^1J_{P-F}$ = 1007.179. $^{19}$F NMR $\delta_{=PF(t\text{-}C_4H_9)}$ −72.140 (m, 1 F), $^1J_{P-F}$ = 1011.658; $\delta_{=PF(t\text{-}C_4H_9)}$ −77.148 (m, 2 F), $^1J_{P-F}$ = 1007.080.

The third compound eluted was found to be ethoxydi-*tert*-butyltrifluorocyclotriphosphazene, $N_3P_3(OC_2H_5)(t\text{-}C_4H_9)_2F_3$ (IV) (1.7 g, 16.1%), mp 40–42 °C. Anal. Calcd for $N_3P_6F_3OC_{10}H_{23}$: C, 34.18; H, 6.55; mol wt 351. Found: C, 34.10; H, 6.91; mol wt 351 (mass spectrum[20]).

$^1$H NMR[21] $\delta_{C(CH_3)_3}$ 1.214 (d), $^3J_{P-H}$ = 19.090; $\delta_{OCH_2CH_3}$ 4.154 (m), $^3J_{P-H}$ = 15.863, $^3J_{H-H}$ = 6.991; $\delta_{OCH_2C_{H_3}}$ 1.369 (t), $^3J_{H-H}$ = 6.991. $^{13}$C NMR $\delta_{C(CH_3)_3}$ 23.545 (d), $^2J_{P-C}$ = 9.637; $\delta_{C(CH_3)_3}$ 31.923 (m), $^1J_{P-C}$ = 136.125, $^2J_{F-C}$ = 26.101, $^3J_{P-C}$ = 2.409; $\delta_{OCH_2CH_3}$ 63.675 (d), $^2J_{P-C}$ = 6.425; $\delta_{OCH_2CH_3}$ 15.922 (d), $^3J_{P-C}$ = 8.031. $^{31}$P NMR $\delta_{=PF(OC_2H_5)}$ 12.581 (m, 1 P), $^1J_{P-F}$ = 892.857; $\delta_{=PF(t\text{-}C_4H_9)}$ 54.299 (m, 2 P), $^1J_{P-F}$ = 1007.441. $^{19}$F NMR $\delta_{=PF(OC_2H_5)}$ −63.862 (m, 1 F), $^1J_{P-F}$ = 892.334; $\delta_{=PF(t\text{-}C_4H_9)}$ −76.033 (m, 1 F), $^1J_{P-F}$ = 1015.625; $\delta_{=PF(t\text{-}C_4H_9)}$ −77.187 (m, 1 F), $^1J_{P-F}$ = 1009.304. IR[22] 1250 (s, $\nu$P=N), 1050 (s, P–O), 990 (m, P–F asym), 920 (m, P–F asym), 895 (m, P–F sym), 835 (s, P–F sym), 805 (s, P–F sym).

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(22) In $cm^{-1}$.

Attempts at introduction of additional *tert*-butyl groups by employing $t$-$C_4H_9Li$:$N_3P_3F_6$ ratios greater than 3:1 were unsuccessful.

**Reaction of $N_3P_3F_6$ with 1 Equiv of $n$-$C_4H_9Li$.** The reaction of $n$-$C_4H_9Li$ (20 mL, 0.03 mol) with $N_3P_3F_6$ (7.5 g, 0.03 mol) in 200 mL of diethyl ether at −78 °C was conducted as previously described. Reduced-pressure (0.02 mmHg) distillation of the product at room temperature gave a colorless liquid which was characterized as *n*-butylpentafluorocyclotriphosphazene, $N_3P_3(n\text{-}C_4H_9)F_5$ (V): 0.67 g (7.5% of theory, lit.[13] 11–14%); bp 25 °C (0.02 mmHg). Anal. Calcd for $N_3P_3F_5C_4H_9$: C, 16.72; H, 3.14; mol wt 287. Found: C, 16.01; H, 3.04; mol wt 287 (mass spectrum[20]).

$^1H$ NMR[21] $\delta_{CH_2(CH_2)_2CH_3}$ 1.992 (m, 2 H); $\delta_{CHCH_2CH_2CH_3}$ 1.631 (m, 2 H); $\delta_{(CH_2)_2CH_2CH_3}$ 1.469 (m, 2 H); $\delta_{(CH_2)_3CH_3}$ 0.960 (t, 3 H), $^3J_{H-H}$ = 7.254. $^{13}C$ NMR $\delta_{C_\alpha}$ 28.207 (m), $^1J_{P-C}$ = 141.709, $^2J_{F-C}$ = 15.474, $^3J_{P-C}$ = 7.737; $\delta_{C_\beta}$ 23.4054 (d), $^2J_{P-C}$ = 4.298; $\delta_{C_\gamma}$ 23.227 (d), $^3J_{P-C}$ = 18.053; $\delta_{C_\Delta}$ 13.408 (s). $^{19}F$ NMR $\delta_{\equiv PF_2}$ −69.714 (m, 2 F), $^1J_{P-F}$ = 934.738; $\delta_{\equiv PF_2}$ −67.874 (m, 2 F), $^1J_{P-F}$ = 929.675; $\delta_{\equiv PF(n\text{-}C_4H_9)}$ −59.977 (d, t, 1 F), $^1J_{P-F}$ = 1009.521, $^3J_{P-F}$ = 11.597. $^{31}P$ NMR $\delta_{\equiv PF_2}$ 9.548, $^1J_{P-F}$ = 925.293; $\delta_{\equiv PF(n\text{-}C_4H_9)}$ 50.211, $^1J_{P-F}$ = 1008.301, $^2J_{P-P}$ = 63.476, $^3J_{P-F}$ = 19.531. IR[22] 1275 (s, $\nu_{P=N}$), 970–750 (s, unresolved, includes P–F).

At higher distillation temperatures (~100 °C), a second product (0.20 g 2.1%), which solidified on cooling, was obtained. The solid, mp 55 °C, was identified as di-*n*-butyltetrafluorocyclotriphosphazene (VI). Anal. Calcd for $N_3P_3F_4C_8H_{18}$: C, 29.53; H, 5.54; mol wt 325. Found: C, 28.48; H, 5.68; mol wt 325 (mass spectrum[20]).

$^1H$ NMR[21] $\delta_{CH_2(CH_2)_2CH_3}$ 1.744 (m, 2 H); $\delta_{CH_2CH_2CH_2CH_3}$ 1.567 (m, 2 H); $\delta_{(CH_2)_2CH_2CH_3}$ 1.434 (m, 2 H); $\delta_{(CH_2)_3CH_3}$ 0.945 (t, 3 H), $^3J_{H-H}$ = 7.172. $^{13}C$ NMR $\delta_{C_\alpha}$ 30.903 (d, t), $^1J_{P-C}$ = 92.843, $^3J_{P-C}$ = 5.158; $\delta_{C_\beta}$ 22.689 (d), $^2J_{P-C}$ = 5.158; $\delta_{C_\gamma}$ 23.508 (d), $^3J_{P-C}$ = 17.193; $\delta_{C_\Delta}$ 13.531 (s). $^{19}F$ NMR $\delta_{\equiv PF_2}$ −68.612, $^1J_{P-F}$ = 928.173. $^{31}P$ NMR $\delta_{\equiv PF_2}$ 9.753 (m, 2 P), $^1J_{P-F}$ = 917.608; $\delta_{\equiv P(n\text{-}C_4H_9)_2}$ 48.294 (t, 1 P), $^2J_{P-P}$ = 35.400. IR[22] 1250 (s, $\nu_{P=N}$), 935 (s, P–F), 825 (m, P–F), 785 (m, P–F).

The residue remaining after the above distillation solidified on cooling. The material, which was gummy and of low solubility, resisted further characterization.

## Results and Discussion

The reaction of *tert*-butyllithium with $N_3P_3F_6$ in diethyl ether gives the partially substituted fluorocyclotriphosphazene derivatives, $N_3P_3(t\text{-}C_4H_9)_nF_{6-n}$ ($n$ = 1–3), and an ethoxy derivative, $N_3P_3(OC_2H_5)(t\text{-}C_4H_9)_2F_3$. Reaction of 1 equiv of *tert*-butyllithium with 1 equiv of $N_3P_3F_6$ in diethyl ether at −78 °C gives the monosubstituted compound, $N_3P_3(t\text{-}C_4H_9)F_5$ (I) (67.4%), and a small amount (2.7%) of the disubstituted compound, $N_3P_3(t\text{-}C_4H_9)_2F_4$ (II). The yield of the disubstituted compound (II) can be increased substantially by the reaction of 2 equiv of *tert*-butyllithium with 1 equiv of $N_3P_3F_6$ at −78 °C. A 1:3 $N_3P_3F_6$:*tert*-butyllithium reaction gives the disubstituted compound (II), the trisubstituted compound, $N_3P_3(t\text{-}C_4H_9)_3F_3$ (III), and an unexpected product, $N_3P_3(OC_2H_5)(t\text{-}C_4H_9)_2F_3$ (IV). These compounds can be separated by column chromatography over silica gel. The source of ethoxide ion for the formation of compound IV is from the cleavage of diethyl ether by *tert*-butyllithium.[23] Reaction of *tert*-butyllithium with $N_3P_3F_6$ in pentane gives only *tert*-butylfluorocyclotriphosphazenes $N_3P_3(t\text{-}C_4H_9)_nF_{6-n}$ $n$ = 1,2 in significantly reduced yields. This observation is consistent with the increased carbanionic character of organolithium reagents in the presence of Lewis bases.

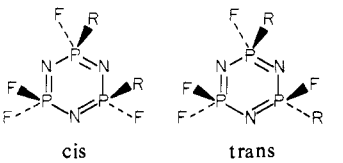
The synthetic results demonstrate a significant increase in the difficulty of effecting higher degrees of substitution. This observation is most directly related to the steric hindrance associated with each of the *tert*-butyl substituents. Similar observations have been made in the reactions of other organometallic reagents[24] and bulky amines[25] with halocyclophosphazenes.

The reaction of *n*-butyllithium with $N_3P_3F_6$ in diethyl ether gives the previously reported[13] mono- and disubstituted cyclotriphosphazenes, $N_3P_3(n\text{-}C_4H_9)F_5$ (V) and $N_3P_3(n\text{-}C_4H_9)_2F_4$ (VI). In contrast to the excellent yields obtained in the *tert*-butyllithium reaction, the yields of *n*-butylfluorocyclotriphosphazenes are poor. This observation confirms our hypothesis that organophosphazenes without α-hydrogen atoms may be prepared in good yields since the degradative routes via the heteroatom-stabilized α anions[16,18] are not available. It is reasonable to expect that one should be able to prepare partially substituted poly(organophosphazenes) using *tert*-butyllithium without the cross-linking observed with other alkyllithium reagents.[18]

The various *tert*-butyl- and *n*-butylfluorocyclophosphazenes have been characterized by elemental analysis and spectroscopic data (MS, NMR, and IR). As expected, two distinct phosphorus environments are observed in the $^{31}P$ NMR spectra of the mono-*tert*-butyl compound (I) and mono-*n*-butyl compound (V). The phosphorus nuclei to which the alkyl group is attached are surprisingly deshielded compared to $\equiv PF_2$ groups. Similar deshielding is observed in the $^{31}P$ NMR spectra of all the *tert*-butyl- and *n*-butyl derivatives prepared in this work. The electron-donating alkyl groups are expected to cause shielding of the phosphorus resonances. A similar reversal of trend has been noted in the NMR spectra of other phosphorus compounds.[26-28] The $^{31}P$ NMR spectra of compounds I and V are complicated by second-order effects. The values of chemical shift and coupling constants have been deduced on the basis of first-order approximations. In the $\equiv PFR$ centers the $^{31}P$ NMR resonances are first order and values for $^2J_{P-P}$ and $^3J_{P-F}$ can be deduced. The $^{19}F$ NMR spectra of monosubstituted compounds I and V indicate three distinct fluorine environments as might be expected.

Disubstituted cyclotriphosphazenes of the type $N_3P_3F_4R_2$ can exist in three isomeric forms: geminal, or 2,2-$N_3P_3F_4R_2$, and nongeminal *cis*-2,4-$N_3P_3F_4R_2$ and *trans*-2,4-$N_3P_3F_4R_2$. The identity of these materials may be established by $^{31}P$ and $^{19}F$ NMR spectroscopy.[11] With this approach the di-*n*-butyl derivative (VI) has been assigned a geminal structure. The $^{31}P$ NMR spectrum of compound VI shows two distinct phosphorus resonances. A small triplet ($J$ = 35.400 Hz) at $\delta$ 48.294 is assigned to the $\equiv P(n\text{-}C_4H_9)_2$ group. The large triplet ($J$ = 917.608 Hz) at $\delta$ 9.753 is assigned to the $\equiv PF_2$ groups. These assignments are further substantiated by the observations of a single fluorine environment in the $^{19}F$ NMR spectrum. While there is no significant structural information contained in the $^1H$ NMR spectrum, the $^{13}C$ data are of value. The significant decrease of $^1J_{P-C}$ and loss of $^2J_{F-C}$ on going from V to VI is supportive of the geminal assignment. The formation of the geminal isomer appears to be the preferred pathway in most organolithium reactions.[4]

The $^1H$ NMR spectrum of the di-*tert*-butyl derivative (II) shows a doublet, with $^3J_{P-H}$ very similar to that observed for the mono-*tert*-butyl derivative (I). These data along with the observation of similr values for $^1J_{P-C}$ and $^2J_{F-C}$ in the $^{13}C$ spectra in compounds I and II suggest a nongeminal configuration for II. The magnitude of $^3J_{P-C}$ is greater than that of $^2J_{P-C}$. Similar observations have been noted in various organophosphorus compounds by McFarlane.[29] The $^{31}P$ NMR spectrum for II shows both $\equiv PF_2$ and $\equiv PFR$ groups, thus confirming the nongeminal assignment. The large triplet ($\delta$ 9.548, $J$ = 903.320 Hz) is assigned to the $\equiv PF_2$ group. The large doublet at $\delta$ 51.270 with a $J$ value of 1021.632 Hz is assigned to the $\equiv PF(t\text{-}C_4H_9)$ centers. The large deshielding of the $\equiv PFR$ center is again noted. The conclusive assignment of structure comes from the $^{19}F$ NMR data. The fluorine atoms of a $\equiv PF_2$ center are inequvalent with respect to R in a cis isomer but are equivalent in a trans isomer. The



cis trans

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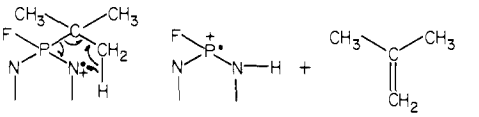
observed $^{19}F$ NMR spectrum of II shows two sets of first-order doublets, thus demonstrating the trans disposition of organic groups and the power of high-field $^{19}F$ NMR for structural work in the study of fluorophosphazenes. There are no observable signals due to the cis isomer.[11] The exclusive formation of the trans isomer represents the first example of a regio- and stereospecific reaction in phosphazene chemistry.

Like the disubstituted derivative (II), the trisubstituted compound, $N_3P_3(t\text{-}C_4H_9)_3F_3$ (III), can have three possible structures: geminal and nongeminal cis and trans. The $^{31}P$ NMR spectrum of compound III shows two distinct phosphorus environments. If compound III were to have a cis structure, then its phosphorus spectrum should be a simple $A_3X_3$ type. Thus a cis structure can be ruled out readily. Since the phosphorus spectrum does not show the presence of $\equiv PR_2$ group, a geminal structure can also be ruled out. Thus, compound III is assigned a trans structure. This conclusion is strongly supported by the $^{19}F$ spectrum for III, which shows two distinct fluorine environments. A cis structure should give rise to a single fluorine environment. The observation of two single doublets in the ratio 2:1 in the $^1H$ NMR spectrum of compound III is in complete agreement with the trans structure proposed.

The argument outlined above can be extended to arrive at the structure of the ethoxy derivative, $N_3P_3(OC_2H_5)(t\text{-}C_4H_9)_2F_3$ (IV). All the NMR spectroscopic data clearly prove a trans structure for compound IV. Therefore, the regio- and stereoselective nature of this process is maintained at the level of trisubstitution. The fact that the same isomer is formed with either the ethoxy or *tert*-butyl reagent as the incoming groups suggests that the stereochemistry is controlled by the substituents on the ring in II.

Infrared spectroscopy is of limited use in structural assignments to organocyclophosphazenes[2,3] and is used for only fingerprinting purposes. All the *tert*-butyl- and *n*-butylfluorocyclotriphosphazenes show characteristic P–N stretching vibrations.

A close look at the mass spectrometry data (Table I[20]) for compounds I–VI reveals several interesting points. In all the *tert*-butyl- and *n*-butylfluorocyclotriphosphazenes, the ions corresponding to the loss of fluorine atoms are weak compared to those corresponding to the loss of the alkyl group(s). This observation indicates that P–C bond cleavage is more facile than P–F bond cleavage. Similar behavior has been observed earlier in arylfluorocyclotriphosphazenes.[30] In the mono-*tert*-butyl compound, I, the molecular ion is the most intense ion, and the most prominent fragment is $N_3P_3F_5H^+$. In compounds II and III the most intense species are $N_3P_3F_4C_4H_{10}^+$ (*m/e* 269) and $N_3P_3F_3C_8H_9^+$ (*m/e* 307), respectively. These species may be thought to be formed by a McLafferty rearrangement of the molecular ion. This process appears to represent a significant fragmentation route for a variety of organophosphazenes.[8,30] The mass spectra of the mono- (V) and disubstituted (VI) *n*-butyl derivatives also exhibit significant alkyl group cleavage.



*m/e* 325 *m/e* 269

We have previously proposed[8] a model for the directive effect in the formation of organophosphazenes in which the electron-releasing ability of the organic function in $N_3P_3F_5R$ results in preferential transfer of nitrogen lone pair electron density to a $\equiv PF_2$ center. The $\equiv PFR$ center is now more susceptible to nulceophilic attack and geminal substitution is favored. This rationale accounts for the structure of the di-*n*-butyl derivative (V) but not those of the *tert*-butyl derivatives, II–IV. The steric requirements of the *tert*-butyl group present a significant barrier to geminal substitution, and consequently a nongeminal process becomes the low-energy pathway. The magnitude of this steric control is demonstrated by the exclusive formation of the trans isomer in the nongeminal series and by the reluctance of the reaction to proceed past the trisubstituted stage.

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**Registry No.** I, 81095-56-9; II, 81095-57-0; III, 81095-58-1; IV, 81095-59-2; V, 650-08-8; VI, 81095-60-5; $N_3P_3F_6$, 15599-91-4; *t*-BuLi, 594-19-4; BuLi, 109-72-8.

**Supplementary Material Available:** A listing of major mass spectral fragments and their relative intensities, Table I (2 pages). Ordering information is given on any current masthead page.

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