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# Deprotonation–Substitution Reactions of Cyclic Methylphenylphosphazenes: Synthesis and Structures of Nongeminal P-Ethyl, P-Phenyl Cyclotriphosphazenes

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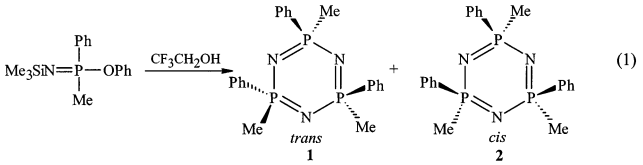
The deprotonation–substitution reactions of both the cis and trans isomers of nongeminally substituted $[(Me)(Ph)P{=}N]_3$ were investigated. Treatment of the trans isomer, **1**, with 3 equiv of *n*-BuLi followed by 3 equiv of MeI gave only nongeminal *trans*-$[(Et)(Ph)P{=}N]_3$, **3**, while the same reaction sequence on *cis*-$[(Me)(Ph)P{=}N]_3$, **2**, gave a mixture of nongeminal di- and trisubstitution products, *cis*-$Et_2MePh_3P_3N_3$, **4**, and *cis*-$Et_3Ph_3P_3N_3$, **5**. These trimers were separated by column chromatography. No changes in the stereochemistry of the rings occurred during these reactions. Compound **4** was also prepared using 2 equiv of the reactants and was then converted to **5** by treatment with a single equivalent of BuLi and MeI. Thermal analysis of the new cyclic trimers indicates that ring-opening polymerization does not occur and that sublimation occurs at ca. 300 °C. The structures of **4** and **5**, obtained by X-ray diffraction, illustrate the basketlike shape of these molecules with an aromatic bowl formed by the phenyl rings on the top rim, while the structure of **3** clearly shows the trans orientation of the substituents. Crystal data for *trans*-$Et_3Ph_3P_3N_3$, **3**, at 20 °C are as follows: $C_{24}H_{30}N_3P_3$ monoclinic, $a = 14.273(2)$ Å, $b = 9.370(2)$ Å, $c = 19.600(3)$ Å, $\beta = 107.16(1)°$, $P2_{1/n}$, $Z = 4$. Crystal data for *cis*-$Et_2MePh_3P_3N_3$, **4**, at 20 °C are as follows: $C_{23}H_{28}N_3P_3$, triclinic, $a = 10.276(2)$ Å, $b = 10.699(2)$ Å, $c = 11.925(2)$ Å, $\alpha = 72.07(2)°$, $\beta = 73.79(1)°$, $\gamma = 85.87(1)°$, $P\bar{1}$, $Z = 2$. Crystal data for *cis*-$Et_3Ph_3P_3N_3$, **5**, at 20 °C are as follows: $C_{24}H_{30}N_3P_3$ monoclinic, $a = 29.488(2)$ Å, $b = 9.8391(1)$ Å, $c = 21.172(2)$ Å, $\beta = 126.30(1)°$, $C2/c$, $Z = 8$.

## Introduction

Phosphazenes, $[RR'PN]_n$, are either cyclic or polymeric compounds consisting of a phosphorus−nitrogen ring or backbone. The types of substituents at phosphorus are widely varied and account for a diverse range of properties for both the cyclic and polymeric systems.[1] Most cyclic phosphazenes have been prepared by nucleophilic substitution of halogen atoms, X, at phosphorus in $[X_2PN]_3$, but this approach generally precludes control of stereochemistry of the substituents on the phosphorus, unless selected sterically bulky and/or electron-releasing nucleophiles are used.[2] We have recently found that high yields of cyclotriphosphazenes with nongeminal methyl and phenyl groups, $[(Me)(Ph)PN]_3$, **1** and **2**, can be prepared from the same *N*-silylphosphoranimines that are used to prepare the polymer analogue poly(methylphenylphosphazene), $[(Me)(Ph)PN]_n$.[3] The process involves simple treatment of a phosphoranimine such as $Me_3SiN{=}P(OPh)(Me)(Ph)$ with $CF_3CH_2OH$ (eq 1). This




(1)

yields both the cis and the trans isomers **1** and **2**, which are readily separated by column chromatography. The cis isomer is particularly interesting since the three phenyl groups on one side of the essentially planar PN ring produce a basketlike shape similar to calixarenes or cyclodextrins.[4,5]

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(1) (a) Wisian-Neilson, P. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: Chichester, England, 1994; Vol. 7, p 3371. (b) Allcock, H. R. *Phosphorus−Nitrogen Compounds*, Academic Press: New York, 1972. (c) Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315.

(2) Lee, S. B.; Song, S.-C.; Jin, J.-I.; Sohn, Y. S. *J. Am. Chem. Soc.* **2000**, *122*, 8315. (b) Brown, D. E.; Allen, C. W. *Inorg. Chem.* **1987**, *26*, 934.

(3) Wisian-Neilson, P.; Johnson, R. S.; Zhang; H.; Jung, J.-H.; Neilson, R. H.; Ji, J.; Watson, W. H. *Inorg. Chem.* **2002**, *41*, 4475.



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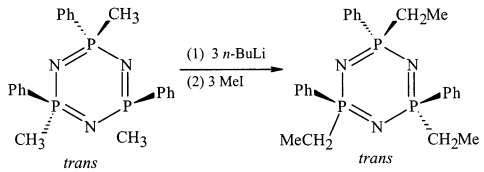
Furthermore, with potentially reactive sites at the methyl and phenyl groups and at the lone pair on nitrogen, both the cis and trans isomers offer access to a large range of new compounds with controlled stereochemistry and reactivity. In this paper we report the first reactions on the methyl groups of cyclic nongeminal methylphenylphosphazene trimers. It is noteworthy that the method reported herein will allow for functionalization at three sites on one side of a rigid, planar PN ring in the case of the cis isomer or on opposite sides for the trans isomer. Such controlled stereochemical functionality will provide access to diverse and novel compounds, e.g., stereospecific transition metal catalysts, shape-specific compounds for molecular recognition, and/or species for stabilization of metal nanoparticles.

## Results and Discussion

**Deprotonation−Substitution Reactions.** The deprotonation of the methyl groups in poly(methylphenylphosphazene), $[(Me)(Ph)PN]_n$, followed by substitution with electrophiles has provided access to a wide range of new phosphazene polymers with a variety of functional groups attached to the polymer by direct P−C linkages.[6] Although deprotonation−substitution reactions have been studied on cyclic phosphazenes with P−C bonded substituents,[7] the lack of availability of the nongeminally substituted compounds has precluded such studies on the cyclic analogues, **1** and **2**, of poly(methylphenylphosphazene). Now that these are readily available and due to the stereochemistry of the isomers, we are exploring the derivative chemistry of these compounds to access new molecules with precise shape and directional functionality.

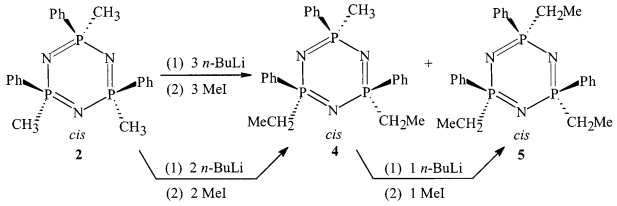
The deprotonation reactions involved treatment of the trans and cis isomers of the cyclic phosphazene, **1** and **2**, with *n*-BuLi in THF at −78 °C. The intermediate phosphazene anion solutions formed from the trans isomer **1** were generally clear, but slightly yellow colored, while deprotonation of the cis isomer **2** formed a white slurry indicative of the lower solubility of the cis anion. When the trans isomer was treated with 3 equiv of *n*-BuLi and then with 3 equiv of the small electrophile MeI, all three methyl groups were readily substituted as demonstrated by $^{31}$P NMR spectroscopy. Better than 70% yields of *trans*-$Et_3Ph_3P_3N_3$, **3**, were obtained after column chromatography (eq 2).




(2)

The new nongeminal cyclic phosphazene **3** was readily characterized by NMR and IR spectroscopy, which clearly demonstrate that only the trans isomer was present and that no ring opening and subsequent rearrangement had occurred in this reaction.[8] The $^{31}$P NMR spectrum consisted of a doublet at 24.7 ppm and triplet at 24.8 ppm with relative intensity of 2:1 as anticipated for the two types of phosphorus environments that result from the trans configuration of the ethyl groups. The phosphorus signal was ca. 5 ppm downfield of that observed for **1**, *trans*-$[(Me)(Ph)P{=}N]_3$,[3] due to increasing the length of the alkyl chain from methyl to ethyl.[9] It is interesting to note that a P−P coupling constant of ca. 4 Hz was observed for **3** while this coupling was not observed for the parent trans compound **1**. The $^1$H and $^{13}$C NMR spectra also clearly support the trans configuration of **3**. In particular, in the $^1$H NMR spectrum, the $CH_3$ resonances of the ethyl groups appeared as two distinct triplets ($J_{HH}$) of doublets ($J_{PH}$) at 1.04 and 0.83 ppm with an intensity of 2:1, while two multiplets were observed at 1.82 and 1.74 ppm for the $PCH_2$ hydrogens in the same 2:1 intensity. A similar 2:1 pattern of multiplets was observed for the phenyl resonances. Although the $^{13}$C NMR spectrum showed two signals each for the P−$CH_2$ (28.45 and 28.54 ppm) carbon atoms, the signals overlapped for the $CH_3$ (5.68 ppm) carbon atoms. The characteristic strong band for the P−N stretching frequency at 1166 $cm^{-1}$ was clearly evident in the IR spectrum.[1b]

By contrast to the trans isomer, sequential treatment of the cis isomer **2** with 3 equiv each of *n*-BuLi and MeI was less straightforward. In this case, both the di- and trisubstituted cyclic phosphazenes, **4** and **5**, were formed in approximately equal proportions (eq 3). This may be due to




(3)

incomplete formation of the intermediate cis phosphazene ion, given the close proximity of these anions in the cis isomer, and to the insolubility of the cis anion. Even when a slight excess of *n*-BuLi (3.5 equiv) was used to compensate for possible traces of moisture and to enhance complete deprotonation, the ratio of **4** to **5** was 20:80. Nonetheless, it is clear that an unusual cis trifunctional organolithium reagent is formed in this process.

Compounds **4** and **5** could be separated by column chromatography and were fully characterized by NMR and IR spectroscopy, elemental analysis, and X-ray diffraction

(4) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, UK, 1989.
(5) Szejtli, J.; Osa, T. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, UK, 1996; Vol. 3: Cyclodextrins.
(6) See, for example: (a) Wisian-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *19*, 2089. (b) Wisian-Neilson, P. *ACS Symp. Ser.* **1994**, *572*, 246. (c) Wisian-Neilson, Zhang, C. *Macromolecules* **1998**, *31*, 9084.
(7) (a) Gallicano, K. D.; Oakley, R. T.; Paddock, N. L.; Sharma, R. D. *Can. J. Chem.* **1981**, *39*, 2654. (b) Calhoun, H. P.; Lindstrom, R. H. Oakley, R. T.; Paddock, N. L.; Todd, S. M. *Chem. Commun.* **1975**, 343.
(8) The $^{31}$P NMR spectrum of the crude mixture contained only the signals for the trans compound **3** and very small signals at 28, 32, and 34 ppm, which were not assigned, but are likely due to complexation of traces of excess MeI to the ring nitrogen atoms.
(9) Heatley, F.; Todd, M. *J. Chem. Soc. A* **1966**, 1152.

as discussed below. In addition, both isomers were prepared separately, as shown in eq 3. When the cis isomer **2** was treated with only 2 equiv of *n*-BuLi and MeI, the major product was the disubstituted product **4**, but the relatively low yield (43%) of this compound indicates that this reaction is complicated by the formation of mono- and trisubstituted products as discussed below. The trisubstituted compound **5** was readily formed in good yield (75%) from the disubstituted compound **4** by treatment with an additional equivalent of *n*-BuLi and MeI (eq 3).

Like the new trans compound **3**, the cis compounds **4** and **5** are white, air-stable compounds that are soluble in most common organic solvents. Each was purified by column chromatography, and crystals were typically grown in ethyl acetate. In addition to characterization by X-ray diffraction (see below), both **4** and **5** showed strong P−N stretching bands at 1162−1166 $cm^{-1}$ in the IR spectra as well as characteristic C−H absorptions around 2900 $cm^{-1}$. The NMR spectra were, however, more informative. First, the $^{31}P$ NMR spectrum for **4** showed two resonances at 20.1 and 24.6 ppm with a relative intensity of 1:2. The signal at 20.1 ppm is in the same region as the phosphorus resonance in the parent cyclic phosphazene, **2**, and clearly corresponds to the $PCH_3$ resonance. In addition to the aromatic resonances, the $^1H$ NMR spectrum for the disubstituted derivative **4** contained one triplet of doublets from the $CH_3$ protons in the ethyl groups at 1.28 ($J_{PH}$ = 19.2 Hz, $J_{HH}$ = 7.5 Hz) and one doublet arising from the methyl group directly bonded to the phosphorus at 1.82 ppm ($J_{PH}$ = 14.1 Hz) with an intensity ratio of 2:1, respectively. The methylene signals appeared at 1.92 ppm as a multiplet. Finally, the proton-decoupled $^{13}C$ NMR spectrum for **4** consisted of a doublet for the methylene carbons of the ethyl group at 28.5 ppm ($J_{PC}$ = 103.4 Hz), a doublet for the unsubstituted methyl group at 23.5 ppm ($J_{PC}$ = 100.2 Hz), and an overlapping doublet of triplets for the $CH_3$ carbon atoms of the ethyl groups at 5.58 ppm ($J_{PC}$ = 2.8, 5.7 Hz), the latter of which results from long-range coupling to phosphorus.

The NMR spectra for the fully derivatized product **5** were much simpler than those for **3** as expected for the symmetric cis configuration. The $^1H$ NMR spectrum exhibited a distinct triplet of doublets at 1.26 ppm ($J_{PH}$ = 19.2 Hz, $J_{HH}$ = 7.5 Hz) arising from the terminal $CH_3$ protons in the ethyl groups, while the methylene protons appeared as a multiplet at 1.92 ppm. As observed for **4**, the $^{13}C$ spectrum of **5** contained an overlapping doublet of triplets at 5.75 ppm ($J_{PC}$ = 2.3, 4.5 Hz) for the $CH_3$ carbon atoms, but a simple triplet of doublets at 28.5 ppm ($J_{PC}$ = 101.5 Hz, $^3J_{PC}$ = 2.7 Hz) was observed for the methylene carbon atoms. The $^{31}P$ NMR spectrum for **5** showed only one signal at 24.5 ppm.

Attempts to deprotonate and substitute only one methyl group on either the cis or trans isomers were unsuccessful. Generally, these reactions gave complex mixtures of unreacted starting material and compounds with varying degrees of substitution. This tendency to deprotonate at more than one site was also observed for $[Me_2PN]_3$ by Paddock et al.[7] The reactions of the trans isomer **1** with either 1 or 2 equiv of the reagents were further complicated by the formation of different mono- and disubstituted stereoisomers as shown by the complex $^{31}P$ NMR spectra. These various isomers were not readily separable by column chromatography and/or recrystallization.

**Table 1.** DSC and TGA Data for Cyclotriphosphazenes **3**, **4**, and **5**

| trimer | DSC $T_m$ (°C) | TGA, % wt loss 250 °C | 300 °C | 350 °C |
|---|---|---|---|---|
| **1** | 97 | 5 | 23 | 92 |
| **2** | 156 | 7 | 32 | 99 |
| **3** | 74 | 2 | 10 | 47 |
| **4** | 95 | 5 | 24 | 96 |
| **5** | 103 | 5 | 14 | 58 |

The use of methyl triflate as an electrophile rather than methyl iodide was also investigated, but only low yields (less than 10%) of the ethyl-substituted cyclics were obtained. These reactions were complicated by the polymerization of THF in the presence of methyl triflate.[10]

**Thermal Properties.** Differential scanning calorimetry (DSC) was used to determine the thermal transitions of the new trimers, **3**, **4**, and **5**. Endothermic peaks corresponding to melting points ($T_m$) were observed at 74, 95, and 103 °C for **3**, **4**, and **5**, respectively (Table 1). These are generally lower than the $T_m$ for **1** and **2** (97 and 157 °C), an effect caused by the longer alkyl chain on the rings. The $T_m$ of the cis isomer is higher than that for the trans isomer. These trends are readily explained by the difference in intermolecular interactions and molecular packing of the ethyl versus methyl substituents and the order in the cis isomer. The DSC data for these new trimers did not show any evidence of transitions indicative of thermal polymerization. The broad endothermic curves observed between 240 and 270 °C can be explained by sublimation or decomposition of **3**, **4**, and **5**.

The thermogravimetric analysis (TGA) data for **3**, **4**, and **5** (Table 1) were all similar, with each showing a one-step weight loss behavior at ca. 250 °C. Compound **4** appears to be slightly less stable than **3** and **5**, presumably due to simple steric effects resulting from two rather than three ethyl substituents on the ring.

**X-ray Structure Studies of Cyclophosphazenes 3, 4, and 5.** The crystal structures of **3**, **4**, and **5** are shown in Figures 1, 2, and 3, respectively. Crystal data are presented in Table 2, and selected bond distances and angles are given in Table 3. Both the cis and trans trisubstituted cyclics **3** and **5** crystallized in the monoclinic system, while the disubstituted compound **4** formed triclinic crystals.

The P(2)−N(1) distance [1.622(2) Å] for **3** is slightly longer than for the rest, but one slightly longer P−N distance was also observed for the trans compound **1**.[3] Otherwise, all the other P−N distances [mean 1.601(11), 1.599(5), 1.603(4) Å] for **3**, **4**, and **5**, respectively] are similar to *cis*-$[(Me)(Ph)P{=}N]_3$,[3] $(Me_2P{=}N)_3$,[11] and $(Ph_2P{=}N)_3$.[12] The

(10) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1990.
(11) Oakley, R. T.; Paddock, N. L.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1977**, *55*, 4206.
(12) Ahmed, F. R.; Singh, P.; Barnes, W. H. *Acta Crystallogr., Sect. B* **1969**, *B25*, 316.

**Table 2.** Crystal Data[a] for **3**, **4**, and **5**

| | **3** | **4** | **5** |
|---|---|---|---|
| formula | $C_{24}H_{30}N_3P_3$ | $C_{23}H_{28}N_3P_3$ | $C_{24}H_{30}N_3P_3$ |
| formula weight | 453.42 | 439.39 | 453.42 |
| space group | $P2_{1/n}$ | $P\bar{1}$ | $C2/c$ |
| $a$, Å | 14.273(2) | 10.276(2) | 29.488(2) |
| $b$, Å | 9.370(2) | 10.699(2) | 9.839(1) |
| $c$, Å | 19.600(3) | 11.925(2) | 21.172(2) |
| α, deg | 90 | 72.07(2) | 90.00 |
| $\beta$, deg | 107.16(1) | 73.79(1) | 126.30(1) |
| $\gamma$, deg | 90 | 85.87(1) | 90.00 |
| Z | 4 | 2 | 8 |
| $V$, Å$^3$ | 2504.6(7) | 1197.7(4) | 4950.6(8) |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.202 | 1.218 | 1.217 |
| $\mu$, mm$^{-1}$ | 0.253 | 0.262 | 0.256 |
| $R_1$ [$I > 2\sigma(I)$][b] | 0.068 | 0.044 | 0.044 |
| $wR_2$ [all data][b] | 0.194 | 0.194 | 0.124 |

[a] Graphite monochromatized Mo Kα radiation, $\lambda = 0.710\ 73$ Å. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

**Table 3.** Selected Bond Lengths [Å] and Angles [deg] for **3**, **4**, and **5**

| | **3** | **4** | **5** |
|---|---|---|---|
| P(1)−N(1) | 1.589(4) | 1.594(2) | 1.601(2) |
| P(1)−N(3) | 1.598(4) | 1.597(2) | 1.604(2) |
| P(2)−N(2) | 1.593(4) | 1.603(2) | 1.598(2) |
| P(2)−N(1) | 1.621(4) | 1.592(2) | 1.606(2) |
| P(3)−N(3) | 1.600(4) | 1.603(2) | 1.598(2) |
| P(3)−N(2) | 1.606(4) | 1.603(2) | 1.608(2) |
| P(1)−C(1) | 1.824(5) | 1.797(3) | 1.802(2) |
| P(1)−C(11) | 1.817(5) | 1.805(3) | 1.809(2) |
| P(2)−C(2) | 1.805(5) | 1.804(3) | 1.800(3) |
| P(2)−C(21) | 1.801(5) | 1.810(3) | 1.814(2) |
| P(3)−C(3) | 1.808(5) | 1.797(2) | 1.792(3) |
| P(3)−C(31) | 1.805(5) | 1.808(3) | 1.813(3) |
| C(1)−C(4) | 1.470(8) | | 1.511(4) |
| C(2)−C(5) | 1.529(6) | 1.463(5) | 1.512(4) |
| C(3)−C(6) | 1.509(8) | 1.520(4) | 1.516(4) |
| C(3)−C(6A) | 1.508(8) | | |
| N(1)−P(1)−N(3) | 117.6(2) | 117.5(1) | 116.5(1) |
| N(2)−P(2)−N(1) | 116.9(2) | 116.9(1) | 117.3(1) |
| N(3)−P(3)−N(2) | 117.4(2) | 117.0(1) | 116.4(1) |
| P(1)−N(1)−P(2) | 121.9(2) | 122.3(1) | 121.8(1) |
| P(2)−N(2)−P(3) | 122.2(2) | 121.1(1) | 120.4(1) |
| P(3)−N(3)−P(1) | 121.9(2) | 122.3(1) | 121.4(1) |
| C(1)−P(1)−C(11) | 102.6(2) | 103.2(1) | 103.4(1) |
| C(2)−P(2)−C(21) | 104.2(2) | 103.8(1) | 103.8(1) |
| C(3)−P(3)−C(31) | 103.3(2) | 103.8(1) | 104.7(1) |

P−aryl distances [mean 1.808(8), 1.808(3), and 1.812(3) Å for **3**, **4**, and **5**, respectively] are close to typical P−C distances in $(Ph_2P{=}N)_3$[11] and $[(Me)(Ph)P{=}N]_3$.[3] While the P−alkyl distances for the cis compounds **4** and **5** are similar to the *cis*-$[(Me)(Ph)P{=}N]_3$ [mean 1.791(2) Å][3] and $(Me_2P{=}N)_3$ [mean 1.805(4) Å],[10] the unique P−alkyl bond in **3** is somewhat longer [1.824(5) Å] presumably due to the steric constraints of the two phenyl groups on the same side of the $P_3N_3$ ring. The mean values of the P−N−P and N−P−N angles in **3** [122.0(1)° and 117.3(3)°], **4** [121.2(7)° and 116.8(5)°], and **5** [121.9(7)° and 117.1(3)°] are typical of those normally encountered in cyclotriphosphazenes.[1b] The exocyclic R−P−R angles in **3**, **4**, and **5**, which average at 103.5(6)°, 103.9(7)°, and 103.6(3)°, respectively, are in good agreement with R−P−R angles of other P−C substituted cyclic phosphazenes and $(Br_2P{=}N)_3$,[12,13] but are larger than

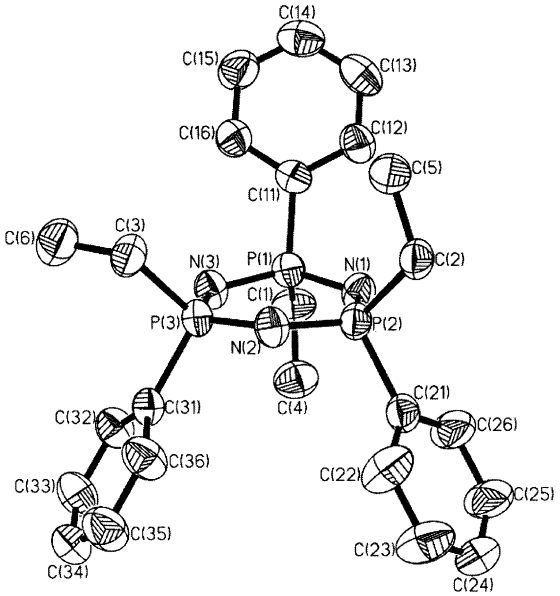



**Figure 1.** Thermal ellipsoid plot of **3**, *trans*-$Et_3Ph_3P_3N_3$ (40% probability ellipsoids for non-hydrogen atoms are shown).

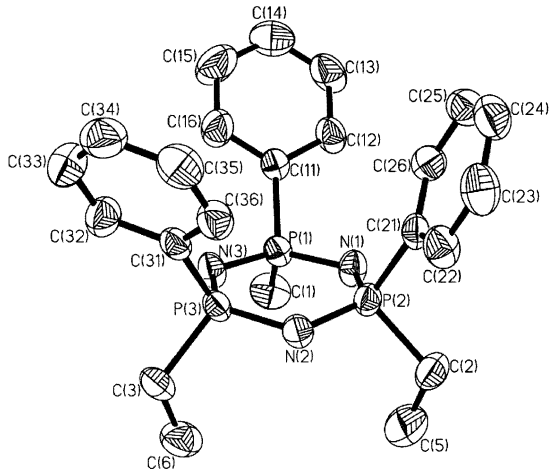



**Figure 2.** Thermal ellipsoid plot of **4**, *cis*-$Et_2MePh_3P_3N_3$ (40% probability ellipsoids for non-hydrogen atoms are shown).

the exocyclic angles of fluorinated, chlorinated, alkoxide, or spirocyclotriphosphazenes.[14] Structure **3** has a trans stereochemistry (Figure 1) with two phenyl groups on the top of the nearly planar $P_3N_3$ ring and one phenyl below the $P_3N_3$ ring. Structures **4** (Figure 2) and **5** (Figure 3) illustrate the basketlike shape of the cis configuration.

The four atoms P(2), P(3), N(1), and N(3) of the $P_3N_3$ ring in compound **3** are essentially coplanar to within 0.002 Å, while the other two atoms, P(1) and N(2), are +0.157 and +0.130 Å out of plane, respectively. Similarly, in the cis compounds **4** and **5**, P(1), P(3), N(1), and N(3) in **4** and P(1), P(2), N(2), and N(3) in **5** are coplanar to within 0.006 and 0.002 Å, respectively. However, the deviate atoms in these compounds are located on the opposite sides of the phosphazene plane, i.e., P(2) +0.083, N(2) −0.160 Å for **4**

(13) (a) Zoer, H.; Koster, D. A.; Wagner, A. J. *Acta Crystallogr., Sect. A* **1969**, *A25*, S107. (b) Giglio, E.; Puliti, R. *Acta Crystallogr.* **1967**, *22*, 304.

(14) (a) Dougill, M. W. *J. Chem. Soc.* **1963**, 3211. (b) Bullen, G. J. *J. Chem. Soc. A* **1971**, 1450. (c) Marsh, W. C.; Trotter, J. *J. Chem. Soc. A* **1971**, 169. (d) Siegel, L. A.; van den Hende, J. H. *J. Chem. Soc. A* **1967**, 817.

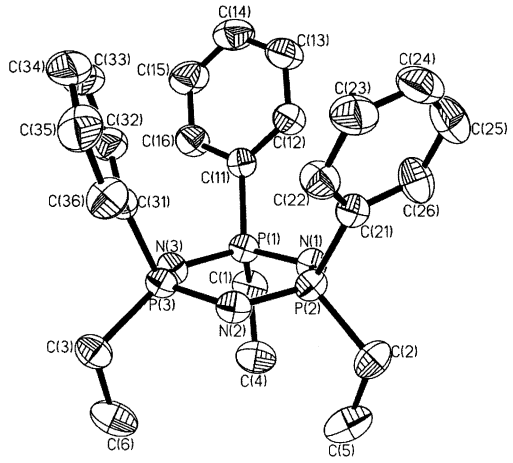



**Figure 3.** Thermal ellipsoid plot of **5**, *cis*-$Et_3Ph_3P_3N_3$ (40% probability ellipsoids for non-hydrogen atoms are shown).

and P(3) −0.296, N(1) +0.175 Å for **5**. Hence, compound **3** has a slight boat shape and **4** and **5** have a chair form to alleviate intramolecular steric repulsions of the cis phenyl groups.[11,12]

The angles between the plane of the cyclophosphazene ring and each of the three phenyl rings are 61.8(2)°, 55.6(2)°, and 55.6(2)° [mean 58.0°] in **3**, 49.1(1)°, 67.6(1)°, and 61.0(1)° [mean 59.7°] in **4**, and 68.5(1)°, 63.4(1)°, and 73.6(1)° [mean 68.5°] in **5**. The phenyl groups opposite the somewhat larger ethyl groups are bent farther from the $P_3N_3$ plane than the phenyl group opposite the smaller methyl group. The angles between the planes of adjacent phenyl rings that are on the same side of the cyclophosphazene ring are 79.2(3)° in **3**, 82.9(1)°, 79.6(1)°, and 76.9(1)° [mean 79.8°] in **4**, and 82.3(1)°, 64.7(1)°, and 70.5(1)° [mean 72.5°] in **5**. Thus, in contrast to the trans compound **3**, the phenyl rings in the cis compounds **4** and **5** have a "propeller" orientation to minimize steric crowding in the solid state.

The synthesis of the new nongeminally substituted ethylphenyl cyclic phosphazene trimers is a significant step toward the preparation of a wide variety of new functionalized molecules with specific stereochemistry, i.e., molecules in which functional groups can be securely anchored to one side of a rigid, planar phosphazene ring or molecules with reactive functionality on opposites sides of the plane. The reactions at the methyl groups in both the cis and trans isomers of $[(Me)(Ph)PN]_3$ reported here demonstrate the utility of the deprotonation−substitution sequence. The use of more complex electrophiles for the synthesis of molecules with novel architecture and reactivity is under investigation.

## Experimental Section

Unless otherwise stated, all reactions were performed in flame-dried or oven-dried glassware by using standard Schlenk techniques. Toluene, benzene, hexanes, and dichloromethane were distilled from $CaH_2$, while THF and diethyl ether were distilled from Na/benzophenone and stored over molecular sieves under nitrogen until they were needed. The *n*-BuLi in hexane, MeI, and methyl trifluoromethanesulfonate were used as received from commercial sources. $[(Ph)(Me)P{=}N]_3$ was prepared by published procedures.[3] All manipulations for the syntheses were done under an atmosphere of dry nitrogen, but cyclic phosphazene products were handled in the atmosphere. NMR spectra were recorded on a SGI/Bruker DRX-400 spectrometer using $CDCl_3$ as a solvent. Positive $^1H$ and $^{13}C$ NMR chemical shifts and $^{31}P$ NMR shifts are downfield from the external references $Me_4Si$ and $H_3PO_4$, respectively. Elemental analyses and IR spectra were obtained on a Carlo Erba Strumentazione CHN Elemental Analyzer 1106 and a Nicolet 560 IR spectrometer, respectively. Thermal data were collected on TA instruments SDT 2960 and DSC 2010.

**X-ray Crystallography.** Crystals of structure **3**, **4**, and **5** were colorless and plate-shaped. The diffraction data of the three structures were collected on a Bruker P4 diffractometer at room temperature. The pertinent crystallographic data are summarized in Table 1. Final unit cell parameters were obtained by a least-squares fit of the angles of ca. 40 accurately centered reflections in the range of $18° < 2\theta < 30°$. Data were recorded using $\omega$ scans. The three structures were solved by direct methods and subsequent difference Fourier syntheses using the SHELXTL-Plus package.[15] All structures were refined anisotropically on $F^2$ (SHELXL97).[16] In the trans structure **3**, disorder appeared for the methyl carbon [C(6)] of one ethyl group and refined in two positions with the site occupancy factors of C(6) 60%, C(6A) 40%. The positions of the disordered atoms were elastically restrained in the final stage of refinement. Hydrogen atoms were constrained with a riding model. Selected bond distances and angles are listed in Table 2. Further details regarding the crystal data and refinement, as well as full tables of bond lengths and angles for each structure reported in this paper, are presented in CIF format in the Supporting Information.

**Synthesis of 3.** In a typical procedure, 1.00 g (2.43 mmol) of *trans*-$[(Me)(Ph)P{=}N]_3$, **1**, was placed in a two-neck, 50 mL round-bottom flask equipped with a magnetic stir bar, a nitrogen inlet adapter, and a rubber septum. Freshly distilled THF (10 mL) was then added to the flask and the mixture was cooled to −78 °C. Then 3 equiv of *n*-BuLi (7.3 mmol, 2.93 mL, 2.5 M in hexane) was added to the solution. The pale yellow solution was stirred for 1.5 h at −78 °C, followed by addition of 3 equiv of MeI (0.45 mL). The mixture was warmed to room temperature and stirred for 12 h. After removal of the volatile components under vacuum, the residue was dissolved in 20 mL of benzene and the mixture was filtered through a glass frit with Celite. The solvent was removed at reduced pressure, giving an oil. This was dissolved in dichloromethane and washed with 1.5 M KOH solution (2 × 30 mL) to remove any HI. The organic layer was separated and solvents were removed using a rotary evaporator. The oily residue was further dried at 65 °C in a vacuum oven for 1 day. The oily product formed a white solid when placed in a refrigerator for 5 days. $^1H$ and $^{31}P$ NMR spectroscopy indicated that only trace amounts of the mono- and disubstituted trans isomers were present. Yield: 0.80 g, 73%. The *trans*-$Et_3Ph_3P_3N_3$, **3**, was further purified by column chromatography [silica gel 60 Å columns (25 × 250 mm) and elution with ethyl acetate/hexanes (1:1)]. 0.75 g, 68%, $R_f$ = 0.70. $^1H$ NMR ($CDCl_3$): $\delta$ 0.83 (td, $P_bCH_2CH_3$, 3 H, $J_{PH}$ = 19.5 Hz, $J_{HH}$ = 7.5 Hz), 1.04 (td, $P_aCH_2CH_3$, 6 H, $J_{PH}$ = 19.3 Hz, $J_{HH}$ = 7.5 Hz), 1.74 (m, $PCH_2Me$, 2 H), 1.82 (m, $PCH_2Me$, 4H), 7.31 (m, 6 H, $C_6H_5$), 7.45 (m, 3 H, $C_6H_5$), 7.80 (m, 4 H, $C_6H_5$), 7.99 (m, 2 H, $C_6H_5$). $^{13}C$ NMR{$^1H$} ($CDCl_3$): $\delta$ 5.68 (overlapping doublet of triplets, $PCH_2CH_3$), 28.45 (d, $P_aCH_2CH_3$, $J_{PC}$ = 99.5

(15) Sheldrick, G. M., *SHELXTL-Plus*; Bruker Analytical X-ray Systems, Inc.: USA, 1990.
(16) Sheldrick, G. M. *SHELX97, Program for Crystal Structure Solution and Refinement*; Institut für Anorganische Chemie: Göttingen, Germany, 1998.

Hz), 28.54 (d, $P_bCH_2CH_3$, $J_{PC}$ = 98.8 Hz), 127.49 (d, $C_6H_5$, $J_{PC}$ = 11.7 Hz), 127.66 (d, $C_6H_5$, $J_{PC}$ = 11.6 Hz), 129.87 (s, $C_6H_5$), 129.96 (d, $C_6H_5$, $J_{PC}$ = 5.8 Hz), 130.06 (d, $C_6H_5$, $J_{PC}$ = 5.0 Hz), 130.00 (s, $C_6H_5$), 138.11 (d, $C_6H_5$, $J_{PC}$ = 120.3 Hz), 138.33 (d, $C_6H_5$, $J_{PC}$ = 120.5 Hz). $^{31}$P NMR{$^1$H} ($CDCl_3$): $\delta$ 24.82 (t, $J_{PP}$ = 3.8 Hz), 24.72 (d, $J_{PP}$ = 3.7 Hz). IR (KBr, neat, cm$^{-1}$): 3073 m, 3055 m, 3009 m, 2969 s, 2934 s, 2906 m, 2877 m, 1961 w, 1896 w, 1590 w, 1479 m, 1457 m, 1437 s, 1403 m, 1276 w, 1263 s, 1166 vs, 1118 s, 1069 m, 1029 s, 997 s, 849 s, 754 s, 719 s, 696 s, 675 s. Anal. Calcd for $C_{24}H_{30}P_3N_3$: C, 63.57, N, 9.27, H, 6.67. Found: C, 64.01, N, 9.06, H, 6.73. mp 74 °C.

**Synthesis of 4 and 5.** Using the same conditions described above for compound **3**, 0.5 g (1.22 mmol) of *cis*-[(Me)(Ph)PN]$_3$, **2**, was treated with *n*-BuLi (3.66 mol) and then MeI (3.66 mol). After workup, the $^1$H and $^{31}$P NMR spectra indicated that the di- and trisubstituted cis isomers were both present. Yield: 0.60 g, 95%. The mixture was purified and the two compounds were separated by column chromatography [silica gel 60 Å columns (25 × 250 mm) and elution with ethyl acetate]. Cis disubstituted **4**, 0.26 g, 43%, $R_f$ = 0.39; cis trisubstituted **5**: 0.30 g, 48%, $R_f$ = 0.67.

**Synthesis of *cis*-$Et_2MePh_3P_3N_3$, 4.** This compound was prepared by a procedure analogous to that used for the preparation of the mixture of **4** and **5** above. However, only 2 equiv of *n*-BuLi and MeI was used in this reaction. The compound was isolated as a white powder in 43% yield using column chromatography. $^1$H NMR ($CDCl_3$): $\delta$ 1.28 (dt, 6 H, $J_{PH}$ = 19.2 Hz, $J_{HH}$ = 7.5 Hz), 1.82 (d, 3 H, $J_{PH}$ = 14.1 Hz), 1.91 (m, 4 H), 7.17 (m, 6 H, $C_6H_5$), 7.25 (m, 3 H, $C_6H_5$), 7.64 (m, 6 H, $C_6H_5$). $^{13}$C NMR{$^1$H} ($CDCl_3$): $\delta$ 5.58 (overlapping doublet of triplets, $PCH_2CH_3$, $J_{PC}$ = 2.9, 5.7 Hz), 23.5 (d, $PCH_3$, $J_{PC}$ = 100.2 Hz), 28.5 (d, $PCH_2CH_3$, $J_{PC}$ = 103.4 Hz), 127.4 (d, $C_6H_5$, $J_{PC}$ = 15.5 Hz), 127.5 (d, $C_6H_5$, $J_{PC}$ = 15.5 Hz), 129.2 (s, $C_6H_5$), 129.3 (s, $C_6H_5$), 129.8 (m, $C_6H_5$), 137.8 (d, $C_6H_5$, $J_{PC}$ = 118.7 Hz), 138.7 (d, $C_6H_5$, $J_{PC}$ = 122 Hz). $^{31}$P NMR{$^1$H} ($CDCl_3$): $\delta$ 20.1, 24.6. IR (KBr, pellet, cm$^{-1}$): 3074 s, 3055 s, 2969 s, 2933 s, 2907 s, 2874 s, 1591 m, 1435 s, 1289 s, 1163 vs, 1122 s, 1028 s, 997 m, 914 s, 890 s, 843 s, 802 s, 732 s, 719 s, 696 s, 676 s, 571 s. Anal. Calcd for $C_{23}H_{28}P_3N_3$: C, 62.87, N, 9.56, H, 6.42. Found: C, 63.35, N, 9.37, H, 6.43. mp 95 °C.

**Synthesis of 5 from 4 (Method 2).** Using procedures described above, compound **4** (0.1 g, 0.23 mmol) in dry THF (5 mL) was sequentially treated with *n*-BuLi (0.23 mmol, 0.091 mL) and then with MeI (0.23 mmol, 0.014 mL) in THF at −78 °C to yield the cis disubstituted (**4**) and trisubstituted (**5**) compounds (75%). Compound **5** was purified by column chromatography [elution with ethyl acetate]. $^1$H NMR ($CDCl_3$): $\delta$ 1.26 (td, $PCH_2CH_3$, 9 H, $J_{PH}$ = 19.2 Hz, $J_{HH}$ = 7.5 Hz), 1.92 (m, $PCH_2CH_3$,6 H), 7.17 (m, 6 H, $C_6H_5$), 7.25 (m, 3 H, $C_6H_5$), 7.64 (m, 6 H, $C_6H_5$). $^{13}$C NMR{$^1$H} ($CDCl_3$): $\delta$ 5.75 (overlapping doublet of triplets, $PCH_2CH_3$, $J_{PC}$ = 2.3, 4.5 Hz), 28.5 (dt, $PCH_2CH_3$, $J_{PC}$ = 101.5 Hz, $^3J_{PC}$ = 2.7 Hz), 127.4 (d, $C_6H_5$, $J_{PC}$ = 15.5 Hz), 129.7 (s, $C_6H_5$), 129.8 (d, $C_6H_5$, $J_{PC}$ = 10.5 Hz), 137.8 (d, $C_6H_5$, $J_{PC}$ = 137.8 Hz). $^{31}$P NMR{$^1$H} ($CDCl_3$): $\delta$ 24.5. IR (KBr, neat, cm$^{-1}$): 3077 m, 3056 m, 3056 m, 2963 s, 2931 s, 2902 s, 2872 s, 1954 m, 1902 m, 1838 m, 1780 m, 1590 s, 1455 s, 1434 s, 1401 m, 1373 m, 1263 s, 1162 s, 1028 s, 997 s, 847 s, 804 s, 750 s, 723 s, 667 s, 577 s. Yield: 75% (0.08 g). Anal. Calcd for $C_{24}H_{30}P_3N_3$: C, 63.57, N, 9.27, H, 6.67. Found: C, 64.01, N, 9.11, H, 6.64. mp 103 °C.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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