collected and identified, and at 930 °C, very small amounts of $(CH_3)_3SiH$, CH_4, and H_2 were found in the off-gas. The remaining light gray solid was heated at 930 °C under a stream of ammonia. The resulting solid is still slightly gray, and the color suggests the presence of residual carbon. A powder X-ray pattern for this material is shown in Figure 2. The pattern is essentially identical with the patterns for the isostructural pure phases of AlN and 2H-SiC, and the diffraction lines are shifted slightly to larger 2θ values from those of pure AlN.[12] Energy-dispersive X-ray analyses unambiguously show the presence of aluminum and silicon in an approximate 5:1 ratio.

(12) The diffraction lines displayed by the mixture have the following values [2θ, deg (hkl)]: 33.816 (100), 36.090 (002), 38.375 (101), 50.110 (102), 60.100 (110), 71.367 (200), 72.124 (112). Close examination of the diffraction patterns does not reveal evidence for the presence of low-temperature α-SiC as might be expected; however, the relatively small amount of silicon in the sample, as evidenced by X-ray analysis, makes identification of a specific SiC phase difficult. Parallel studies of the system $[(CH_3)_3Si]_3Al/PH_3$ reveal formation of AlP and SiC. In this case, the binaries are not isostructural, and the powder X-ray diffractions of the separate components do not severely overlap. We observe SiC with diffuse diffraction lines, and the majority of the SiC is amorphous.

On the basis of these results and the findings from our earlier studies of the pyrolysis of $\{[(CH_3)_3Si]_2AlNH_2\}_2$,[4] it appears that aluminum nitride containing small amounts of SiC is obtained from pyrolysis of these molecular aminosilylaluminum precursors. At this time, additional detailed processing studies of these precursors under a variety of conditions and extensive microstructure characterization of the resulting ceramic products are in progress.

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Registry No. $[(CH_3)_3Si]_3Al\cdot Et_2O$, 75441-10-0; $(CH_3)_3SiH$, 993-07-7; $\{[(CH_3)_3Si]_2Al(NH_2)_2\}Al$, 117251-56-6; CH_4, 74-82-8; AlN, 24304-00-5; SiC, 409-21-2.

Supplementary Material Available: Tables SI-SV, giving a full description of experimental data for the X-ray analysis, anisotropic temperature factors, hydrogen atom positional parameters, and all bond distances and bond angles (7 pages); Table SVI, giving calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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Substitution Reaction of Hexachlorocyclotriphosphazene with Trimethylaluminum

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The reaction of hexachlorocyclotriphosphazene with trimethylaluminum yields the fully substituted hexamethylcyclotriphosphazene and a ring-opened linear phosphazene salt. The substitution pathway that yields the fully substituted cyclic product was determined by monitoring the reactions of several methylchlorocyclotriphosphazenes with trimethylaluminum with the use of gas chromatography and ^{31}P NMR spectroscopy. The reaction was found to proceed via both geminal and nongeminal substitution pathways, depending on the species undergoing substitution. The degree of ring opening that occurred was observed to decrease with increasing methyl substitution of the phosphazene ring. The new products prepared were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, infrared spectroscopy, mass spectrometry, and elemental analysis.

Introduction

The preparation of highly alkylated phosphazenes is an area of concentrated interest. The most thoroughly examined means of synthesis of highly alkylated phosphazenes involves the reaction of halophosphazenes with organometallic reagents.[1] The studies of the reaction of organometallic reagents with chlorocyclotriphosphazenes have produced a wide variety of mono- and dialkylated cyclic chlorotriphosphazenes.[2-7] However, complete replacement of the chlorine atoms of the cyclic trimeric phosphazene ring with alkyl substitutents has not yet been achieved by direct substitution reactions with organometallic reagents. Studies of the reaction of cyclic chlorophosphazenes with various organometallic reagents have been used as models for similar reactions with the poly(dichlorophosphazene) polymer.[8] The reactions of organometallic reagents with poly(dichlorophosphazene) have resulted in substitution, but these reactions are also accompanied by cleavage of the phosphazene chain.[9,10]

The reactions of organometallic reagents with chlorocyclotriphosphazenes are some of the most complex in main-group chemistry. The substitution pathway has not always been well-defined and in many cases involves complex intermediates. The reactions of Grignard reagents with chlorocyclotriphosphazenes are found to yield bicyclophosphazenes, while these reactions in the presence of an organocopper reagent are found to proceed via a metal-halogen-exchange pathway to yield mono- and dialkylated chlorocyclotriphosphazenes.[2,4] Reactions with simple organolithium reagents have primarily been found to result in cleavage of the phosphazene ring.[14,15] Recently, the reaction of methyl-

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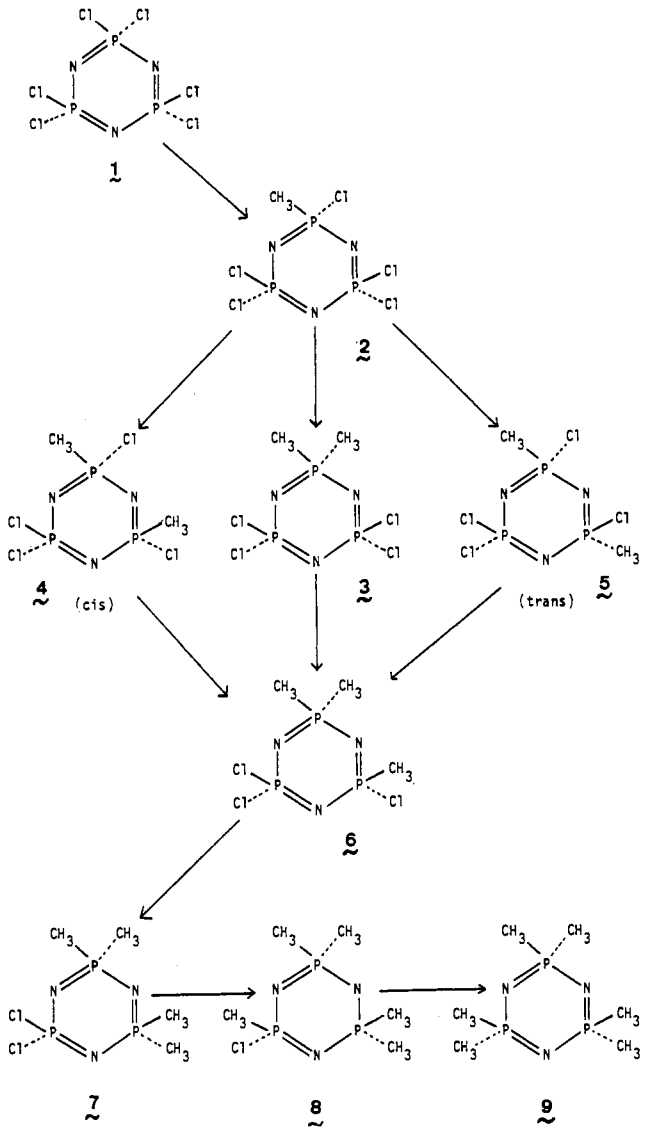
Scheme I



lithium with $N_3P_3Cl_6$ has been found to follow a metal–halogen-exchange pathway yielding substituted products.[16] Higher degrees of substitution have not yet been achieved by these methods. However, higher degrees of substitution have been achieved by the reaction of aminocyclophosphazenes and Grignard reagents followed by removal of the amine functionality.[17]

We have shown, in a preliminary communication, that high degrees of alkylation can be achieved by the reaction of trimethylaluminum and hexachlorocyclotriphosphazene.[18,19] This allowed for the preparation of 1,1,3,3-tetramethyl-5,5-dichlorocyclotriphosphazene (**7**). In this paper a detailed description of the reaction is presented. It was found, by further studies and under forcing conditions, that the reaction yielded the fully substituted hexamethylcyclotriphosphazene (**9**) and a new fully alkylated linear phosphazene salt, heptamethyltriphosphazene hydrochloride (**10**). It was possible to determine, by using gas chromatography, the substitution pathway that yielded the fully substituted hexamethylcyclotriphosphazene (**9**). The substitution reaction exhibited both geminal and nongeminal substitution pathways, with the geminal pathway predominating. The degree of ring opening was observed to decrease with increasing methyl substitution of the phosphazene ring.

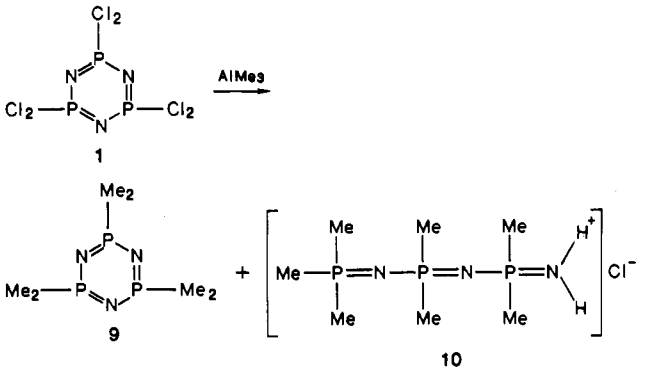
Table I. Reactions of Methylchlorocyclotriphosphazenes with Trimethylaluminum (TMA)

compd	mmol of phosphazene	equiv of TMA (concn)	time, h	% yield of **9**
$N_3P_3Cl_6$ (**1**)	7.2	12.0 (neat)	7.0	43
$N_3P_3Cl_6$ (**1**)	14.4	12.0 (2.0 M)[a]	130.0	44
$N_3P_3(CH_3)Cl_5$ (**2**)	7.7	11.0 (neat)	4.0	48
$N_3P_3(CH_3)Cl_5$ (**2**)	15.3	11.0 (2.0 M)[a]	82.0	52
$N_3P_3(CH_3)_2Cl_4$ (**3**)	8.1	10.0 (neat)	4.0	62
$N_3P_3(CH_3)_2Cl_4$ (**3**)	16.2	10.0 (2.0 M)[a]	80.0	63
$N_3P_3(CH_3)_3Cl_3$ (**6**)	3.5	9.0 (2.0 M)[a]	55.0	72
$N_3P_3(CH_3)_4Cl_2$ (**7**)	3.8	8.0 (2.0 M)[a]	55.0	85

[a] Reactions were run in 2.0 M solutions of TMA in toluene.

Results and Discussion

Overall Reaction. The direct reaction of hexachlorocyclotriphosphazene with trimethylaluminum (TMA) allowed for the preparation of hexamethylcyclotriphosphazene (**9**) in modest yield. This is the first example of complete replacement of the chlorine atoms of compound **1** with alkyl substituents resulting in good



yield. The substitution reaction was accompanied by a ring-opening reaction that yielded a linear phosphazene salt, heptamethyltriphosphazene hydrochloride (**10**), of structure similar to those previously reported.[19,20] The cyclic and linear compounds (**9** and **10**) were found to be the major products of the reaction. The substitution pathway that yielded compound **9** was found to be dependent on the number and positions of the methyl groups present on the phosphazene ring. The substitution pathway that the reaction followed is shown in Scheme I.

Substitution Behavior. The reaction of hexachlorocyclotriphosphazene (**1**) with trimethylaluminum (TMA) proceeded by both geminal and nongeminal substitution pathways. The substitution pathway was determined by monitoring the reaction of TMA with various methylchlorocyclotriphosphazene derivatives with the use of capillary gas chromatography and ^{31}P NMR spectroscopy. Monitoring these reaction with gas chromatography allowed for the synthesis and isolation of 1,1,3-trimethyl-3,5,5-trichlorocyclotriphosphazene (**6**) and 1,1,3,3-tetramethyl-5,5-dichlorocyclotriphosphazene (**7**)[18] in modest yields. The determination of the substitution pathway was accomplished by the examination of the reaction of TMA with hexachlorocyclotriphosphazene (**1**), 1-methyl-1,3,3,5,5-pentachlorocyclotriphosphazene (**2**), 1,1-dimethyl-3,3,5,5-tetrachlorocyclotriphosphazene (**3**), 1,1,3-trimethyl-3,5,5-trichlorocyclotriphosphazene (**6**), and 1,1,3,3-tetramethyl-5,5-dichlorocyclotriphosphazene (**7**). The yield of the fully methylated compound **9** was dependent on the number of methyl groups present on the starting phosphazene. These results are shown in Table I.[21] This

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(21) Each reaction was repeated without monitoring to obtain the reaction yield.

effect was also observed in the study of the reactions of TMA with diphenylalkylchlorophosphazenes.[19]

Preparation and Characterization of Reaction Intermediates. The intermediates observed in the reaction of compound **1** with TMA were prepared for standardization of the gas chromatograph. The preparation and characterization data for compounds **2**[4] and **3**[2] used in this study have been reported elsewhere. Compounds **4** and **5** were not obtained in pure form, but enriched samples were obtained by incomplete reaction of compound **2** with TMA followed by separation on silica gel. Confirmation of the structures of compounds **4** and **5** were obtained by comparison with reported ^1H and ^{31}P NMR spectroscopic data.[17] Compounds **6** and **7** were prepared by incomplete reaction of compound **3** with TMA. Compound **6** was isolated from a mixture of compounds **3**, **6**, and **7** by chromatography on silica gel. Compound **7** was easily separated from a mixture with compound **9**, and characterization data for compounds **7** and **9** are reported elsewhere.[18]

The new cyclic phosphazene, compound **6**, was characterized by a combination of ^1H, ^{13}C, and ^{31}P NMR spectroscopy, infrared spectroscopy, and mass spectrometry. The infrared spectrum for compound **6** consisted of two bands for the P=N stretching vibration found at 1165 and 1202 cm^{-1} and two bands for the CH_3 stretch at 2910 and 2980 cm^{-1}. The mass spectrum gave the molecular ion at m/z 285.

The ^1H NMR spectrum of compound **6** consisted of three separate resonances. The resonance for the methyl group of the PCH_3Cl unit was observed at 2.04 ppm (J_{PCH} = 17.5 Hz, J_{PNPCH} = 2.0 Hz). The resonance of the protons of the methyl group of the $P(CH_3)_2$ unit that is cis to the methyl group of the PCH_3Cl unit was found at 1.62 ppm (J_{PCH} = 14.4 Hz). The resonance of the protons of the methyl group of the $P(CH_3)_2$ unit that is trans to the methyl group of PCH_3Cl was found at 1.70 ppm (J_{PCH} = 14.2 Hz).

The proton-decoupled ^{13}C NMR spectrum consisted of three separate resonances. The resonance for the carbon of the methyl group of PCH_3Cl was found at 26.6 ppm (J_{PC} = 135.0 Hz, J_{PNPC} = 5.6 Hz). The resonances of the carbon atoms of the $P(CH_3)_2$ unit could not be unambigously assigned and were found as a overlapping set of resonances centered at 20.9 ppm (J_{PC} = 91.4 Hz).

The proton-decoupled ^{31}P NMR spectrum for compound **6** consisted of three resonances. The resonance for the phosphorus atom of the $P(CH_3)_2$ unit was found at 35.7 ppm (J_{PNP} < 2.0 Hz). The resonance for the phosphorus atom of the PCH_3Cl unit was found at 39.4 ppm (J_{PNP} < 2.0 Hz). The resonance for the phosphorus atom of the PCl_2 unit was found at 19.7 ppm (J_{PNP} < 2.0 Hz). These assignments were confirmed by examination of the proton-coupled spectrum.

The proton decoupled ^{31}P NMR spectrum of the linear species, compound **10**, in $CDCl_3$ consisted of three signals. The resonance for the phosphorus atom of $P(CH_3)_3$ was observed at 26.4 ppm (J_{PNP} = 7.2 Hz) as a doublet. The phosphorus atom of the central $P(CH_3)_2$ unit was observed at 17.8 ppm (J_{PNP} = 7.2 Hz, J_{PNP} = 8.8 Hz) as a multiplet. The resonance for the phosphorus atom of the $P(CH_3)_2NH_2$ group was observed at 31.8 ppm (J_{PNP} = 8.8 Hz) as a doublet. The assignment of the chemical shift values was confirmed by examination of the proton-coupled ^{31}P NMR spectrum. The infrared spectrum of this compound consisted of a broad strong band for the phosphazene P=N band at 1260 cm^{-1}. The terminal NH_2 stretch was observed as two bands at 3140 and 3190 cm^{-1}. The presence of the chloride ion was confirmed by addition of an ether solution of $AgNO_3$ to a methylene chloride solution of compound **10**, which precipitated AgCl.

Reaction of Compound 1 with TMA. The reaction of compound **1** with TMA was carried out in neat reagent and in 2.0 M solutions of TMA in toluene.[22] In both experiments the yield of compound **9** was approximately 40% (Table I). Quantitatively monitoring the reactions of compound **1** with gas chromatography proved to be difficult due to the poor response of compound **1** with the flame ionization detector. In these experiments gas chromatography was used to qualitatively identify the intermediates as the reactions proceeded. In each case all of the intermediates displayed in Scheme I were shown to be present at some time in the reaction. There were no unidentified components present. This was confirmed by examination of the ^{31}P NMR spectra of the samples.

It was observed that both geminal and nongeminal substitution pathways occur in the early stages of the replacement of the chlorine atoms on the phosphazene ring (Scheme I). The initial reaction of TMA with compound **1** produced the monomethylated intermediate, compound **2**. This molecule was then substituted both geminally and nongeminally to yield the disubstituted compound **3** nd the cis- and trans-disubstituted compounds **4** and **5**. This was confirmed by the analysis of the reactions of compound **2** with TMA under two different sets of conditions. The three dimethylated intermediates, compounds **3–5**, then reacted to yield the trimethylated compound **6**. From this point the reaction was found to proceed solely along a geminal substitution pathway. This was confirmed by reaction of compounds **6** and **7** with TMA.

Reaction of Compound 2 with TMA. The reaction of compound **2** with 11.0 equiv of neat TMA at 130 °C was monitored by gas chromatography, and it was observed that initially compound **2** reacted to give the three different compounds, **3–5**, shown in Scheme I. The plot of the percent composition of the products present versus time for this reaction is shown in Figure 1 (supplementary material) and these results are tabulated in Table II (supplementary material).[23] It was observed that under these reaction conditions geminal substitution of compound **2** was favored. The geminal- and nongeminal-disubstituted compounds **3–5** then reacted with TMA to yield the trimethylated compound **6**. This compound when formed substituted geminally with the TMA to yield the tetramethylated compound **7**. The reaction of compound **6** with TMA was rapid, and only a small amount was detected early in the reaction. The further substitution of compound **7** was found to be more difficult. Compound **7** apparently reacted slowly to give intermediate **8**, which substituted rapidly to yield compound **9**. Only compounds **7** and **9** were detected in the latter stages of the reaction. The presence of compound **8** was not confirmed in any of the reactions studied, indicating that, once formed, it reacted very rapidly to yield compound **9** (48%, Table I).

The reaction of compound **2** under less forcing conditions yielded slightly different results. This experiment was carried out at 110 °C with 11.0 equiv of TMA as a 2.0 M solution in toluene. The plot of these results (Table III (supplementary material)) versus time is shown in Figure 2. Again, the reaction was observed to proceed via both the geminal and nongeminal substitution pathways. However, in this case the trans nongeminal product, compound **5**, was slightly favored while compounds **3** and **4** were found to be present in roughly equivalent amounts early in the reaction, as shown in Figure 2. The trimethylated compound **6** was detected in roughly the same percent composition as found for compounds **3** and **4**. Again, compound **7** was found to reach a high percent composition and disappeared slowly as the reaction proceeded to completion. Compound **9** was obtained in 52% yield (Table I) at the completion of the reaction.

The reaction of the dimethylated compounds **3–5** proceeded by a geminal substitution pathway. This was confirmed by the reactions of compounds **3**, **6**, and **7** with TMA. It was not possible in our laboratories to prepare significant quantities of compounds **4** and **5** for study. However, from the results obtained in the reactions of TMA with compound **2**, it was apparent that there were no other substitution products present in the reaction. This does not rule out the possibility of trace amounts of other substituted products being present that could not be detected by the techniques used.

Reaction of Compound 3 with TMA. The reaction of compound **3** with TMA was examined under two different sets of conditions.

(22) A 6.0-equiv excess of TMA was used in each study to ensure completion of the reactions in a reasonable amount of time.

(23) The values given for the present composition represent the amount of each component present with respect to the total amount of cyclic products obtained.

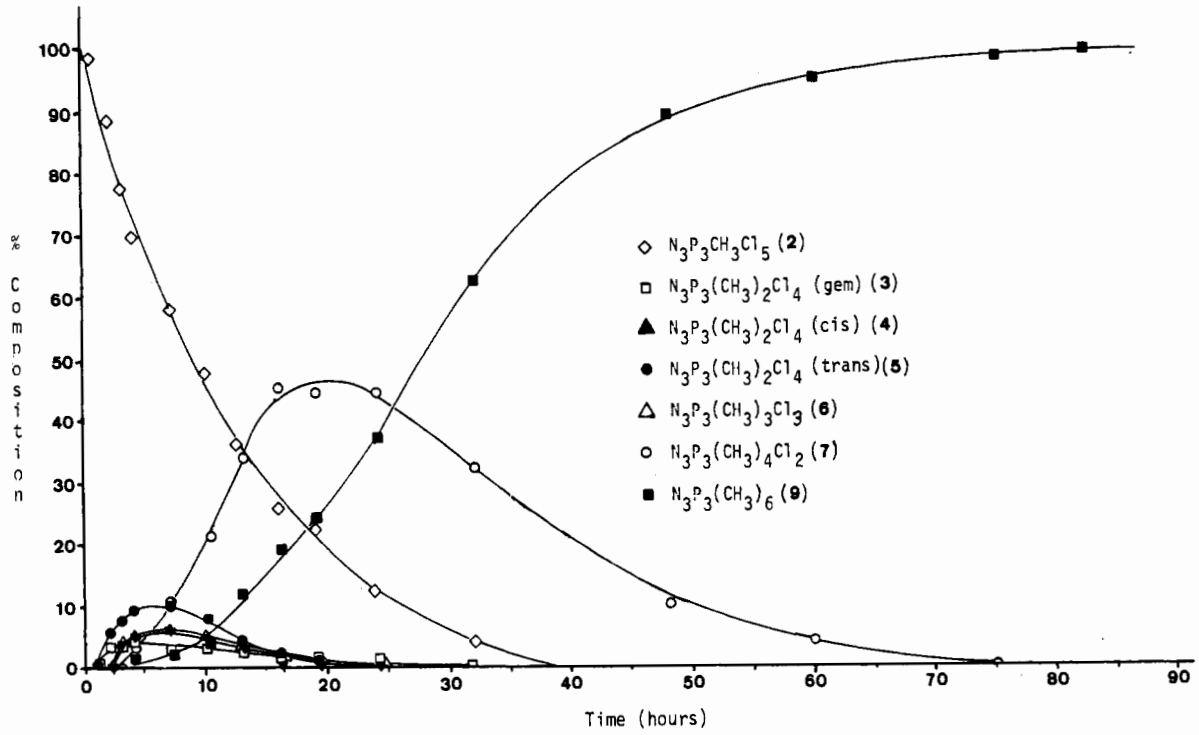

Figure 2. Plots of the percent composition of products versus time for the reaction of compound **2** with 11.0 equiv of TMA (2.0 M in toluene) at 110 °C.

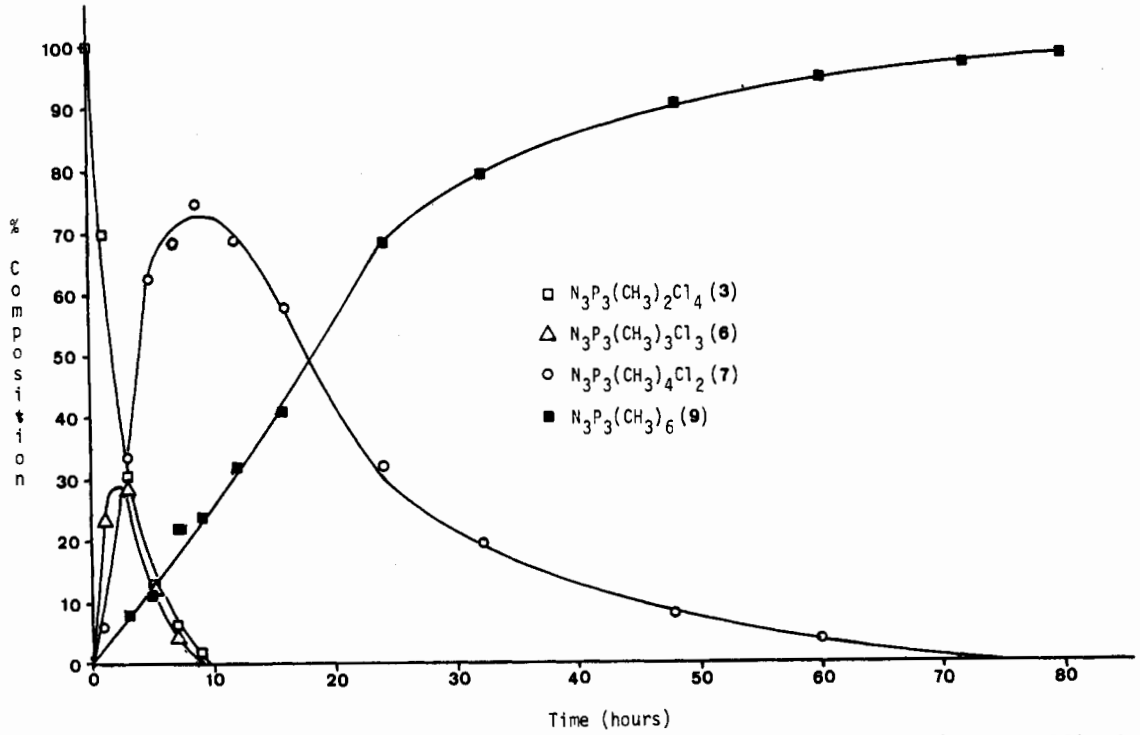

Figure 4. Plots of the percent composition of products versus time for the reaction of compound **3** with 10.0 equiv of TMA (2.0 M in toluene) at 110 °C.

The reaction of compound **3** with 10.0 equiv of neat TMA at 130 °C was rapid and complete in 4 h. The plot of the percent composition of the intermediates present versus the reaction time is shown in Figure 3 and Table IV (supplementary material). The reaction of compound **3** with TMA was observed to proceed solely by a geminal substitution pathway (Scheme I). Again only compounds **7** and **9** were observed in the latter stages of the reaction. Compound **9** was obtained in 62% yield (Table I).

The reaction of compound **3** with 10.0 equiv of TMA as a 2.0 M solution in toluene at 110 °C allowed for the optimization of the preparation of compounds **6** and **7**. The plot of these results (Table V (supplementary material)) is shown in Figure 4. The trimethylated compound **6** reached a maximum percent composition (28%) at 3.0 h. Stopping the reaction at this point allowed for the isolation of compound **6**. At 9.0 h compound **7** reached maximum percent composition, and halting the reaction at this point allowed for the isolation of good yields of compound **7**. Again, there was no evidence of other substitution products being present. At the end of the reaction the fully substituted compound **9** was obtained in 63% yield (Table I).

Reaction of Compound 6 with TMA. The reaction of compound **6** with 9.0 equiv of TMA as a 2.0 M solution in toluene at 110 °C was performed and monitored by gas chromatography. The plot of the percent composition versus the reaction time is shown

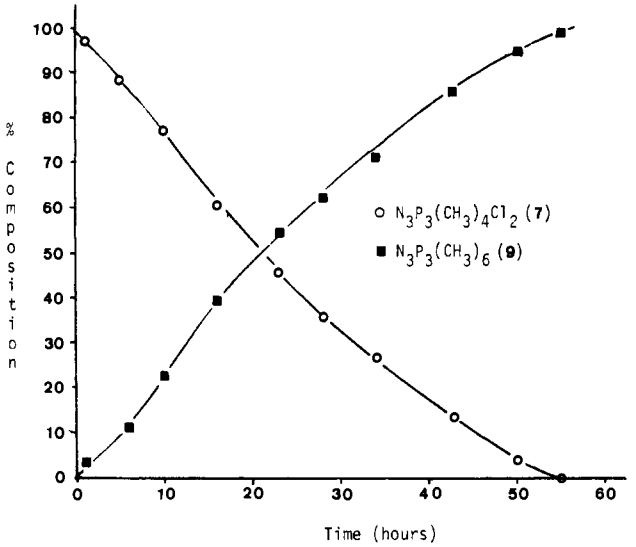

Figure 5. Plots of the percent composition of products versus time for the reaction of compound **6** with 9.0 equiv of TMA (2.0 M in toluene) at 110 °C.

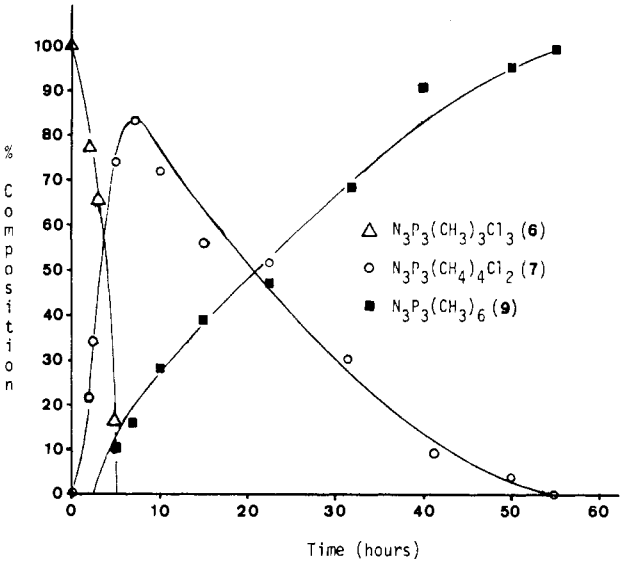

Figure 6. Plots of the percent composition of products versus time for the reaction of compound **7** with 8.0 equiv of TMA (2.0 M in toluene) at 110 °C.

in Figure 5 (Table VI (supplementary material)). Compound **6** was observed to react rapidly with the TMA and was not detectable after 5.0 h. This gave compound **7**, which reached a high-percent composition at 7.0 h (84%). Reaction of compound **7** was again slow, and the reaction reached completion in 60 h. The final product, compound **9**, was obtained in 72% yield (Table I).

Reaction of Compound 7 with TMA. The reaction of compound **7** with 8.0 equiv of TMA as a 2.0 M solution of TMA in toluene at 110 °C was monitored by gas chromatography. The plot of the percent composition versus the reaction time is shown in Figure 6 (Table VII (supplementary material)). This experiment demonstrated that compound **7** was the least reactive of the methylated phosphazenes studied. Again, there was no indication of the presence of compound **8** in the reaction mixture, suggesting that, once formed, this intermediate reacted very rapidly with the TMA to give compound **9**. The reaction was complete in 60 h, and 85% yield (Table I) of compound **9** was obtained.

Ring-Opening Reaction. We have previously reported the ring-opening reaction of diphenylchlorocyclotriphosphazene. This reaction yielded both the fully substituted species and a linear phosphazene salt.[16] Therefore the possibility of this process occurring in the reaction studied here was examined. In this experiment the hexachlorocyclotriphosphazene was reacted with TMA, and then a nonaqueous reaction workup was employed. The material obtained yielded the fully substituted compound **9** and the new linear phosphazene salt (**10**).

The results obtained show that reaction of hexachlorocyclotriphosphazene (**1**) with TMA yields both the fully substituted cyclic and linear compounds. The degree of ring opening that occurred was found to decrease with increasing methyl substitution. The substitution reaction of hexachlorocyclotriphosphazene proceeds via both geminal and nongeminal substitution pathways. The reactions of compounds **1** and **2** were found to proceed via both substitution pathways, while the reactions of compounds **3**, **6**, and **7** proceeded solely by a geminal substitution pathway. The yield of the fully substituted phosphazene, compound **9**, increased with increasing methyl substitution of the phosphazene starting material.

Experimental Section

Materials. All reactions were carried out under inert nitrogen atmosphere by using Schlenk techniques. Subsequent reaction workups were carried out in a well-ventilated fume hood. The hexachlorocyclotriphosphazene used was supplied by Shin Nisso Kako Co. and was used as obtained. The mono- and dimethylchlorocyclotriphosphazenes (compounds **2** and **3**) were prepared by reported methods.[2,4] The trimethylaluminum (TMA) was obtained from the Ethyl Corp. as a neat liquid and used as obtained. It should be noted that great care should be employed when neat liquid TMA is used because of the risk of spontaneous combustion in the atmosphere. The trimethylaluminum reagent was handled via syringe by using Schlenk techniques. Toluene was distilled from sodium metal before use.

Analytical Equipment. The ^{31}P NMR spectra were obtained in $CDCl_3$ on a 200-MHz Bruker NMR spectrometer operating at 81.02 MHz with a capillary of 85% phosphoric acid as the external standard. The ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a 270-MHz Bruker FT NMR spectrometer operating at 270.02 and 67.93 MHz with tetramethylsilane as the internal reference. The infrared spectra were recorded on a Nicolet MX1 FTIR spectrometer. The mass spectral data for the molecules discussed are reported elsewhere.[17,24]

The gas chromatographic studies were carried out by using a Hewlett-Packard 5790A Series gas chromatograph equipped with a flame ionization detector and a 3390A reporting integrator. The capillary column used was made of fused silica coated with cross-linked dimethylsilicone. Sampling was done isothermally at 125 °C, and the injector and detector temperatures were maintained at 200 and 350 °C. The column flow was 1.0 mL/min. The calibration curves were prepared for each component. It was found that the detector response was a linear function of the number of methyl groups on the phosphazene ring. Since compounds **4** and **5** were not readily available, the calibration curve used for compound **3** was used to determine the percent composition of these intermediates present.

Preparation of $N_3P_3(CH_3)_6$ (9). Neat TMA (2.8 mL, 29 mmol) was added to $N_3P_3Cl_6$ (**1**) (1.00 g, 3.0 mmol) carefully via syringe. The reaction mixture was then heated at 130 °C in a thermoregulated oil bath for 8 h. The homogeneous mixture was cooled to room temperature, and dry methylene chloride (20 mL) was added via syringe. The reaction mixture was then opened to the atmosphere and transferred to a beaker (300 mL) containing methylene chloride (150 mL) cooled to 0 °C. The cooled solution was then poured carefully into an aqueous solution of NaOH (1.0 M, 125 mL) at 0 °C. The aqueous layer was then saturated with NaCl and extracted with methylene chloride (100 mL). The combined extracts were dried over anhydrous magnesium sulfate and filtered. Removal of the solvent yielded a pale white powder (0.33 g). Sublimation (100 °C, 0.03 mmHg) yielded pure $N_3P_3(CH_3)_6$ (**9**) (0.28 g, 43%; mp 193–196 °C (lit mp, 195–196 °C[25])).

Preparation of $N_3P_3(CH_3)_3Cl_3$ (6). Neat TMA (6.4 mL, 66 mmol) was added carefully via syringe to a solution of $N_3P_3(CH_3)_2Cl_4$ (**3**) (2.0 g, 6.5 mmol) in toluene (26.0 mL). The reaction mixture was then heated at reflux for 1.5 h, cooled to 0 °C in an ice bath, opened to the atmosphere, and diluted into a beaker (500 mL) containing methylene chloride (200 mL, 0 °C). The cooled solution was then poured carefully into a beaker (1.0 L) containing an aqueous solution of NaOH (1.0 M, 200 mL) cooled to 0 °C. The mixture was transferred to a separatory funnel and shaken vigorously. The methylene chloride layer was separated, and the aqueous layer was extracted with additional methylene

(24) Harris, P. J.; Jackson, L. A. *Org. Mass Spectrom.* **1986**, *21*, 377.
(25) Searle, H. T.; Dyson, J.; Ranganathan, T. N.; Paddock, N. L. *J. Chem. Soc., Dalton Trans.* **1975**, 203.

chloride (200 mL). The combined extracts were dried with anhydrous magnesium sulfate, and the solvent was removed to yield a white powder (1.66 g). The crude product, a mixture of $N_3P_3(CH_3)_2Cl_4$ (**3**), $N_3P_3(CH_3)_3Cl_3$ (**6**), and $N_3P_3(CH_3)_4Cl_2$ (**7**), was separated by chromatography on silica gel. $N_3P_3(CH_3)_2Cl_4$ (**3**) was eluted first with a 90/10 mixture of hexane/methylene chloride. The desired $N_3P_3(CH_3)_3Cl_3$ (**6**) was then eluted with methylene chloride. Elution with ethyl acetate gave $N_3P_3(CH_3)_4Cl_2$ (**7**). Sublimation (100 °C, 0.03 mmHg) of the resulting material yielded the pure compound **9** (0.45 g, 24%; mp 189.5–192.0 °C).[26]

Preparation of $N_3P_3(CH3)_4Cl_2$ (7). Neat TMA (6.4 mL, 66.0 mmol) was added carefully to a solution of $N_3P_3(CH_3)_2Cl_4$ (**3**) (2.0 g, 6.5 mmol) in toluene (26.0 mL). The reaction mixture was heated at reflux for 12 h and then cooled to 0 °C. The mixture was then treated as described above for the preparation of $N_3P_3(CH_3)_3Cl_3$ (**6**). Extraction of the aqueous base and drying with anhydrous magnesium sulfate followed by removal of the solvent yielded the crude product. Sublimation (100 °C, 0.03 mmHg) of the crude material yielded the pure compound (0.72 g, 42%; mp 240–242 **C**). The remaining aqueous layer was saturated with NaCl and extracted with methylene chloride (2 × 200 mL). The combined extracts were dried with anhydrous magnesium sulfate, and removal of the solvent yielded $N_3P_3(CH_3)_6$ (**9**) (0.28 g, 19%).

Attempted Isolation of *cis*- and *trans*-$N_3P_3(CH_3)_2Cl_4$ (4 and 5). The incomplete reaction of $N_3P_3(CH_3)Cl_5$ (**2**) with 11.0 equiv of TMA as a 2.0 M solution with toluene for 6 h yielded a mixture of products. Column chromatography on silica using hexane as the elutant allowed for the removal of $N_3P_3(CH_3)Cl_5$ (**2**). A solution of hexane/methylene chloride (90/10) eluted a mixture of the three dimethylated products. Further chromatography on silica gel using hexane allowed for the isolation of nearly pure compound **5**. Compound **4** was obtained as a mixture with compound **3**. These materials were used to confirm the presence of intermediates **4** and **5** in the reactions studied.

GC Analysis of Reactions. The gas chromatographic study of the reaction of TMA with the various methylated phosphazenes was accomplished according to the following general procedure. In reactions with neat TMA, the phosphazene was placed in a small round-bottom flask with a reflux condenser attached, the flask was sealed with a serum stopper, and the phosphazene was purged with nitrogen. The appropriate amount of TMA was added via syringe, and the reaction mixture was stirred and heated to 130 °C in a thermoregulated oil bath. When toluene was used as the solvent, the phosphazene was dissolved and then TMA was added via syringe. The reaction mixture was heated to reflux.

Aliquots were then taken with respect to time and diluted into methylene chloride. The sample solution was added slowly to an aqueous solution of 1.0 M NaOH. The aqueous solution was saturated with NaCl and extracted with methylene chloride. The organic phases were combined and dried over anhydrous magnesium sulfate and filtered. Removal of the solvent yielded the sample, which was analyzed by gas chromatography.

Isolation of the Linear Phosphazene (10). $N_3P_3Cl_6$ (**1**) (1.00 g, 2.8 mmol) was placed in a reaction flask, and the flask was sealed with a serum stopper. The vessel was flushed with dry nitrogen via inlet and outlet stainless steel needles. Neat TMA (3.3 mL, 34.2 mmol) was added carefully via syringe. A reflux condenser was attached, and the reaction mixture was heated to 130 °C for 12 h. At the end of this time the reaction mixture was cooled to room temperature and diluted with methylene chloride (25 mL). The solution was then stirred rapidly, and dry methanol was added slowly to destroy the remaining TMA. After precipitation of the salts, the mixture was decanted and the remaining material was extracted with methylene chloride (2 × 25 mL). The solvent was removed from the combined extracts to yield an oil (0.73 g). This material was dissolved in methylene chloride; addition of hexane precipitated an oil. The mother liquor was removed from the oil and the solvent removed to yield a pale yelllow material (0.35 g). This material was sublimed to yield hexamethylcyclotriphosphazene (**9**) (0.25 g, 40%). The remaining oil (0.38 g, 47%), consisted of mostly (<90%) the linear phosphazene (**10**).[27]

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Registry No. **1**, 940-71-6; **2**, 71332-21-3; **3**, 6204-32-6; **4**, 94235-14-0; **5**, 94235-15-1; **6**, 107651-59-2; **7**, 86748-46-1; **9**, 6607-30-3; **10**, 117146-21-1; $AlMe_3$, 75-24-1.

Supplementary Material Available: Tables II–VII, listing percent composition of reaction products, and Figures 1 and 3, showing plots of percent composition of reaction products versus time (8 pages). Ordering information is given on any current masthead page.

(26) The present composition given for compound **10** was estimated from the proton-decoupled ^{31}P NMR spectrum of the mixture.

(27) Anal. Calcd for $N_3P_3(CH_3)_3Cl_3$ (**6**): C, 12.58; H, 3.17; N, 14.67. Found: C, 12.74; H, 3.22; N, 14.49.