and added slowly to the reaction mixture via syringe. The ice bath was removed, and the solution was allowed to warm to room temperature. The ^{31}P NMR spectrum of the solution showed that two phosphorus compounds were present (**8** and **10**). The products were separated by vacuum distillation. Compound **8** was obtained as the major product with a ^{31}P NMR signal at 32.8 ppm. It was characterized by NMR spectroscopy and elemental analysis.

Preparation of 10. The silane $(CH_2SiMe_2Cl)_2$ (3.48 g, 16.2 mmol) was dissolved in CH_2Cl_2 (40 mL). The solution was cooled to 0 °C, and 1 equiv of the phosphoranimine **1** was added slowly via syringe. The solution was allowed to warm to room temperature. Solvent was removed and the product **10**, formed together with **8**, was purified by distillation. Compound **10**, an unstable, reactive liquid, was difficult to obtain in high purity. Therefore, **10** was used to synthesize the derivative **11**.

Preparation of 11. A fresh sample of compound **10** (3.5 g, 10 mmol) was dissolved in Et_2O (25 mL) in a flask equipped with a N_2 inlet, septum, and stirring bar. The solution of **10** was cooled to −78 °C, and 1 equiv of MeLi (7.1 mL, 1.4 M solution in Et_2O) was added slowly via syringe. The reaction mixture was stirred while the cold bath was allowed to slowly warm to room temperature. Hexane (25 mL) was added to help precipitate the solids, the mixture was filtered, and the solvent was removed. Vacuum distillation afforded **11**, as a colorless liquid that was characterized by NMR spectroscopy and elemental analysis.

Preparation of the Siloxane Derivatives 12–15. In a typical experiment, compound **1** (4.5 g, 18.2 mmol) was dissolved in CH_2Cl_2 (35–40 mL), in a flask equipped with a magnetic stirrer, a nitrogen inlet, and a rubber septum. The solution of **1** was cooled to 0 °C, and the corresponding dichlorosiloxane (9.1 mmol) was added slowly via syringe. The mixture was stirred for 1 h and then allowed to warm to room temperature. The solvent and Me_3SiCl were removed under reduced pressure. The remaining product was purified by distillation.

Preparation of 16. Although compound **16** could be prepared by the above procedure, a higher yield was obtained when **1** was added to 1 equiv of dichlorotetramethyldisiloxane dissolved in CH_2Cl_2. Solvent removal and distillation gave **16** as a colorless, reactive liquid.

Preparation of 17. In a flask equipped with a magnetic stirrer, N_2 inlet, and septum, **16** (1.5 g, 4.8 mmol) was dissolved in Et_2O (10 mL) and cooled to −78 °C. One equivalent of MeLi (Et_2O solution) was added via syringe. The solution was stirred at −78 °C for 1 h and then allowed to warm slowly to room temperature. Hexane (25 mL) was added, the mixture was filtered, and the solvent was removed under reduced pressure. Compound **17** was isolated by vacuum distillation as a colorless liquid.

Preparation of 18. In the same manner, **16** (8.2 mmol) was treated with 1 equiv of *n*-BuLi to give **18** as a colorless, distillable liquid.

Thermolysis of 15. A sample of **15** (2.2 g) was transferred to a heavy-walled glass ampule and degassed by the freeze–pump–thaw method. The ampule was sealed under vacuum and then heated at 185 °C for 3 days. The ampule then contained a solid product and a clear liquid. No volatile products were obtained when the contents of the ampule were subjected to a high vacuum. The clear liquid was removed with a pipet, and the remaining solid was identified as $(Me_2PN)_n$ by ^{31}P NMR spectroscopy. The clear liquid was purified by distillation and was identified as **19** by NMR spectroscopy and elemental analysis.

Cothermolysis of 13 with 1. Compounds **1** (3.2 g, 13 mmol) and **13** (1.5 g, 2.6 mmol) were transferred into a heavy-walled glass ampule, degassed, and sealed as described above. The ampule was heated at 185 °C for 4 days and then opened and attached to the vacuum line. The volatile byproduct was condensed into a cooled flask (−196 °C) and identified as $CF_3CH_2OSiMe_3$ by ^1H NMR spectroscopy. The nonvolatile products of the thermolysis were dissolved in CH_2Cl_2. The ^{31}P NMR spectrum of this mixture showed peaks at 8.9, 16.9, and 25.0 ppm. Addition of hexane caused the precipitation of the phosphazenes $(Me_2PN)_n$ (^{31}P NMR 7.0 ppm) and $(Me_2PN)_4$ (^{31}P NMR 25.7 ppm). Proton NMR analysis of the solution indicated the presence of the siloxane byproduct **19a**.

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(Vinyloxy)chlorocyclotetraphosphazenes. The Use of Two-Dimensional ^{31}P NMR Spectroscopy in Phosphazene Chemistry†

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The reactions of the lithium enolate of acetaldehyde, $LiOCHCH_2$, with octachlorocyclotetraphosphazene, $N_4P_4Cl_8$, led to the series of (vinyloxy)chlorocyclotetraphosphazenes $N_4P_4Cl_{8-n}(OCH{=}CH_2)_n$ (n = 1, 2). The qualitative and quantitative analysis of the ^{31}P NMR spectrum of the mixture of bis isomers, $N_4P_4Cl_6(OCH{=}CH_2)_2$, was accomplished by a combination of *J*-resolved homonuclear 2-D NMR, $^{31}P\{^1H\}$ homonuclear shift-correlated 2-D NMR spectroscopy, and mixture simulation techniques. This represents the first demonstration of the use of 2-D NMR methods to solve problems in phosphazene chemistry. The reaction of $LiOCHCH_2$ is unique in the reactions of $N_4P_4Cl_8$ in that the 2,4-$N_4P_4Cl_6(OCH{=}CH_2)_2$ isomers are the major products. The composition of the $N_3P_3Cl_3(OCH{=}CH_2)_3$ mixture was also determined in order to shed light on the stereochemical course of the lithium enolate reactions.

Introduction

The reactions of oxygen-based nucleophiles with cyclophosphazenes have received increased attention recently. We have been particularly interested in the reactions of the enolate anion of acetaldehyde with cyclotriphosphazenes.[1-3] The reaction of the ambidentate enolate anion occurs exclusively at the oxygen end of the nucleophile, leading to (vinyloxy)cyclotriphosphazenes.[1] These materials represent a new class of organofunctional cyclophosphazene monomers, and certain of these may be transformed into novel polymeric materials.[4] The extension of these reactions to other enolate anions has been noted.[1,5] The stereochemical pathway followed in the formation of the series $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ (n = 1–6) is predominantly nongeminal[2] and is exclusively nongeminal for the series $N_3P_3F_{6-n}(OCH{=}CH_2)_n$ (n = 1–5).[3] In this paper, we report the reactions of the enolate anion of acetaldehyde with octachlorocyclotetraphosphazene, $N_4P_4Cl_8$. These studies have allowed us to expand the range of available (vinyloxy)phosphazene polymer precursors and to explore the stereochemical pathway followed in the less widely studied tetrameric series. We also report, for the first time, the use of two-dimensional ^{31}P NMR spectroscopy

† The general term cyclotetraphosphazene is used in this paper to represent cyclotetra(λ^5-phosphazene).

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to solve complex problems in phosphazene chemistry.

Experimental Section

Octachlorocyclotetraphosphazene, $N_4P_4Cl_8$ (Shin Nisso Kako Co., Ltd.), was used as received. The tris(vinyloxy)trichlorocyclotriphosphazene, $N_3P_3Cl_3(OCH{=}CH_2)_3$, isomeric mixture was prepared by a previously reported procedure.[2] *n*-Butyllithium (1.55 M in hexane) was obtained from Aldrich. Tetrahydrofuran, THF (Aldrich), was distilled from sodium–benzophenone ketyl. Petroleum ether (bp 35–55 °C) was distilled from sodium ribbon. Silica gel (40 μm) for flash chromatography was obtained from Baker. All NMR spectra (in $CDCl_3$) were measured on a Bruker WM-250 spectrometer with an Aspect 3000 computer. The operating frequencies were 250.1 (^{1}H), 62.9 (^{13}C), and 101.2 MHz (^{31}P). Tetramethylsilane (Me_4Si) was used as an internal reference for ^{1}H and ^{13}C NMR measurements. For ^{31}P NMR, 85% H_3PO_4 was used as an external standard. Chemical shifts downfield of the reference were assigned a positive sign. ^{13}C and ^{31}P NMR spectra were recorded under conditions of broad-band decoupling. NMR simulations were carried out with a locally modified version of DNMR-3.[6] The inverse gated-decoupled ^{31}P NMR spectral measurements along with the spectral measurements and calculations for T_1 relaxation rates (inversion-recovery method) were done by using standard Bruker microprograms. The ^{31}P homonuclear *J*-resolved and homonuclear spin-correlated (COSY-45) 2-D NMR spectra were obtained with modified Bruker microprograms. Both programs were modified by introducing recovery pulses so that relaxation delays, and therefore total acquisition time, could be reduced. In addition, composite π pulses were substituted into the *J*-resolved microprogram for more accurate spin inversion.[7] The data matrix for the *J*-resolved spectrum was 1024 × 512 points, and that for the COSY spectrum was 1024 × 256 points. The transformations for both spectra were done in the absolute-value mode with phase-shifted sine-bell window functions in both dimensions and zero-filling in the F_1 dimensions. Total acquisition time was approximately 12 h for each spectrum. Infrared (IR) spectra were obtained as thin films (NaCl disks) on a Nicolet 6000 series spectrophotometer. Mass spectra were recorded on a Finnigan 4610 spectrometer operating at 80 eV. Elemental analyses were performed by Robertson Laboratory, Inc.

Preparation of the $N_4P_4Cl_7OCH{=}CH_2$ (1) and $N_4P_4Cl_6(OCH{=}CH_2)_2$ Mixture (2). A solution of 35 mL (0.054 mol) of *n*-butyllithium was added to 150 mL of THF in a previously described[8] air-sensitive reagent vessel. The mixture was stirred overnight to allow for complete formation of the lithium enolate, $LiOCH{=}CH_2$, which was then added slowly to 15.00 g (0.032 mol) of $N_4P_4Cl_8$ in 200 mL of THF at −40 °C under a nitrogen atmosphere. The resulting mixture was allowed to warm to room temperature overnight while being stirred. The solvent was removed and extracted with petroleum ether. Following addition of activated charcoal, filtration, and removal of petroleum ether, 13.33 g of a pale yellow-green liquid was obtained. A 3.43-g sample of this material was purified by using flash chromatography[9] with petroleum ether as the eluant. After elution of unreacted $N_4P_4Cl_8$, 0.97 g (28.3% of theory) of a colorless liquid, bp 95 °C (0.02 mmHg), was obtained. Anal. Calcd for $N_4P_4Cl_7OCH{=}CH_2$ (**1**): C, 5.10; H, 0.64; mol wt 468. Found: C, 5.04; H, 0.74; mol wt 468 (mass spectrum).[10]

^{1}H NMR:[11] $\delta(\equiv POCH{=}CH_2)$ 6.52 (complex multiplet), $\delta(\equiv POCH{=}CH_2$ (trans)) 5.02 (complex multiplet), $\delta(\equiv POCH{=}CH_2$ (cis)) 4.71 (complex multiplet). ^{13}C NMR: $\delta(\equiv POCH{=}CH_2)$ 140.6, $^1J_{CH}$ = 191, $^2J_{PC}$ = 0.12; $\delta(\equiv POCH{=}CH_2)$ 103.3, $^1J_{CH}$ = 157, $^3J_{PC}$ = 0.21. ^{31}P NMR:[12] $\delta(\equiv PClOR)$ −10.0, $^2J_{PNP}$ = 27.1; $\delta(\equiv PCl_2$ (4, 8)) −3.7, $^2J_{PNP}$ = 50.6; $\delta(PCl_2$ (6)) −5.6, $^4J_{P6P}$ = −0.95. IR:[13] 3083 (w, CH str), 1643 (s, C=C str), 1303 (s, PN str), 1113 (s, PO str), 1037 (s), 932 (m), 884 (m), 775 (m).

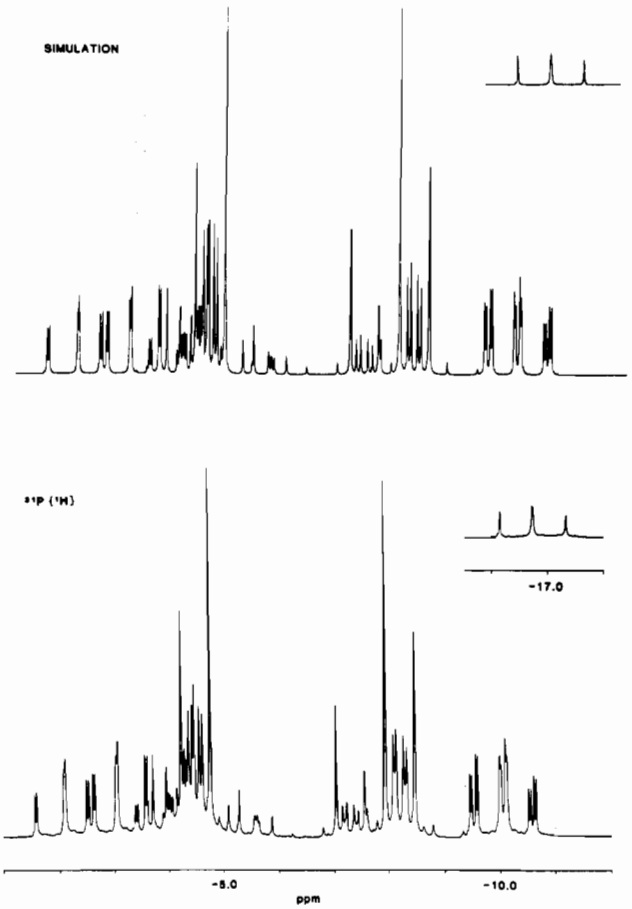

Figure 1. Simulated and observed $^{31}P\{^1H\}$ NMR spectra of the $N_4P_4Cl_6(OCH{=}CH_2)_2$ mixture.

Continued elution produced 1.25 g (36.4% theory) of a second colorless liquid, bp 100 °C (0.02 mmHg). Anal. Calcd for $N_3P_3Cl_4(OCH{=}CH_2)_2$: C, 10.04; H, 1.26; mol wt 476. Found: C, 10.16; H, 1.28; mol wt 476 (mass spectrum).[10]

^{1}H NMR:[11] $\delta(\equiv POCH{=}CH_2)$ 6.54, $\delta(\equiv POCH{=}CH_2$ (trans)) 5.08, $\delta(\equiv POCH{=}CH_2$ (cis)) 4.81. IR:[13] 3083 (w, CH str), 1644 (s, C=C str), 1311 (s, PN str), 1114 (s, PO str), 1036 (s), 932 (m), 883 (m), 786 (m).

Attempts at isomer separation by HPLC, TLC, and column chromatography were not completely successful. The isomeric composition was however established by two-dimensional NMR (vide infra).

Analysis of the $N_3P_3Cl_3(OCH{=}CH_2)_3$ ^{31}P NMR. The individual components and the mixture ^{31}P NMR spectrum of $N_3P_3Cl_3(OCH{=}CH_2)_3$ were simulated by using DNMR-3 to yield the following parameters: geminal $\delta(\equiv PCl_2$ (A)) 27.1, $\delta(\equiv PCl(OCH{=}CH_2)$ (M)) 18.4, $^2J_{AM}$ = 71.1, $\delta(\equiv P(OCH{=}CH_2)$ (X) 2.9, $^2J_{AX}$ = 72.1, $^2J_{MX}$ = 79.6; cis nongeminal $\delta(\equiv PCl(OCH{=}CH_2))$ 18.9; trans nongeminal $\delta(\equiv PCl(OCH{=}CH_2)$ (A)) 19.2, $\delta(\equiv PCl(OCH{=}CH_2)$ (B)) 19.0, $^2J_{AB}$ = 64.5.

Results and Discussion

The reaction of the enolate anion of $LiOCHCH_2$ with $N_4P_4Cl_8$ proceeds smoothly to give moderate yields of the mono- (**1**) and disubstituted (**2**) chlorocyclotetraphosphazenes (eq 1). The ^{1}H

$$N_4P_4Cl_8 + n\text{LiOCHCH}_2 \rightarrow N_4P_4Cl_{8-n}(OCH{=}CH_2)_n + n\text{LiCl} \quad (1)$$

and ^{13}C NMR spectra of the monosubstituted derivative, **1**, clearly demonstrate that the substituent is in the vinyloxy rather than the β-carbonyl form; i.e., the enolate anion undergoes reaction at the oxygen end of the ambident nucleophile. The ^{1}H NMR spectrum of **2** indicates that the disubstituted derivatives are also in the vinyloxy form. This reactivity pattern was found in all previous enolate anion/phosphazene reactions.[1,2,4] The ^{31}P NMR and IR spectra of **1** are consistent with a monosubstituted cyclotetraphosphazene. The mass spectrum (Table SI, supplementary material) of **1** establishes the stoichiometry of the material. The fragmentation pattern suggests a similar propensity

(6) The original version of the computer program DNMR-3 was written by: Kleier, D. A.; Binsch, G. J. *Magn. Reson. Relat. Phenom., Proc. Congr. Ampere, 16th, 1970* **1971**, *3*, 146. Local modifications are described in: Bushweller, C. H.; Bhat, G.; Letendre, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 65.
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(10) Mass spectrometry data are available as supplementary material. The monoisotope is based on ^{35}Cl.
(11) Chemical shifts are in ppm, and coupling constants are in Hz; only the center of the ^{1}H multiplet is reported.
(12) R = $-OCH{=}CH_2$; the vinyloxy-substituted phosphorus atom is labeled 2.
(13) In cm^{-1}.

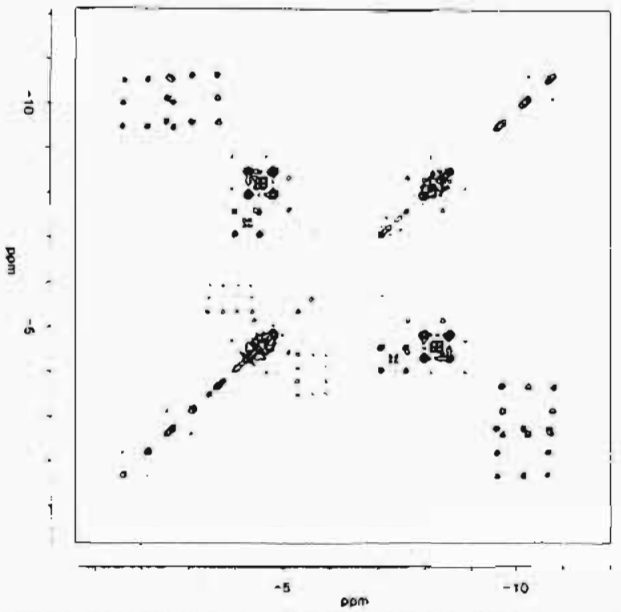

Figure 2. $^{31}P\{^1H\}$ homonuclear shift-correlated 2-D NMR spectrum of the $N_4P_4Cl_6(OCH{=}CH_2)_2$ mixture.

for either phosphorus–chlorine or phosphorus–vinyloxy cleavage. The other noteworthy feature of the mass spectrum is the importance of the ring contraction to give trimeric species as abundant fragments. The importance of this mode of fragmentation has previously been established for cyclotetraphosphazenes.[14] Similar processes occur in the mass spectrum of the bis isomers.

A mixture of bis isomers, **2**, was also isolated. Attempts to effect isomeric separation using traditional column or flash chromatography were unsuccessful, and analytical HPLC separation provided only two components. The complexity of the ^{31}P NMR spectrum of **2** (Figure 1) indicates the presence of more than two components, so an alternative approach to the analysis of the composition of the mixture was sought. The work of Colguhoun and McFarlane[15] has shown that the technique of $^{31}P\{^1H\}$ homonuclear *J*-resolved two-dimensional (2-D) NMR spectroscopy can be successfully applied to assignment of a complex ^{31}P NMR spectrum of a mixture of phosphorus compounds. Consequently, we have applied *J*-resolved 2-D NMR along with $^{31}P\{^1H\}$ homonuclear shift-correlated 2-D NMR spectroscopy to make assignments in the ^{31}P NMR spectrum of **2**.

Before the analysis of the mixture of **2** was undertaken, several important points about the system were noted. In our analysis of the ^{31}P NMR spectra of the series $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ we established that the chemical shifts of the $\equiv PCl(OCH{=}CH_2)$ centers are upfield of the $\equiv PCl_2$ and downfield of the $\equiv P(OCH{=}CH_2)_2$ centers.[2] Positional isomers in the tetrameric series are easily distinguished by their ^{31}P NMR spectra.[16,17] The cis- and trans-2,4-substituted isomers $N_4P_4X_6Y_2$ yield AA′XX′ patterns while the corresponding 2,6-isomers give A_2X_2 patterns. The geminal (2,2) derivative exhibits an A_2MX spectrum.

In the ^{31}P NMR spectrum of **2** (Figure 1), the upfield and downfield halves of the two AA′XX′ patterns resulting from the 2,4-isomers can be paired from the large intensity differences between the two patterns. This indicates a significant difference in the relative amounts of the cis and trans isomers. Since the

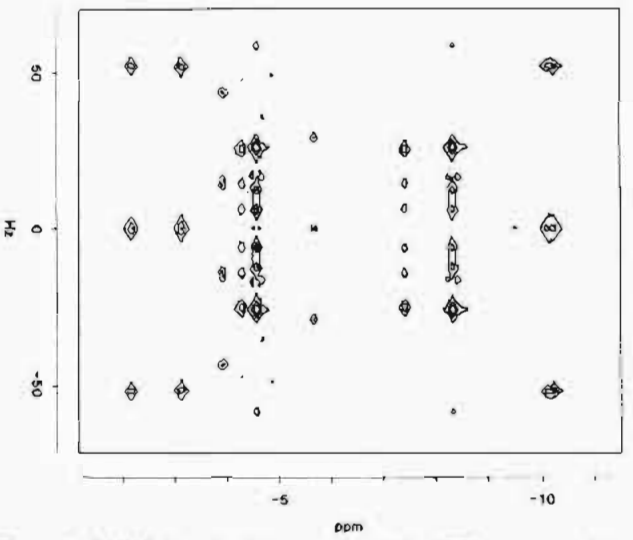

Figure 3. $^{31}P\{^1H\}$ *J*-resolved homonuclear 2-D NMR spectrum of the $N_4P_4Cl_6(OCH{=}CH_2)_2$ mixture.

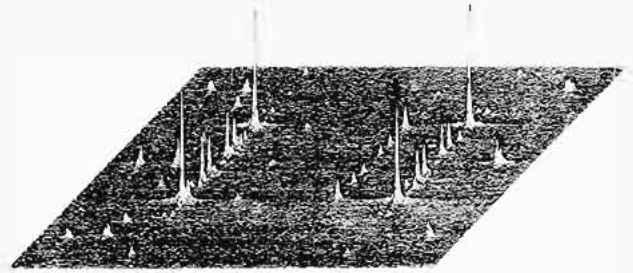

Figure 4. $^{31}P\{^1H\}$ *J*-resolved 2-D NMR stacked plot for the $N_4P_4Cl_6(OCH{=}CH_2)_2$ mixture.

intensities of the two A_2X_2 patterns from the 2,6-isomers are almost equal, a $^{31}P\{^1H\}$ homonuclear shift-correlated 2-D NMR spectrum (Figure 2) was obtained. In this spectrum, the off-diagonal correlation peaks from the 2,6-isomers can be seen in the lower right- and upper left-hand corners. From these peaks it is seen that, as in the case of the 2,4-isomers, the respective chemical shifts of the $\equiv PCl_2$ and $\equiv PCl(OCH{=}CH_2)$ centers for one A_2X_2 pattern occur upfield of the corresponding chemical shifts of the other 2,6-isomer. An examination of the $^{31}P\{^1H\}$ shift-correlated spectrum also allows for corroboration of the chemical shift assignments of the 2,4-isomers and shows that the A_2 part of the A_2MX pattern of the 2,2-isomer is masked by the downfield ($\equiv PCl_2$) resonances from the other isomers. The remaining resonances of the A_2MX pattern are easily discernible.

Each of the spectra of the individual components of the mixture were simulated in turn. The identifiable transition frequencies for the A_2X_2 and AA′XX′ systems can be substituted into the standard equations for these systems. The fine tuning of the parameters was accomplished by using the static simulation program in the DNMR-3 system. The A_2MX system was solved directly from the simulation program. The individual transitions of the A_2X_2 system (2,6-isomers) can be readily assigned directly from the $^{31}P\{^1H\}$ mixture spectrum. Most of the higher intensity transitions of the AA′XX′ systems (2,4-isomers) can also be directly assigned; however, the four weak outer transitions are difficult to identify. Similarly, the $\equiv P(OCH{=}CH_2)_2$ and upfield $\equiv PCl_2$ centers of the 2,2-isomer can be directly assigned, but the downfield $\equiv PCl_2$ center (the A_2 part of the A_2MX spin system) is masked by other resonances.

In order to locate the hidden transitions, a $^{31}P\{^1H\}$ *J*-resolved 2-D NMR spectrum of the mixture of isomers was obtained (Figures 3 and 4). The A_2 part of the A_2MX system can be observed by viewing slices along the F_1 dimension of the tilted spectrum. The outer transitions of the AA′XX′ pattern can also be easily seen in an F_1 slice (Figure 5). The approximate chemical shifts of all centers can also be obtained from the F_2 projection

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Table I. ^{31}P Chemical Shifts and Coupling Constants for the $N_4P_4Cl_6(OCH{=}CH_2)_2$ Isomers[a,b]

isomer	case	δ(A)	δ(B)	δ(M)	$^2J_{AA}$	$^2J_{AX}$	$^2J_{XX}$	$^4J_{AM,MX}$	$^2J_{AX}$
2,4 major	AA'XX'	−4.52	−8.17		79.5	53.7	31.0	−0.6	
2,4 minor	AA'XX'	−4.24	−7.27		67.8	52.3	32.7	−1.0	
2,6 major	A_2X_2	−3.09	−10.07			53.7			
2,6 minor	A_2X_2	−2.14	−9.98			54.1			
geminal	A_2MX	−3.89	−5.56	−16.72		60.7		−0.6	30.3

[a] Chemical shifts are in ppm from 85% H_3PO_4 (external standard). [b] Coupling constants are in Hz.

Table II. Percent Distribution of Isomers for $N_4P_4Cl_6(OCH{=}CH_2)_2$

isomer	by integration[a]	by simulation fit
2,4 major	50.1	47.3
2,4 minor	12.8	14.1
2,6 major	17.3	17.7
2,6 minor	12.3	13.1
geminal	7.5	7.8

[a] Inverse gated-decoupled ^{31}P spectrum used.

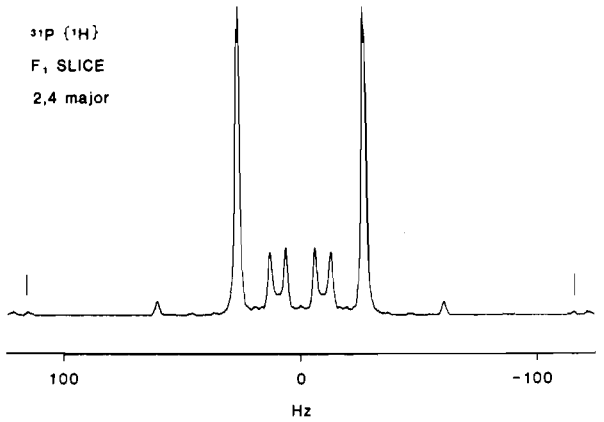

Figure 5. F_1 slice showing the major 2,4-$N_4P_4Cl_6(OCH{=}CH_2)_2$ isomer in the *J*-resolved homonuclear 2-D NMR spectra.

of the tilted *J*-resolved 2-D NMR spectrum (Figure 6). This spectrum is equivalent to an ^1H broad-band, ^{31}P homonuclear decoupled spectrum of the mixture of isomers and therefore shows a single peak for each of the 11 different phosphorus environments in the mixture. Accurate coupling constants and chemical shifts for each of the isomers were obtained by computer simulation of the individual spin systems (Figure S1, supplementary material). The data may be found in Table I. The mixture spectrum was matched to the composite of the individual spectra by varying the contributions of each of the components, thus allowing for calculation of the relative concentration of each species (Table II).

While the ^{31}P NMR data allow for unambiguous identification of positional isomers, the stereochemistry of the individual components of the sets of 2,4- and 2,6-isomers cannot be made with certainty. A similar problem was noted in the study of the bis(vinyloxy)cyclotriphosphazenes $N_3P_3Cl_4(OCH{=}CH_2)_2$.[2] At the third stage of substitution of the trimeric system, the stereochemistry of the nongeminal isomers can be assigned from the ^{31}P NMR spectra. The cis isomer exhibits an A_3 spectrum while the trans isomer exhibits an AB_2 pattern. We reinvestigated the $N_3P_3Cl_3(OCH{=}CH_2)_3$ system and, upon simulation of the NMR spectrum of the mixture, found 27.2% of the cis, 51.3% of the trans, and 21.5% of the geminal isomer. The observed cis:trans ratio is 1.6:3 while the ratio expected solely on a statistical basis is cis:trans = 1:3; i.e., a cis preference is observed at the tris stage of substitution. It is reasonable to suggest that the cis preference is also manifested in $N_3P_3Cl_4(OCH{=}CH_2)_2$. A similar cis preference has been observed in the formation of $N_3P_3Cl_4(OPh)_2$.[18] In the absence of further definitive data, we can extend the inference from the results of the $N_3P_3Cl_3(OCH{=}CH_2)_3$ analysis and tentatively assign a cis configuration to the major 2,4-

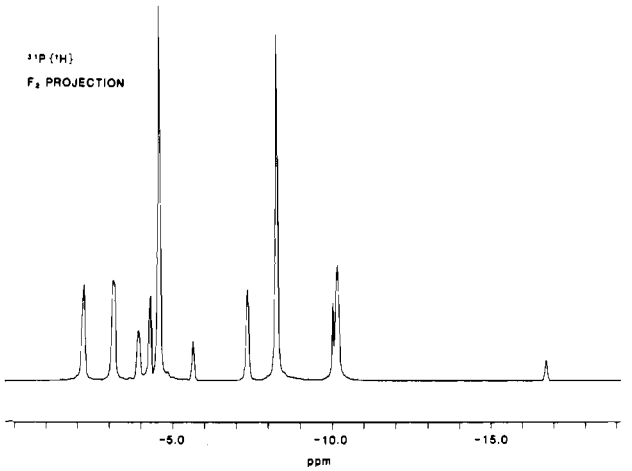

Figure 6. F_2 projection of the tilted *J*-resolved homonuclear 2-D NMR $^{31}P\{^1H\}$ spectrum of the $N_4P_4Cl_6(OCH{=}CH_2)_2$ mixture.

$N_4P_4Cl_6(OCH{=}CH_2)_2$ isomer. No significant stereochemical preference is observed in the formation of the 2,6-isomers. We have previously suggested that the cis preference observed in certain reactions of unsaturated nucleophiles with cyclophosphazenes arises from an electrostatic attraction between the electron-rich nucleophile and the electron-poor phosphazene substituent.[19]

The pathway followed in the reaction of $LiOCH{=}CH_2$ with $N_4P_4Cl_8$ is unique in that the 2,4-isomers are the major products. By way of contrast, the analogous reaction with sodium phenoxide[20] and certain less reactive amines such as *tert*-butylamine,[21] benzylamine,[22] *N*-methylaniline,[23] and aziridine[24] provides 2,4- and 2,6-disubstituted hexachlorocyclotetraphosphazenes in comparable quantities. More reactive nucleophiles such as dimethylamine,[25] methylamine,[22] and ethylamine[26] give high relative yields of the 2-trans-6 derivatives.

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Registry No. **1**, 106820-70-6; *cis*-2,4-**2**, 106820-71-7; *trans*-2,4-**2**, 106820-72-8; *cis*-2,6-**2**, 106820-73-9; *trans*-2,6-**2**, 106820-74-0; *gem*-**2**, 106820-75-1; $LiOCH{=}CH_2$, 2180-63-4; $N_4P_4Cl_8$, 2950-45-0.

Supplementary Material Available: Table SI, showing major mass spectral fragments and their relative intensities, and Figure S1, showing the simulated $^{31}P\{^1H\}$ NMR spectra for each component of the $N_4P_4Cl_6(OCH{=}CH_2)_2$ mixture (3 pages). Ordering information is given on any current masthead page.

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