Synthesis and Spectroscopy of $N_3P_3X_5OCH{=}CH_2$ (X = Cl, F, OCH_3, OCH_2CF_3, $N(CH_3)_2$) and $N_3P_3X_4(OCH{=}CH_2)_2$ (X = Cl, $N(CH_3)_2$). Correlations of Ultraviolet Photoelectron Spectroscopy and Nuclear Magnetic Resonance Data to Electronic and Geometrical Structure

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The syntheses of the vinyloxycyclotriphosphazene derivatives $N_3P_3X_5OCH{=}CH_2$ (X = OMe, OCH_2CF_3) and the $N_3P_3(NMe_2)_4(OCH{=}CH_2)_2$ isomeric mixture along with improved preparations of $N_3P_3X_5OCH{=}CH_2$ (X = F, NMe_2) are reported. The interactions between the vinyloxy function and the cyclophosphazene in these and the previously reported $N_3P_3Cl_5$ ($OCH{=}CH_2$) and $N_3P_3F_{6-n}(OCH{=}CH_2)_n$ (n = 1−4) have been examined by ultraviolet photoelectron spectroscopy (UPS) and NMR spectroscopy. The UPS data for the chloro and fluoro derivatives show a strong electron-withdrawing effect of the phosphazene on the olefin that is mediated with decreasing halogen substitution. The ^1H and ^{13}C NMR data for $N_3P_3X_5OCH{=}CH_2$ (X = F, Cl, OMe, OCH_2CF_3, NMe_2) show significant changes as a function of the phosphazene substituent. There is a linear correlation between the β-carbon chemical shift on the vinyloxy unit and the phosphorus chemical shift at the vinyloxyphosphorus centers. The chemical shifts of the different phosphorus centers on each ring are also related in a linear fashion. These relationships may be understood in terms of the relative electron donor−acceptor abilities of the substituents on the phosphazene ring. The ^1H NMR spectra of the $N_3P_3(NMe_2)_4(OCH{=}CH_2)_2$ isomeric mixture allow for assignment of the relative amounts of cis and trans isomers. A model for the observed cis preference in the formation of $N_3P_3Cl_4(OCH{=}CH)_2$ is presented.

Introduction

The reactions of enolate anions with halocyclophosphazenes lead to a wide range of vinyloxycyclophosphazenes.[1−7] We have explored the reactions of the simplest of these species, i.e., the enolate of acetaldehyde, in detail and reported the synthesis of the following derivatives: $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ (n = 1−6),[1,2,6] $N_3P_3F_{6-n}$ $(OCH{=}CH_2)_n$ (n = 1−5),[4] and $N_4P_4Cl_{8-n}$ $(OCH{=}CH_2)_2$ (n = 1, 2).[5] Our interest in these materials has been focused on two areas: new organofunctional phosphazene monomers that can be converted to carbon chain polymers with cyclophosphazenes as substituents[8,9] and questions involving regio- and stereochemical control in the substitution reactions of cyclophosphazenes.[10] The purpose of the current investigation is an exploration of the reactions of $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ (n = 1, 2) with a variety of nucleophiles in order to extend the range of available organofunctional cyclophosphazene monomers. The disubstituted materials are also of interest in the question of the isomer distribution in the formation of $N_3P_3Cl_4(OCH{=}CH_2)_2$.[2,5] Additionally, the availability of a series of new, closely related compounds allows continuation of our long-term interest in the NMR spectroscopy of cyclophosphazene derivatives with a particular focus in looking for systematic trends in NMR data. A preliminary report of selected aspects of this investigation has appeared.[7]

Experimental Section

Materials and Methods. Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (Nippon Soda), was converted to $N_3P_3Cl_5OCH{=}CH_2$ (**1**),[6] the $N_3P_3Cl_4(OCH{=}CH_2)_2$ isomeric mixture (**2**),[2] $N_3P_3F_6$,[11] and the $N_3P_3F_{6-n}(OCH{=}CH_2)_n$ [n = 2 (**3**), 3 (**4**), 4 (**5**)] nongeminal isomeric mixtures[4] by previously reported procedures. *n*-Butyllithium (1.55 *m* in hexane) was obtained from Aldrich. Tetrahydrofuran (THF) and diethyl ether (Aldrich) were distilled from sodium/benzophenone. Trifluoroethanol and 40% aqueous dimethylamine were obtained from Aldrich. Other solvents and reagents were obtained from standard sources and used as received. Reactions, which necessitated anhydrous conditions, were carried out in magnetically stirred solutions under N_2 utilizing standard Schlenk line techniques.

NMR spectra were recorded on a Bruker WM250 spectrometer with an Aspect 3000 computer. Operating frequencies were 250.1 MHz (^1H), 62.9 MHz (^{13}C), and 101.12 MHz (^{31}P). Tetramethylsilane (^1H and ^{13}C) was used as an internal reference, and 85% H_3PO_4 (^{31}P) was used as an external reference. Chemical shifts upfield from the reference were given a negative sign. Broadband ^1H decoupling was used for ^{13}C and ^{31}P spectra. NMR simulations were carried out with a locally modified

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version of DNMR-3.[12] Infrared spectra were obtained as thin films on NaCl disks on a Nicolet 6000 series spectrophotometer. Mass spectra were recorded on a Finnigan 4610 spectrometer operating at 80 eV. Photoelectron spectra were obtained on a Perkin-Elmer PS-18 spectrometer using the He(I) resonance line (21.22 eV) as the excitation source. All data represent the average of three or more runs. Xenon was the internal calibrant. Elemental analyses were performed by Robertson Laboratory (P.O. Box 927, Madison, NJ 07940).

Preparation of $N_3P_3F_5OCH{=}CH_2$ (6). A 250 mL sidearm flask fitted with a magnetic stirrer and septum was alternately evacuated and backfilled with nitrogen three times. The vessel was put under nitrogen pressure, filled with 100 mL of dry THF, and 55 mL (0.085 mol) of an *n*-butyllithium solution, which after being stirred for 12 h yielded approximately 0.085 mol of the lithium enolate of acetaldehyde.[2] The solvent mixture was removed by vacuum distillation at room temperature into a liquid nitrogen cooled trap. The vessel was then backfilled with nitrogen, and 100 mL of dry THF was added to the lithium enolate. A separate 250 mL round-bottom flask was fitted with a magnetic stirrer, filled with 20 g (0.08 mol) of $N_3P_3F_6$, and fitted with an addition funnel with a septum. The phosphazene-containing vessel was placed in an ice−water bath, partially evacuated, and backfilled with nitrogen, and 50 mL of dry THF was added. The enolate solution was transferred to the addition funnel and slowly added to the phosphazene solution, which was allowed to warm to room temperature and then transferred to a 250 mL round-bottom flask. This flask was fitted with a 20 cm long, 14 mm bore column filled with stainless steel wool that had an evacuated jacket coated on the inside with a silver mirror. A microdistillation head/condenser and a 250 mL collection flask were added, and the vessel was put under nitrogen gas pressure. The solution was slowly heated until the rate of distillation noticeably dropped. The remaining solution was placed in a 50 mL round-bottom flask and fractionally distilled. Four fractions were collected and the final two determined to be greater than 99% pure product (^{1}H NMR). These fractions were combined to give 2.44 g (11.2% of theory) of a colorless liquid, bp (68−72 °C). This compound has been previously prepared using a different method and was identified from the reported ^{1}H and ^{31}P NMR data.[1,4]

Preparation of $N_3P_3(OCH_2CF_3)_5OCH{=}CH_2$ (7). A 250 mL round-bottom flask was filled with 1.3 g (0.056 mol) of sodium under nitrogen pressure, was placed in a room-temperature water bath, and was charged with 100 mL of dry diethyl ether. Then 5.63 g (0.0563 mol) of 2,2,2-trifluoroethanol was added over a 30 min period. The reaction was allowed to proceed for about 2 h until hydrogen gas evolution ceased. A 250 mL round-bottom flask containing 4 g (0.01 mol) of $N_3P_3Cl_5(OCH{=}CH_2)$ was alternately evacuated and backfilled with nitrogen three times followed by 25 mL of dry diethyl ether. The sodium trifluoroethoxide solution was transferred into the phosphazene-containing flask. The resulting solution was stirred for 12 h and filtered, and the solvent was removed. The resulting oil was distilled to give 6.41 g (84.6% of theory) of a colorless liquid, bp 75 °C (0.02 mmHg). Anal. Calcd for $N_3P_3(OCH_2CF_3)_5(OCH{=}CH_2)$: C, 21.40; H, 1.93; mol wt, 673. Found: C, 21.59; H, 2.08; mol wt, 673 (mass spectrum).[13] ^{1}H NMR:[14] δ(≡POC*H*=CH_2) 6.41, $^3J_{PH}$ = 7.6; δ(≡POCH=C*H*$_2$ (cis)) 4.99, $^3J_{HH}$ = 13.6, $^4J_{PH}$ = 2.1; δ(≡POCH=C*H*$_2$ (trans)) 4.71, $^3J_{HH}$ = 5.9, $^2J_{HH}$ = 2.3, $^4J_{PH}$ 2.1; δ(≡POC*H*$_2$CF$_3$) 4.21−4.36 (complex multiplet). ^{13}C NMR: δ(≡PO*C*H=CH_2) 141.2, $^1J_{CH}$ = 193, $^2J_{CP}$ 5.5; δ(≡POCH=*C*H_2) 102.2, $^1J_{CH}$ = 161.2, $^3J_{CP}$ = 10.1; δ(≡PO*C*H$_2$F$_3$) 63.3, $^1J_{CH}$ = 36.4, $^2J_{CP}$ = 2.7, $^2J_{CF}$ = 38.5; δ(≡P(OCH$_2$*C*F$_3$) 122.7, $^1J_{CF}$ = 277.1, $^3J_{CP}$ = 6.7. ^{31}P NMR: δ(≡P(OCH$_2$CF$_3$)$_2$) 17.7, J_{PP} = 91.7; δ(≡P(OCH$_2$CF$_3$)(OCH=CH_2)) 14.1.

Preparation of $N_3P_3(OCH_3)_5OCH{=}CH_2$ (8). A 250 mL round-bottom flask was charged with 100 mL of anhydrous methanol followed by 1.26 g (0.0548 mol) of sodium, and the apparatus was placed under nitrogen pressure. After the sodium had all reacted and hydrogen gas evolution ceased, 3.9 g (0.011 mol) of $N_3P_3Cl_5(OCH{=}CH_2)$ was added to the solution by syringe. The mixture was allowed to react for 12 h and was filtered, and the solvent was removed. The resulting oil was distilled twice to give 0.51 g (14% of theory) of a colorless liquid, bp 85 °C (0.02 mmHg). A considerable amount of the product decomposed and polymerized during the distillations, and a second distillation was needed to remove the impurities that distilled with the product. ^{1}H NMR:[14] δ(≡POC*H*=CH_2) 6.42, $^3J_{PH}$ = 6.7; δ(≡POCH=C*H*$_2$(cis)) 4.72, $^3J_{HH}$ = 13.6, $^4J_{PC}$ = 1.7; δ(≡POCH=C*H*$_2$ (trans)) 4.38, $^3J_{HH}$ = 5.9, $^2J_{HH}$ = 1.7, $^4J_{PH}$ = 1.9; δ(≡P(OC*H*$_3$) 3.51, 3.53, 3.55, $^3J_{CH}$ = 3.6. ^{13}C NMR: δ(≡POC*H*=CH_2) 142.0, $^2J_{CP}$ = 5.3; δ(≡POCH=*C*H_2) 98.9, $^3J_{CP}$ = 10.3; δ(≡P(OCH$_3$)) 52.4. ^{31}P NMR: δ(≡P(OCH$_3$)$_2$) 21.0, $^3J_{pp}$ = 83.9; δ(≡P(OCH$_3$)(OCH=CH_2)) 17.7.

Preparation of $N_3P_3[N(CH_3)_2]_5OCH{=}CH_2$ (9). A 250 mL round-bottom flask was charged with 3.9 g (0.011 mol) of $N_3P_3Cl_5(OCH{=}CH_2)$, 100 mL of toluene, 50 mL (0.40 mol) of a 40% solution of dimethylamine in water, and 4 g (0.1 mol) of NaOH. The solution was stirred vigorously for 12 h, washed twice with 100 mL of water, and dried over anhydrous $MgSO_4$. After removal of the solvent and distillation of the resulting oil, 1.3 g (39% of theory) of a colorless liquid, bp = 70 °C (0.03 mmHg), was obtained. This compound has been previously prepared by a different method and was identified from the reported ^{1}H, ^{13}C, and ^{31}P NMR data.[2]

Preparation of $N_3P_3[N(CH_3)_2]_4(OCH{=}CH_2)_2$ (10). This compound was prepared using the same procedure as for $N_3P_3(N(CH_3)_2)_5(OCH{=}CH_2)$ except that 2.16 g (0.0595 mol) of $N_3P_3Cl_4(OCH{=}CH_2)_2$, 50 mL of toluene, 1 g (0.03 mol) of NaOH, and 25 mL (0.20 mol) of a 40% solution of dimethylamine in water were used. After distillation, 1.71 g (71.8% of theory) of a colorless liquid, bp = 90 °C (0.02 mmHg), was obtained. Anal. Calcd for $N_3P_3(N(CH_3)_2)_4(OCH{=}CH_2)_2$: C, 36.37; H, 7.56; mol wt, 397. Found: C, 36.65; H, 7.95; mol wt, 397 (mass spectrum).[13] ^{1}H NMR:[14] δ(≡P(OC*H*=CH_2) 6.47; δ(≡POCH=C*H*$_2$ (cis)) 4.60, $^3J_{HH}$ = 13.7; δ(≡POCH=C*H*$_2$ (trans)) 4.23, $^3J_{HH}$ = 5.9; δ(≡PN(C*H*$_3$)$_2$OCH=CH_2 (cis)) 2.59, $^3J_{PH}$ = 12.3; δ(≡PN(C*H*$_3$)OCH=CH_2 (trans)) 2.58, $^3J_{PH}$ = 12.2; δ(≡P(N(C*H*$_3$)$_2$)$_2$ (cis)) 2.51, 2.53, $^3J_{PH}$ = 11.4, 11.5; δ(≡P(N(C*H*$_3$)$_2$ (trans)) 2.52, $^3J_{PH}$ = 11.4. ^{13}C NMR: δ (≡POC*H*=CH_2) 143.2; δ(≡POCH=C*H*$_2$) 96.8; δ(PN(C*H*$_3$)) 36.3, 36.4. ^{31}P NMR: δ[≡P(N(CH$_3$)$_2$ (cis)] 27.4, $^3J_{PP}$ = 49.2; δ(≡PN(CH$_3$)$_2$OCH=CH$_2$(cis)) 22.8; δ(≡P(N(CH$_3$)$_2$(trans)) 27.5, $^3J_{PP}$ = 49.7; δ(≡PN(CH$_3$)$_2$OCH=CH$_2$ (trans)) 23.1; δ(≡P(N(CH$_3$)$_2$)$_2$) 26.3, $^3J_{PP}$ = 50.0; δ(≡P(OCH=CH$_2$)$_2$) 14.6.

Results and Discussion

The reactions of $N_3P_3Cl_5OCH{=}CH_2$ (**1**) with nucleophiles typically utilized in cyclophosphazene chemistry[10,15,16] lead to moderate yields of the persubstituted vinyloxyphosphazene monomers, $N_3P_3X_5OCH{=}CH_2$ [X = OCH_2CF_3 (**7**), OMe (**8**), NMe_2 (**9**)]. Good yields of crude **8** were obtained; however, significant decomposition occurred during distillation. Rearrangements leading to decomposition have been noted for other persubstituted alkoxycyclophosphazenes.[15,16] The mechanism of the phosphazene−phosphazane rearrangement has recently been elucidated.[17] The ionic intermediates that arise in the course of the rearrangement potentially could initiate polymerization of the vinyloxy moiety in **8**. Thus, both the rearrangement and polymerization of **8** contribute to the low isolated yield of pure material. The previously reported perfluoroderivative, $N_3P_3F_5OCH{=}CH_2$ (**6**), was prepared in somewhat improved yields using a modified procedure. The volatility of **6** is comparable to that of the solvents used in its preparation, which is a major reason for the low isolated yields. The higher yields noted in

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Table 1. Ionization Energies for Selected Vinyloxycyclotriphosphazenes[a]

phosphazene	I_1	I_2	I_3
$N_3P_3F_5OCH{=}CH_2$ (**6**)	10.61 ± 0.01	11.36 ± 0.02	12.88 ± 0.01
$N_3P_3F_4(OCH{=}CH_2)_2$ (**3**)	10.09 ± 0.01	10.78 ± 0.1	12.3[b]
$N_3P_3F_3(OCH{=}CH_2)_3$ (**4**)	10.10 ± 0.01	10.57 ± 0.04	12.06
$N_3P_3F_2(OCH{=}CH_2)_4$ (**5**)	*c*	10.32 ± 0.03	11.66 ± 0.02
$N_3P_3Cl_5OCH{=}CH_2$ (**1**)	10.48 ± 0.01	11.10 ± 0.01	

[a] All values refer to vertical ionization potentials in electronvolts. [b] Approximate value. [c] Could not be resolved.

the preparation of **3**−**5** are consistent with this proposal. The isomeric mixtures of $N_3P_3F_{6-n}(OCH{=}CH_2)_n$ [n = 2 (**3**), 3 (**4**), 4 (**5**)] and $N_3P_3(NMe_2)_4(OCH{=}CH_2)_2$ (**10**) were prepared directly from $N_3P_3F_6$ and $N_3P_3Cl_4(OCH{=}CH_2)_2$, respectively. These results demonstrate the viability of synthesis of a variety of vinyloxyphosphazene monomers from the readily available[2,5,6] vinyloxychlorophosphazene precursors.

The nature of the interaction between the vinyloxy function and the cyclophosphazene moiety was explored using NMR and ultraviolet photoelectron spectroscopy (UPS). Despite the extensive and ongoing interest in the electronic structure of the cyclophosphazenes,[10−15,18−21] surprisingly few reports of valence shell ionization data have appeared.[22−24] Earlier studies have involved systematic variations in ionization potentials (IP) of persubstituted trimers, tetramers, and larger rings[22] and in the $N_3P_3F_{6-n}(C_6H_5)_n$ (n = 1−4) series.[23] UPS data for selected vinyloxycyclotriphosphazenes are reported in Table 1. Overlap of bands and resulting ambiguities obviated determination of the ionization potentials of other members in the series. The assignment of the spectra is based on the composite molecule approach[25] starting from the known spectra of $N_3P_3F_6$ [22,24] and the organic substituents.[26] The results obtained in the phenylfluorophosphazene study[23] also provide a guide for the assignment of the spectra obtained for **3**−**6**. The close agreement in the data for cis and trans isomers noted in the phenyl series[23] suggests that no significant information was lost by using mixtures of the nongeminal isomers **3**−**5**. The out-of-plane π orbital ionization in $N_3P_3F_6$ occurs at 11.4 eV and the in-plane π ionization at 13.1 eV.[22,24] Replacement of fluorine atoms by phenyl groups leads to destabilization of these orbitals and hence a decrease in their respective ionization potentials.[23] Consequently, the vertical ionization potentials, I_2 and I_3 in Table 1, can be confidentially assigned to the phosphazene out-of-plane and in-plane π orbital ionizations. This leaves I_1 as being derived from the $OCH{=}CH_2$ moiety, which is in agreement with previous observations of the general range of energies associated with this functional group.[26] The π ionization in alkyl vinyl ethers typically occurs between 8.7 and 9.6 eV,[27,28] and the $\pi_{C=C}$ band in vinyl acetate occurs at 9.85 eV.[29] While the actual value is somewhat dependent on conformational effects,[26−28] the general trend is stabilization with increased electron-withdrawing effect of R in $ROCH{=}CH_2$. The strong electron-withdrawing effect previously established for the $N_3P_3F_5$ moiety[23,30] is clearly manifested in I_1 for **6** (10.61 eV). A moderation of the phosphazene electron-withdrawing effect as fluorine atoms are replaced by vinyloxy groups is also observed (Table 1). The first ionization in $N_3P_3Cl_6$ occurs at 10.26 eV,[22] and consequently, the I_1 of **1** is expected to correspond to an orbital containing both π_{PN} and $\pi_{C=C}$ contributions. The similar ranges of ionization energies for chlorophosphazenes and the vinyloxy unit preclude definitive assignment in these and the related derivatives. The I_2 peak in **1** is most reasonably assigned to the Cl lone pair ionization. The general range of I_1 for **1** again demonstrates the strong electron-withdrawing effect of the pentahalocyclotriphosphazene, resulting in an olefinic center in which the π electron density is polarized toward the inorganic ring. The magnitude of the olefin perturbation by the cyclophosphazenes is greater than that in vinyl acetate (a reference point for electron-withdrawing behavior in well-understood olefins).

The vinyl region in the ^{1}H NMR spectra of the vinyloxyphosphazenes is typical of an ABX system, found for example in vinyl acetate, with the addition of phosphorus coupling and was successfully simulated as such. The proton−proton coupling constants are unremarkable and follow previously noted trends. The similarity of behavior of all three structurally unique protons suggests that anisotropic contributions are not significant, and hence, the variation arises from the differing group electronegativities (**1** > **7** > **8** > **9**) of the $N_3P_3X_5$ substituents. The ^{1}H NMR parameters of vinyl acetate are in the range of the more, but not most, electron-withdrawing cyclophosphazene substituents.

The ^{13}C NMR shifts are of particular interest in the examination of electronic effects.[30] In general, the origins of variations in olefinic α-carbon shifts are not obvious, but the β-carbon shifts can be correlated to electronic perturbations induced by substituent effects.[31] The β-carbon shifts in the series $N_3P_3X_5$-$OCH{=}CH_2$ increase with increasing electronegativity of the phosphazene substituent from 95.4 ppm (**9**) to 104.3 ppm (**1**). The chemical shift increase with increased substituent electronegativity indicates the dominance of the paramagnetic term in the ^{13}C shielding for these molecules. Since the diamagnetic term controls the ^{1}H shifts, the substituent/shift trends are in opposite directions, but both show the increasing polarization of olefin electron density toward the phosphazene with increased substituent electronegativity.

The ^{31}P chemical shifts of the vinyloxy-substituted phosphorus atoms show a progressive deshielding with increased substituent electronegativity. This general trend indicates the dominance of the diamagnetic term in the ^{31}P shielding for the systems under investigation. The connection between the ^{31}P and the β-^{13}C chemical shifts of the vinyloxyphosphorus centers is clearly demonstrated in the linear correlation[32] shown in Figure 1. The negative slope reflects the opposite controlling factors (paramagnetic vs diamagnetic) for the ^{13}C and ^{31}P

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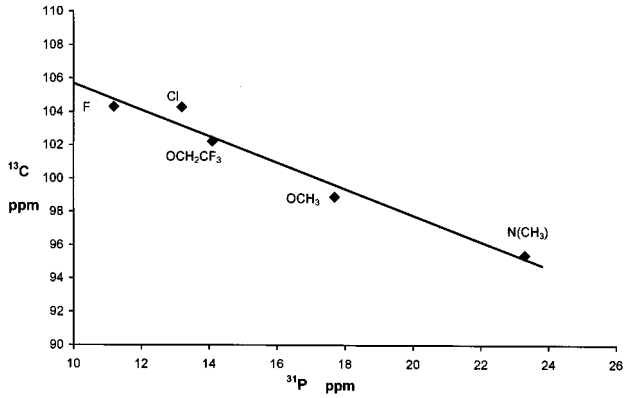

Figure 1. Correlation of the ^{13}C and ^{31}P chemical shifts for the β-carbon atom in the vinyloxy unit and the $\equiv$P(X)OCH$=$CH$_2$ center in the series $N_3P_3X_5OCH{=}CH_2$ (X = F, Cl, OCH_2CF_3, OCH_3, $N(CH_3)_2$).

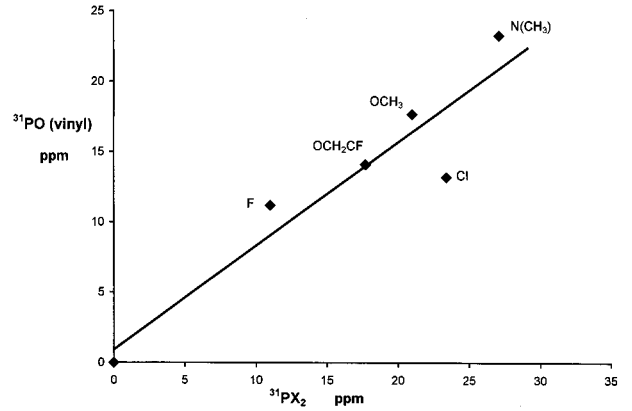

Figure 2. Correlation of the ^{31}P chemical shifts for the series $N_3P_3X_5$-$OCH{=}CH_2$ (X = F, Cl, OCH_2CF_3, OCH_3, $N(CH_3)_2$).

chemical shifts. The linear relationship between the carbon and phosphorus shifts demonstrates that the electron density in the exocyclic olefin is controlled by the electronic structure of the phosphorus atom to which the vinyloxy group is attached. The plot of the ^{31}P chemical shifts for the $\equiv$PX(OCH$=$CH$_2$) centers vs the $\equiv$PX$_2$ centers shown in Figure 2 is linear with a zero (or nearly zero) intercept.[33] As in the other cases noted above, the data for **1** are anomalous. The positive slope and linearity demonstrate a direct correlation between the electronic effects operative at the $\equiv$PX(OCH$=$CH$_2$) center and the distant phosphorus sites on the ring. Consequently, any electronic effects arising from the interaction of the phosphazene substituents and the vinyloxy moiety are manifested in an equivalent fashion across the cyclophosphazene ring. This investigation is the first to clearly demonstrate quantitative relationships involving transmission of electronic effects across the cyclophosphazene ring system. The value of $^2J_{pp}$ in cyclotriphosphazenes is proportional to the sum of the electronegativies of the substituents on the two phosphorus atoms in question.[34] The distant phosphorus atom contributes to the magnitude of J_{pp} between the remaining two centers when very large differences in substituent electronegativities are involved.[35] With the

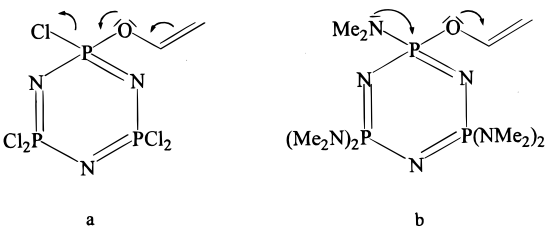

Figure 3. Effect of phosphazene substituents on olefin electron density in vinyloxycyclophosphazenes for electron-withdrawing (a) and electron-donating (b) groups.

exception of the low value for **1**, the increase in $^2J_{pp}$ in the order **7** (91.7) > **8** (83.9) > **1** (64.1) > **9** (49.1) is qualitatively consistent with the effect of substituent electronegativity.

A simple model for rationalization of the spectroscopic observations can be obtained from a consideration of the relative donor−acceptor properties of the different exocyclic groups in question. In the case where the cosubstituent is an electron-withdrawing entity such as a chlorine or fluorine atom, electron density is removed from the phosphorus center, and this increased electropositive nature at phosphorus results in a strong polarization of electron density in the vinyloxy group away from the olefin (Figure 3a). This behavior is reminiscent of the role of the acyl group on the vinyloxy center in vinyl acetate and is demonstrated in the similarity of both the UPS and NMR data between vinyl acetate and **1** or **6**. When the cosubstituent exhibits electron-donating properties, a different situation is obtained. The dimethylamino moiety has previously been established as a strong electron-donating group to phosphorus atoms in cyclophosphazene derivatives.[36] Thus, the dimethylamino group in **9** will transfer electron density to the phosphorus centers, thereby reducing its ability to polarize electron density from the vinyloxy unit toward the phosphazene (Figure 3b). Under these conditions, the oxygen lone pair electrons are free to interact with the olefin, leading to an electron-rich substituent that resembles a vinyl ether. The NMR data for **9** reflect the electron-rich nature of the olefin and thus are consistent with the proposed model. The precise nature of the mechanism of transmission of electronic effects is currently under investigation.

The NMR spectra of the isomeric mixture **10** were investigated in order to establish the structural identity of individual components. If one assumes that no isomerization occurs during the dimethylaminolysis of **2**, then the isomeric composition of **10** is identical to that of **2**. The fact that pure 2,4,6-*cis*-$N_3P_3Cl_3(OPh)_3$ is converted to 2,4,6-*cis*-$N_3P_3[N(CH_3)_2]_3(OPh)_3$ without any isomerization[37] is a strong precedent for the absence of cleavage of the strong phosphorus−oxygen bonds (a necessary step for cis−trans isomerization) during reaction of the vinyloxy phosphazenes, **2**, with dimethylamine.[38] The use of the analysis of the ^{1}H NMR spectra of dimethylaminated cyclophosphazenes for structural assignment of the precursor is well established.[36] It has been previously established from ^{31}P NMR studies of **2** that very little of the geminal isomer, 2,2-$N_3P_3Cl_4(OCH{=}CH_2)_2$, is formed and that either the cis or the trans isomer is formed in a modest excess over the other

(32) A linear least-squares fit of the data gives a correlation coefficient of 0.981. If the data for **1** is omitted, the correlation coefficient increases to 0.996.

(33) A linear least-squares fit of the data gives a correlation coefficient of 0.79, which improves to 0.98 when the data for **1** are omitted and further improves to 0.99 when the zero intercept (0, 0) is included as a data point.

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(38) If the cis and trans isomers were in equilibrium, then the observed ratios would arise from thermodynamic control. However, the isomeric stability of 2,4,6-*cis*-$N_3P_3Cl_3(OPh)_3$ and the high thermodynamic barrier to phosphorus−oxygen bond cleavage suggest that the products once formed do not undergo isomerization and the observed ratios arise from kinetic control.

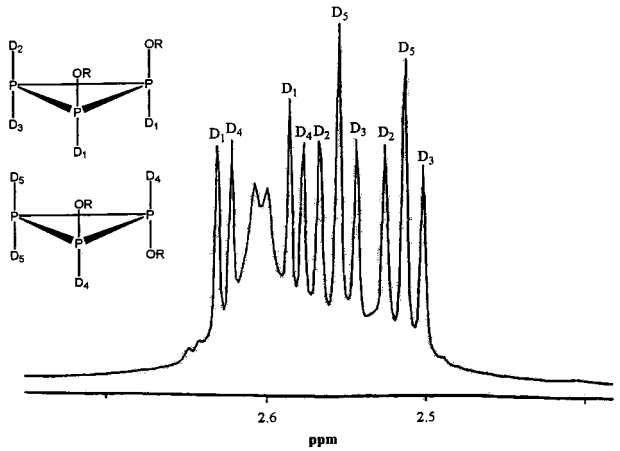

Figure 4. Assignment of the dimethylamino region of the ^{1}H NMR spectrum of $N_3P_3[N(CH_3)_2]_4(OCH{=}CH_2)_2$. The cyclophosphazene ring is represented as a triangle with phosphorus atoms at the vertexes. D represents the dimethylamino substituent, and R represents the vinyl group.

isomer.[2] Arguments involving relative chemical shifts[2] and the established cis preference at the trisubstituted stage[5] lead to the suggestion that the cis isomer predominates. The dimethylamino region of the ^{1}H NMR spectrum of **10** would be expected to consist of three sets of doublets (doublets from phosphorus coupling) with an intensity ratio of 2:1:2 from the three different sets of dimethylamino groups in the *cis*-2,4-$N_3P_3[N(CH_3)_2]_4(OCH{=}CH_2)_2$ isomer, and two doublets of equal intensity for the *trans*-2,4-$N_3P_3[N(CH_3)_2]_4(OCH{=}CH_2)_2$ isomer (see Figure 4 for structural representations of each isomer). It would also be expected that the three sets of $\equiv P[N(CH_3)_2]_2$ proton signals would be upfield of the two sets of $\equiv P[N(CH_3)_2](OCH{=}CH_2)$ proton signals based on the greater group electronegativity of the vinyloxy substituent. The same relative chemical shift pattern is observed for the dimethylamino protons in the phenoxy analogues *cis*-2,4-$N_3P_3[N(CH_3)_2]_4(OPh)_2$ and *trans*-2,4-$N_3P_3[N(CH_3)_2]_4(OPh)_2$.[37] The observation of three doublets upfield of two doublets is evident in the ^{1}H NMR spectrum (Figure 4) of **10**. The two broad components in the downfield portion of the spectrum are the result of the virtual coupling, a long-range-coupling phenomenon that is commonly observed in dimethylamino cyclophosphazene derivatives.[37,39] The resonances arising from the dimethylamino group labeled D_5 (Figure 4) can then be immediately assigned as the $\equiv P[N(CH_3)_2]_2$ centers from the trans isomer, since the intensity of this doublet is expected, and observed, to be about twice that of the other doublets. The other two doublets in the $\equiv P[N(CH_3)_2]_2$ region can be provisionally assigned as D_2 and D_3, with interchange of these assignments possible. The absolute assignments of these two pairs of resonances are not necessary for determining the isomeric composition. The groups D_1 and D_4 are assigned on the basis of the correlation of intensity with those of D_5 vs D_2 and D_3. Integration of this ^{1}H spectrum, the ^{31}P spectrum of the same sample, and the ^{31}P spectrum of the original $N_3P_3Cl_4(OCH{=}CH_2)_2$ isomeric mixture (**2**) gives the composition results shown in Table 2. The geminal compound was disregarded for this comparison. These results convincingly show that the cis isomer is formed in a slight excess over the trans isomer. This observation is in marked contrast to the reaction pathway followed by saturated species such as alkoxides and fluoroalkoxides where a strong trans preference exists.[10]

Table 2. Isomeric Composition of $N_3P_3Cl_4(OCH{=}CH_2)_2$

compound	method	cis	trans
$N_3P_3(N(CH_3)_2)_4(OCH{=}CH_2)_2$	^{1}H NMR	56.1	43.9
$N_3P_3(N(CH_3)_2)_4(OCH{=}CH_2)_2$	^{31}P NMR	54.3	45.7
$N_3P_3Cl_4(OCH{=}CH_2)_2$	^{31}P NMR	53.4	46.6

The origins of the observed stereoselectivity in cyclophosphazene substitution reactions has been a fundamental question since the early days of structure assignment for partially substituted cyclophosphazene derivatives. The early focus was on ground-state electronic effects leading to postulation of a selective transfer of electron density to a cis or trans position.[40] Relatively low-level MO calculations give some support to this line of reasoning.[41] However, with the recognition of the dominant influence of mechanistic effects in regio- and stereochemical control,[10] the focus has shifted to considerations of the relationship of the incoming reagent to the substrate structure. The various models considered for stereochemical preferences in the reactions of oxyanions with cyclophosphazenes have been summarized elsewhere.[10] The cis preference observed in the vinyloxy system is counterintuitive and is best rationalized in terms of a model wherein the electron-rich enolate anion undergoes a donor−acceptor interaction with the electron-deficient vinyloxy substitutent on the cyclophosphazene in **1**. This alignment of the nucleophile on the same side of the phosphazene ring as the vinyloxy substituent leads to a cis preference in the substitution pathway. This proposal can be supported in terms of literature precedents and experimental observations. The stereochemistry of a wide variety of organic reactions has been discussed in terms of a $\pi-\pi$ stacking model involving the electrostatic attraction of electron-rich and electron-deficient π electron moieties.[42,43] In the reactions of oxyanions with halocyclophosphazenes, cis steroselective is only observed when the hydrocarbon component of the oxyanion has carbon−carbon π bonds. Previous work has demonstrated the strong polarization of organic π electron systems by a directly attached cyclophosphazene ring.[23] The present study has shown that this strong π electron polarization effect is effectively transmitted through an oxygen atom separating the organic π system from the phosphazene ring. This combination of the delocalized, electron-rich enolate anion entering group and the electron-deficient olefin center in the vinyloxy phosphazene substituent provides the $\pi-\pi$ stacking environment that leads to the observed cis preference.

In summary, the present study reports the first quantitative correlations between changes in phosphosphazene substituents and variations in exocyclic group electronic structure. In the series of cyclophosphazenes in this investigation, the ^{31}P NMR chemical shifts are controlled by the local diamagnetic term and there is a quantitative correlation between ^{31}P chemical shifts at different sites on the phosphazene ring. The application of NMR spectroscopy has also allowed for establishment of a cis stereoselective pathway in the formation of the $N_3P_3Cl_4(OCH{=}CH_2)_2$ isomeric mixture. The observed stereoselectivity has been related to the electronic structure of the vinyloxy substituent on the cyclophosphazene.

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