into the vacant $2b_1$ acceptor orbital of a SO_2 ligand when it is η^1 bonded through S.[24] As a consequence, the SO_2 plane lies almost perpendicular to the equatorial coordination plane of the Fe atom.

In attempting to explain why the ArNSO ligand show a greater tendency to adopt η^2 as opposed to η^1 coordination than does SO_2, it should be borne in mind that irrespective of the η^1 vs. η^2 balance, η^2-(NS) is markedly preferred over η^2-(SO) in ArNSO complexes despite steric effects favoring the latter (cf. ref 5). It seems likely that in a molecule X=S=O, π bonding would decrease X = O > NAr. (It is consistent with this supposition that MeN–SO, 1.525 (4) Å,[25] is much longer than O–SO, 1.4321 Å,[29] whereas MeNS–O is 1.451 (5) Å[25]). Consequently, there would be an increase in the energy of the filled N–S–O π orbital (the equivalent of $1b_1$ in SO_2), which would have greater oxygen 2p character than nitrogen, and a decrease in the energy of the vacant N–S–O π^* orbital (the equivalent of $2b_1$ in SO_2), which would have greater nitrogen 2p character than oxygen. The former is thus able to compete more effectively with the n orbital as an electron donor, while the latter becomes a better acceptor. If, as proposed above, the Fe–ArNSO bond is largely back-bonding in character, it would be centered on the S–N bond so that η^2-(NS) bonding would be preferred to η^2-(SO) and, in our compounds, to η^1-(S). In other systems, the relative energies of the relevant metal donor and acceptor orbitals will obviously determine which of the bonding alternatives is adopted. Increasing the electron-withdrawing ability of the Ar group will lower the energy of the π^* orbital, increase the back-bonding to the η^2-(NS)-ArNSO ligand from the metal while reducing that to the CO ligands, and consequently lower the ν(CO) frequencies (Table I).

Nature of the $[Fe_2(CO)_9]$–ArNSO Product. We have suggested that the red compound obtained from the reaction of $[Fe_2(CO)_9]$ and various ArNSO species is $[Fe(CO)_4(ArNSO)]$. The presence of three absorption bands due to its IR-active ν(CO) vibrations is consistent with axially substituted trigonal-bipyramidal coordination about the iron atom but does not define it unambiguously. The frequencies of these vibrations are relatively low (for $[Fe(CO)_5$ ν(CO) = 1997, 2022, 2031, and 2114 cm^{-1}) which implies that the ArNSO ligand is acting here as a poorer π acceptor than CO, though better than PPh_3, and therefore cannot be either η^1-(S) or η^2-(NS) bonded. We suggest that it is η^1-(N) bonded via the lone pair on the N atom so that there is a N to Fe σ bond, possibly with some back-bonding into the NSO π^* orbital (the equivalent of the SO_2 $2b_1$ orbital). This mode of bonding has not been observed previously in ArNSO complexes, but it has been reported for the sulfur diimide derivative $[PtCl_2(C_2H_4)(\eta^1$-(N)-*t*-BuNSN-*t*-Bu)].[30]

Registry No. I (Ar = 4-$MeOC_6H_4$, R = Ph), 85134-75-4; I (Ar = 4-MeC_6H_4, R = Ph), 85134-76-5; I (Ar = 4-FC_6H_4, R = Ph), 85134-77-6; I (Ar = C_6H_5, R = Ph), 85134-78-7; I (Ar = 4-ClC_6H_4, R = Ph), 85134-79-8; I (Ar = 4-BrC_6H_4, R = Ph), 85134-80-1; I (Ar = 4-$NO_2C_6H_4$, R = Ph), 85134-81-2; I (Ar = 4-$NO_2C_6H_4$, R = 4-$MeOC_6H_4$), 85134-83-4; I (Ar = 4-$NO_2C_6H_4$, R = 4-MeC_6H_4), 85134-85-6; I (Ar = 4-$NO_2C_6H_4$, R = 4-ClC_6H_4), 85134-86-7; I (Ar = 4-$NO_2C_6H_4$, R = $PhCH_2$), 85134-87-8; I (Ar = 4-ClC_6H_4, R = 4-MeC_6H_4), 85134-88-9; I (Ar = 4-BrC_6H_4, R = 4-MeC_6H_4), 85134-89-0; I (Ar = 4-$NO_2C_6H_4$, R = MeO), 85115-71-5; I (Ar = 4-$NO_2C_6H_4$, R = EtO), 85115-72-6; I (Ar = 4-$NO_2C_6H_4$, R = *i*-PrO), 85134-92-5; II, 13463-40-6; $Fe((4\text{-}MeOC_6H_4)Ph_2P)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)$, 85134-82-3; $Fe((4\text{-}MeC_6H_4)Ph_2P)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)$, 85134-84-5; $[Fe(PPh_3)(MeC(CH_2O)_3P)(CO)_2(4\text{-}MeC_6H_4NSO)]$, 85134-90-3; $[Fe(PPh_3)(MeC(CH_2O)_3P)(CO)_2(PhNSO)]$, 85134-91-4; $[Fe(PPh_3)(MeC(CH_2O)_3P)(CO)_2(4\text{-}ClC_6H_4NSO)]$, 85115-68-0; $[Fe(PPh_3)(MeC(CH_2O)_3P)(CO)_2(4\text{-}BrC_6H_4NSO)]$, 85115-69-1; $[Fe(PPh_3)(MeC(CH_2O)_3P)(CO)_2(4\text{-}NO_2C_6H_4NSO)]$, 85115-70-4; $[Fe(Me(CH_2O)_3P)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$, 85115-73-7; $[Fe(PPh_3)_2(MeNC)(CO)(4\text{-}NO_2C_6H_4NSO)]$, 85115-74-8; $[Fe(PPh_3)_2(EtNC)(CO)(4\text{-}NO_2C_6H_4NSO)]$, 85115-75-9; $[Fe(PPh_3)_2(C_6H_{11}NC)(CO)(4\text{-}NO_2C_6H_4NSO)]$, 85115-76-0; $[Fe(PPh_3)_2(PhCH_2NC)(CO)(4\text{-}NO_2C_6H_4NSO)]$, 85115-77-1; $[Fe_2(CO)_9]$, 15321-51-4; $[FeB(CO)_3]$ (B = benzylideneacetone), 38333-35-6; $[Fe(PPh_3)_3(CO)_2]$, 15739-18-1; $[Fe(PPh_3)_2(CO)(CNCH_2Ph)(NNC_6H_4F\text{-}4)]BF_4$, 85097-64-9; $[Fe(PPh_3)_2(CO)_2(C_2(CN)_4)]$, 85097-65-0; $[Fe(PPh_3)_2(CO)_2(O_2CMe)_2]$, 85097-66-1.

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(Vinyloxy)chlorocyclotriphosphazenes

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The reactions of the lithium enolate of acetaldehyde, $LiOCHCH_2$, with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, lead to the series of (vinyloxy)chlorocyclotriphosphazenes, $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ (n = 1–6). Evidence for the occurrence of all possible geometrical and positional isomers in the series has been obtained from the ^{31}P NMR spectra. The principal products are the nongeminal species with comparable amounts of cis and trans isomers being formed. Small amounts of the geminal isomers are also observed. The mono- and pentasubstituted derivatives have been converted to their dimethylamino derivatives, $N_3P_3(OCH{=}CH_2)_{6-n}[N(CH_3)_2]_n$ (n = 1, 5).

Introduction

Although there have been extensive investigations into the reactions of amines[1-3] and more recently of organometallic reagents[4] with cyclophosphazenes, the corresponding reactions with alcohols have received considerably less attention. Detailed studies of the substitution pattern followed in the reactions of phenoxide[5] and the trifluoroethoxide[6] ions with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, have appeared. Less detailed studies of the reactions of other selected alkoxides with

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$N_3P_3Cl_6$ have also been carried out.[7] In all cases a nongeminal pathway is preferred. Recently, we have shown that the ambident enolate anions undergo reactions with the hexahalocyclotriphosphazenes $N_3P_3X_6$ (X = F, Cl) to yield the (vinyloxy)pentahalocyclotriphosphenes $N_3P_3X_5OCR{=}CH_2$.[8] The favorable combination of the hard acid (phosphorus(V)) with the hard base (oxygen) leads to exclusive attack at the oxygen end of the enolate anion and thus provides a route to previously inaccessible vinyl alcohol derivatives. In this paper, we present the synthesis and characterization of the series of (vinyloxy)chlorocyclotriphosphazenes $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ (n = 1–6). This study is of interest in terms of exploring the substitution pathway of oxygen-based nucleophiles with cyclophosphazenes. These materials are also new organofunctional phosphazenes which can serve as precursors to new monomeric and polymeric phosphazene derivatives.[9]

Experimental Section

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (Ethyl Corp.), was recrystallized from petroleum ether to a constant melting point of 113 °C. *n*-Butyllithium (1.6 M solution in hexane) was obtained from Aldrich. Tetrahydrofuran (THF) (Aldrich) was distilled from sodium–benzophenone ketyl. Petroleum ether (bp 35–55 °C), benzene,[10] and ethyl acetate (Fisher) were distilled by standard procedures. NMR spectra (in $CDCl_3$) were recorded on a Brucker WM 250 spectrometer operating at 250.1 MHz (^{1}H), 62.9 MHz (^{13}C), and 101.2 MHz (^{31}P). Tetramethylsilane (Me_4Si) was used as 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 upfield of the reference are assigned a negative sign. ^{13}C and ^{31}P NMR spectra were recorded under conditions of broad-band decoupling. Infrared (IR) spectra were obtained as their thin films (NaCl disks) on a Beckman IR 20A spectrometer. Mass spectra were recorded on a Perkin-Elmer RMU-6D spectrometer operating at 80 eV. Elemental analyses were performed by Integral Microanalytical Laboratories. The NMR spectra of mixtures were simulated by using a locally modified version of the computer program DNMR3.[11] The "spectral vector output" (i.e., an intensity parameter) of DNMR3 was modified to accommodate the calculation of spectra composed on several overlapping subspectra.

Preparation of $N_3P_3Cl_5OCH{=}CH_2$ (1) and $N_3P_3Cl_4(OCH{=}CH)_2$ (2). A solution of 10.5 g (30.2 mmol) of $N_3P_3Cl_6$ was treated with 70.0 mmol of $LiOCH{=}CH_2$.[12] A 2-g sample of the product was separated by flash chromatography[13] to yield 0.92 g (44.3% of theory) of $N_3P_3Cl_5OCH{=}CH_2$ (**1**) as previously described.[8] Continued elution from the column yielded 0.70 g (32.80% theory) of a colorless liquid, bp 55–57 °C (0.02 mmHg). Anal. Calcd for $C_4H_6Cl_4N_3O_2P_3$ (**2**): C, 13.22; H, 1.58; mol wt 361. Found: C, 13.15; H, 1.72; mol wt 361 (mass spectrum).

^{1}H NMR:[14] $\delta(\equiv POCH{=}CH_2)$ = 6.6–6.4 (complex multiplet), $\delta(\equiv POCH{=}CH_2(\text{trans}))$ = 5.2–5.0 (complex multiplet), $\delta(\equiv POCH{=}CH_2(\text{cis}))$ = 4.9–4.8 (complex multiplet). ^{31}P NMR: for nongeminal isomers $\delta(\equiv PCl_2)$ = 24.8, $\delta(\equiv PCl(OCH{=}CH_2))$ = 15.8 ($^2J_{PP}$ = 67.3), $\delta(\equiv PCl(OCH{=}CH_2))$ = 15.6 ($^2J_{PP}$ = 67.5); for geminal isomer $\delta(\equiv PCl_2)$ = 24.5 (d, 2 P) ($^2J_{PP}$ = 68.4), $\delta(\equiv P(OCH{=}CH_2)_2)$ = –0.6 (t, 1 P) ($^2J_{PP}$ = 69.0). IR:[15] 1645 (s, C=C str), 1220 (s, PN str), 1105 (s, PO str), 1030 (m), 925 (m, PCl), 885 (m, PCl), 785 (m, PCl).

Preparation of $N_3P_3Cl_3(OCH{=}CH_2)_3$ (3) and $N_3P_3Cl_2(OCH{=}CH_2)_4$ (4). The lithium enolate prepared from *n*-C_4H_9Li (45 mL, 72 mmol) and THF (80 mL) was added to a solution of $N_3P_3Cl_6$ (7.5 g, 21.7 mmol) in THF (70 mL) at room temperature. The reaction mixture was stirred for 5 days and worked up as before to give 7.0 g of a pale yellow liquid. A 2.0-g sample of this liquid was purified by using flash chromatography. The following compounds were obtained in succession: $N_3P_3Cl_5OCH{=}CH_2$ (**1**), 0.15 g (6.71% of theory); $N_3P_3Cl_4(OCH{=}CH_2)_2$ (**2**), 0.35 g (15.34% of theory). The third compound eluted was distilled under reduced pressure to yield 0.40 g (17.18% of theory) of a colorless liquid, (bp 90 °C (0.05 mmHg). Anal. Calcd for $C_6H_9Cl_3N_3O_3P_3$ (**3**): C, 19.43; H, 2.43; mol wt 369. Found: C, 19.12; H, 2.41; mol wt 369 (mass spectrum).

^{1}H NMR:[14] $\delta(\equiv POCH{=}CH_2)$ = 6.6–6.4 (complex multiplet), $\delta(\equiv POCH{=}CH_2(\text{trans}))$ = 5.1–5.0 (complex multiplet), $\delta(\equiv POCH{=}CH_2(\text{cis}))$ = 4.8–4.6 (complex multiplet). ^{31}P NMR:[16] $\delta(\equiv PCl_2)$ = 27.3, $\delta(\equiv PCl(OCH{=}CH_2))$ = 18.0, $\delta(\equiv P(OCH{=}CH_2)_2)$ = 3.0. IR:[15] 1640 (s, C=C str), 1230 (s, PN str), 1120 (s, PO str), 1025 (s), 930 (m, PCl), 900 (m, PCl), 790 (m, PCl).

The fourth compound obtained was distilled under reduced pressure to give 0.52 g (21.88% of theory) of a viscous liquid, bp 96 °C (0.05 mmHg). Anal. Calcd for $C_8H_{12}Cl_2N_3O_4P_3$ (**4**): C, 25.40; H, 3.17; mol wt 377. Found: C, 24.53; H, 2.90; mol wt 377 (mass spectrum).

^{1}H NMR:[14] $\delta(-OCH{=}CH_2)$ = 6.6–6.4 (complex multiplet), $\delta(-OCH{=}CH_2(\text{trans}))$ = 5.1–4.9 (complex multiplet), $\delta(-OCH{=}CH_2(\text{cis}))$ = 4.8–4.7 (complex multiplet). ^{31}P NMR: for geminal isomer $\delta(\equiv PCl_2)$ = 28.9, $\delta(\equiv P(OCH{=}CH_2)_2)$ = 5.7 ($^2J_{PP}$ = 75.7); for nongeminal isomers $\delta(\equiv PCl(OCH{=}CH_2))$ = 21.6, $\delta(\equiv P(OCH{=}CH_2)_2)$ = 6.1 ($^2J_{PP}$ = 83.4), $\delta(\equiv PCl(OCH{=}CH_2))$ = 21.4, $\delta(\equiv P(OCH{=}CH_2)_2)$ = 6.1 ($^2J_{PP}$ = 80.6). IR:[15] 1645 (s, C=C str), 1230 (s, PN str), 1115 (s, PO str), 1025 (s), 930 (m, PCl), 905 (m, PCl), 785 (m, PCl).

Preparation of $N_3P_3Cl(OCH{=}CH_2)_5$ (5) and $N_3P_3(OCH{=}CH_2)_6$ (6). The reaction of the lithium enolate prepared from *n*-C_4H_9Li (85 mL, 136 mmol) and THF (160 mL) with $N_3P_3Cl_6$ (6.0 g, 17.2 mmol) in THF (100 mL) was carried out as described above to yield 5.6 g of a pale yellow liquid. A 1.0-g sample of this liquid was purified by using flash chromatography with petroleum ether–ethyl acetate (97/3) as the eluant. The first product obtained was a viscous liquid, which was distilled under reduced pressure to give 0.36 g (30.78% of theory) of a colorless liquid, bp 105 °C (0.05 mmHg). Anal. Calcd for $C_{10}H_{15}ClN_3O_5P_3$ (**5**): C, 31.13; H, 3.89; mol wt 385. Found: C, 30.39; H, 3.70; mol wt 385 (mass spectrum).

^{1}H NMR:[14] $\delta(-OCH{=}CH_2)$ = 6.7–6.4 (complex multiplet), $\delta(-OCH{=}CH_2(\text{trans}))$ = 5.1–5.0 (complex multiplet), $\delta(-OCH{=}CH_2(\text{cis}))$ = 4.9–4.6 (complex multiplet). ^{31}P NMR: $\delta(\equiv PCl(OCH{=}CH_2))$ = 23.9, $\delta(\equiv P(OCH{=}CH_2)_2)$ = 8.7 ($^2J_{PP}$ = 85.0). ^{13}C NMR: $\equiv PCl(OCH{=}CH_2)$ group $\delta(C_\alpha)$ = 141.0 (d) ($^3J_{PC_\alpha}$ = 8.5), $\delta(C_\beta)$ = 102.7 (d) ($^3J_{PC_\beta}$ = 12.2); $\equiv P(OCH{=}CH_2)_2$ group $\delta(C_\alpha)$ = 141 (s), $\delta(C_\beta)$ = 101.8 (m) ($^2J_{PC_\beta}$ = 12.2). IR:[15] 1645 (s, C=C str), 1240 (s, PN str) 1110 (s, PO str), 1025 (s), 920 (m, PCl), 860 (m, PCl), 770 (m, PCl).

The next product was distilled under reduced pressure to yield 0.30 g (25.15% of theory) of a viscous liquid, bp 110 °C (0.05 mmHg). Anal. Calcd for $C_{12}H_{18}N_3O_6P_3$ (**6**): C, 36.64; H, 4.58; mol wt 393. Found: C, 35.88; H, 4.01; mol wt 393 (mass spectrum).

^{1}H NMR:[14] $\delta(-OCH{=}CH_2)$ = 6.5 (center of a complex multiplet), $\delta(-OCH{=}CH_2(\text{trans}))$ = 4.9 (center of a complex multiplet), $\delta(-OCH{=}CH_2(\text{cis}))$ = 4.5 (center of a complex multiplet, ^{13}C NMR: $\delta(C_\alpha)$ = 141.6 (d) (J_{PC_α} = 2.4), $\delta(C_\beta)$ = 101.3 (m). ^{31}P NMR: $\delta(\equiv P(OCH{=}CH_2)_2)$ = 11.3 (s). IR:[15] 1645 (s, C=C str), 1245 (s, PN str), 1130 (s, PO str), 1010 (s), 865 (m), 810 (m), 760 (m), 690 (m).

Preparation of $N_3P_3(OCH{=}CH_2)(NMe_2)_5$ (7). The reaction of $N_3P_3Cl_5OCH{=}CH_2$ (**1**) (2.5 g, 7.1 mmol) with an excess of anhydrous dimethylamine (10.5 g, 233.3 mmol) in chloroform (100 mL) at 0 °C was allowed to proceed for 24 h. After removal of the solvent, the oily residue was extracted with petroleum ether (250 mL). The amine hydrochloride and petroleum ether were removed, and the remaining liquid was distilled to yield 2.0 g (71.8% of theory) of a colorless liquid, bp 90 °C (0.05 mmHg). Anal. Calcd for $C_{12}H_{33}N_8OP_3$ (**7**): C, 36.18; H, 8.29; mol wt 398. Found: C, 37.67; H, 8.12; mol wt 398 (mass spectrum).

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^{1}H NMR:[14] $\delta(\equiv POCH{=}CH_2) = 6.6$ (m) (J_{HH}(trans) = 13.6, J_{HH}(cis) = 5.9, $^3J_{PH}$ = 7.6), $\delta(\equiv POCH{=}CH_2$ (trans)) = 4.6 (m) (J_{HH}(trans) = 13.6, J_{HH}(*gem*) = 2.2, $^3J_{PH}$ = 2.0), $\delta(\equiv POCH{=}CH_2$ (cis)) = 4.2 (m) (J_{HH}(cis) = 5.9, J_{HH}(*gem*) = 2.2, $^4J_{PH}$ = 1.8), $\delta(\equiv P(OCH{=}CH_2)(NMe_2)) = 2.7$ (d) ($^3J_{PH}$ = 11.8), $\delta(\equiv P(NMe_2)_2) = 2.6$ (d) ($^3J_{PH}$ = 11.4). ^{31}P NMR: $\delta(\equiv P(OCH{=}CH_2)(NMe_2)) = 23.3$ (t, 1 P) ($^2J_{PP}$ = 47.6), $\delta(\equiv P(NMe_2)_2) = 27.1$ (d, 2 P) ($^2J_{PP}$ = 50.6). ^{13}C NMR: $\delta(C_\alpha = 142.7$ (d) (J_{PC_α} = 6.1), $\delta(C_\beta) = 95.4$ (d) (J_{PC_β} = 9.8), $\delta(\equiv P(OCH{=}CH_2)(NMe_2)) = 35.8$ (d) (J_{PC} = 2.4), $\delta(\equiv P(NMe_2)_2) = 35.6$ (s). IR:[15] 2880 (s, CH str), 1640 (s, C=C str), 1460 (s, $\delta_{as}(CH_3)$), 1275 (s, PN str), 1190 (s), 1120 (s, PO str), 1060 (m), 880 (m, PN), 750 (m), 670 (m).

Preparation of $N_3P_3(OCH{=}CH_2)_5NMe_2$ (8). Anhydrous dimethylamine (10.0 g, 222 mmol) was added to a solution of $N_3P_3Cl(OCH{=}CH_2)_5$ (**5**) (0.5 g, 1.4 mmol) in toluene (50 mL) at 0 °C, and the reaction was allowed to proceed as above. The resultant liquid was distilled under reduced pressure to give 0.45 g (87.8% of theory) of a colorless liquid, bp 105 °C (0.05 mmHg). Anal. Calcd for $C_{12}H_{21}N_4O_5P_3$ (**8**): C, 36.92; H, 5.38; mol wt 350. Found: C, 36.37; H, 5.18; mol wt 350 (mass spectrum).

^{1}H NMR:[14] $\delta(-OCH{=}CH_2) = 6.5$ (center of a complex multiplet), $\delta(-OCH{=}CH_2$ (trans)) = 4.9 (center of a complex multiplet), $\delta(-OCH{=}CH_2$ (cis)) = 4.6 (center of a complex multiplet), $\delta(-NMe_2) = 2.7$ (d) ($^3J_{PH}$ = 12.2). ^{13}C NMR: $\equiv P(OCH{=}CH_2)(NMe_2)$ group $\delta(C_\alpha) = 99.6$ (d) (J_{PC_α} = 11.0, $\delta(C_\beta = 142.3$ (J_{PC_β} = 7.32), $\delta(-NMe_2) = 36.3$ (d) ($^3J_{PC}$ = 3.7); $\equiv P(OCH{=}CH_2)_2$ group $\delta(C_\alpha) = 141.8$ (s), $\delta(C_\beta) = 100.4$ (m). ^{31}P NMR: $\delta(\equiv P(OCH{=}CH_2)(NMe_2)) = 22.2$, $\delta(\equiv P(OCH{=}CH_2)_2) = 11.7$ ($^2J_{PP}$ = 74.6). IR:[15] 2920 (m, CH str), 1645 ns, C=C str), 1240 (s, PN str), 1125 (s, PO str), 1010 (s), 920 (m, PN), 870 (m, PN), 810 (m), 770 (m), 695 (m).

Results and Discussion

There are two possible routes of reaction for an ambident enolate anion leading to derivativization of either the oxygen end or the carbon end of the nucleophile.[17] We have previously shown that the phosphazene is attacked by the oxygen end of the enolate anion in the formation of the monosubstituted derivatives.[8] The ^{1}H and ^{13}C NMR spectra of all the new compounds reported in this investigation closely resemble those of the monosubstituted derivative. In particular, the proton spectra resemble that of vinyl acetate with additional phosphorus coupling and there are no alkyl or carbonyl carbon atoms observed in the ^{13}C NMR spectra.[18] The NMR spectra of authentic phosphazenes with β-carbonyl functions (the hypothetical product resulting from the attack on the carbon end of the enolate) have recently been reported and differ significantly from the products of the enolate anion reactions.[19] Consequently, we may conclude that the reaction generally leads to the vinyloxy derivatives as shown in eq 1. These materials are stable to air and atmospheric moisture.

$$N_3P_3Cl_6 + n\text{LiOC}_2H_3 \rightarrow N_3P_3Cl_{6-n}(OCH{=}CH_2)_n + n\text{LiCl} \quad (1)$$
$$n = 1\text{–}6$$

The monosubstituted derivative, **1**, has an AB_2 ^{31}P NMR spectrum appropriate to the proposed structure. Further characterizational details were previously reported.[8] The chlorine atoms in **1** were removed by the reaction of **1** with dimethylamine to give $N_3P_3[N(CH_3)_2]_5OCH{=}CH_2$. The ^{1}H and ^{31}P NMR spectra of this derivative are consistent with the formulation given above. The fact that **1** can be derivatized leaving the vinyl group intact demonstrates that one can potentially prepare a series of organofunctional phosphazene monomers of the type $N_3P_3X_5OCH{=}CH_2$ starting with **1**.

A mixture of bis isomers, **2**, which resisted further chromatographic separation, was isolated. The absence of mono- or trisubstituted species was confirmed by mass spectrometry.

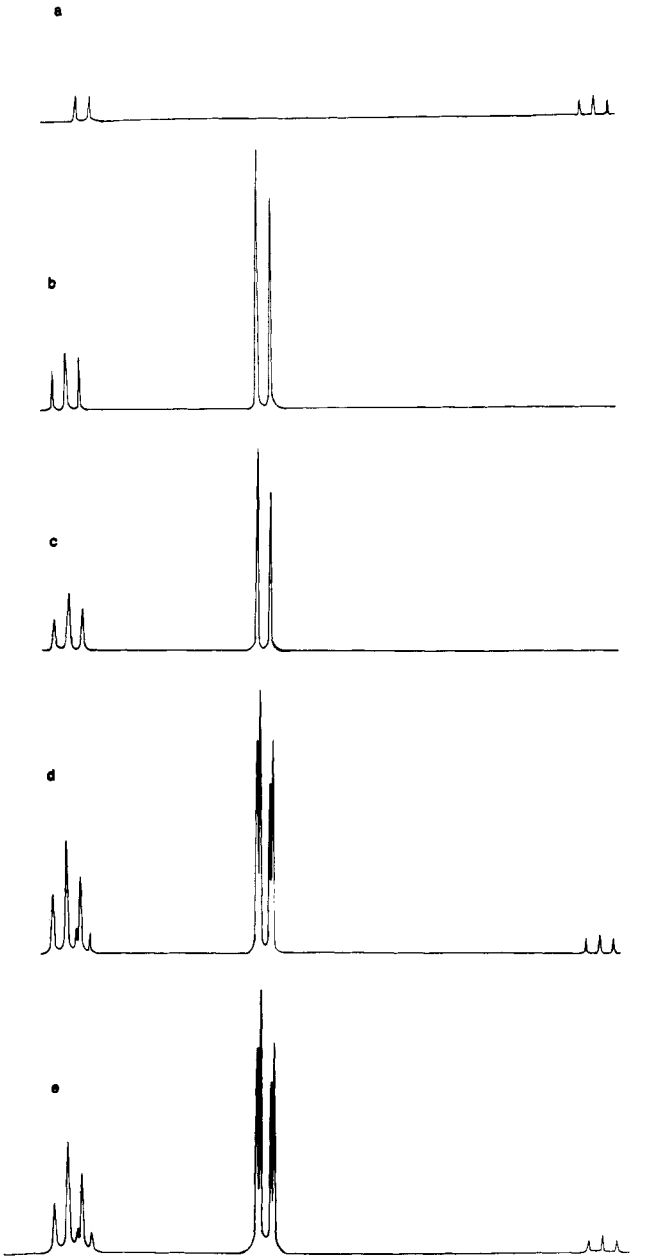

Figure 1. Simulated and observed ^{31}P NMR spectra for $N_3P_3Cl_4(OCH{=}CH_2)_2$: (a) simulated spectrum of 2,2-$N_3P_3Cl_4(OCH{=}CH_2)_2$; (b) simulated spectrum of the less abundant 2,4-$N_3P_3Cl_4(OCH{=}CH_2)_2$ isomer; (c) simulated spectrum of the more abundant 2,4-$N_3P_3Cl_4(OCH{=}CH_2)_2$ isomer; (d) simulated spectrum of the mixture of the $N_3P_3Cl_4(OCH{=}CH_2)_2$ isomers: (e) observed spectrum of the mixture of the $N_3P_3Cl_4(OCH{=}CH_2)_2$ isomers.

The ^{31}P NMR spectrum of **2** (Figure 1) clearly shows the existence of all three positional and geometric isomers of the composition $N_3P_3Cl_4(OCH{=}CH_2)_2$. The NMR parameters for each isomer were estimated from the mixture spectrum and used to simulate the individual spectra. The mixture spectrum was matched to the composite of the individual spectra (Figure 1) by varying the contributions of each of the components, thus allowing for calculation of the relative concentration of each species.[20] There is a low-intensity A_2X spectrum (Figure 1a) in which the A part is in the $\equiv PCl_2$ chemical shift range while the X part is in the general range

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(20) The ^{31}P line widths are visibly different for different phosphorus environments in the mixture. Thus, different T_2 values were required for each environment. The values best reproducing the individual spectra: geminal $\equiv PCl_2$, 0.06; geminal $\equiv P(OCH{=}CH_2)_2$, 0.18; nongeminal $\equiv PCl(OCH{=}CH_2$, 0.06; nongeminal $\equiv PCl_2$ 0.035.

found in $N_3P_3(OCH{=}CH_2)_6$. The A_2X spectrum, with A being $\equiv PCl_2$, is consistent only with the geminal isomer. Excluding spirocyclic species, this is the first example of a geminal $N_3P_3Cl_4(OR)_2$ species formed in the reactions of nucleophiles derived from alcohols with $N_3P_3Cl_6$. The nongeminal isomers both exhibit AB_2 spectra (Figure 1b,c) with identical A regions. In the B ($\equiv PCl(OCH{=}CH_2)$) region the chemical shifts are slightly different. The relative abundances of each isomer as obtained from the simulation study are 4% geminal and 43 and 53%, respectively, for the two nongeminal isomers. This characterization of the mixture of bis isomers by high-field ^{31}P NMR and simulation studies demonstrates the value of this approach in both qualitative and quantitative studies of phosphazene substitution reactions. The proton NMR spectrum of the mixture is, as expected, complex. In the region associated with H_a ($-OCH_a{=}CH_2$), there is a triplet[21] in low abundance, which is slightly upfield from the H_a resonances for $\equiv PCl(OCH{=}CH_2)$ environment. The intensity of the triplet increases as one goes through the $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ series, and so it may be taken as an indicator of the amount of species containing the $\equiv P(OCH{=}CH_2)_2$ center in a mixture.

Given the propensity for trans isomer formation observed in the reactions of cyclotriphosphazenes with alkyl- and dialkylamines,[2,22] *tert*-butyllithium,[23] and the trifluoroethoxide ion,[6] it is tempting to suggest that the isomer in greatest abundance is *trans*-2,4-$N_3P_3Cl_4(OCH{=}CH_2)_2$. Any assignment of this type must be considered as tenuous since there is very little knowledge of isomer ratios in the reactions of $N_3P_3Cl_6$ with oxygen bases and a few reactions of cyclotriphosphazenes with nucleophiles such as phenyllithium[24] and the phenoxide ion[25] appear to give the cis isomer predominantly. In the case of the bis(dimethylamino)chlorocyclotriphosphazenes, the ^{31}P NMR chemical shift for the $\equiv PClN(CH_3)_2$ center is more positive for the trans (compared to the cis) isomer.[26] In $N_3P_3Cl_4(OCH{=}CH_2)_2$, the less abundant nongeminal isomer has the more positive chemical shift for the $\equiv PCl(OCH{=}CH_2)$ center. These observations also cast doubt on the suitability of assigning the trans configuration to the more abundant isomer in **2**.

The results presented above indicate interesting differences in the reaction pattern in the reactions of $N_3P_3Cl_6$ with $LiOCH{=}CH_2$ and $NaOCH_2CF_3$. In the latter system, the geminal isomer was not observed and the trans isomer was in significantly greater abundance (trans:cis > 5:1).[6] There are not sufficient data to speculate on the reasons for these differences. In particular the roles of the counterion and the solvent bear further investigation.

The sample, **3**, with the stoichiometry $N_3P_3Cl_3(OCH{=}CH_2)_3$ has a complex ^1H NMR spectrum with evidence for the $\equiv P(OCH{=}CH_2)_2$ center in small amounts. The ^{31}P NMR spectrum of **3** shows evidence for all three isomers (geminal, cis-2,4,6, trans-2,4,6). A doublet of doublets in the $\equiv P(OCH{=}CH_2)_2$ region along with a triplet (center lines of doublet of doublets merged) in the $\equiv PCl_2$ region confirms the presence of the geminal (2,2,4) isomer. The $\equiv PCl(OCH{=}CH_2)$ region contains peaks from the geminal isomer, a large singlet corresponding to the cis isomer, and an AB_2 pattern assignable to the trans isomer. The overlap of all of these resonances precludes the obtaining of quantitative information concerning isomer ratios. The pattern established at the level of disubstitution is qualitatively maintained, i.e. predominantly nongeminal with traces of the geminal product being observed.

The ^{31}P NMR spectrum of **4**, the tetrasubstituted sample, again indicates the existence of all three isomers. The geminal isomer is in very low abundance and is characterized by an AX_2 spectrum with A in the $\equiv PCl_2$ and X in the $\equiv P(OCH{=}CH_2)_2$ region. There are two sets of closely spaced A_2X spectra covering the $\equiv PCl(OCH{=}CH_2)_2$ and $\equiv P(OCH{=}CH_2)_2$ regions, which correspond to the nongeminal cis and trans isomers in nearly equal amounts.

The pentasubstituted derivative, **5**, exhibits an AB_2 ^{31}P NMR spectrum, which is approaching AX_2. In aminophosphazene derivatives, materials that appear to be $N_3P_3Cl(NR_2)_5$ are often hydrochlorides of $N_3P_3(NR_2)_6$,[2] so we carried out the reaction of **5** with dimethylamine to yield $N_3P_3N(CH_3)_2(OCH{=}CH_2)_5$, thus providing chemical structure proof of the proposed formulation of **5**.

The ^{31}P NMR spectrum of the hexasubstituted material, **6**, has the expected singlet in the $\equiv P(OCH{=}CH_2)_2$ region. The ^1H NMR spectrum shows a curious anomaly in that there is an increase in the number of lines in the H_a region over what is observed in **1**. The origins of this complication are unclear, but it does suggest different environments for the exocyclic substituents.

In summary, it has been shown that the reaction of the lithium enolate of acetaldehyde with $N_3P_3Cl_6$ leads to the complete series of compounds of the type $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$. The nongeminal pathway is favored. This new, and to date most complete, series of organofunctional phosphazenes can be expected to form the basis of extensive new incorporation of cyclophosphazenes into polymeric systems.[9] Of particular interest is the possibility that the nongeminal species will be reagents for novel cross-linking and related reactions. Work along these lines is currently in progress in our laboratory.

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Registry No. **1**, 82056-02-8; **2** (isomer 1), 85167-43-7; **2** (isomer 2), 85167-50-6; **2** (isomer 3), 85167-51-7; **3** (isomer 1), 85167-44-8; **3** (isomer 2), 85167-52-8; **3** (isomer 3), 85201-85-0; **4** (isomer 1), 85167-45-9; **4** (isomer 2), 85167-53-9; **4** (isomer 3), 85167-54-0; **5**, 85167-46-0; **6**, 85167-47-1; **7**, 85167-48-2; **8**, 85167-49-3; $N_3P_3Cl_6$, 940-71-6; $LiOCH{=}CH_2$, 2180-63-4.

(21) Doublet of doublets with $J_{PH} \simeq J_{HH}$.
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