evaporated to dryness. The white, crystalline residue, after recrystallization from diethyl ether, gave a mass spectrum with a parent ion at 569 amu. It melted at 82-83 °C and had a ^{31}P NMR spectrum that was interpreted as an AB_2 spin system, as reported in Table I.

Displacement of Imidazole from II by $NaOCH_2CF_3$ To Form $[NP(OCH_2CF_3)_2]_3$. Compound II (0.961 g, 1.79×10^{-3} mol) in tetrahydrofuran (100 mL) was placed in a round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and an addition funnel. To this solution was added sodium trifluoroethoxide in tetrahydrofuran, prepared from sodium (1.25 g, 0.054 mol) and excess trifluoroethanol (a fivefold excess of $NaOCH_2CF_3$ over that required for total imidazole replacement). The reaction mixture was stirred overnight at 23 °C, and the excess sodium trifluoroethoxide was deactivated with a small amount of aqueous hydrochloric acid. The solvent was then removed, and the resultant oil was dissolved in benzene and washed with water. The benzene layer was separated, and the solvent was removed. Sublimation yielded a white solid (0.2922 g, 23%), mp 44-49 °C (lit. 49-50 °C). A mass spectrum showed a parent ion at 729 amu that indicated the presence of $[NP(OCH_2CF_3)_2]_3$. No partly substituted phosphazene species were detected from the mass spectrum, and no evidence of peaks from imidazolyl residues were seen.

Reaction between *N*-Methylimidazole and $(NPCl_2)_3$. All of the following manipulations were carried out under a nitrogen atmosphere. *N*-Methylimidazole (1.5 g, 0.03 mol) was vacuum-distilled from potassium hydroxide and was added to a solution prepared by dissolving $(NPCl_2)_3$ (1 g, 0.003 mol) in tetrahydrofuran (70 mL). A yellow precipitate developed immediately following addition of the *N*-methylimidazole. The reaction mixture was stirred for 20 min, and the yellow precipitate was collected by filtration in a Schlenk filter funnel. It was washed with tetrahydrofuran and dried under vacuum. The product was insoluble in tetrahydrofurn, benzene, acetonitrile, and diethyl ether. It reacted with water or ethanol with decomposition. This salt proved difficult to purify because of its insolubility and sensitivity to hydrolysis. Microanalysis of the crude product suggested a composition close to that of VII, but accurate correspondence between theory and the analysis results could not be obtained.

Reactions of Species of Type VII. A stirred suspension of VII (prepared as described above) (0.5 g) in tetrahydrofuran (100 mL) was treated under dry nitrogen with excess *n*-butylamine (6.3 g, 0.0862 mol). The yellow solid dissolved slowly, with bleaching of the color. A ^{31}P NMR spectrum of the concentrated reaction mixture showed a clean spectrum identical with that of an authentic sample of $[NP(NHC_4H_9)_2]_3$ (see Table I). Similarly, VII (0.5 g) was allowed to react with imidazole (5.8 g, 0.862 mol) in tetrahydrofuran (100 mL). A ^{31}P NMR spectrum showed the presence of II only (Table I). Methylamine (100 mL) reacted with a stirred suspension of VII (0.5 g) in tetrahydrofuran (100 mL) at 0 °C during 2 days under dry nitrogen to yield $[NP(NHCH_3)_2]_3$, identified by its ^{31}P NMR spectrum (Table I).

A solution of sodium trifluoroethoxide, prepared from trifluoroethanol (8.62 g, 0.0862 mol) and sodium hydride in tetrahydrofuran (175 mL), was filtered and added to a stirred solution of VII (0.5 g) in tetrahydrofuran (100 mL). After reaction for 2 days at 25 °C the mixture was concentrated. A ^{31}P NMR spectrum gave unambiguous evidence for the presence of $[NP(OCH_2CF_3)_2]_3$ as the only phosphorus-containing species present (see Table I).

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. HL 11418). We thank R. D. Minard for the mass spectrometric data and P. J. Harris and A. J. Freyer for the ^{31}P NMR data.

Organometallic Phosphazenes: Synthesis and Rearrangement of Propynyl- and Propadienylcyclotriphosphazenes

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Abstract: A new series of 1,1-dialkyltetrachlorocyclotriphosphazenes with prop-2-ynyl (VI), prop-1,2-dienyl (V), and prop-1-ynyl (XII) substituents have been prepared. These syntheses involve the reactions of cuprio- or lithiophosphazene anions (II or IX) with prop-2-ynyl bromide which lead initially to the formation of the prop-2-ynyl complexes (VI). The prop-2-ynyl side group was found to undergo an alumina-initiated rearrangement to the prop-1,2-dienyl group (V), and both compounds VI and V underwent a methyllithium-initiated rearrangement to the prop-1-ynyl derivatives (XII). These organometallic-initiated rearrangements were monitored by ^{31}P NMR spectroscopy. The structural characterization of all the new compounds is described, and the NMR results, together with the various rearrangements, are discussed in terms of electronic interactions between the C_3H_3 group and the phosphazene ring. The formation of the lithiophosphazene anion (IX, R = CH_3) was studied by low-temperature ^{31}P NMR spectroscopy, and the results are discussed in terms of the electron distribution within the phosphazene ring.

The synthesis of phosphazene compounds with organic substituents bound to the skeleton through direct phosphorus–carbon bonds has received considerable attention in recent years.[2-6] Phosphazene compounds that contain unsaturated organic substituents are of particular interest.[5-8] Olefinic or acetylenic side groups can serve as sites for many different types of organic transformations or as building blocks for polymerization or oligomerization reactions.[7] Acetylenic phosphazenes can be used as ligands for transition metals.[8,9]

The general route employed for the synthesis of this class of compounds has, until now, involved the reactions of organometallic reagents with halophosphazenes.[2-4,7,8] a procedure that is often accompanied by side reactions such as ring coupling or skeletal cleavage.[2-4,7,8]

In this paper we describe a new route for the synthesis of organo-substituted phosphazenes with acetylenic side groups. The

(1) For a previous paper in this series see: Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. *Inorg. Chem.*, in press.
(2) DuPont, J. F.; Allen, C. W. *Inorg. Chem.* **1978**, *17*, 3093.
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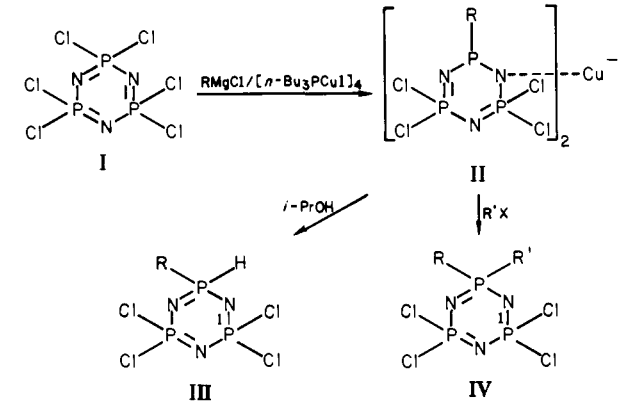
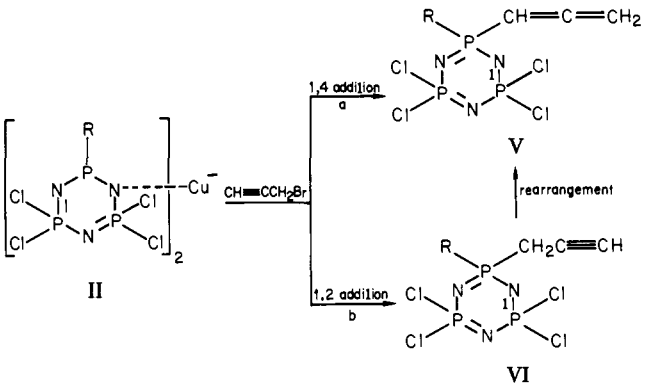
Scheme I



Scheme II



approach taken involves the reaction of various metallophosphazene intermediates[5,6,10,11] with the unsaturated electrophile, prop-2-ynyl bromide. The main advantage of this reaction route over the conventional organometallic approach is that the side reactions that lead to phosphazene degradation can be virtually eliminated.

Results and Discussion

The Primary Reaction. In recent publications we described the synthesis[10,11] and subsequent reactions[5,6,10,11] of a new group of metallophosphazene complexes, of general formula, II. These metallophosphazenes (II, R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, i-C_4H_9, t-C_4H_9, or allyl) can be synthesized readily by the reaction of hexachlorocyclotriphosphazene, I, with the appropriate Grignard reagent in the presence of $[n\text{-}Bu_3PCuI]_4$.[10]

Subsequent reaction of complexes of type II with 2-propanol yields hydridophosphazenes, III,[10,11] while reaction with alkyl halides leads to 1,1-dialkylphosphazenes, IV (Scheme I).[5,6]

In this work, metallophosphazenes of type II were allowed to react with prop-2-ynyl bromide. These reactions were found to yield mixtures of compounds V and VI (R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, i-C_4H_9, t-C_4H_9, or allyl). Compounds VI possess a prop-2-ynyl group bound to the phosphazene ring, whereas compounds V contain a prop-1,2-dienyl substituent. The ratio of these two species appeared to be dependent not only on the type of alkyl group, R, bound to the metallophosphazene in II but also on the isolation and purification procedure employed. In principle, these products could result from the reaction of prop-2-ynyl bromide with II in one of two ways, as shown in Scheme II. However, as will be shown later, the operative mechanism involves 1,2 addition to give VI followed by rearrangement to V. This rearrangement is catalyzed either by copper(I) salts present in solution[13] or when VI interacts with neutral alumina[13] during the removal of copper salts from the product.

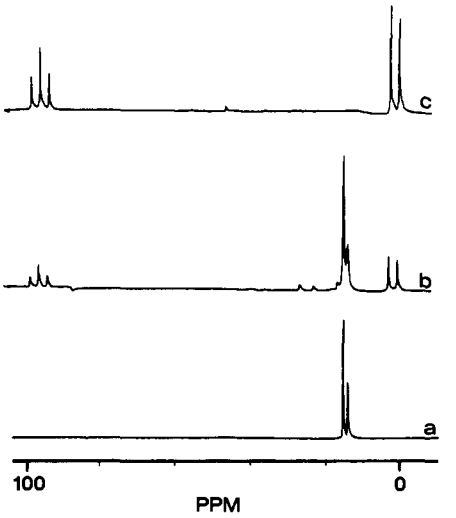
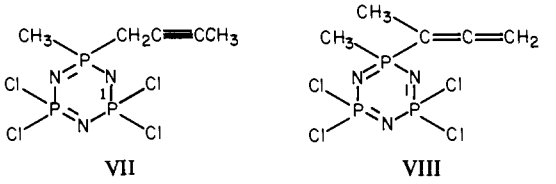


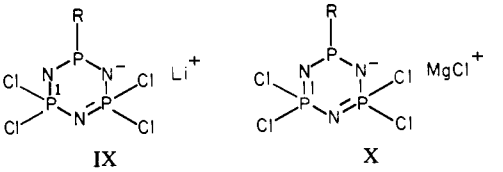
Figure 1. Changes in the ^{31}P NMR spectrum following addition of methyllithium to methylhydridotetrachlorocyclotriphosphazene (III, R = CH_3) at −70 °C. The differences between spectra a, b, and c are discussed in the text.

A number of experiments were carried out in an attempt to distinguish between these two pathways. In order to explore possibility (a), we allowed the metallophosphazene II (R = CH_3) to react with but-2-ynyl bromide. This reaction was chosen for the following reasons. Earlier work[5] had shown that the reaction of metallophosphazene II (R = CH_3) with prop-2-ynyl bromide led almost exclusively to the prop-1,2-dienyl compound V (R = CH_3). Although 1,4-conjugate addition to but-2-ynyl bromide may be somewhat more sterically hindered than with prop-2-ynyl bromide, at least a small amount of this type of product would be expected if the conjugate addition pathway was indeed operative. However, the only product isolated from the reaction of II (R = CH_3) with but-2-ynyl bromide was VII. *No* products such as VIII, derived from a conjugate addition type reaction,



were observed. This result suggests that conjugate addition *does not* occur during the reaction of metallophosphazenes, II, with acetylenic halides. Thus, it appears that compounds V are formed from compounds VI either by a copper(I)-catalyzed rearrangement or during the isolation procedure. This prospect will be discussed in a later section.

Synthesis of Lithio- and Magnesiophosphazenes. In view of the results obtained with cupriophosphazenes, it became clear that the synthesis of prop-2-ynyl substituted phosphazenes VI in a pure state required the use of a metallophosphazene species that did not contain copper. This was achieved by the low-temperature metallation[14] of hydridophosphazenes III with methyllithium to yield IX (or with methylmagnesium chloride to yield X). Al-



though both of these new types of metallophosphazenes were extremely reactive and decomposed if warmed to room temperature, it was possible to obtain the ^{31}P NMR spectrum of com-

(10) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.
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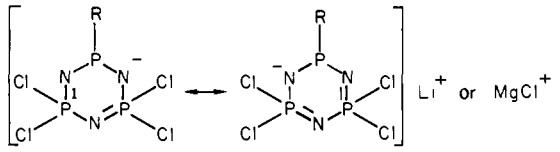
pound IX (R = CH_3) by generating the compound in the cooled probe of an NMR spectrometer.[15]

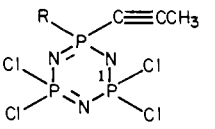
A typical series of proton-decoupled ^{31}P NMR spectra are shown in Figure 1. The initial spectrum, a, contains resonances at 17.6 and 13.8 ppm, assigned to the starting material III (R = CH_3).[10,16] Spectrum b was derived from the reaction mixture after addition of $\simeq 1/2$ equiv of methyllithium, and spectrum c was obtained after addition of ≥ 1 equiv. Spectrum c, assigned to compound IX (R = CH_3), was interpreted as an AX_2 spin system.[17] The resonance for the phosphorus atom bound to the alkyl group occurred at 97.1 ppm as a triplet (J_{PNP} = 93 Hz). The position of resonance for this nucleus displayed a large downfield shift compared to the parent compound and appeared in the same general region as for alkyldiaminophosphines, R'P-$(NR_2)_2$.[18] The resonance assigned to the PCl_2 nuclei occurred at 2.9 ppm as a doublet (J_{PNP} = 93 Hz). This position of resonance is shifted upfield from that of the parent hydridophosphazene, and this is presumed to result from a negative charge buildup in the phosphazene ring. The phenomenon can be rationalized in terms of the variation in π-electron density distribution about the phosphazene ring by consideration of the "island" theory of bonding in phosphazene molecules.[19,20] A buildup of negative charge in one of the P–N–P islands will concentrate toward the end of the island bearing the most electronegative substituents, i.e., the PCl_2 groups. This effect would cause a greater magnetic shielding and thus generate an upfield shift for the position of this nucleus. This type of perturbation of the phosphazene π-bonding system has been discussed before[6] and can be detected from crystal structure data for various phosphazenes.[21-24]

These results can be rationalized best if the metallophosphazenes IX (and X) are viewed as resonance hybrids of the canonical forms described in XI, with the negative charge symmetrically distributed about the N–(R)P–N segment of the phosphazene ring.



XI

Reaction of Lithio- or Magnesiophosphazenes with Prop-2-ynyl Bromide. The extremely high reactivity of compounds IX or X precluded their isolation. However, if these complexes were generated by the reaction of methyllithium (or methylmagnesium chloride) with the hydridophosphazenes III and were then immediately allowed to react with prop-2-ynyl bromide, the products isolated were either compounds V, VI, or XII (in each case R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, i-C_4H_9, t-C_4H_9, or allyl). The specific products, or mixture of products, isolated from these reactions were found to be dependent on the amount of organometallic reagent used for the metalation of the hydridophosphazenes and on the reaction time. Thus, if the metalation reactions were carried out with a deficiency of the organometallic reagent, the final products isolated were always compounds VI. On the other hand, if the metalation reactions were effected with a slight excess of the organometallic reagent, the products consisted of mixtures of compounds V, VI, and XII. However, if these reaction mixtures were stirred at low temperatures for prolonged periods of time, compounds XII could be isolated in pure form in high yield. These results again suggested that a rearrangement of the prop-2-ynyl side group occurs in these reactions. In this case the rearrangement was apparently initiated by an excess of the organometallic reagent used to generate the metallophosphazene. This prospect is considered in the following sections.



XII

The Prop-2-ynyl and Prop-1,2-dienyl Rearrangements. As discussed earlier, the first type of rearrangement observed was that of the prop-2-ynyl compounds, VI, to the prop-1,2-dienyl compounds, V, a rearrangement apparently catalyzed either by copper(I) salts or by neutral alumina. The second type was of compounds VI to XII, apparently via V. This rearrangement appeared to be initiated by an organometallic reagent. The following series of experiments were carried out in an attempt to determine the exact course of these different rearrangements.

Pure samples of each of the prop-2-ynyl compounds VI (R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, i-C_4H_9, t-C_4H_9, or allyl) were synthesized via the reaction of the corresponding lithiophosphazene IX with prop-2-ynyl bromide (see Experimental Section). These compounds were then allowed to react with $[n\text{-}Bu_3PCuI]_4$. These reactions were carried out to explore the possibility that the rearrangement of compounds VI to V was catalyzed by copper(I) species. At the end of a 24-h period, no prop-1,2-dienyl-substituted compounds were observed.

In a second series of reactions, pure samples of compounds VI were dissolved in CH_2Cl_2 and filtered through neutral alumina. After this procedure had been repeated 2–3 times, complete rearrangement of the side groups to the prop-1,2-dienyl compounds V had occurred. This procedure allowed the isolation of all compounds V (R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, i-C_4H_9, t-C_4H_9, or allyl) in pure form. These results demonstrated conclusively that the rearrangement of compounds VI to V was catalyzed by neutral alumina and not by copper(I) salts.

The rearrangement of a terminal acetylene group to an allene, initiated simply by alumina, has been observed only in a limited number of cases.[25-28] The hydrogen atom involved in the migration must initially be adjacent to a second multiply bonded atom,[25,26] or adjacent to any functional group which will increase its acidity.[27,28] It is possible that both these factors are important in the rearrangement of the prop-2-ynylphosphazenes VI to the prop-1,2-dienyl-substituted compounds V. The activation of the protons of a methyl or methylene group attached to a phosphazene ring[29] or phosphoryl group[30] is well documented and has been attributed to d orbital interactions. The possibility also exists of an electronic interaction between the prop-1,2-dienyl group and the phosphazene skeleton.[31-33]

(15) ^{31}P NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer operating at 40 MHz in the Fourier transform mode. The data were processed with the use of a Nicolet 1080 computer. Unless otherwise stated, all spectra were obtained with broad-band proton decoupling. The rearrangements were monitored by ^{31}P NMR techniques (rather than by ^{13}C NMR methods) because (a) the rearrangement rates were too high to permit the multiple scans required for a well-resolved ^{13}C spectrum, (b) the ^{31}P technique is especially sensitive to changes in the electron-directing characteristics of groups attached to a phosphazene ring, and (c) phosphorus-phosphorus couplings of 2 Hz or greater are present.

(16) Positive chemical shifts are downfield from external phosphoric acid.

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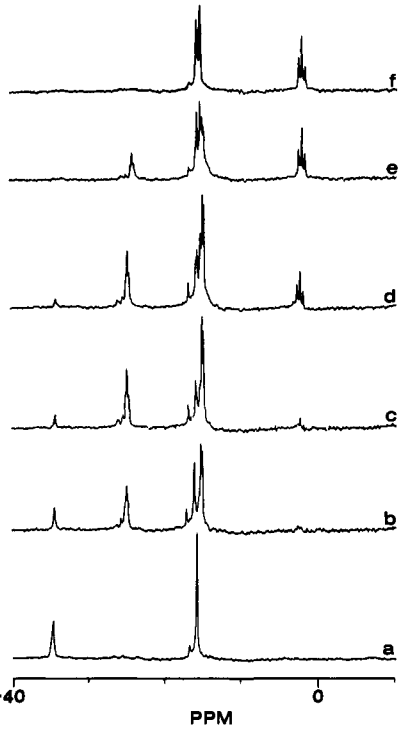


Figure 2. Changes in the ^{31}P NMR spectrum during rearrangement of the prop-2-ynyl-substituted phosphazene (VI, R = CH_3) to the prop-1,2-dienyl derivative to the prop-1-ynyl compound, initiated by methyllithium.

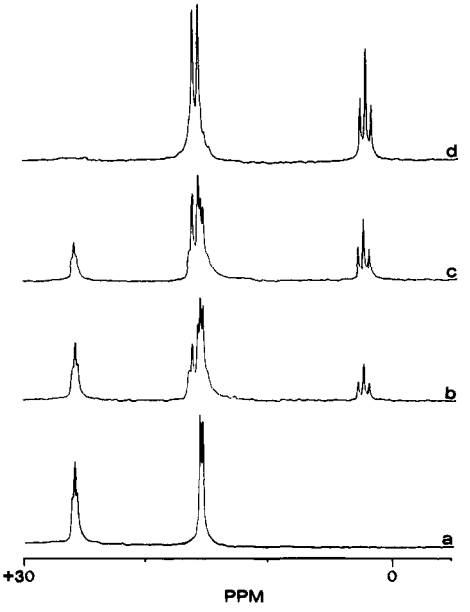
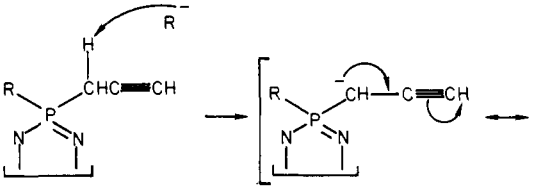


Figure 3. ^{31}P NMR spectral changes following the addition of a small quantity of methyllithium to a solution of the prop-1,2-dienyl-substituted phosphazene (VI, R = CH_3).

The Prop-2-ynyl and Prop-1,2-dienyl to Prop-1-ynyl Rearrangements.[5] Peripheral observations had suggested that these rearrangement reactions were initiated by traces of organometallic reagents. This possibility was explored by the following series of experiments. A pure sample of compound VI (R = CH_3) was treated with a small quantity of methyllithium. The reaction was monitored by ^{31}P NMR spectroscopy,[15] and a typical series of spectra are shown in Figure 2. The initial spectrum, a, shows resonances at 34.3 (triplet) and 19.4 ppm (doublet),[16] assigned to the starting material VI, R = CH_3 (see Table II in the supplementary material). This spectrum was obtained before the addition of any organometallic reagent. A small quantity of methyllithium was then introduced into the NMR tube, and the ^{31}P NMR spectrum was scanned at intervals. As the reaction proceeded, peaks at 25.9 (triplet) and 18.6 ppm (doublet) (spectra b and c) appeared. These resonances were assigned to the prop-1,2-dienyl-substituted compound V (R = CH_3). After nearly all of the starting material had been consumed (spectrum c), peaks at 18.8 (doublet) and 2.5 ppm (triplet) began to appear (spectra d and e). These resonances were assigned to the prop-1-ynyl compound XII (R = CH_3). After completion of the reaction (spectrum f), the only resonances present were those assigned to compound XII (R = CH_3).

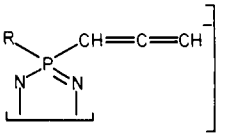
It was also found that the reactions of V with a small amount of methyllithium led exclusively to the formation of compounds XII. A typical series of ^{31}P NMR spectra for the methyllithium-induced rearrangement of V (R = CH_3) to XII (R = CH_3) is shown in Figure 3. Spectrum a is for the starting material, with resonances at 25.9 (triplet) and 18.6 ppm (doublet). Addition of the methyllithium (spectra b, c, and finally d) led eventually to complete formation of XII (R = CH_3), with peaks at 18.8 (doublet) and 2.5 ppm (triplet). Thus, it was concluded that complete rearrangement of the prop-2-ynyl compound VI (R = CH_3) to the prop-1-ynyl compound XII (R = CH_3) probably takes place via an intermediate formation of the prop-1,2-dienyl complex V (R = CH_3).

The overall rearrangement presumably takes place by way of the corresponding anions.[34] Abstraction of an α-proton from VI



VI

XIII



XIV

and successive proton abstraction reactions by XIV on VI to yield V continue until only a low concentration of VI remains. Further α-proton abstraction from V, rearrangement of the anion, and proton abstraction by the rearranged species yields XII.

A related process has been observed[35,36] in the rearrangement of acetylenic-substituted thioethers (XV). However, this reaction

$$\underset{\text{XV}}{\text{RSCH}_2\text{C}{\equiv}\text{CH}} \xrightarrow{\text{base}} \text{RSC}{\equiv}\text{CCH}_3$$

is reversible. All attempts to reverse the prop-2-ynyl- to prop-1-ynylphosphazene rearrangement have been unsuccessful. It is possible that the stability of the prop-1-ynyl derivative (XII) reflects an electronic interaction between the acetylenic group and the phosphazene ring.

Proof of Structure of Compounds V, VI, and XII. All the new phosphazene compounds synthesized in this study were characterized by infrared and ^1H, ^{13}C, and ^{31}P NMR spectroscopy, mass spectrometry (low and high resolution), and, in representative cases, elemental analysis. These data are listed in Tables I–IV (supplementary material).

The mass spectral data[37] for compounds V, VI, XII (R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *i*-C_3H_7, *i*-C_4H_9, *t*-C_4H_9, or allyl), and VII synthesized in this work are listed in Table I. All the compounds displayed a strong parent ion with a characteristic Cl_4 isotope pattern. The fragmentation pathways observed involved loss of alkyl and C_3H_3 groups as well as chlorine. However, from the

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interpretation of these data, it was impossible to distinguish between isomers of structures V, VI, and XII.

The infrared spectra[38] of compounds V, VI, VII, and XII were consistent with the proposed structures. In each case an intense absorbance between 1100 and 1300 cm^{-1} was observed, a characteristic of the PN skeleton in cyclic phosphazene compounds.[28] The C≡C absorbance[40] for the prop-2-ynyl compounds, VI, and the prop-1-ynyl, XII, was observed between 2010 and 2120 cm^{-1}, but in most cases it was extremely weak. However, the absorbance assigned to the C=C=C stretch for compounds V (between 1930 and 1980 cm^{-1})[40] was always relatively intense and proved extremely useful in the identification of these compounds. Other bands in the infrared spectra of species V, VI, VII, and XII were tentatively assigned to C—H, P—C, C—C, and P—Cl absorbances.[6,40] The proton-decoupled ^{31}P NMR spectra[15,16] of compounds V, VI, VII, and XII (listed in Table II of the supplementary material) were all interpreted as simple AB_2 spin systems.[17] The resonance for the phosphorus atom bound to the alkyl groups appeared as a triplet in the proton-decoupled spectra. However, these resonances broadened in the proton-undecoupled ^{31}P NMR spectra, due to unresolved proton–phosphorus couplings. By contrast, the other resonances observed in these spectra, a doublet, centered between 20.5 and 18.6 ppm assigned to the PCl_2 groups, remained virtually unaffected following removal of the proton-decoupling frequencies.

It is of interest that a dramatic ^{31}P upfield shift (and in some cases an increase in the P–P coupling constant) of the alkylated phosphorus accompanied the rearrangement of the C_3H_3 group from prop-2-ynyl to prop-1-ynyl. Thus, for the series VI, V, XII (R = CH_3), the phosphorus resonance for the prop-2-ynyl derivative occurred at 34.3 ppm, the prop-1,2-dienyl compound occurred at 25.9 ppm, and the prop-1-ynyl complex occurred at 2.5 ppm. This effect is perhaps a consequence of electronic interactions between the prop-1,2-dienyl group or the prop-1-ynyl group and the π system of the phosphazene ring.[31-33] An X-ray crystal structure analysis, currently under way, will help to clarify this point.

The alkyl groups bound to the phosphazene ring in compounds V, VI, VII and XII were all characterized by a combination of ^1H and ^{13}C NMR spectroscopy. The ^1H NMR data[41] are listed in Table III; the ^{13}C NMR data[42] are listed in Table IV (both tables are included in the supplementary material). In some cases, from an interpretation of the ^1H NMR data, it was possible to distinguish between V, VI, or XII. In many cases, however, the ^1H NMR spectra appeared as a complex pattern of overlapping resonances that could not be interpreted easily. By contrast, analysis of the ^{13}C NMR spectra of all compounds synthesized in this work provided a complete proof of structure. Certain trends appear to be consistent throughout the data sets. The resonances for the carbon atoms bonded directly to the phosphazene ring always appeared as a doublet of triplets,[6] due to coupling to the near (J_{PC}) and remote (J_{PNPC}) phosphorus nuclei. Resonances for carbon atoms two or three bonds removed from the phosphazene ring appeared as doublets in most cases. For the series of compounds VI, V, and XII (R = CH_3), the chemical shift of the methyl group carbon atom increased from 17.6 ppm for the prop-2-ynyl compound to 20.0 ppm for the prop-1,2-dienyl compound to 23.2 ppm for the prop-1-ynyl complex. The values of the coupling constants J_{PC} and J_{PNPC} for this methyl carbon, as well as the α-carbon of the C_3H_3 group, also increase in this order. For the α-carbon atom of the C_3H_3 group, the increase in J_{PC} is quite dramatic. This value increases from 88.8 Hz for the prop-2-ynyl compound to 131.7 Hz for the prop-1,2-dienyl derivative to 213.9 Hz for the prop-1-ynyl complex.

All these effects can be rationalized in terms of increasing electronic interactions between the C_3H_3 substituent and the phosphazene ring.[31-33] For the series of compounds VI (R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9), the chemical shift of the α-carbon of the prop-2-ynyl substituent decreased from 25.5 ppm (R = CH_3) to 24.2 ppm (R = C_2H_5) to 22.1 ppm (R = i-C_3H_7) to 19.4 (R = t-C_4H_9). These results can be rationalized simply in terms of the electron-donating ability of the alkyl group.[43] This increases the electron density at phosphorus and thus increases the shielding effect at the α-carbon of the C_3H_3 group. Thus, the ^{13}C NMR spectra of alkyl-substituted phosphazene compounds contain valuable information about the various interactions between the phosphazene ring and the organic side group.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was supplied by Ethyl Corp. and was purified by sublimation, followed by two recrystallizations from hexane. Organometallic reagents were obtained from Aldrich or Alfa-Ventron. Prop-2-ynyl bromide (Aldrich) was used without further purification. Tetrahydrofuran (Fisher) was distilled into the reaction flask under an atmosphere of dry nitrogen from sodium benzophenone ketyl drying agent. The reagents, $[n\text{-}Bu_3PCuI]_4$[44] and but-2-ynyl bromide[45] were synthesized by published procedures. All manipulations involving organometallic reagents or air-sensitive intermediates were carried out under an atmosphere of dry nitrogen.

Synthesis of Cupriophosphazenes (II). The metallophosphazenes, II, were all synthesized in an identical manner.[6,10] Hexachlorocyclotriphosphazene (I) (5.0 g, 0.014 mol) and $[n\text{-}Bu_3PCuI]_4$ (4.0 g, 0.0025 mol) were stirred together in THF (150 mL) at −78 °C. The Grignard reagent (25 mL of a 3 M solution in diethyl ether or THF) was added dropwise over a period of ≃30 min. This reaction mixture was then stirred for 16 h, and the temperature was allowed to rise slowly to ≃25 °C. These complexes were not isolated but were allowed to react in situ, as described in the following sections.

Synthesis of Hydridophosphazenes (III). These compounds were prepared from the cupriophosphazenes (II) by published procedures.[10,11] Compounds III (R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7) were sublimed from the reaction mixture, as described previously. Compounds III (R = i-C_4H_9, t-C_4H_9, allyl) were distilled from the reaction residue at 120 °C under reduced pressure.

Synthesis of Prop-1,2-dienyl Compounds (V). A solution of prop-2-ynyl bromide (80% in toluene, 5 mL) was added dropwise to a solution of the cupriophosphazene (II) prepared as described previously. The reaction mixture was then stirred for 24 h. The solvent was removed under reduced pressure, and the products were dissolved in toluene (250 mL). The organic layer was then washed with aqueous HCl (10% solution, 250 mL) and dried over $MgSO_4$, and the solvent was removed under reduced pressure to leave the crude product. This mixture was purified by filtration of a solution in CH_2Cl_2 through neutral alumina, followed by recrystallization from hexane to leave the product as white crystals. In some cases filtration of the CH_2Cl_2 solution through neutral alumina had to be repeated two or three times to effect complete conversion to the prop-1,2-dienyl-substituted compound.

Synthesis of Lithio- and Magnesiophosphazenes. All of these compounds were prepared in an identical manner. The following is a typical procedure. Methylhydridotetrachlorocyclotriphosphazene (III, R = CH_3) (5.0 g, 0.017 mol), prepared as described previously, was dissolved in THF (150 mL), and the solution was cooled to −78 °C. Methyllithium (as a lithium bromide complex, 11 mL of a 1.5 M solution in diethyl ether, 0.016 mol) or methylmagnesium chloride (5.5 mL of a 3 M solution in THF, 0.016 mol) was then added carefully. The temperature of the reaction mixture during addition of the organometallic reagent was not allowed to rise above −70 °C. This mixture was then stirred for a further 30 min at −78 °C. These complexes were not isolated but were

(38) Infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrometer. The samples were prepared as KBr disks.

(39) Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972.

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(41) Proton NMR spectra were obtained with the use of either a Bruker WP-200 spectrometer operating at 200 MHz, a JEOL JNM-PS-100 spectrometer operating at 100 MHz, or a Varian Associates EM-360 spectrometer operating at 60 MHz. All spectra were recorded on a solution of the sample in $CDCl_3$ and are referenced to internal tetramethylsilane at δ 0.

(42) Carbon NMR spectra were obtained with the use of either a Bruker WP-200 spectrometer operating at 80 MHz or a Varian Associates CFT-20 spectrometer operating at 20 MHz. All spectra were recorded on a solution of the sample in either $CDCl_3$ or C_6D_6 and are referenced to internal tetramethylsilane at 0 ppm.

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(45) Black, D. K.; Landor, S. R.; Patel, A. N.; Whiter, P. F. *Tetrahedron Lett.* **1963**, 483.

reacted in situ, as described in the following sections.

Preparation of Prop-2-ynyl Compounds (VI). A solution of prop-2-ynyl bromide (3 mL, 80% solution in toluene) was added rapidly to the solution of lithio- or magnesiophosphazene, synthesized as described in the preceding section. The mixture was then stirred for 2 h during which time the temperature was allowed to warm to 25 °C. The solvent was then removed under vacuum, and the products were extracted with hot hexane (4 × 50 mL portions). The resultant hexane layer was concentrated by removal of some of the solvent under vacuum, and recrystallization at −10 °C left the product as white crystals.

Preparation of Prop-1-ynyl Compounds (XII). A solution of the lithio- or magnesiophosphazene was prepared as described previously, except that 15 mL of the methyllithium reagent (0.023 mol) or 7.7 mL of the methylmagnesium chloride solution (0.023 mol) was used. A solution of prop-2-ynyl bromide (3 mL, 80% in toluene) was added slowly to this solution, and the mixture was stirred at −80 °C for 6 h. The temperature was then allowed to rise to 25 °C, and the solvent was removed under vacuum. The products were extracted with hot hexane (4 × 50 mL portions) and were recrystallized from hexane.

Attempted Copper-Initiated Rearrangement of Prop-2-ynyl-Substituted Phosphazenes (VI) to Prop-1,2-dienyl-Substituted Complexes (V). A pure sample of the prop-2-ynyl-substituted phosphazene (VI) (100 mg, ≃0.3 mmol) and $[n\text{-}Bu_3PCuI]_4$ (20 mg, 0.012 mmol) was dissolved in $CDCl_3$ (1 mL), and the solution was filtered into an NMR tube. The ^1H NMR spectrum of this mixture showed only resonances in the region δ 1–3.0. No olefinic proton resonances corresponding to the prop-1,2-dienyl compound were observed. This mixture was allowed to stand for 24 h. At the end of this time the ^1H NMR spectrum was rescanned. No difference existed between this spectrum and the initial spectrum. Thus, it was concluded that no rearrangement of the C_3H_3 side group had occurred.

The Alumina-Initiated Rearrangement of Prop-2-ynyl-Substituted Phosphazenes (VI) to Prop-1,2-dienyl-Substituted Phosphazenes (V). A pure sample of the prop-2-ynyl-substituted phosphazene (VI) (1.0 g, ≃2.80 mmol) was dissolved in CH_2Cl_2 (10 mL). This solution was introduced on to a chromatography column (2.5 cm × 7 cm) packed with neutral alumina (Brockman Activity I) and eluted with CH_2Cl_2 (200 mL). The product was isolated by removal of the solvent under vacuum. The filtration through alumina was repeated two or three times to bring about complete conversion to the prop-1,2-dienyl complex. These compounds were then recrystallized from hexane.

Organometallic-Initiated Rearrangement of Prop-2-ynyl-Substituted Phosphazenes (V) to Prop-1-ynyl-Substituted Derivatives (XII). Pure prop-2-ynyl-substituted phosphazenes (VI) (1.0 g, ≃2.8 mmol) were dissolved in THF (50 mL), and the solutions were cooled to −78 °C. Methyllithium (0.20 mL, as a lithium bromide complex, 1.5 M in diethyl ether) was then introduced into the reaction vessels and the mixtures were stirred at −78 °C for 4 h. At the end of this time the temperatures of the reaction mixtures were slowly allowed to rise to 25 °C and the solvent was removed under vacuum. The products were dissolved in hexane, filtered, and recrystallized to leave the prop-1-ynyl-substituted phosphazenes (XII) as white crystals. Typical yields were 90–96%.

Organometallic-Initiated Rearrangement of Prop-1,2-dienyl Phosphazenes (V) to Prop-1-ynyl-Substituted Complexes (XII). A pure sample of the prop-1,2-dienyl-substituted phosphazene compounds (V) (1.0 g, ≃2.8 mmol) was dissolved in THF (50 mL), and the solution was cooled to −78 °C. A solution of methyllithium (as a lithium bromide complex, 0.20 mL, 1.5 M solution in diethyl ether) was then added to the phosphazene solution, and the mixture was stirred for 6 h at −78 °C. At the end of this time the temperature was allowed to rise to 25 °C, and the solvent was removed under vacuum. The products were dissolved in hexane and filtered. The final product, the prop-1-ynyl-substituted phosphazenes (XII), was isolated by recrystallization from hexane. Typical yields were 90–95%.

^{31}P NMR Monitoring of the Rearrangement of the Prop-2-ynylphosphazene to the Prop-1-ynyl Complex. A pure sample of the prop-2-ynylphosphazene (VI, R = CH_3) (0.10 g, 0.3 mmol) was dissolved in a mixture of THF-d_8 (0.5 mL) and THF (1.5 mL) and filtered into an NMR tube (10-mm o.d.) under an atmosphere of dry nitrogen. (The deuterio compound was needed as an NMR lock.) The tube was then sealed with a septum cap. The sample was introduced into the probe of the spectrometer, and the temperature was gradually lowered to −70 °C. The spectrum was then scanned. An aliquot of methyllithium (0.1 mL, as a lithium bromide complex, 1.5 M solution in diethyl ether) was then syringed into the NMR tube through the septum. Any methane gas evolved was vented from the tube with a second syringe needle. The spectrum was then rescanned at intervals.

^{31}P NMR Monitoring of the Rearrangement of the Prop-1,2-dienylphosphazene to the Prop-1-ynylphosphazene. This reaction was carried out in an identical manner to the preceding experiment. However, the prop-1,2-dienylphosphazene, V (R = CH_3) was used.

^{31}P NMR Monitoring of the Synthesis of the Lithiophosphazene (IX, R = CH_3). A pure sample of methylhydridotetrachlorocyclotriphosphazene (III, R = CH_3) was dissolved in a mixture of THF-d_8 (0.5 mL) and THF (2.0 mL) and was filtered into an NMR tube (10-mm o.d.) under an atmosphere of dry nitrogen. The tube was then sealed with a septum cap and was introduced into the NMR probe, and the temperature was lowered slowly to −70 °C. The spectrum of the sample was obtained. Methyllithium (0.25 mL, as a lithium bromide complex, 1.5 M in diethyl ether) was then introduced into the tube with a syringe through the septum cap in 2 or 3 aliquots. Any gas pressure in the tube was vented with a second syringe needle. The spectrum of the mixture was obtained between each addition of the lithium reagent.

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Supplementary Material Available: Tables I–IV for dialkylphosphazenes showing mass spectral and elemental analysis data (Table I), ^{31}P NMR data (Table II), ^1H NMR data (Table III), and ^{13}C NMR data (Table IV) (15 pages). Ordering information is given on any current masthead page.