methylamino)phenyl moiety is a better electron-releasing group than the phenyl group.[25] Alternatively, in a nonplanar phosphazene derivative, the ortho hydrogen atoms on the aryl ring may undergo hydrogen bonding with cis fluorine atoms, thereby blocking cis attack. This effect is expected to be more significant for the *p*-(dimethylamino)phenyl derivative, where the ring hydrogen atoms are more acidic than in the phenyl derivatives. A thorough examination of factors involved in control of isomer distribution will have to await detailed mechanistic and thermodynamic investigations.

A 6:1 molar reaction of $(CH_3)_2NC_6H_4MgBr$ with $P_3N_3F_6$ was undertaken in an attempt to obtain the hexakis[*p*-(dimethylamino)phenyl]cyclotriphosphazene. The only cyclophosphazene isolated was the trisubsituted derivative *trans*-2,4,6-$P_3N_3F_3[C_6H_4N(CH_3)_2]_3$ which is obtained in low yields. The structural assignment follows from NMR data. The ^{19}F NMR spectrum shows two sets of doublets in the $\equiv PFR$ region which is consistent with the trans disposition of fluorine atoms. The ^1H NMR spectrum shows two resolved resonances in the $N(CH_3)_2$ region in a ratio of 2:1 which can be assigned to the two different aryl environments which are the consequence of a trans structure.

The low yield and apparent reluctance of the reaction to proceed past the level of trisubstitution can be understood in terms of both the previously established low reactivity of the *p*-(dimethylamino)phenyl Grignard reagent and also decomposition reactions. Ring-opening degradation is the primary mode of reaction in the interactions of Grignard[5] and organolithium[7] reagents with hexachlorocyclotriphosphazene. At the stage of trisubstitution of $P_3N_3F_6$, the point may be reached where the barrier to additional substitution is high and the ring nitrogen atoms become sufficiently basic to allow coordination of the organometallic reagent, thus initiating ring opening[5] and giving the large amounts of insoluble residue observed. The tendency toward formation of the trans isomer is again noted in the formation of the trisubstituted derivative. Reaction of the organometallic reagent at the trans rather than the cis position may be related to the expected steric constraints favoring trans attack in bimolecular reactions and/or the factors previously discussed relating to stereochemical control in the formation of the disubstituted derivatives.

It has been shown that one may convert a $\equiv PFC_6H_5$ center, in a phosphazene derivative, to a $\equiv(C_6H_5)_2$ center via the Friedel–Crafts reaction.[26] In this investigation, the reaction of [*p*-(dimethylamino)phenyl]fluorophosphazenes with aluminum chloride in benzene (or deuteriobenzene) proved to be a successful method for the conversion of a $\equiv PFC_6H_4N(CH_3)_2$ center to a $\equiv P(C_6H_5)C_6H_4N(CH_3)_2$ center. Excess aluminum chloride was used to account for deactivation of the Lewis acid by coordination to a $N(CH_3)_2$ group. The yields ranged from excellent in the reaction of $P_3N_3F_5C_6H_4N(CH_3)_2$ to moderate in the reaction of 2,4-$P_3N_3F_4[C_6H_4N(CH_3)_2]_2$. The factors which favor nongeminal substitution in the organometallic reactions are not operative in the Friedel–Crafts reaction, where a mechanistic pathway based on phosphorus–halogen ionization is believed to prevail.[2,3] Consequently, the electron-releasing *p*-(dimethylamino)phenyl group will stabilize a phosphonium ion[18] which is created from a $\equiv PFC_6H_5N(CH_3)_2$ center and hence favors geminal substitution. The structures were established in each case by consideration of the NMR data. The ^{19}F spectra show resonances only in the $\equiv PF_2$ region, and the phosphorus–ortho hydrogen coupling constants in the ^1H spectra are in the range previously observed for a geminal arrangement of aryl groups.[24] The tetrasubstituted derivative $P_3N_3F_2(C_6H_5)_2[C_6H_4N(CH_3)_2]_2$ is expected to exhibit two isomeric forms arising from cis and trans disposition of identical aryl substituents. While there is no direct NMR evidence on this point, the $N(CH_3)_2$ resonance in the ^1H spectrum is considerably broadened, suggesting unresolved lines within the band envelope.

Acknowledgment. This work was supported, in part, by the Office of Naval Research and the National Science Foundation.

Registry No. $P_3N_3F_5[p\text{-}C_6H_4N(CH_3)_2]$, 53968-86-8; $\{P_3N_3F_4[p\text{-}C_6H_4N(CH_3)_2]\}_2$, 75232-92-7; *cis*-2,4-$P_3N_3F_4[p\text{-}C_6H_4N(CH_3)_2]_2$, 75232-93-8; *trans*-2,4-$P_3N_3F_4[p\text{-}C_6H_4N(CH_3)_2]_2$, 75232-94-9; *trans*-2,4,6-$P_3N_3F_3[p\text{-}C_6H_4N(CH_3)_2]_3$, 75232-95-0; 2,2-$P_3N_3F_4(C_6H_5)[p\text{-}C_6H_4N(CH_3)_2]$, 75232-96-1; 2,2-$P_3N_3F_4(C_6D_5)[p\text{-}C_6H_4N(CH_3)_2]$, 53968-88-0; $P_3N_3F_2(C_6D_5)_2[p\text{-}C_6H_4N(CH_3)_2]_2$, 75232-97-2; *p*-$BrC_6H_4N(CH_3)_2$, 586-77-6; *p*-$LiC_6H_4N(CH_3)_2$, 13190-50-6; $P_3N_3F_6$, 15599-91-4.

(25) In the original form, the electron-releasing effect was via a π mechanism.[15] However recent work[1] has shown that there are no significant aryl–phosphazene π interactions.

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The Pennsylvania State University, University Park, Pennsylvania 16802

Synthesis of Alkylphosphazenes via Copper–Phosphazene Intermediates[1,2]

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Received June 25, 1980

A new reaction route has been developed for the synthesis of a hitherto inaccessible series of 1,1-dialkyltetrachlorocyclotriphosphazenes, $N_3P_3Cl_4RR'$ (III), where R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *i*-C_4H_9, *t*-C_4H_9, or allyl and R' = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, or allyl. The high-yield route involves the interaction of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, with alkyl Grignard reagents in the presence of $[n\text{-}Bu_3PCuI]_4$, followed by treatment with alkyl halides. The structural characterization of these compounds by NMR and mass spectrometric techniques is discussed, together with the reaction mechanism.

The synthesis of linear or cyclic alkyl-substituted phosphazene compounds has attracted considerable attention in recent years but has met with only limited success. Cyclic alkyl- or arylphosphazenes that contain side groups bound to the phosphazene skeleton through direct phosphorus–carbon bonds are useful models[3] for preliminary macromolecular reactivity studies or "monomers" for polymerization reactions.[4,5]

(1) For a previous paper in this series see: Allcock, H. R.; Evans, T. L.; Fuller, T. J. *Inorg. Chem.* **1980**, *19*, 1026.

(2) A preliminary communication on this work has appeared: Harris, P. J.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1979**, 714.

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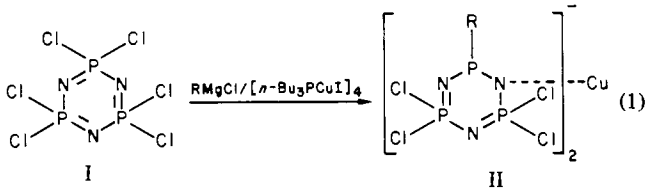
The general routes normally employed for the synthesis of alkyl- or aryl-substituted phosphazenes involve a nucleophilic attack by an organolithium or Grignard reagent on a halophosphazene.[6-12] However, in many of these reactions, P–N bond cleavage can be competitive with halogen replacement. Thus, phosphazene degradation accompanies substitution. We have recently demonstrated that hexachlorocyclotriphosphazene reacts with alkyl or aryl Grignard reagents by two competing mechanisms, leading to either alkylated phosphazenes or phosphazene dimers.[12]

One of the objectives of our current research is to design *alternative* synthetic routes for the formation of alkyl- or aryl-substituted cyclic or high phosphazenes to permit halogen replacement at phosphorus without extensive degradation of the P–N skeleton.

In this paper we describe an entirely new approach to the synthesis of alkylcyclophosphazenes. This versatile route involves the reaction of a metallophosphazene intermediate with an alkyl halide. Because the nucleophile in these reactions is the phosphazene and not the alkyl group, degradation of the phosphazene skeleton is virtually eliminated.

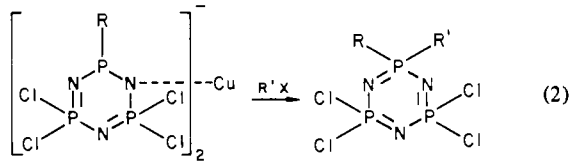
Results and Discussion

Overall Reaction. In a recent publication[13,14] we described the formation of a series of metallophosphazene compounds of general fromula II. These complexes (II) (R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *i*-C_4H_9, $CH_2CH{=}CH_2$) are synthesized readily via the reaction of hexachlorocyclotriphosphazene (I) with the appropriate Grignard reagent in the presence of [*n*-$Bu_3PCuI]_4$ (eq 1). The mechanism of this reaction has been discussed previously.[14]



I II

In this paper the results of the reactions of such metallophosphazene complexes (II) with various alkyl halides are discussed. These reactions led to the high-yield formation of 1,1-dialkyltetrachlorocyclotriphosphazene compounds of general formula III (eq 2).



II III

Compounds of structure III were isolated when the R group was 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, and $CH_2CH{=}CH_2$ and when the R′ group was CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, and $CH_2CH{=}CH_2$. All compounds of type III were volatile, air- and moisture-stable, white crystalline products. This series represents the broadest range of alkylphosphazenes yet synthesized.[15]

Proof of Structure of III. The structures of the 1,1-dialkyltetrachlorocyclotriphosphazene compounds III prepared in this study were determined by a combination of 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–V.

All compounds of structure III gave a strong parent ion in the mass spectrum[16] with a characteristic Cl_4 isotope pattern. The mass spectral data for all species of type III are listed in Table I. A detailed description of the fragmentation patterns of these 1,1-dialkylphosphazene compounds will be discussed in a later paper.

The retention of the phosphazene ring in species III was confirmed by the use of infrared[17] and ^{31}P NMR spectroscopy.[18,19] The infrared spectra[17] showed intense absorbances between 1100 and 1300 cm^{-1}, a characteristic of the PN skeleton in cyclic phosphazene compounds.[15] Other bands in the infrared spectrum were assigned to C–H, P–C, (C=C), and P–Cl vibrations.[20-22] These data and the tentative assignments are listed in Table II (available as supplementary material).

The ^{31}P NMR spectra[18,19] of species III (listed in Table III) were interpreted as simple AB_2 spin systems.[23] The resonance from the phosphorus atom bound to the two alkyl groups appeared as a triplet centered between 35.7 and 54.8 ppm.[19] The resonance broadened in the proton-undecoupled ^{31}P NMR spectrum, due to unresolved proton–phosphorus couplings. By contrast, the other resonance in the spectrum, assigned to the PCl_2 group, remained virtually unchanged when proton decoupling was removed. An interesting feature of the ^{31}P NMR chemical shift of the alkylated phosphorus atom was the observation that the more electron-donating alkyl groups caused a greater *de*shielding of this nucleus and, thus, generated a downfield shift for the position of resonance. This effect has been noted[24-26] in the NMR spectra of other phosphorus compounds and has been rationalized by quantum mechanical arguments.[27] The position of resonance assigned to the two phosphorus atoms linked to chlorine always appeared as a doublet centered between 17.7 and 19.3 ppm.[19] This resonance is shifted upfield from the position observed for the phosphorus nuclei in hexachlorocyclotriphosphazene (I) (19.8 ppm).[15,19] The greater shielding is presumed to be a consequence of the

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(16) Mass spectral data were obtained with the use of an AEI MS-902 mass spectrometer.
(17) Infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrometer and were run as KBr disks.
(18) ^{31}P NMR spectra were recorded on a JEOL JHM-PS-100 spectrometer operating at 40 MHz in the Fourier transform mode. The data were processed with use of a Nicolet 1080 computer.
(19) All ^{31}P NMR spectra were recorded on a solution of the compound in $CDCl_3$. Positive chemical shifts are downfield from external phosphoric acid.
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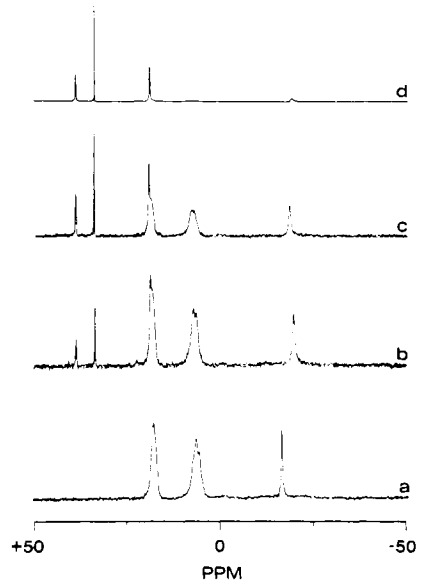


Figure 1. ^{31}P NMR spectral changes following the addition of methyl iodide to a solution of II (R = CH_3) in tetrahydrofuran at 25 °C. Spectrum *a* is the reaction mixture before addition of the alkyl halide. Spectra b, c, and d are of the reaction mixture after 45 min, 2 h, and 4 h, respectively.

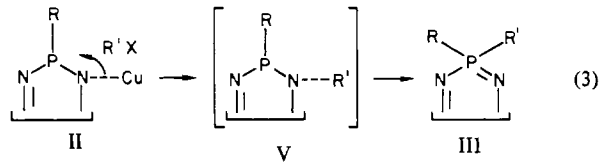
presence of the alkyl groups in species III. Such phenomena can be rationalized in terms of variations in π-electron distribution around the phosphazene ring by consideration of the "island" theory of π bonding in cyclic phosphazene compounds.[28,29] The presence of electron-donating alkyl groups at one end of a P–N–P island will allow electron density to drift toward the opposite end of the island, i.e., toward the phosphorus atoms bound to the chlorine atoms. The buildup of electron density on this phosphorus atom would cause a greater magnetic shielding and, thus, generate an upfield shift in the position of resonance of this atom. This type of perturbation of the π bonding in cyclic phosphazenes has been detected before, from X-ray crystal structure data for various alkylphosphazenes.[30-35]

The alkyl groups bound to the phosphazene ring in compounds III were characterized by a combination of ^1H and ^{13}C NMR spectroscopy. In many cases the ^1H NMR spectra[36,37] (listed in Table IV, available as supplementary material) consisted of a complex pattern of overlapping resonances that could not be readily interpreted. However, in most cases, the ^{13}C NMR spectra[38,39] (listed in Table V, available as supplementary material) were well-resolved first-order spectra, from which the position of resonance of every carbon atom and a value for each P–C coupling constant could be determined.[40] The carbon atoms bound directly to the phosphazene ring always appeared as a doublet of triplets, from coupling to the near (J_{PC}) and the remote (J_{PNPC}) phosphorus atoms. Carbon atoms that were two or three bonds removed from the phosphazene ring appeared as doublets, coupled only to the nearby phosphorus nucleus. The peak assignments and coupling constants[41] are listed in Table V.

The Reaction Mechanism. ^{31}P NMR Changes. An attempt was made to deduce the mechanism of the reaction between metallophosphazenes, II, and the various alkyl halides used in this study (see Table VI), by the use of ^{31}P NMR spectroscopy.[18,19] A typical series of spectra (for the reaction of II, R = CH_3 with CH_3I) are shown in Figure 1. The initial spectrum showed resonances at 14.8, 4.3, and 3.0 ppm for the metallophosphazene and at −18.4 ppm from the *n*-Bu_3P ligand coordinated to copper. (This assignment was confirmed by comparison with the spectrum of a sample of $[n\text{-}Bu_3PCuI]_4$.) All the peaks in the initial spectrum are broadened, probably from coupling to copper. As the reaction proceeded, the only resonances that appeared were those assigned to the dialkylphosphazene product III (in this case, III, R = CH_3, R′ = CH_3, with resonances at 35.7 (t) and 18.0 ppm (d)) and a resonance between 35 and 31 ppm (s) assigned to the complex $n\text{-}Bu_3P^+RX^-$ (in this case $n\text{-}Bu_3P^+MeI^-$, with a resonance at 31.7 ppm). This complex was formed in a secondary reaction between the alkyl halide and the *n*-Bu_3P ligand. The assignment was confirmed by comparison with the ^{31}P NMR spectrum of an authenic sample of the phosphonium salt.

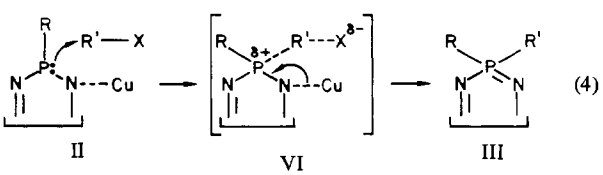
Limitations of the Reaction. Certain limitations exist to the scope of the reaction. The metallophosphazene complexes II reacted only with allyl bromide or with primary alkyl iodides. (This was determined by the absence of a change in the ^{31}P NMR spectrum of the reaction mixtures when other halides were used.) The reactivity of the metallophosphazene II (R = CH_3) was even more limited; this complex reacted only with allyl bromide or methyl iodide. None of the other alkyl iodides studied reacted with II (R = CH_3). The alkyl halides used are listed in Table VI.

Reaction Pathway. Two plausible pathways are suggested for the reaction between the metallophosphazenes II and alkyl halides: (1) an initial replacement of copper at nitrogen by the alkyl group to give a species such as V, followed by a migration of the alkyl group from nitrogen to phosphorus, with concurrent reformation of the phosphazene skeleton (reaction 3), or (2) an initial coordination of the lone pair of electrons



(3)

at phosphorus to the alkyl halide to form the phosphazenium intermediate or transition state VI, followed by a rapid or concurrent loss of copper, and subsequent re-formation of the phosphazene skeleton to yield the final product III (reaction 4).



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(36) ^1H NMR spectra were recorded on a JEOL-JNM-100 spectrometer operating at 100 MHz in the Fourier transform mode.
(37) All ^1H NMR spectra were recorded on a solution of the sample in $CDCl_3$ and are referenced to internal tetramethylsilane at $\delta = 0$.
(38) ^{13}C NMR spectra were recorded on a Varian Associates CFT 20 spectrometer.
(39) All ^{13}C NMR spectra were recorded on a solution of the sample in $CDCl_3$ and are referenced to internal tetramethylsilane at 0 ppm. All spectra were recorded with broad-band ^1H decoupling.
(40) In some cases spectra were also obtained at 50 MHz to confirm peak assignments. The instrument used was a Bruker WP-200 spectrometer.
(41) No attempt was made to determine the absolute signs of any of the coupling constants.

Table I. Characterization Data of Dialkylphosphazenes

compd	% yield	mp, °C	mass spectral data found	mass spectral data calcd		elemental analysis data % found	elemental analysis data % calcd
$N_3P_3Cl_4(CH_3)_2$	84	176	305	305	C	7.86	7.82
					H	2.03	1.95
					N	13.74	13.68
					P	30.46	30.29
					Cl	46.09	46.25
$N_3P_3Cl_4(CH_3)(C_2H_5)$	76	115	319	319	C	11.15	11.21
					H	2.42	2.49
					N	13.13	13.08
					P	28.30	28.97
					Cl	44.10	44.23
$N_3P_3Cl_4(CH_3)(n\text{-}C_3H_7)$	73	121	333	333	C	14.35	14.32
					H	3.02	2.98
					N	12.45	12.53
					P	27.88	27.76
					Cl	42.26	42.38
$N_3P_3Cl_4(CH_3)(n\text{-}C_4H_9)$	58	113	347	347	C	17.13	17.19
					H	3.39	3.43
					N	12.16	12.04
					P	26.58	26.64
					Cl	40.78	40.69
$N_3P_3Cl_4(CH_3)(i\text{-}C_3H_7)$	60	51	333	333	C	14.96	14.32
					H	3.05	2.98
					N	12.38	12.53
					P	27.78	27.76
					Cl	42.04	42.38
$N_3P_3Cl_4(CH_3)(i\text{-}C_4H_9)$	51	91	347	347	C	17.31	17.19
					H	3.33	3.43
					N	12.07	12.04
					P	26.55	26.64
					Cl	40.63	40.69
$N_3P_3Cl_4(CH_3)(t\text{-}C_4H_9)$	49	67	347	347	C	17.50	17.19
					H	3.22	3.43
					N	11.98	12.04
					P	26.53	26.64
					Cl	40.58	40.69

compd	% yield	mp, °C	mass spectral data found	mass spectral data calcd	mol wt found	mol wt calcd
$N_3P_3Cl_4(C_2H_5)_2$	69	141	333	333	332.8830	332.8841
$N_3P_3Cl_4(C_2H_5)(n\text{-}C_3H_7)$	71	122	347	347	346.9001	346.8998
$N_3P_3Cl_4(C_2H_5)(n\text{-}C_4H_9)$	66	85	361	361	360.9181	360.9153
$N_3P_3Cl_4(C_2H_5)(i\text{-}C_3H_7)$	60	78	347	347	346.9008	346.8998
$N_3P_3Cl_4(C_2H_5)(i\text{-}C_4H_9)$	51	100	361	361	360.9159	360.9153
$N_3P_3Cl_4(C_2H_5)(t\text{-}C_4H_9)$	44	69	361	361	360.9179	360.9153
$N_3P_3Cl_4(n\text{-}C_3H_7)_2$	70	164	361	361	360.9171	360.9153
$N_3P_3Cl_4(n\text{-}C_3H_7)(n\text{-}C_4H_9)$	65	137	375	375	374.9318	374.9311
$N_3P_3Cl_4(n\text{-}C_3H_7)(i\text{-}C_3H_7)$	48	95	361	361	360.9166	360.9153
$N_3P_3Cl_4(n\text{-}C_3H_7)(i\text{-}C_4H_9)$	39	121	375	375	374.9322	374.9311
$N_3P_3Cl_4(n\text{-}C_3H_7)(t\text{-}C_4H_9)$	40	112	375	375	374.9313	374.9311
$N_3P_3Cl_4(n\text{-}C_4H_9)_2$	67	143	389	389	388.9474	388.9467
$N_3P_3Cl_4(n\text{-}C_4H_9)(i\text{-}C_3H_7)$	47	122	375	375	374.9334	374.9311
$N_3P_3Cl_4(n\text{-}C_4H_9)(i\text{-}C_4H_9)$	31	102	389	389	388.9469	388.9467
$N_3P_3Cl_4(n\text{-}C_4H_9)(t\text{-}C_4H_9)$	28	36	389	389	388.9477	388.9467

compd	% yield	mp, °C	mass spectral data found	mass spectral data calcd		elemental analysis data % found	elemental analysis data % calcd
$N_3P_3Cl_4(C_3H_5)(CH_3)$	84	90	331	331	C	14.57	14.41
					H	2.37	2.40
					N	12.53	12.61
					P	27.78	27.92
					Cl	42.52	42.64
$N_3P_3Cl_4(C_3H_5)(C_2H_5)$	81	105	345	345	C	17.33	17.29
					H	3.00	2.88
					N	12.12	12.10
					P	26.91	26.80
					Cl	40.55	40.92
$N_3P_3Cl_4(C_3H_5)(n\text{-}C_3H_7)$	78	130	359	359	C	20.06	19.94
					H	3.17	3.33
					N	11.61	11.63
					P	25.64	25.76
					Cl	39.91	39.34
$N_3P_3Cl_4(C_3H_5)(n\text{-}C_4H_9)$	75	98	373	373	C	22.60	22.40
					H	3.41	3.37
					N	11.38	11.20

Table I (*Continued*)

compd	% yield	mp, °C	mass spectral data found	mass spectral data calcd	elemental analysis data	% found	% calcd
					P	24.46	24.80
					Cl	37.96	37.86
$N_3P_3Cl_4(C_3H_5)(i\text{-}C_3H_7)$	69	69	359	359	C	20.47	19.94
					H	3.37	3.33
					N	11.68	11.63
					P	25.83	25.76
					Cl	39.36	39.34
$N_3P_3Cl_4(C_3H_5)(i\text{-}C_4H_9)$	65	91	373	373	C	22.22	22.40
					H	3.68	3.73
					N	11.41	11.20
					P	25.01	24.80
					Cl	37.81	37.86
$N_3P_3Cl_4(C_3H_5)(t\text{-}C_4H_9)$	56	93	373	373	C	22.69	22.40
					H	3.64	3.73
					N	11.14	11.20
					P	24.48	24.80
					Cl	37.78	37.86
$N_3P_3Cl_4(C_3H_5)_2$	62	86	357	357	C	19.94	20.05
					H	2.85	2.79
					N	11.63	11.69
					P	25.75	25.90
					Cl	39.69	39.55

Table III. Dialkylphosphazene ^{31}P NMR Data

compd	chem shift, ppm $P(R)_2$	chem shift, ppm $P(Cl)_2$	coupling const J_{PNP}, Hz
$N_3P_3Cl_4(CH_3)_2$	35.7 (t)	18.0 (d)	8.9
$N_3P_3Cl_4(CH_3)(C_2H_5)$	41.8 (t)	18.3 (d)	<2
$N_3P_3Cl_4(CH_3)(n\text{-}C_3H_7)$	39.6 (t)	18.2 (d)	2.8
$N_3P_3Cl_4(CH_3)(n\text{-}C_4H_9)$	39.9 (t)	18.0 (d)	2.1
$N_3P_3Cl_4(CH_3)(i\text{-}C_3H_7)$	46.1 (t)	17.9 (d)	<2
$N_3P_3Cl_4(CH_3)(i\text{-}C_4H_9)$	38.3 (t)	17.7 (d)	<2
$N_3P_3Cl_4(CH_3)(t\text{-}C_4H_9)$	50.4 (t)	18.1 (d)	<2
$N_3P_3Cl_4(C_2H_5)_2$	48.1 (t)	19.2 (d)	<2
$N_3P_3Cl_4(C_2H_5)(n\text{-}C_3H_7)$	45.8 (t)	18.7 (d)	<2
$N_3P_3Cl_4(C_2H_5)(n\text{-}C_4H_9)$	46.3 (t)	18.7 (d)	<2
$N_3P_3Cl_4(C_2H_5)(i\text{-}C_3H_7)$	52.5 (t)	18.8 (d)	3.7
$N_3P_3Cl_4(C_2H_5)(i\text{-}C_4H_9)$	44.7 (t)	18.3 (d)	<2
$N_3P_3Cl_4(C_2H_5)(t\text{-}C_4H_9)$	56.8 (t)	18.6 (d)	7.0
$N_3P_3Cl_4(n\text{-}C_3H_7)_2$	43.6 (t)	18.5 (d)	<2
$N_3P_3Cl_4(n\text{-}C_3H_7)(n\text{-}C_4H_9)$	44.1 (t)	18.5 (d)	<2
$N_3P_3Cl_4(n\text{-}C_3H_7)(i\text{-}C_3H_7)$	50.3 (t)	18.6 (d)	3.8
$N_3P_3Cl_4(n\text{-}C_3H_7)(i\text{-}C_4H_9)$	42.4 (t)	18.0 (d)	<2
$N_3P_3Cl_4(n\text{-}C_3H_7)(t\text{-}C_4H_9)$	54.3 (t)	18.2 (d)	7.2
$N_3P_3Cl_4(n\text{-}C_4H_9)_2$	44.5 (t)	18.4 (d)	<2
$N_3P_3Cl_4(n\text{-}C_4H_9)(i\text{-}C_3H_7)$	51.1 (t)	19.0 (d)	4.3
$N_3P_3Cl_4(n\text{-}C_4H_9)(i\text{-}C_4H_9)$	42.9 (t)	17.9 (d)	<2
$N_3P_3Cl_4(n\text{-}C_4H_9)(t\text{-}C_4H_9)$	54.8 (t)	18.2 (d)	7.2
$N_3P_3Cl_4(C_4H_5)_2$	37.8 (t)	19.3 (d)	2.3
$N_3P_3Cl_4(C_3H_5)(CH_3)$	36.9 (t)	18.5 (d)	<2
$N_3P_3Cl_4(C_3H_5)(C_2H_5)$	43.1 (t)	19.2 (d)	<2
$N_3P_3Cl_4(C_3H_5)(n\text{-}C_3H_7)$	40.9 (t)	18.9 (d)	<2
$N_3P_3Cl_4(C_3H_5)(n\text{-}C_4H_9)$	41.4 (t)	18.9 (d)	<2
$N_3P_3Cl_4(C_3H_5)(i\text{-}C_3H_7)$	47.6 (t)	18.9 (d)	5.5
$N_3P_3Cl_4(C_3H_5)(i\text{-}C_4H_9)$	39.8 (t)	18.5 (d)	<2
$N_3P_3Cl_4(C_3H_5)(t\text{-}C_4H_9)$	52.3 (t)	19.2 (d)	9.3

Although it is not possible to rule out definitely either of these two possibilities, the available evidence favors the second pathway. That evidence is as follows. (a) No resonances from an intermediate such as V were observed during the ^{31}P NMR monitoring of the reaction. (Such a rearrangement would be expected to be slow at low temperatures.) If pathway 3 were correct, a species such as V should be detected, unless the migration of the alkyl group was more rapid than cleavage of the N–Cu bond. This is unlikely. (b) The reaction does not proceed with secondary or tertiary halides (which should be more reactive than primary alkyl halides), and this suggests that the reaction is limited by the steric requirements of the intermediate or transition state. These factors would be important if pathway 4 were the correct one. Finally, (c) the extremely low reactivity of the metallophosphazene II (R = CH_3) suggests that a buildup of electron density at phosphorus is necessary before the reaction will proceed. This again favors pathway 4, in which the electron-donating ability of the alkyl group would enhance the reactivity of the lone pair of electrons at phosphorus and thus enhance the ability of compound II to form a phosphazenium intermediate or transition state such as VI. This effect would not be observed in pathway 3, where the alkyl group bound to phosphorus should have little effect on the charge buildup at nitrogen.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (I) was supplied by Ethyl Corp. and was purified by sublimation, followed by two recrystallizations from hexane. The alkyl halides and Grignard reagents were obtained from Aldrich or Alfa-Ventron. Tetrahydrofuran (THF) was distilled into the reaction flask under an atmosphere of dry nitrogen from a sodium benzophenone ketyl drying agent. The reagent, [*n*-

Table VI[a]

R in metallophosphazene II	alkyl halide CH_3I	C_2H_5I	$n\text{-}C_3H_7I$	$n\text{-}C_4H_9I$	$i\text{-}C_3H_7I$	$i\text{-}C_4H_9I$	$t\text{-}C_4H_9I$	(allyl)Br
CH_3	P	NR	NR	NR	NR	NR	NR	P
C_2H_5	P	P	P	P	NR	NR	NR	P
$n\text{-}C_3H_7$	P	S	P	P	NR	NR	NR	P
$n\text{-}C_4H_9$	P	S	S	P	NR	NR	NR	P
$i\text{-}C_3H_7$	P	P	P	P	NR	NR	NR	P
$i\text{-}C_4H_9$	P	P	P	P	NR	NR	NR	P
$t\text{-}C_4H_9$	P	P	P	P	NR	NR	NR	P
allyl	S	S	S	S	NR	NR	NR	P

[a] P = product isolated and characterized; S = products detected by ^{31}P NMR analysis; NR = no reaction took place as determined by ^{31}P NMR analysis.

$Bu_3PCuI]_4$, was prepared by standard methods.[42] All reactions were carried out under an atmosphere of dry nitrogen.

Synthesis of Metallophosphazenes II. The syntheses of the metallophosphazenes II were all carried out in an identical manner; the following procedure is typical. 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 −80 °C. The Grignard reagent (25 mL of a 3 M solution in THF or ether) was added dropwise over a period of ≃30 min. The reaction mixture was then stirred for 16 h, and the temperature was allowed to rise slowly to ≃25 °C. These complexes II were not isolated but were allowed to react with alkyl halides, as described in the next section.

Reaction of II with Alkyl Halides. Initially, all the reactions listed in Table VI were monitored by ^{31}P NMR spectroscopy. A 3-mL aliquot of the solution in THF, prepared as previously described, was withdrawn under a blanket of dry nitrogen and introduced into a nitrogen-filled NMR tube. The alkyl halide (2 mL) was then added carefully and the mixture allowed to stand for 25 h. At the end of this time, the ^{31}P NMR of the mixture was scanned. A spectrum such as that in part a in Figure 1 indicated that no reaction had taken place. A spectral pattern as shown in spectrum d in Figure 1 indicated that a reaction had occurred. Only when a reaction was observed by ^{31}P NMR monitoring, was that reaction repeated on a large scale and were the products isolated. This was done in the following manner.

Isolation of Products. A solution of II in THF, prepared as described previously, was cooled to 0 °C and the alkyl halide (0.07 mol) added dropwise over ≃30 min. This mixture was stirred for 48 h, and the temperature was allowed to rise to 25 °C. The solvent was then 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 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.

(42) Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 9.

Acknowledgment. We thank the Office of Naval Research for the support of this work.

Registry No. I, 940-71-6; II (R = CH_3), 75083-25-9; II (R = C_2H_5), 75083-26-0; II (R = n-C_3H_7), 75083-27-1; II (R = n-C_4H_9), 75083-28-2; II (R = i-C_3H_7), 75083-29-3; II (R = i-C_4H_9), 75083-30-6; II (R = t-C_4H_9), 75083-31-7; II (R = C_3H_5), 75083-32-8; III (R = R′ = CH_3), 6204-32-6; III (R = CH_3, R′ = C_2H_5), 72474-25-0; III (R = CH_3, R′ = n-C_3H_7), 72474-26-1; III (R = CH_3, R′ = n-C_4H_9), 72474-27-2; III (R = CH_3, R′ = i-C_3H_7), 72474-28-3; III (R = CH_3, R′ = i-C_4H_9), 75067-44-6; III (R = CH_3, R′ = t-C_4H_9), 72474-20-5; III (R = R′ = C_2H_5), 75067-45-7; III (R = C_2H_5, R′ = n-C_3H_7), 75067-46-8; III (R = C_2H_5, R′ = n-C_4H_9), 75067-47-9; III (R = C_2H_5, R′ = i-C_3H_7), 75067-48-0; III (R = C_2H_5, R′ = i-C_4H_9), 75067-49-1; III (R = C_2H_5, R′ = t-C_4H_9), 75067-50-4; III (R = R′ = n-C_3H_7), 75067-51-5; III (R = n-C_3H_7, R′ = n-C_4H_9), 75067-52-6; III (R = n-C_3H_7, R′ = i-C_3H_7), 75067-53-7; III (R = n-C_3H_7, R′ = i-C_4H_9), 75067-54-8; III (R = n-C_3H_7, R′ = t-C_4H_9), 75067-55-9; III (R = R′ = n-C_4H_9), 75082-97-2; III (R = n-C_4H_9, R′ = i-C_3H_7), 75067-56-0; III (R = n-C_4H_9, R′ = i-C_4H_9), 75067-57-1; III (R = n-C_4H_9, R′ = t-C_4H_9), 75067-58-2; III (R = C_3H_5, R′ = CH_3), 72474-22-7; III (R = C_3H_5, R′ = C_2H_5), 75067-59-3; III (R = C_3H_5, R′ = n-C_3H_7), 75067-60-6; III (R = C_3H_5, R′ = n-C_4H_9), 75067-61-7; III (R = C_3H_5, R′ = i-C_3H_7), 72474-29-4; III (R = C_3H_5, R′ = i-C_4H_9), 75067-62-8; III (R = C_3H_5, R′ = t-C_4H_9), 72474-21-6; III (R = R′ = C_3H_5), 72474-23-8; CH_3I, 74-88-4; C_2H_5I, 75-03-6; n-C_3H_7I, 107-08-4; n-C_4H_9I, 542-69-8; C_3H_5Br, 106-95-6; $[n\text{-}Bu_3PCuI]_4$, 28132-72-1.

Supplementary Material Available: Table II, dialkylphosphazene infrared data, Table IV, dialkylphosphazene ^1H NMR data, and Table V, dialkylphosphazene ^{13}C NMR data (26 pages). Ordering information is given on any current masthead page.

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Reaction of Triphenylphosphine with Tetrasulfur Tetranitride: Synthesis and Structure of 1,5-Bis(triphenylphosphinimino)cyclotetrathiazene, $(Ph_3P{=}N)_2S_4N_4$

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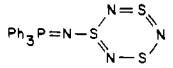
Received December 11, 1979

The reaction of triphenylphosphine with S_4N_4 in acetonitrile yields 1,5-bis(triphenylphosphinimino)cyclotetrathiazene, $(Ph_3P{=}N)_2S_4N_4$, as well as smaller amounts of the tetrasulfur pentanitride salt of the tris(triphenylphosphinimino)sulfonium cation, $(Ph_3P{=}N)_3S^+$. The crystal and molecular structure of $(Ph_3P{=}N)_2S_4N_4$ has been determined by single-crystal X-ray diffraction. The crystals of $(Ph_3P{=}N)_2S_4N_4$ are monoclinic, of space group $P2_1/c$, with a = 10.306 (1) Å, b = 19.473 (5) Å, c = 17.804 (1) Å, β = 94.03(1)°, V = 3564.1 Å^3, Z = 4, and D_{calcd} = 1.37 g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final R = 0.043 and R_w = 0.060 for 3303 reflections with $I > 3\sigma(I)$. The structure consists of a 1,5-disubstituted S_4N_4 cage, the two exocyclic triphenylphosphinimino ligands being oriented in equatorial and axial directions, with the mean d(P–N) = 1.592 Å and ∠P–N–S = 122.6°. The asymmetry of the ligand orientation distorts the S_4N_4 unit from the ideal C_{2v} symmetry. The otherwise symmetry-related S–N bonds fall into two classes: (i) d(S–N) = 1.630 (4)–1.675 (4) Å and (ii) d(S–N) = 1.583 (4)–1.613 (4) Å. The substituted sulfur atoms are separated by 3.727 (2) Å, but the two unsubstituted sulfurs remain only 2.452 (2) Å apart, indicating significant σ bonding between these two atoms.

Introduction

The reaction of triphenylphosphine with tetrasulfur tetranitride was first reported in 1961 by Krauss and Jung, who described the preparation of triphenylphosphiniminocyclotrithiazene, $Ph_3P{=}N\text{-}S_3N_3$ (**1**), in 11% yield.[2] This compound had been described earlier by Fluck, Becke-Goehring, and Dehoust,[3] who isolated it in low yield as a side product of the reaction of triphenylphosphine ylide and S_4N_4. No attempt was made at the time to rationalize the formation of **1**, nor were any other products (apart from Ph_3PS) observed. Later, however, Fluck and Reinisch examined the reaction of $PhPCl_2$ with S_4N_4,[4] and although they were unable to isolate any sulfur-containing compound, they did suggest a mechanism



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0020-1669/81/1320-0016$01.00/0