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Reactions between Alkyl Grignard Reagents and Aminophosphazenes: Synthesis of Alkylchlorocyclotriphosphazenes[1]

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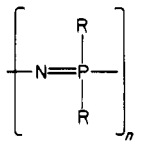
The reactions between alkyl Grignard reagents and aminophosphazenes have been investigated. The products formed when 1,3,5-tris(dimethylamino)-1,3,5-trichlorocyclotriphosphazene (**4**) reacts with alkyl Grignard reagents depend on the concentrations of the reagents in solution, on the solvent employed, and on the method of product isolation. Reaction between **4** and CH_3MgBr in diethyl ether, followed by treatment with triethylamine, results in chlorine replacement to yield the trialkylphosphazene, **5**, and an ethoxy-substituted product, **6**. Formation of **5** is favored by increases in the concentration of **4** and use of a larger excess of Grignard reagent. Similar results were obtained when C_2H_5MgBr was used. The proposed mechanism for the replacement of chlorine by ethoxy involves an interaction between the phosphazene substrate, magnesium species in solution, and diethyl ether solvent. Chlorine replacement by 4-chlorobutoxy side groups predominates when **4** reacts with CH_3MgCl in tetrahydrofuran. Compounds of formula $N_3P_3Cl_3R_3$ (**2**) were prepared by the reaction of **5** with hydrogen chloride in refluxing toluene. Species $N_3P_3Cl_4R_2$ were synthesized by allowing 1,3,5,5-tetrakis(dimethylamino)-1,3-dichlorocyclotriphosphazene (**14**) to react with excess Grignard reagent in diethyl ether to yield the dialkyl species **15** (R = CH_3, C_2H_5). The reaction between **15** and hydrogen chloride in refluxing toluene yields 1,3-dialkyl-1,3,5-trichloro-5-(dimethylamino)cyclotriphosphazene (**16**). Removal of the last dimethylamino residue was accomplished by treatment of **16** with hydrogen chloride in a sealed tube at 100 °C. Structural characterization was obtained for all the new cyclophosphazenes by elemental analysis, mass spectrometry, infrared spectroscopy, and NMR (^{31}P, ^{13}C, ^{1}H) spectroscopy. NMR evidence is presented for the presence of geometrical isomers.

The reactions between cyclic halophosphazenes and main-group organometallic reagents are important for several reasons. First, a need exists for new synthetic routes for the preparation of high molecular weight poly(organophosphazenes) such as **1** that contain



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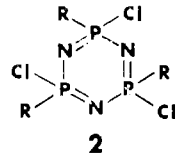
alkyl or aryl side groups attached to the skeleton through P–C bonds.[2] These materials should have physical properties that are markedly different from those of conventional poly(organophosphazenes) that contain alkoxy- or amino side groups.[3] One prospective method for the preparation of macromolecules of type **1** involves the reactions of organometallic reagents with halophosphazene high polymers such as $(NPCl_2)_n$ or $(NPF_2)_n$.[4] Experimentally, it is found that these reactions are often complicated by skeletal-degradation, metal–halogen-exchange, and proton-abstraction processes. Such reactions have been studied at the small-molecule level.[5-7]

Second, organosubstituted cyclotriphosphazenes can function as polymerization "monomers".[8,9] For instance, the thermal ring-opening polymerization of species such as **2** or **3** should



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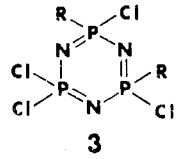

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generate high polymeric linear phosphazenes with both alkyl and chloro side groups. Subsequent replacement of the chlorine atoms would allow the controlled introduction of a wide range of different organic side groups and permit the synthesis of noncrystalline, mixed-substitutent polymers.[10] These studies could also yield valuable information about the mechanism of phosphazene ring-opening polymerizations.[11]

Third, compounds **2** and **3**, as well as the analogous high polymers, may serve as interesting substrates for reactions with transition-metal anions. Several transition-metal-containing cyclic phosphazenes have been synthesized, but as yet, no high polymeric species exist.[12] If accessible, these would be of considerable interest as polymeric catalysts or electroactive materials.

Recently, we described the synthesis of a wide range of monoalkylpentachlorocyclotriphosphazenes, $N_3P_3Cl_5R$, and 1,1-dialkylcyclotriphosphazenes, $N_3P_3Cl_4RR'$.[13] The thermal po-

(1) This work was presented in part at the 187th National Meeting of the American Chemical Society, St. Louis, MO, April 8–13, 1984.
(2) Fully alkyl-substituted polyphosphazenes have been prepared from small-molecule alkylphosphorus–nitrogen–silicon precursors, but the reported molecular weights are lower than those of alkoxy- or amino-substituted polyphosphazenes prepared by the polymer substitution route; see: Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848.
(3) For example, some alkoxy- and aminophosphazenes are unstable at moderate temperatures; see: (a) Ferrar, W. T.; DiStefano, F. V.; Allcock, H. R. *Macromolecules* **1980**, *13*, 1345. (b) Cheng, T. C.; Mochel, V. D.; Adams, H. E.; Longo, T. F. *Macromolecules* **1980**, *13*, 158. (c) O'Brien, J. P.; Ferrar, W. T.; Allcock, H. R. *Macromolecules* **1979**, *12*, 108. (d) Allcock, H. R.; Kolich, C. H.; Kossa, W. C. *Inorg. Chem.* **1977**, *16*, 3362.
(4) (a) Allcock, H. R.; Chu, C. T.-W. *Macromolecules* **1979**, *12*, 551. (b) Allcock, H. R.; Evans, T. L.; Patterson, D. B. *Macromolecules* **1980**, *13*, 201. (c) Evans, T. L.; Patterson, D. B.; Suszko, P. R.; Allcock, H. R. *Macromolecules* **1981**, *14*, 218.
(5) Allcock, H. R.; Desorcie, J. L.; Harris, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 2814.
(6) (a) Allen, C. W.; Bright, R. P. *Inorg. Chem.* **1983**, *22*, 1291. (b) Ramachandran, K.; Allen, C. W. *J. Am. Chem. Soc.* **1982**, *104*, 2396. (c) Blumentritt, J.; Moeller, T. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 263. (d) Biddlestone, M.; Shaw, R. A. *Phosphorus Relat. Group V Elem.* **1973**, *3*, 95. (e) Paddock, N. L.; Ranganathan, T. N.; Todd, S. M. *Can. J. Chem.* **1971**, *49*, 164.
(7) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(8) (a) Allcock, H. R.; Patterson, D. B. *Inorg. Chem.* **1977**, *16*, 197. (b) Allcock, H. R.; Schmutz, J. L.; Kosydar K. M. *Macromolecules* **1978**, *11*, 179. (c) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1975**, *8*, 377.
(9) (a) Allcock, H. R.; Ritchie, R. J.; Harris, P. J. *Macromolecules* **1980**, *13*, 1332. (b) Allcock, H. R.; Connolly, M. S. *Macromolecules*, in press.
(10) A mixture of **2** (R = CH_3) and the analogous cyclotetraphosphazene has been reported to underto thermal ring-opening polymerization, but the resulting polymer was not derivatized to replace hydrolytically unstable P–Cl bonds: Prons, V. N.; Grinblat, M. P.; Klebanskii, A. L. *Zh. Obshch. Khim.* **1971**, *41*, 482.
(11) Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972.
(12) (a) Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim. M. Y. *Inorg. Chem.* **1981**, *20*, 716. (b) Allcock, H. R.; Wagner, L. J.; Levin, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 1321. (c) Allcock, H. R.; Suszko, P. R.; Wagner, L. J. Whittle, R. R.; Boso, B. *J. Am. Chem. Soc.* **1984**, *106*, 4966. (d) Allcock, H. R.; Riding, G. H.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, 106, 5561.
(13) (a) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221. (b) Allcock, H. R.; Harris, P. J. *Inorg. Chem.* **1981**, *20*, 2844. (c) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11. (d) Allcock, H. R.; Connolly, M. S.; Whittle, R. R. *Organometallics* **1983**, *2*, 1514.

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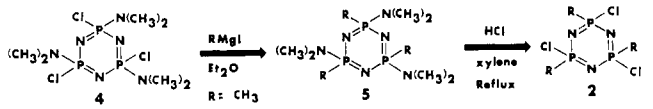
lymerization of the monoalkyl compounds and subsequent chlorine replacement reactions have already been explored.[9] In 1960, in a brief paper, Tesi and Slota[14] reported the preparation of 1,3,5-trimethyl-1,3,5-trichlorocyclotriphosphazene, $(NPClCH_3)_3$, by treatment of 1,3,5-tris(dimethylamino)-1,3,5-trichlorocyclotriphosphazene (**4**) with an excess of methylmagnesium iodide



in ether to yield 1,3,5-tris(dimethylamino)-1,3,5-trimethylcyclotriphosphazene (**5**, R = CH_3) as the only product. The formation of $(NPClCH_3)_3$ (**2**, R = CH_3) was accomplished by the reaction of **5** with hydrogen chloride in refluxing xylene.

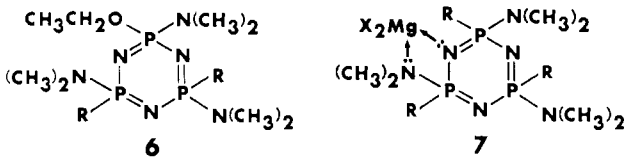
Through our attempts to repeat this reaction sequence, we have found that the nature of the products formed when **4** reacts with alkyl Grignard reagents is influenced by several factors. These include the concentration of the reagents in solution, the nature of the solvent employed, and the method by which the products are isolated. Here, we describe these effects, together with a detailed procedure for the high-yield synthesis of 1,3,5-trialkyl-1,3,5-trichlorocyclotriphosphazenes (**2**) and 1,3-dialkyl-1,3,5,5-tetrachlorocyclotriphosphazenes (**3**). The thermal ring-opening polymerization behavior of **2** and **3** will be discussed in another paper.

Results and Discussion

Reaction between 4 and CH_3MgBr: General Features. An initial attempt was made to repeat the work of Tesi and Slota.[14] 1,3,5-Tris(dimethylamino)-1,3,5-trichlorocyclotriphosphazene[15] (**4**) was treated with methylmagnesium bromide[16] at 25 °C in diethyl ether. A threefold excess of Grignard reagent for each P–Cl bond was employed.

After 48 h, and after the formation of a white precipitate, it was clear from ^{31}P NMR spectra that all the starting material (**4**) had been consumed (Figure 1a).[17] However, the identity of the products could not be deduced from the NMR spectra. The unreacted Grignard reagent was then destroyed by treatment with 2-propanol. Subsequent treatment with triethylamine, followed by chromatography,[18] yielded two products, identified as **5** (R = CH_3) and 1,3,5-tris(dimethylamino)-1,3-dimethyl-5-ethoxycyclotrisphosphazene (**6**, R = CH_3). The yields were 46% and 44%, respectively. The structural proof for **5** and **6**, as well as an explanation for the introduction of the ethoxy groups, will be discussed later.

Unless triethylamine is employed in this reaction sequence, species **5** and **6** are not isolated. Instead, the products appear to



be phosphazenylmagnesium complexes of the type shown in **7**. The ^{31}P NMR spectrum,[17] shown in Figure 1a, is consistent with this interpretation. The treatment with triethylamine yielded the spectrum shown in Figure 1b, in which the resonances centered at 27 ppm are from compound **5** and those at 30 and 19 ppm are from compound **6**. The spectrum is complicated by the presence of different cis and trans isomers. The formation of phosphazenylmagnesium complexes such as **7** seems reasonable in view of

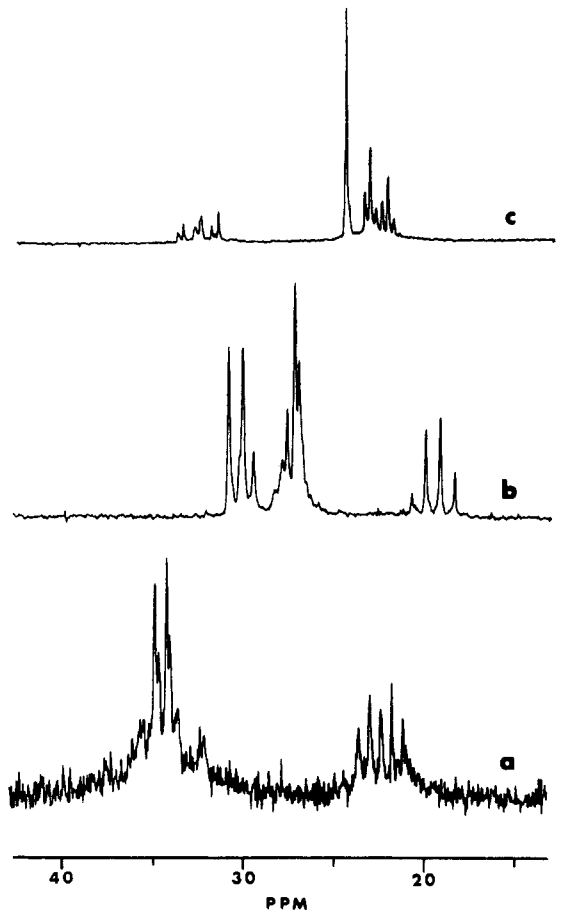


Figure 1. ^{31}P NMR spectra: (a) the product mixture obtained from the reaction between **4** and CH_3MgBr in diethyl ether (note the absence of **4**, with an expected chemical shift at 27.8 ppm); (b) **5** and **6** obtained from the reaction between **4** and CH_3MgBr in diethyl ether followed by treatment with triethylamine; (c) **12** and **13** obtained from the reaction between **4** and CH_3MgCl in tetrahydrofuran at 66 °C.

the skeletal basicity of aminophosphazenes[11] and the well-known ability of tertiary amines to complex with Grignard reagents.[19]

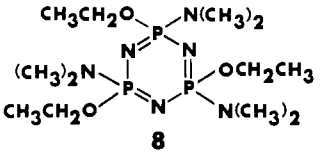
Method for the High-Yield Synthesis of 5. In practical terms, compound **6** is an undesirable side product from the reaction between **4** and CH_3MgBr. Thus, an attempt was made to modify the reaction conditions to increase the yield of product **5** at the expense of **6**. As will be discussed, ethoxy side groups are derived from the diethyl ether solvent. Hence, it seemed likely that chlorine replacement by ethoxy residues could be minimized by increases in the concentrations of **4** and CH_3MgBr and by the use of a larger excess of Grignard reagent for each P–Cl bond.

A sample of **4** was cooled to −78 °C[20] and a 3.0 M solution of methylmagnesium bromide[16] (6 equiv/P–Cl bond) in diethyl ether was added. The solution was stirred at 25 °C for 48 h, and the products were isolated as described earlier. A mixture of **5** and **6** was again obtained, but the yield of **5** had increased to 87% and the yield of **6** (R = CH_3) was reduced to 5%. The use of C_2H_5MgBr in place of CH_3MgBr yielded similar quantities of **5** and **6** (R = C_2H_5).

Mechanism of Ethoxy Group Introduction. The replacement of chlorine by ethoxy during the reaction between **4** and alkyl Grignard reagents was of some interest. In addition, it was found that compound **4** reacts with magnesium bromide in diethyl ether to yield (after treatment with triethylamine) compound **8** in 81% yield.

The most likely mechanism for the formation of **8** is outlined in Scheme I. This mechanism is similar to the one proposed for

(14) Tesi, G.; Slota, P. J. *Proc. Chem. Soc. London* **1960**, 404.
(15) Keat, R.; Shaw, R. A. *J. Chem. Soc.* **1965**, 2215.
(16) Identical results were obtained when methylmagnesium iodide was employed in place of methylmagnesium bromide.
(17) ^{31}P NMR spectra were recorded with the use of a Varian CFT-20 spectrometer operating at 32 MHz. Positive chemical shifts are downfield from external phosphoric acid. Spectra were recorded with broad-band ^1H decoupling.
(18) Chromatographic separations were carried out with the use of a Waters Prep 500 liquid chromatograph equipped with silica columns.
(19) Ashby, E. C.; Reed, R. *J. Org. Chem.* **1966**, *31*, 971.
(20) Addition of the Grignard reagent at reduced temperatures was found to increase the yield of **5** slightly.



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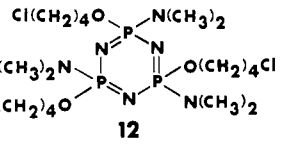
the Lewis acid catalyzed cleavage of aliphatic ethers by organic acid chlorides.[21] An initial interaction between **4** and magnesium bromide generates a phosphonium ion type intermediate, **9**. Similar complexes are believed to form when $(NPCl_2)_3$ reacts with $AlCl_3$ during Friedel–Crafts arylation reactions.[22] Species **9** reacts with diethyl ether solvent to form an oxonium ion, **10**. Cleavage of the ether then occurs to form **11** with expulsion of bromoethane. The final product, **8**, is produced after treatment with triethylamine.

The evidence that supports this mechanism is as follows: First, no reaction was observed when **4** was treated with diethyl ether in the absence of magnesium bromide. Second, no reaction occurs when hexachlorocyclotriphosphazene $(NPCl_2)_3$ and $MgBr_2$ are allowed to interact in diethyl ether for several days. Also, when the reaction is carried out with a mixture of **4** and $(NPCl_2)_3$, compound **4** is converted to **8** but $(NPCl_2)_3$ is recovered unchanged. This suggests the need for a strong Lewis acid–Lewis base interaction. As mentioned previously, cyclic phosphazenes that contain amino side groups are significantly more basic than their perhalo counterparts.[11] Third, significant quantities of bromomethane were detected when **4** was converted to **8**.[23] No chloroethane was detected. Thus, only the more labile, as well as the more abundant, bromide ion is expelled during the ether cleavage step. Finally, treatment with triethylamine is necessary before product **8** can be isolated. As with the reaction between **4** and RMgBr, failure to carry out this procedure yields products that appear to be magnesium salt adducts of the cyclophosphazene.

Reactions in Tetrahydrofuran Solvent. The reaction between **4** and CH_3MgCl in tetrahydrofuran (THF) was also investigated. Previous studies have demonstrated that reactions between halophosphazenes and organometallic reagents in THF may proceed through either metal–halogen exchange or substitution pathways.[5,13] No reaction was detected when a THF solution of **4** was allowed to interact with CH_3MgCl at 25 °C for 48 h. However, at 66 °C a reaction occurred that yielded two new cyclotriphosphazenes. These were identified as 1,3,5-tris(dimethylamino)-1,3,5-tris(4-chlorobutoxy)cyclotriphosphazene (**12**) and



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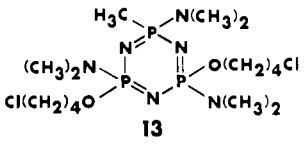
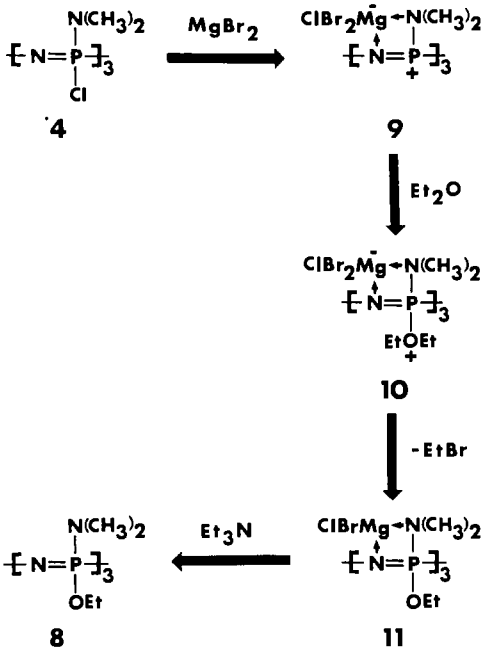


13

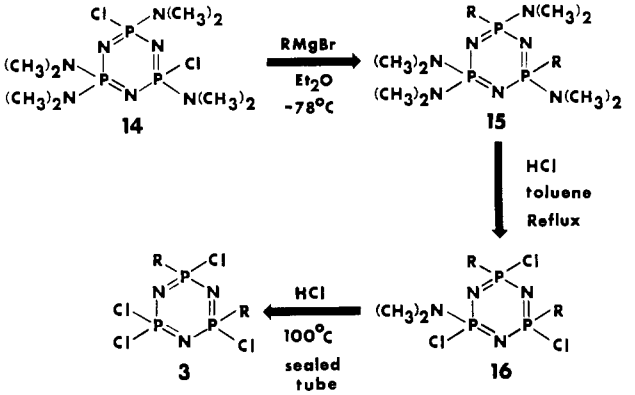
1,3,5-tris(dimethylamino)-1,3-bis(4-chlorobutoxy)-5-methylcyclotriphosphazene (**13**). These compounds were isolated as relatively unstable, colorless oils in 38% and 54% yields, respectively. They could not be purified by vacuum distillation; significant decomposition occurred above 80 °C. Alkoxyphosphazenes are known to undergo rearrangements to phospha*zanes* at elevated temperatures.[11] Moreover, such reactions are assisted by the presence of alkyl halides.

Phosphazenylmagnesium complexes are apparently not formed when **4** reacts with CH_3MgCl in THF. Treatment of the reaction mixture with triethylamine is not a requirment for product isolation (see Experimental Section). Also, a ^{31}P NMR spectrum[17] of the crude reaction mixture (Figure 1c) revealed resonances associated with compounds **12** and **13** only. No phosphazenylmagnesium species were detected. The resonance at 24 ppm was assigned to **12**, while the resonances centered at 33 and 22 ppm were assigned to **13**. As will be discussed later, three stereoisomers of **13** are apparently formed. The superior coordinating ability of THF (compared to diethyl ether) is believed to prevent the formation of long-lived phosphazenylmagnesium complexes. However, the fact that alkoxy-substituted products predominate suggests that interactions involving cyclotriphosphazenes, magnesium species, and solvent do occur in this medium. A refluxing solution of **4** and $MgCl_2$ in THF gave an 85% yield of **12**.[24] No reaction was detected when a solution of **4** in THF (containing no $MgCl_2$) was refluxed for 48 h.[24]

Scheme I



Scheme II



Reactions between 5 and Hydrogen Chloride. Compounds of type **5** (R = CH_3, C_2H_5) reacted smoothly with anhydrous hydrogen chloride in boiling toluene to yield 1,3,5-trialkyl-1,3,5-trichlorocyclotriphosphazenes (**2**).[14] These compounds are white, air-stable solids.

Compounds **2** were the only products isolated even when the starting material, **5**, was contaminated with small amounts of **6** (5–10%). As mentioned previously, the thermal stability of alkoxyphosphazenes is diminished significantly in the presence of reagents such as alkyl halides or hydrogen halides that can quaternize the skeletal nitrogen atoms.[11] Hence, the reaction conditions required to remove the dimethylamino substituents are probably sufficient for alkoxyphosphazene rearrangement and subsequent decomposition.

Synthesis of 1,3-Dialkyl-1,3,5,5-tetrachlorocyclotriphosphazenes. It was expected that 1,3-dialkyl-1,3,5,5-tetrachlorocyclo-

(21) Johnson, F. In "Friedel-Crafts and Related Reactions"; Olah, G. Ed.; Interscience: New York, 1965; Vol. IV, p 1.
(22) Acock, K. G.; Shaw, R. A.; Wells, F. G. B. *J. Chem. Soc.* **1964**, 121.
(23) Gaseous products were analyzed by VPC using a Varian 3700 gas chromatograph equipped with a 2-m Chromosorb 102 column. Products were identified by comparison of retention times with authentic samples.
(24) No reaction was detected at 25 °C.

Table II. Cyclotriphosphazene ^{31}P NMR Data[a,17]

compd	chem shift, ppm				coupling const, Hz
$N_3P_3[N(CH_3)_2]_3(CH_3)_3$ (5)	P(N)(C)	28.0			singlet[b]
	P(N)(C)	29.3	P(N)(C)	28.3	$J_{PNP} = 10.5$[c]
$N_3P_3[N(CH_3)_2]_3(CH_3)_2(OCH_2CH_3)$ (6)	P(N)(C)	31.4	P(N)(O)	19.3	$J_{PNP} = 24.2$
	P(N)(C)	30.8	P(N)(O)	20.2	$J_{PNP} = 24.2$
$N_3P_3[N(CH_3)_2]_3(CH_2CH_3)_3$ (5)	P(N)(C)	33.9			singlet[b]
	P(N)(C)	34.2	P(N)(C)	33.5	$J_{PNP} = 8.0$[c]
$N_3P_3[N(CH_3)_2]_3(CH_2CH_3)_2(OCH_2CH_3)$ (6)	P(N)(C)	36.5	P(N)(O)	20.1	$J_{PNP} = 18.9$
	P(N)(C)	36.1	P(N)(O)	20.1	$J_{PNP} = 18.9$
	P(N)(C)	36.8	P(N)(O)	21.0	$J_{PNP} = 19.2$
$N_3P_3[N(CH_3)_2]_3(OCH_2CH_3)_3$ (8)	P(N)(O)	24.1			singlet
$N_3P_3[N(CH_3)_2]_3(CH_3)(OCH_2CH_2CH_2CH_2Cl)_2$ (13)	P(N)(C)	34.0	P(N)(O)	22.6	$J_{PNP} = 29.9$
	P(N)(C)	33.4	P(N)(O)	22.7	$J_{PNP} = 29.8$
	P(N)(C)	34.0	P(N)(O)	22.1	$J_{PNP} = 29.9$
$N_3P_3[N(CH_3)_2]_3(OCH_2CH_2CH_2CH_2Cl)_3$ (12)	P(N)(O)	24.3			singlet
$N_3P_3Cl_3(CH_3)_3$ (2)	P(C)(Cl)	39.6			singlet[b]
	P(C)(Cl)	42.0	P(C)(Cl)	40.8	unresolved[c]
$N_3P_3Cl_3(CH_2CH_3)_3$ (2)	P(C)(Cl)	48.0			singlet[b]
	P(C)(Cl)	50.8	P(C)(Cl)	49.3	unresolved[c]
$N_3P_3[N(CH_3)_2]_4(CH_3)_2$ (15)	P(N)(C)	30.9	$P(N)_2$	23.0	$J_{PNP} = 19.9$
	P(N)(C)	30.5	$P(N)_2$	23.4	$J_{PNP} = 21.6$
$N_3P_3[N(CH_3)_2]_4(CH_2CH_3)_2$ (15)	P(N)(C)	36.1	$P(N)_2$	22.9	$J_{PNP} = 15.4$
	P(N)(C)	35.7	$P(N)_2$	23.2	$J_{PNP} = 17.3$
$N_3P_3Cl_3(CH_3)_2[N(CH_3)_2]$ (16)	P(C)(Cl)	41.7	P(N)(Cl)	26.9	unresolved
	P(C)(Cl)	40.5	P(N)(Cl)	26.4	$J_{PNP} = 4.6$
	P(C)(Cl)	39.9	P(N)(Cl)	27.7	$J_{PNP} = 8.3$
$N_3P_3Cl_3(CH_2CH_3)_2[N(CH_3)_2]$ (16)	P(C)(Cl)	49.6	P(N)(Cl)	28.1	unresolved
	P(C)(Cl)	48.0	P(N)(Cl)	29.2	unresolved
$N_3P_3Cl_4(CH_3)_2$ (3)	P(C)(Cl)	39.7	$P(Cl)_2$	22.1	unresolved[b]
	P(C)(Cl)	41.1	$P(Cl)_2$	22.0	unresolved[c]
$N_3P_3Cl_4(CH_2CH_3)_2$ (3)	P(C)(Cl)	47.4	$P(Cl)_2$	23.3	unresolved[b]
	P(C)(Cl)	48.9	$P(Cl)_2$	23.0	unresolved[c]

[a] Spectra were recorded on a solution of the compound in $CDCl_3$. [b] Cis isomer. [c] Trans isomer.

triphosphazenes (**3**) should also be accessible via reactions similar to those described for the preparation of **5** and **2**. 1,3,5,5-Tetrakis(dimethylamino)-1,3-dichlorocyclotriphosphazene (**14**) reacts with excess Grignard reagent (9 equiv/P–Cl bond) in ether to yield 1,3,5,5-tetrakis(dimethylamino)-1,3-dialkylcyclotriphosphazenes (**15**) exclusively (Scheme II). No ethoxy-substituted compounds were detected. Both the methyl and ethyl derivatives of **15** were isolated as colorless oils.

Compounds **15** reacted with anhydrous hydrogen chloride in refluxing toluene to form 1,3-dialkyl-1,3,5-trichloro-5-dimethylaminocyclotriphosphazene (**16**). The methyl derivative is a white crystalline solid, but the ethyl derivative is a colorless oil. More forcing conditions were required for the complete deamination of **5** (see Experimental Section). The final dimethylamino residue could not be removed even after prolonged treatment with hydrogen chloride in refluxing toluene, xylene, chloroform, acetonitrile, or butyronitrile. These results are compatible with previous studies.[25,26] For instance, hexakis(dimethylamino)cyclotriphosphazene, $N_3P_3(NMe_2)_6$, reacts with hydrogen chloride in refluxing xylene with removal of only one of the two $-NMe_2$ groups attached to each ring phosphorus atom.[25]

Compounds **16** did react with an excess of anhydrous hydrogen chloride in a sealed glass tube at 100 °C to form the desired 1,3-dialkyl-1,3,5,5-tetrachlorocyclotriphosphazenes (**3**).[27] Both the methyl and the ethyl derivatives of **3** are white, crystalline solids. Unlike compounds **2** and the methyl derivative of **3**, the ethyl derivative of **3** is less stable to hydrolysis than previously reported alkylhalocyclotriphophazenes.[5,13]

Cyclotriphosphazene Structural Characterization and Stereochemistry. All the compounds prepared in this study were characterized by a combination of mass spectrometry (low and high resolution), elemental microanalysis, infrared spectroscopy, and ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. These data are listed in Table I (supplementary material) and Tables II and III.

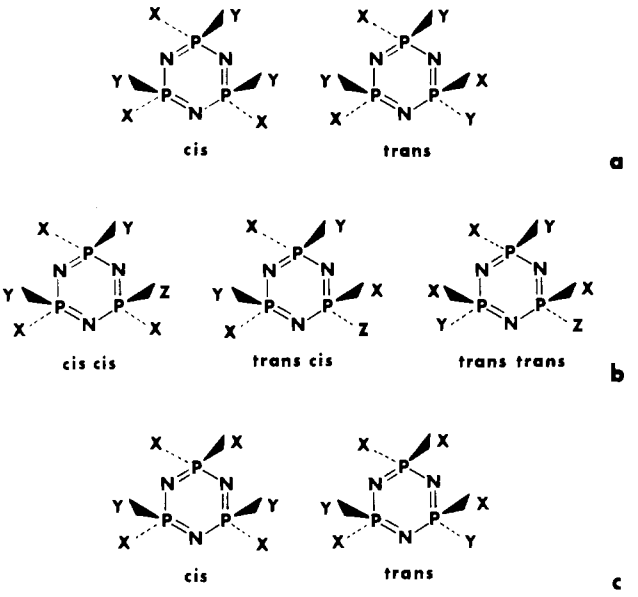


Figure 2. Possible geometrical isomers for cyclotriphosphazenes having the formulas (a) $N_3P_3X_3Y_3$, (b) $N_3P_3X_3Y_2Z$, and (c) $N_3P_3X_4Y_2$.

The parent ion mass spectral data[28] for all the compounds synthesized are listed in Table I (supplementary material). In each case, the correct parent ion was clearly detected. Compounds **2**, **3**, **12**, **13**, and **15** also yielded the expected chlorine isotope patterns. The elemental analysis data[29] are also presented in Table I.

(25) Nabi, S. N.; Shaw, R. A.; Stratton, C. *Chem. Ind. (London)* **1969**, 166.
(26) Clare, P.; Sowerby, D. B.; Green, B. *J. Chem. Soc., Dalton Trans.* **1972**, 2374.
(27) Chivers, T.; Oakley, R. T.; Paddock, N. L. *J. Chem. Soc. A* **1970**, 2324.
(28) Electron impact mass spectral data were obtained with the use of an AEI MS 902 spectrometer.
(29) Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN 37921.

The infrared spectra[30] for all the cyclotriphosphazenes were consistent with the proposed structures. In each case an intense absorbance existed between 1150 and 1250 cm^{-1}. This is a characteristic of the skeletal structure of cyclotriphosphazenes.[11] Other bands were detected for C–H, P–C, P–O, and P–Cl absorbances.

The most useful technique for determining the structure of the cyclotriphosphazenes prepared in this study was NMR (^{31}P, ^{1}H, ^{13}C) spectroscopy.[17,31,32] These data are listed in Tables II and III. As mentioned previously, the ^{31}P NMR spectra (Table II) of the cyclotriphosphazenes reported here are, in some cases, complicated by the presence of two or three geometrical isomers. The possible isomers (excluding enantiomers) for all the compounds prepared are shown in Figure 2.[33] Two isomers may exist for species having the general formula $N_3P_3(X)_3(Y)_3$ or $N_3P_3(X)_4(Y)_2$, while three isomers are possible for $N_3P_3(X)_3(Y)_2(Z)$.[34]

The individual isomers for compounds **2** (R = CH_3, C_2H_5) and **3** (R = CH_3) were isolated by using liquid chromatography techniques.[18] All other compounds were isolated as isomeric mixtures that resisted further chromatographic separation. However, by collection of several fractions as they were chromatographed, it was possible to obtain samples that were enriched with individual isomers. Examination of these samples by ^{31}P NMR spectroscopy[17] provided a qualitative measure of the relative abundance and number of isomers present. The organic side groups were identified by inspection of the high-field ^{1}H and ^{13}C NMR spectra (Table III).[31,32]

The reaction between **4** and RMgBr was carried out with the use of the trans isomer of **4**. This is the most readily obtained isomer from the reaction between $(NPCl_2)_3$ and 6 equiv of dimethylamine.[15] The most abundant (>90%) isomer of **5** (R = CH_3, C_2H_5) was assigned the trans configuration on the basis of the AB_2 pattern in the ^{31}P NMR spectrum. Only a small amount of the cis isomer (singlet) was detected. Two isomers of **6** (R = CH_3) were formed ($\simeq$70:30 relative abundance), even though three are possible (Figure 2). All three isomers of **6** (R = C_2H_5) were formed in nearly equal quantities.

The ^{31}P NMR spectrum of **8**, obtained from the reaction between **4** (trans isomer) and diethyl ether solvent in the presence of $MgBr_2$, consisted of a singlet at 24.1 ppm (Table II). However, the configuration of **8** is uncertain because the ^{31}P NMR spectra of **4** (both cis and trans) are also singlets.[35] The ^{1}H NMR signal for the dimethylamino groups is complex, and this suggests a trans configuration. However, only a single resonance was found in the ^{13}C NMR spectrum for this same side group.

The reaction between **4** (trans isomer) and CH_3MgCl in THF yielded all three of the possible isomers for compound **13**, while only a single resonance in the ^{31}P NMR spectrum was observed for **12**. Again, the ^{1}H NMR signal for the dimethylamino groups in **12** is complex, but only a single resonance exists in the ^{13}C NMR spectrum for this group. The NMR spectrum (^{31}P, ^{1}H, ^{13}C) of **12**, obtained from the reaction between **4** and THF solvent in the presence of $MgCl_2$, was identical with the spectrum for the product **12** obtained from the Grignard reaction.

A mixture of the cis and trans isomers ($\simeq$40:60) of compound **2** (R = CH_3, C_2H_5) resulted from treatment of **5** (R = CH_3, C_2H_5) with hydrogen chloride in refluxing toluene. As described earlier, the samples of **5** used were predominantly trans (>90%).[36] Pure samples of the isomers of **2** (R = CH_3, C_2H_5) were isolated by liquid chromatography.[18] As expected, the ^{31}P NMR spectrum of the cis isomers consisted of a singlet, while two resonances were found for the trans isomer. The ^{1}H and ^{13}C NMR data (Table III) were consistent with these assignments.

For the preparation of the dialkylcyclotriphosphazenes, **3**, the cis isomer of **14** was allowed to react with RMgBr. This is the most readily obtained isomer from the reaction between $(NPCl_2)_3$ and 8 equiv of dimethylamine.[15] The product, **15** (R = CH_3, C_2H_5), was a mixture ($\simeq$50:50) of the cis and trans species. Treatment with hydrogen chloride in refluxing toluene yielded three isomers of **16** (R = CH_3) and two isomers of **16** (R = C_2H_5). When heated with hydrogen chloride in a sealed tube, these isomeric mixtures yielded a mixture of two isomers ($\simeq$70:30) of **3** (CH_3, C_2H_5). These were isolated (R = CH_3 only) by liquid chromatography.[18] Attempted chromatography of the ethyl derivatives appeared to result in decomposition, presumably via hydrolysis. The most abundant isomer of **3** is believed to have the cis configuration. This is based on a comparison of its ^{31}P NMR spectrum (Table II) with those of compounds **2**. In these, the resonances for the PRCl groups of the cis isomers are upfield from that of the trans species. The assignment was confirmed for compounds **3** (R = CH_3) by inspection of the high-field ^{1}H and ^{13}C NMR spectra (Table III).

Experimental Section

Materials. Hexachlorocyclotriphosphazene was supplied by the Firestone Tire and Rubber Co. and was purified by sublimation. Dimethylamine (Matheson) was dried over sodium before use. The dimethylamino-substituted phosphazenes, *trans*-$N_3P_3Cl_3(NMe_2)_3$ and *cis*-$N_3P_3Cl_2(NMe_2)_4$, were prepared by the method of Keat and Shaw.[15] The Grignard reagents were obtained commercially from Alfa-Ventron as 3.0 M solutions in diethyl ether or tetrahydrofuran. Tetrahydrofuran, diethyl ether, and toluene were distilled into the reaction flask under an atmosphere of dry nitrogen from a sodium–benzophenone ketyl drying agent. Xylene, acetonitrile, and butyronitrile were dried over calcium hydride before use. Chloroform was distilled from P_2O_5. Anhydrous magnesium chloride (Aldrich) and magnesium bromide etherate (Aldrich) were dried for several days in vacuo at 160–170 °C. Triethylamine (Aldrich) and anhydrous hydrogen chloride (Matheson) were used as received. All reactions (except those involving HCl) were carried out under an atmosphere of dry nitrogen using typical Schlenk-tube techniques.

Reaction between 4 and CH_3MgBr. To a solution of $N_3P_3Cl_3(NMe_2)_3$ (**4**) (5.0 g, 0.013 mol) in diethyl ether (120 mL) was added CH_3MgBr (40 mL of a 3.0 M solution in diethyl ether). The solution was stirred at 25 °C for 48 h. The precipitate that formed was allowed to settle to the bottom of the flask, and a 2-mL aliquot of the supernatent solution was transferred via syringe into a nitrogen-filled NMR tube and was analzyed.[17] The ^{31}P NMR spectrum is shown in Figure 1a.

The reaction solution was then cooled to 0 °C, and tetrahydrofuran (150 mL) was added to dissolve the precipitated material. The solution was then added dropwise to a mixture of 2-propanol (30 mL) and hexane (200 mL) at 0 °C. The resulting precipitate was removed by filtration, and triethylamine (50 mL) was added to the filtrate. Filtration and solvent removal under reduced pressure yielded 4.1 g of a yellow oil. The ^{31}P NMR spectrum of the product mixture in diethyl ether solvent is shown in Figure 1b.[17] Liquid chromatography,[18] using methylene chloride/ethanol (90:10) solvent, yielded $N_3P_3(NMe_2)_3(CH_3)_3$ (**5**, 46%) and $N_3P_3(NMe_2)_3(CH_3)_2(OCH_2CH_3)$ (**6**, 44%).[16] The compounds were further purified by vacuum distillation: **5**, 103 °C (1.5 mm); **6**, 110 °C (1.5 mm).

High-Yield Synthesis of 5. A flask containing $N_3P_3Cl_3(NMe_2)_3$ (**4**) (15 g, 0.04 mol) was cooled to −78 °C.[20] The Grignard reagent (250 mL of a 3.0 M solution in diethyl ether) was added dropwise over a period of 60 min. After the addition was complete, the solution was warmed slightly in an ice water bath. After 5 min, the ice bath was removed and the solid residue was carefully dispersed using a spatula. (*Caution*! Grignard reagents are highly reactive. Care should be exercised to prevent contact with moisture.) The solution was then allowed to warm slowly to room temperature and was stirred for 48 h. At the end of this time, the solution was cooled to 0 °C and THF (300 mL) was added. The solution was then added dropwise to a mixture of 2-propanol (150

(30) Infrared spectra were recorded on a Perkin-Elmer 283B infrared spectrometer. The samples were prepared as thin films (NaCl disks) or as KBr pellets.
(31) ^{1}H NMR spectra were recorded with the use of a Bruker WP-200 spectrometer operating at 200 MHz. Chemical shifts are relative to tetramethylsilane at δ 0.
(32) ^{13}C NMR spectra were recorded with the use of a Bruker WP-200 spectrometer operating at 50 MHz. All spectra are referenced to internal tetramethylsilane at 0 ppm and were recorded with broad-band ^{1}H decoupling.
(33) For compounds of type $N_3P_3(X)_3(Y)_2(Z)$, the first isomeric designation refers to the configuration of the X ligands while the second refers to the configuration of the Y ligands.
(34) Geminal isomers are also possible, but these would not be expected from any of the reactions carried out in this study.
(35) Keat, R.; Ray, S. K.; Shaw, R. A. *J. Chem. Soc.* **1965**, 7193.
(36) It has been reported (see ref 25) that organohalocyclotriphosphazenes undergo cis–trans isomerization in the presence of dimethylamine hydrochloride (a byproduct of the deamination reaction) in refluxing xylene solvent.

Table III. Cyclotriphosphazene ^1H and ^{13}C NMR Data[a,b]

compd	signal	^1H NMR (δ)[31]	^{13}C NMR (ppm)[32]	coupling const, Hz
$N_3P_3[N(CH_3)_2]_3(CH_3)_3$ (5)	$-N(CH_3)_2$	2.39 (d)	34.94 (s)	$J_{PNCH} = 11.7$
		2.40 (d)	34.79 (s)	$J_{PNCH} = 11.7$
	$-CH_3$	1.24 (d)	15.53 (d, m)	$J_{PCH} = 14.9$
		1.28 (d)		$J_{PC} = 124.8$
				$J_{PCH} = 14.9$
$N_3P_3[N(CH_3)_2]_3(CH_3)_2(OCH_2CH_3)$ (6)	$-N(CH_3)_2$	2.52 (m)	35.69 (s)	
			35.27 (s)	
	$-CH_3$	1.38 (m)	15.75 (d, m)	$J_{PC} = 127.7$
	$-OCH_2CH$	3.81 (m)	58.90 (m)	
	$-OCH_2CH_3$	1.19 (t)	15.08 (m)	$J_{HCCH} = 7.1$
$N_3P_3[N(CH_3)_2]_3(CH_2CH_3)_3$ (5)	$-N(CH_3)_2$	2.59 (d)	36.04 (s)	$J_{PNCH} = 11.0$
		2.60 (d)	35.97 (s)	$J_{PNCH} = 10.9$
	$-CH_2CH_3$	1.66 (m)	23.34 (d, m)	$J_{PC} = 127.5$
	$-CH_2CH_3$	1.09 (d, t)	6.57 (m)	$J_{PCCH} = 19.0$
				$J_{HCCH} = 7.6$
$N_3P_3[N(CH_3)_2]_3(CH_2CH_3)_2(OCH_2CH_3)$ (6)	$-N(CH_3)_2$	2.50 (d)	36.17 (d)	$J_{PNCH} = 11.5$
			36.63 (d)	$J_{PNC} = 1.6$
				$J_{PNC} = 2.3$
	$-CH_2CH_3$	1.58 (m)	22.54 (d, m)	$J_{PC} = 126.3$
	$-CH_2CH_3$	0.99 (m)	6.58 (m)	
	$-OCH_2CH_3$	3.78 (m)	59.81 (m)	
	$-OCH_2CH_3$	1.13 (t)	15.78 (m)	$J_{HCCH} = 7.0$
$N_3P_3[N(CH_3)_2]_3(OCH_2CH_3)_3$ (8)	$-N(CH_3)_2$	2.56 (m)	36.01 (s)	
	$-OCH_2CH_3$	3.83 (m)	59.60 (m)	
	$-OCH_2CH_3$	1.19 (t)	15.41 (m)	$J_{HCCH} = 7.1$
$N_3P_3[N(CH_3)_2]_3(CH_3)(OCH_2CH_2CH_2CH_2Cl)_2$ (13)	$-N(CH_3)_2$	2.52 (m)	36.21 (s)	
			35.72 (s)	
	$-CH_3$	1.40 (d)	15.90 (d, m)	$J_{PCH} = 15.1$
				$J_{PC} = 126.5$
	$-OCH_2CH_2CH_2CH_2Cl$	3.77 (m)	62.81 (m)	
	$-OCH_2CH_2CH_2CH_2Cl$	1.75 (m)	27.09 (s)	
			27.01 (s)	
	$-OCH_2CH_2CH_2CH_2Cl$	1.75 (m)	28.63 (s)	
			28.58 (s)	
	$-OCH_2CH_2CH_2CH_2Cl$	3.49 (t)	44.02 (s)	$J_{HCCH} = 6.0$
$N_3P_3[N(CH_3)_2]_3(OCH_2CH_2CH_2CH_2Cl)_3$ (12)	$-N(CH_3)_2$	2.54 (m)	36.47 (s)	
	$-OCH_2CH_2CH_2CH_2Cl$	3.76 (m)	63.22 (m)	
	$-OCH_2CH_2CH_2CH_2Cl$	1.76 (m)	27.33 (s)	
	$-OCH_2CH_2CH_2CH_2Cl$	1.76 (m)	28.86 (s)	
	$-OCH_2CH_2CH_2CH_2Cl$	3.48 (t)	44.36 (s)	$J_{HCCH} = 6.1$
$N_3P_3Cl_3(CH_3)_3$[c] (2)	$-CH_3$	2.03 (d)	25.91 (d)	$J_{PCH} = 11.2$
				$J_{PC} = 140.6$
$N_3P_3Cl_3(CH_3)_3$[d] (2)	$-CH_3$	2.10 (d, t)	27.43 (d, t)	$J_{PCH} = 17.4$
		2.07 (d, d)	26.65 (ddd)	$J_{PNPCH} = 1.6$
				$J_{PCH} = 14.1$
				$J_{PNPCH} = 1.5$
				$J_{PC} = 131.2$
				$J_{PNPC} = 2.9$
				$J_{PC} = 135.9$
				$J_{PNPC} = 2.5$
$N_3P_3Cl_3(CH_2CH_3)_3$[c] (2)	$-CH_2CH_3$	2.15 (m)	31.94 (d)	$J_{PC} = 134.4$
				$J_{PCCH} = 26.5$
	$-CH_2CH_3$	1.26 (d, t)	6.22 (s)	$J_{HCCH} = 7.6$
$N_3P_3Cl_3(CH_2CH_3)_3$[d] (2)	$-CH_2CH_3$	2.20 (m)	33.19 (d, t)	$J_{PC} = 126.0$
			32.64 (d, d)	$J_{PNPC} = 2.7$
				$J_{PC} = 132.2$
				$J_{PNPC} = 2.1$
	$-CH_2CH_3$	1.31 (m)	6.29 (s)	
			6.15 (s)	
$N_3P_3[N(CH_3)_2]_4(CH_3)_2$ (15)	$-N(CH_3)_2$	2.53 (m)	36.17 (s)	
			35.94 (s)	
	$-CH_3$	1.42 (d)	16.42 (d, m)	$J_{PCH} = 14.1$
		1.38 (d)		$J_{PCH} = 13.5$
				$J_{PC} = 127.9$
$N_3P_3[N(CH_3)_2]_4(CH_2CH_3)_2$ (15)	$-N(CH_3)_2$	2.54 (d)	36.33 (m)	$J_{PNCH} = 10.8$
		2.53 (d)		$J_{PNCH} = 11.3$
	$-CH_2CH_3$	1.61 (m)	22.47 (d, m)	$J_{PC} = 125.8$
			22.01 (d, m)	$J_{PC} = 125.6$
	$-CH_2CH_3$	1.04 (d, t)	6.67 (m)	$J_{PCCH} = 18.9$
				$J_{HCCH} = 7.5$
$N_3P_3Cl_3(CH_3)_2[N(CH_3)_2]$ (16)	$-N(CH_3)_2$	2.71 (d)	36.05 (s)	$J_{PNCH} = 17.0$
		2.68 (d)	35.80 (s)	$J_{PNCH} = 16.8$
		2.67 (d)	35.62 (s)	$J_{PNCH} = 16.8$
	$-CH_3$	2.03 (m)	26.02 (d, m)	$J_{PC} = 137.6$

Table III (*Continued*)

compd	signal	^{1}H NMR (δ)[31]	^{13}C NMR (ppm)[32]	coupling const, Hz
$N_3P_3Cl_3(CH_2CH_3)_2[N(CH_3)_2]$ (16)	$-N(CH_3)_2$	2.54 (d)	35.97 (s)	$J_{PNCH} = 16.8$
		2.52 (d)	35.75 (s)	$J_{PNCH} = 16.7$
	$-CH_2CH_3$	2.01 (m)	32.65 (d, m)	$J_{PC} = 140.7$
	$-CH_2CH_3$	1.08 (m)	6.29 (m)	
$N_3P_3Cl_4(CH_3)_2$[c] (3)	$-CH_3$	2.09 (d, d)	25.80 (ddd)	$J_{PCH} = 14.4$
				$J_{PNPCH} = 3.1$
				$J_{PC} = 135.8$
				$J_{PNPC} = 3.6$
$N_3P_3Cl_4(CH_3)_2$[d] (3)	$-CH_3$	2.12 (ddd)	26.82 (ddd)	$J_{PCH} = 17.5$
				$J_{PNPCH} = 3.1$
				$J_{PC} = 131.0$
				$J_{PNPC} = 3.0$
$N_3P_3Cl_4(CH_2CH_3)_2$ (3)	$-CH_2CH_3$	2.21 (m)	32.61 (d, m)	$J_{PC} = 125.9$
			31.93 (d, m)	$J_{PC} = 132.8$
	$-CH_2CH_3$	1.28 (m)	6.02 (m)	

[a] Spectra were recorded on a solution of the compound in $CDCl_3$. [b] d = doublet; t = triplet; s = singlet; m = unresolved multiplet. [c] Cis isomer. [d] Trans isomer.

mL) and hexane (800 mL) cooled to 0 °C. The solution was filtered, and triethylamine (300 mL) was added to the filtrate. Filtration and solvent removal yielded a mixture of **5** and **6**.[16] The products were separated by liquid chromatography[18] and were purified by vacuum distillation: R = CH_3, **5** (87%) 103 °C (1.5 mm), **6** (5%) 110 °C (1.5 mm); R = C_2H_5, **5** (75%) 110 °C (1.5 mm), **6** (12%) 115 °C (1.5 mm).

Reaction between 4 and Diethyl Ether in the Presence of $MgBr_2$. A solution of $N_3P_3Cl_3(NMe_2)_3$ (**4**) (4.0 g, 0.011 mol) and magnesium bromide (8.6 g, 0.047 mol) in diethyl ether (150 mL) was stirred for 72 h at 25 °C. At the end of this time, the solution was cooled to 0 °C and THF (100 mL) was added, followed by addition of triethylamine (75 mL). The solution was filtered, and the solvent was removed under reduced pressure to yield $N_3P_3(NMe_2)_3(OCH_2CH_3)_3$ (**8**) (3.5 g, 81%) as a colorless oil. The product was further purified by vacuum distillation (120 °C (1.5 mm)).

Stability of $(NPCl_2)_3$ in Diethyl Ether in the Presence of $MgBr_2$. A solution of $(NPCl_2)_3$ (4.0 g, 0.012 mol) and magnesium bromide (8.6 g, 0.047 mol) in diethyl ether (150 mL) was stirred for 72 h. At the end of this time, the solution was cooled to 0 °C and THF (100 mL) was added, followed by triethylamine (75 mL). The solution was filtered and the solvent removed under reduced pressure to yield 3.4 g of unchanged $(NPCl_2)_3$.

A similar reaction was carried out with a solution of $N_3P_3Cl_3(NMe_2)_3$ (**4**) (2.0 g, 0.005 mol), $(NPCl_2)_3$ (2.0 g, 0.006 mol), and magnesium bromide (8.6 g, 0.047 mol) in diethyl ether (150 mL). Following purification as described above, a mixture was isolated that consisted of $N_3P_3(NMe_2)_3(OCH_2CH_3)_3$ (**8**) and unreacted $(NPCl_2)_3$, as determined by ^{31}P NMR spectroscopy.[17]

Isolation of Gaseous Products. A solution of $N_3P_3Cl_3(NMe_2)_3$ (**4**) (2.5 g, 0.007 mol) and magnesium bromide (5.5 g, 0.030 mol) in diethyl ether (75 mL) was stirred for 24 h. During this time, a stream of nitrogen was passed over the reaction mixture, through a trap cooled to −196 °C (500 mL) and through an oil "bubbler". The cold trap was then evacuated, allowed to warm to 25 °C, and back-filled with nitrogen. Samples of the collected liquid and vapor were withdrawn from the collection vessel and subjected to VPC analysis.[23] Bromomethane and diethyl ether solvent were detected.

Reaction between 4 and CH_3MgCl in THF. To a solution of $N_3P_3Cl_3(NMe_2)_3$ (**4**) (5.0 g, 0.013 mol) in THF (120 mL) was added CH_3MgCl (40 mL of a 3.0 M solution in THF). The solution was then heated at reflux (66 °C) for 24 h.[24] At the end of this time, a 2-mL aliquot was transferred via syringe into a nitrogen-filled NMR tube and was analyzed.[17] The ^{31}P NMR spectrum is shown in Figure 1c.

Aqueous hydrochloric acid (300 mL, 4%) was then added, and the mixture was extracted with diethyl ether (2 × 300 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to yield 6.6 g of a colorless oil. Liquid chromatography[18] using methylene chloride solvent yielded $N_3P_3(NMe_2)_3(OCH_2CH_2CH_2CH_2Cl)_3$ (**12**) (38%) and $N_3P_3(NMe_2)_3(CH_3)(OCH_2CH_2CH_2CH_2Cl)_2$ (**13**) (54%).

Reaction between 4 and THF in the Presence of $MgCl_2$. A solution of $N_3P_3Cl_3(NMe_2)_3$ (**4**) (2.0 g, 0.005 mol) and magnesium chloride (1.2 g, 0.013 mol) in THF (60 mL) was heated (66 °C) for 48 h.[24] Water (150 mL) was then added, and the mixture was extracted with diethyl ether (2 × 150 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to yield $N_3P_3(NMe_2)_3(OCH_2CH_2CH_2CH_2Cl)_3$ (**12**) (2.5 g, 85%) as a colorless oil.

Syntheses. $N_3P_3Cl_3R_3$ (2). A solution of $N_3P_3(NMe_2)_3R_3$ (R = CH_3, C_2H_5) (**5**) (35 g) in toluene (300 mL) was heated to reflux (110 °C). Anhydrous hydrogen chloride was then bubbled through the solution for either 2 h (R = CH_3) or 4 h (R = C_2H_5). At the end of this time, the solution was allowed to cool to room temperature and the precipitated dimethylamine hydrochloride was removed by filtration. The solvent was removed under reduced pressure to yield $N_3P_3Cl_3R_3$ (**2**) as a white, crystalline solid: R = CH_3, 76%; R = C_2H_5, 67%. The product was then purified by recrystallization from either heptane (R = CH_3) or hexane (R = C_2H_5), followed by sublimation at 56 °C (0.55 mm). The two geometrical isomers of **2** were separated by liquid chromatography[18] using methylene chloride as the eluent. Mp: R = CH_3, cis 160–162 °C, trans 144–146 °C; R = C_2H_5, cis 113–115 °C, trans 60–62 °C.

$N_3P_3(NMe_2)_4R_2$ (15). A flask containing $N_3P_3Cl_2(NMe_2)_4$ (**14**) (15 g, 0.04 mol) was cooled to −78 °C. The Grignard reagent (250 mL of a 3.0 M solution in diethyl ether) was added dropwise over a period of 60 min. After the addition was complete, the solution was warmed slightly in an ice water bath. After 5 min, the ice bath was removed and the solid residue was carefully dispersed using a spatula. (*Caution*! Grignard reagents are highly reactive. Care should be exercised to prevent contact with moisture). The solution was then allowed to warm slowly to room temperature and was stirred for 48 h. At the end of this time, the solution was cooled to 0 °C and THF (300 mL) was added. The solution was then added dropwise to a mixture of 2-propanol (150 mL) and hexane (800 mL) cooled to 0 °C. The solution was filtered, and triethylamine (300 mL) was added to the filtrate. Filtration and solvent removal yielded **15** as a yellow oil. The product was then purified by vacuum distillation: R = CH_3, 116 °C (0.8 mm) 75%; R = C_2H_5, 125 °C (0.8 mm) 65%.

$N_3P_3Cl_3R_2(NMe_2)$ (16). A solution of $N_3P_3(NMe_2)_4R_2$ (**15**) (25 g) in toluene (300 mL) was heated to reflux. Anhydrous hydrogen chloride was then bubbled through the mixture for either 8 h (R = CH_3) or 15 h (R = C_2H_5). At the end of this time, the solution was allowed to cool to room temperature and the precipitated dimethylamine hydrochloride was removed by filtration. The solvent was removed under reduced pressure to yield $N_3P_3Cl_3R_2(NMe_2)$ (**16**) as a white solid (R = CH_3, 75%) or as a colorless oil (R = C_2H_5, 70%). The product was purified by recrystallization from hexane followed by sublimation (50 °C (0.1 mm); R = CH_3; mp 80–95 °C) or by vacuum distillation (100 °C (0.1 mm); (R = C_2H_5). No reaction was detected after prolonged treatment of **16** with hydrogen chloride in refluxing toluene, xylene, chloroform, acetonitrile, or butyronitrile.

$N_3P_3Cl_4R_2$ (3). A Pyrex tube (18-mm o.d. × 540-mm length) with a constriction 70 mm from the open end was charged with $N_3P_3Cl_3R_2(NMe_2)$ (**16**) (3.0 g). Anhydrous hydrogen chloride gas (1.6 L, 0.043 mol) was then condensed into the tube at −196 °C. The tube was sealed at the constriction, wrapped in aluminum gauze, and allowed to warm to room temperature. The sealed tube was then heated in an oil bath at 100 °C for either 3 days (R = CH_3) or 8 days (R = C_2H_5). (*Caution*! precautions should be taken to guard against pressure-induced shattering of the glass tube.) The tube was then removed from the oil bath and allowed to cool to room temperature. The tube was opened, and the contents were extracted with toluene. The insoluble dimethylamine hydrochloride was removed by filtration, and the solvent was removed under reduced pressure to give $N_3P_3Cl_4R_2$ (**3**) as a white solid: R = CH_3, 52%; R = C_2H_5, 45%. The product (R = CH_3) was purified by recrystallization from heptane followed by sublimation (60 °C (0.1 mm)). Com-

pound **3** (R = C_2H_5) was purified by sublimation (60 °C (0.1 mm); mp 59–67 °C). The two geometrical isomers of **3** (R = CH_3) were separated by liquid chromatography[18] using CH_2Cl_2/C_6H_{14} (60:40) solvent (mp: cis, 152–154 °C; trans, 134–137 °C). Attempted chromatography of **3** (R = C_2H_5) resulted in extensive decomposition, presumably by hydrolysis.

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Supplementary Material Available: Table I for cyclotriphosphazenes showing mass spectral and elemental analysis data (2 pages). Ordering information is given on any current masthead page.

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Reduction of Cysteinesulfenato and Cysteinesulfinato Derivatives of Cobalt(III) by Chromium(II)

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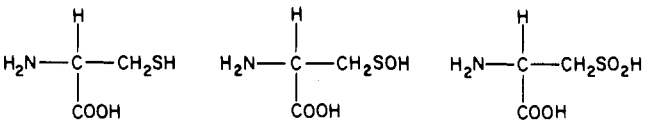
The reductions of the (cysteinesulfenato)bis(ethylenediamine)cobalt(III), abbreviated $[Co(en)_2(CysO)]^{2+}$, and the (cysteinesulfinato)bis(ethylenediamine)cobalt(III), abbreviated $[Co(en)_2(CysO_2)]^{2+}$, complexes by Cr(II) proceeded rapidly. The actual reduction of the cysteinesulfenato derivative was too fast to be measured directly but was estimated to be $>3 \times 10^4$ M^{-1} s^{-1}. Two electrons were rapidly consumed by the oxidant. It was postulated that one of these was used in inner-sphere attack by Cr(II) at the sulfur atom and the other remained on the sulfur ligand producing a radical intermediate. Three fast reactions followed reduction: the first was attributed to S–O bond fission ($k^{25°C}$ = 39.5 s^{-1}, $\Delta H^{\ddagger} = 10 \pm 1$ kcal/mol, $\Delta S^{\ddagger} = -16 \pm 3$ eu), the second was assigned to formation of an encounter pair from two radical ions followed by coupling to give the cystine dimer of Cr(III) ($k^{25°C} = 5.4 \pm 0.2$ s^{-1}, $\Delta H^{\ddagger} = 11 \pm 2$ kcal/mol, $\Delta S^{\ddagger} = -19 \pm 6$ eu), and the third reaction was attributed to the Cr(II)-catalyzed aquation of the dimeric Cr(III)–cystine product ($k^{25°C} = 2.9 \pm 0.4$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 9 \pm 2$ kcal/mol, $\Delta S^{\ddagger} = -26 \pm 11$ eu). The reduction of the cysteinesulfinato derivative occurred by attack of Cr(II) at sulfur to produce the Cr(III)–sulfur-bonded intermediate of cysteinesulfinic acid ($k^{25°C} = (1.46 \pm 0.07) \times 10^3$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 4.4 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -29 \pm 1$ eu). This was followed by a slow Cr(II)-catalyzed aquation of the Cr(III)–sulfinic acid product ($k^{25°C} = (2.5 \pm 0.1) \times 10^{-3}$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 21 \pm 2$ kcal/mol, $\Delta S^{\ddagger} = -1 \pm 5$ eu). These results are compared to work done on related systems.

The oxidation–reduction chemistry of metal-coordinated sulfur-containing organic ligands has received considerable attention over the past decade primarily as a result of the observation that sulfur (from the amino acids cysteine or methionine) is frequently found either close to the active site or directly bonded to the metal centers of proteins having important redox functions.[1,2] Bennett and his co-workers[3-5] first showed that thiolato sulfur could serve as an extremely efficient electron-transfer bridge between metal centers. Balahura and Lewis[6] found that a coordinated cysteine ligand having a sulfur atom directly bonded to the cobalt(III) center was rapidly reduced by Cr(II), again utilizing the sulfur as a bridge. Electron transfer via a noncoordinated thioether function in the reduction of methylcysteine and methionine complexes of cobalt(III) did not occur. Instead, reduction was found to take place through the coordinated carboxylate function.[6]

In an impressive series of reduction experiments[3,7] and X-ray structural studies,[8,9] it was shown that the remarkable efficiency of thiolate sulfur in mediating electron transfer to $(en)_2Co^{III}$ (where en is ethylenediamine) was due to its ability to exert a very strong ground-state trans effect (GSTE), thus decreasing the activation energy required for electron transfer. Sulfur was not, however, able to exert a similar effect in the corresponding $(en)_2Cr^{III}$ complexes. Nevertheless, since iron is frequently found in the active site of proteins and since the electron-transfer chemistry of iron is usually faster than that of cobalt, it is a reasonable conjecture that sulfur is present in these proteins because of its electron-mediating abilities.

Other sulfur-containing amino acids appear to be involved in biological transformations, including the oxidation products of cysteine (**1**), that is cysteinesulfenic acid (**2**) and cysteinesulfinic acid (**3**).



1 **2** **3**

Sulfenic acids (RSOH) in general are very unstable, elusive species,[10-18] and indeed, only a few have ever been isolated.[19-23] The instability of the sulfenic acid moiety is attributed to its high reactivity as either a nucleophile or an electrophile. The observation that protein sulfenic acids may play a regulatory role in enzyme-catalyzed reactions provides a particularly strong incentive for studying the chemistry of these species.[24] In an important

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