RECENT ADVANCES IN PHOSPHAZENE (PHOSPHONITRILIC) CHEMISTRY

H. R. ALLCOCK

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received November 8, 1971

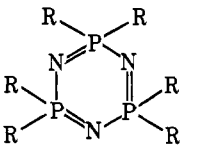
Contents

I. Introduction

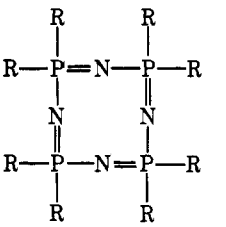
A. FOREWORD

The borderline between inorganic and organic chemistry has been a fertile area for dramatic advances during the past decade, and nowhere is this more obvious than in the field of phosphorus–nitrogen chemistry. In particular, the study of cyclic and open-chain phosphazenes (phosphonitriles) has attracted wide attention, not only from the synthetic and mechanistic points of view, but also with respect to their unusual structural characteristics and their place in high polymer chemistry.

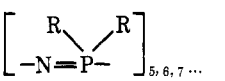
Cyclo- and polyphosphazenes have the general structures shown in **1**–**4** with the series extending from the cyclic trimers (**1**) through the cyclic tetramers (**2**) and higher cyclic oligomers (**3**), to high polymers (**4**) in which the degree of polymerization, n, may exceed 15,000. The side group, R, can vary from halogeno or pseudohalogeno to organic units such as alkyl, aryl, alkoxy, aryloxy, mercapto, alkylamino, or arylamino. Most cyclic trimers and tetramers are stable, white, crystalline solids with "organic"-type physical properties and solubilities, whereas the high polymers vary from rubbery elastomers to thermoplastics according to the nature of the substituent groups.



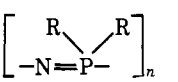
1



2

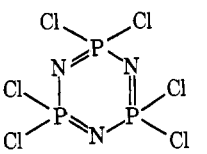


3

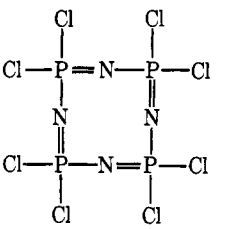


4

The synthetic chemistry of the majority of known cyclo- and polyphosphazenes is based on the reactions of two compounds, hexachlorocyclotriphosphazene (**5**) (also known as phosphonitrilic chloride trimer) and octachlorocyclotetraphosphazene (**6**). More than 1000 compounds have been synthesized *via* these two precursors.

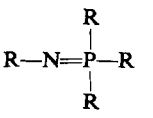


5

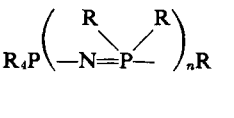


6

Although the bulk of this review will be devoted to cyclic and high polymeric derivatives of structures **1**–**4**, occasional reference will be made to the closely related monophosphazenes or phosphinimines of structure **7**, and particularly to the



7



8

linear oligomers of structure **8**, where n is in the range of 1 to ~10. Indeed, there is a close synthetic relationship between linear species, such as **8**, and cyclic phosphazenes, as will be discussed later in detail.

It is also worthwhile to note the relationship of phosphazenes of structure **1–4** and **8** to other inorganic and organometallic systems.[1] The analogy with organosiloxanes, $(O–SiR_2)_n$, is perhaps the most obvious, especially when the broad polymeric series and polymerization characteristics are compared. From a structural and bonding point of view, the cyclic phosphazenes can be compared to arsenic–nitrogen analogs, $(N{=}AsR_2)_n$, and to sulfur–nitrogen heterocycles, such as thiazyl halides, $(N{=}SX)_3$, or sulfanuric halides, $(N{=}S(O)X)_3$. However, the phosphazenes are apparently unique in offering both broad synthetic versatility and extensive polymeric sequences, and this undoubtedly explains the widespread fundamental and technological interest in these compounds.

B. HISTORICAL BACKGROUND

Although cyclo- and polyphosphazene chemistry has been intensively investigated only since the mid 1950's, the preliminary groundwork was laid down during the nineteenth century. In 1834, Liebig and Wöhler obtained a small amount of hexachlorocyclotriphosphazene (**5**) from the reaction of ammonium chloride with phosphorus pentachloride[2]. Later work by Gerhardt,[3,4] Laurent,[5] Gladstone and Holmes,[6–8] and Wichelhaus[9] deduced the composition and molecular weight of this material. Preliminary clues about the hydrolytic, ammonolytic, and thermal behavior of chlorophosphazenes were available by the 1890's from the work of Gladstone,[10–14] Besson,[15–19] Couldridge,[20,21] and Stokes.[22–26] A classic paper by Schenck and Römer[27] in 1924 outlined procedures for the synthesis of chlorophosphazenes which form the basis of present day preparative and manufacturing methods.

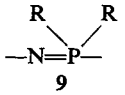
The subsequent development in the late 1950's and early 1960's of techniques for the replacement of halogen in halophosphazenes by organic substituents permitted the synthesis of a wide variety of organophosphazenes. Simultaneously, the structures of these compounds were extensively investigated by X-ray diffraction, vibrational spectroscopy, nmr, and other physical techniques. Much of this structural work has been of considerable importance for an understanding of the electronic structures of phosphazenes and related "pseudo-aromatic" systems. A great deal of the recent synthetic work in phosphazene chemistry has been stimulated by interest in the development of hydrolytically stable inorganic-backbone high polymers. The first synthesis of these unusual materials was accomplished in 1965, and subsequent work has indicated that this aspect constitutes an important area for the future development of phosphazene chemistry.

A number of earlier reviews on this subject have appeared. The basic inorganic chemistry prior to 1943 was discussed in detail by Audrieth, Steinman, and Toy.[28] Developments up to 1961 were reviewed by Paddock and Searle,[29] Haber,[30] and Gribova and Ban-yuan.[31] Comprehensive reviews by Shaw, Fitzsimmons, and Smith[32] and Schmulbach[33] appeared in 1962, while the review by Paddock in 1964[34] emphasized the structural work. Shaw, Keat, and Hewlett[35] discussed experimental techniques in 1965. Yvernault and Casteignau[35a] have also reviewed the subject. During the past 7 years significant new advances have occurred in the structural chemistry of phosphazenes, in new reactions and reaction mechanisms, and in phosphazene high polymer chemistry. In this review, special emphasis will be placed on the most recent work, and the background material will be limited to that required for an appreciation of the current developments.

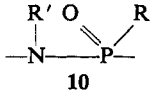
C. NOMENCLATURE

There is currently much confusion about the naming of inorganic heterocyclic compounds and polymers.[1] For phosphorus–nitrogen compounds, at least four different nomenclature systems are currently in use. These are (1) the "phosphazene" notation, (2) the "phosphonitrilic" terminology, (3) the "hydroazaphosphorine" system, and (4) the "phosphinimine" or "phosphazo" notation. The more systematic "phosphazene" based system will be used in this review.

The basis of the phosphazene nomenclature system is that compounds which contain the repeating unit **9** are defined as *phosphazenes*, whereas those which have the structure shown in **10** are called *phosphazanes*. A ring system is indicated



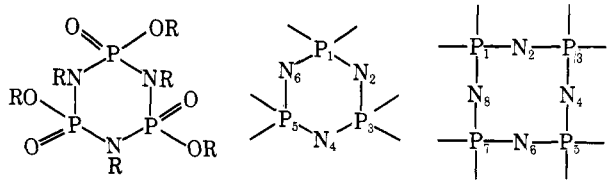
9



10

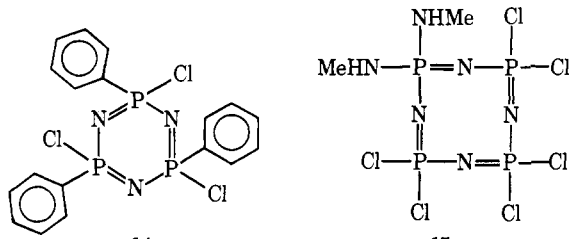
by the prefix cyclo, and the degree of polymerization is specified by tri, tetra, penta, . . . , poly. Thus compounds of structure **1** are called *cyclotriphosphazenes*, those of type **2** are *cyclotetraphosphazenes*, and species of structure **4** are *polyphosphazenes*. Derivatives of structure **11** are called cyclotri-

(1) H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York, N. Y., 1967.
(2) J. Liebig, *Justus Liebigs Ann. Chem.*, **11**, 139 (1834).
(3) C. Gerhardt, *Ann. Chim. Phys.*, [3] **18**, 188 (1846).
(4) C. Gerhardt, *C. R. Acad. Sci.*, **22**, 858 (1846).
(5) A. Laurent, *ibid.*, **31**, 356 (1850).
(6) J. H. Gladstone and J. D. Holmes, *J. Chem. Soc.*, **17**, 225 (1864).
(7) J. H. Gladstone and J. D. Holmes, *Ann. Chim. Phys.*, [4] **3**, 465 (1864).
(8) J. H. Gladstone and J. D. Holmes, *Bull. Soc. Chim. Fr.*, [2] **3**, 113 (1865).
(9) H. Wichelhaus, *Ber.*, **3**, 163 (1870).
(10) J. H. Gladstone, *Justus Liebigs Ann. Chem.*, **76**, 74 (1850).
(11) J. H. Gladstone, *J. Chem. Soc.*, **2**, 121 (1850).
(12) J. H. Gladstone, *ibid.*, **3**, 135 (1851).
(13) J. H. Gladstone, *ibid.*, **3**, 353 (1851).
(14) J. H. Gladstone, *Justus Liebigs Ann. Chem.*, **77**, 314 (1851).
(15) A. Besson, *C. R. Acad. Sci.*, **111**, 972 (1890).
(16) A. Besson, *ibid.*, **114**, 1264 (1892).
(17) A. Besson, *ibid.*, **114**, 1479 (1892).
(18) A. Besson and G. Rosset, *ibid.*, **143**, 37 (1906).
(19) A. Besson and G. Rosset, *ibid.*, **146**, 1149 (1908).
(20) W. Couldridge, *J. Chem. Soc.*, **53**, 398 (1888).
(21) W. Couldridge, *Bull. Soc. Chim.*, **50**, 535 (1888).
(22) H. M. Stokes, *Amer. Chem. J.*, **17**, 275 (1895).
(23) H. N. Stokes, *Ber.*, **28**, 437 (1895).
(24) H. N. Stokes, *Amer. Chem. J.*, **18**, 629 (1896).
(25) H. N. Stokes, *ibid.*, **18**, 780 (1896).
(26) H. N. Stokes, *ibid.*, **19**, 782 (1897).
(27) R. Schenck and G. Römer, *Ber.*, **57B**, 1343 (1924).
(28) L. F. Audrieth, R. Steinman, and A. D. F. Toy, *Chem. Rev.*, **32**, 109 (1943).
(29) N. L. Paddock and H. T. Searle, in "Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeleus and A. G. Sharpe, Ed., Vol. 1, p 348, 1959.
(30) C. P. Haber, *Chem. Soc., Spec. Publ.*, **No. 15**, 115 (1961).
(31) I. A. Gribova and U. Ban-yuan, *Russ. Chem. Rev.*, **30**, 1 (1961).
(32) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962).
(33) C. D. Schmulbach, *Progr. Inorg. Chem.*, **4**, 275 (1962).
(34) N. L. Paddock, *Quart. Rev., Chem. Soc.*, **18**, 168 (1964).
(35) R. A. Shaw, R. Keat, and C. Hewlett, *Prep. Inorg. React.*, **2**, 1, (1965).
(35a) T. Yvernault and G. Casteignau, *Bull. Soc. Chim. Fr., Mem.*, 1469 (1966).



11 12 13

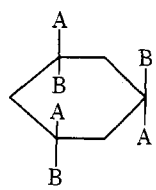
phospha*zanes*. The numerical system to be used in this review is depicted in **12** and **13**, with the numbering commencing at phosphorus.[36] Thus, compound **14** is called 1,3,5-trichloro-1,3,5-triphenylcyclotriphosphazene, or, simply, *nongeminal* trichlorotriphenylcyclotriphosphazene. Compound **15** would



14 15

be called 1,1-bis(methylamino)-3,3,5,5,7,7-hexachlorocyclotetraphosphazene or *geminal* bis(methylamino)hexachlorocyclotetraphosphazene. The name can be expanded to denote the number of classical double bonds in the skeleton. For example, compound **15** could be described as a cyclotetraphospha*zatetraene*. However, this designation will not be used here unless the rings are partly saturated. Derivatives such as **7** and **8** can be named in a straightforward manner as mono-, di-, tri-, tetraphosphazenes, etc., and, for this class of compounds, an indication of the number of classical double bonds is useful.

Opportunities exist with the cyclic derivatives for the formation of geometrical isomers. These can usually be described adequately with the use of the familiar cis–trans notation. For example, structure **16** is that of a trans nongeminal isomer.



16

The other nomenclature systems are of more limited applicability. The older, "phosphonitrilic" notation is still in common use. Derivatives such as **1**, **5**, and **14** are known as phosphonitrilic trimers, and **2**, **6**, and **15** are phosphonitrilic tetramers. However, this system cannot be applied systematically to a wide range of phosphorus–nitrogen derivatives. The same is true of the hydroazaphosphorine notation, which results from the strict use of IUPAC heterocyclic nomenclature. As an example, a simple compound such as $(NPBr_2)_4$ would be assigned the name, 2,2,4,4,6,6,8,8-octabromo-2,2,-4,4,6,6,8,8-octahydro-1,3,5,7,2,4,6,8-tetraphosphocine. For obvious reasons, this system is not generally used by the research workers in this field.

(36) It should be noted that some authors begin their numbering at nitrogen.

II. Structure of Phosphazenes

A considerable amount of research has been directed toward the elucidation of the structures of phosphazenes. Two aspects of the structural work have been of particular interest: (a) the determination of molecular geometries and (b) investigations into the nature of phosphorus–nitrogen bonding. X-Ray diffraction studies form the basis of the structural work, and these will be reviewed first.

A. X-RAY DIFFRACTION STUDIES

1. Molecular Shapes and Conformations

Approximately 30 cyclo- and polyphosphazenes have been investigated by X-ray diffraction techniques (Table I). The results of single crystal studies confirm that those compounds which have the formula $(NPR_2)_{3-8}$ are cyclic, while fiber diagram work indicates that the rubbery materials of formula $(NPR_2)_n$ are long-chain polymers.

Cyclic phosphazenes are found with both planar and puckered phosphorus–nitrogen rings. Unlike organic aromatic species, moderate puckering of the ring appears to have little or no influence on molecular stability. As shown in Table I, $(NPF_2)_3$,[37] $(NPCl_2)_3$,[38,38a] and $N_3P_3FCl_5$[39] have planar or nearly planar rings (Figure 1), but the other trimeric systems studied are puckered.

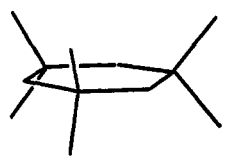


Figure 1. Structure of $(NPF_2)_3$ or $(NPCl_2)_3$.[37,38]

The majority of tetramers and higher cyclic species examined to date are nonplanar. The exceptions are $(NPF_2)_4$,[40] which forms a regular planar ring, and the cyclic pentamer, $(NPCl_2)_5$, which achieves near-planarity by indentation and loss of a regular cyclic shape[41] (Figure 2). Octachlorocyclotetraphosphazene, $(NPCl_2)_4$, exists in two crystallographic modifications. The stable T form contains chair-shaped rings,[42] and the metastable K form contains molecules in a tub conformation.[43] The bromophosphazene, $(NPBr_2)_4$, occupies a similar conformation to that of the K form of $(NPCl_2)_4$.[43a] An unusual conformation is found for $[NP(OMe)_2]_8$, in which the cyclic octameric ring consists of two planar sections joined by a "step" (Figure 3).[44]

The conformation of one high polymer, $(NPF_2)_n$, has been

(37) W. M. Dougill, *J. Chem. Soc.*, 3211 (1963).
(38) A. Wilson and D. F. Carroll, *ibid.*, 2548 (1960).
(38a) G. J. Bullen, *J. Chem. Soc. A*, 1450 (1971).
(39) R. Olthof, *Acta Crystallogr., Sect. B*, **25**, 2040 (1969).
(40) H. M. McGeachin and F. R. Tromans, *J. Chem. Soc.*, 4777 (1961).
(41) A. W. Schlueter and R. A. Jacobson, *J. Chem. Soc. A*, 2317 (1968).
(42) A. J. Wagner and A. Vos, *Acta Crystallogr., Sect. B*, **24**, 707 (1968).
(43) R. Hazekamp, T. Migchelson, and A. Vos, *Acta Crystallogr.*, **15**, 539 (1962).
(43a) H. Zoer and A. J. Wagner, *Acta Crystallogr., Sect. B*, **28**, 252 (1972).
(44) N. L. Paddock, J. Trotter, and S. H. Whitlow, *J. Chem. Soc. A*, 2227 (1968).

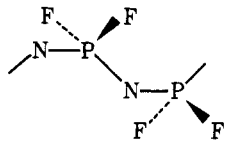
Table I

Structural Data for Phosphazenes and Phosphazanes[a]

Compound	P–N bond length, Å	N–P–N bond angle, deg	P–N–P bond angle, deg	R–P–R bond angle, deg	Skeletal structure	Ref
$(NPF_2)_3$	1.57	119.4	120.3	<99.9	Planar ring	37
$(NPF_2)_4$	1.51	122.7	147.4	99.9	Planar ring	40
$(NPF_2)_n$	1.52	119.0	136.0	95.0	Cis–trans planar chain	46
$N_3P_3FCl_5$	1.56	118.5	121.5	100.5	Planar ring	39
$(NPCl_2)_3$	1.58	118.4	121.4	101.3	Very slightly puckered ring	38a
$(NPCl_2)_4$	1.57	121.2	131.3	102.8	Puckered ring (K form)	43
$(NPCl_2)_4$	1.56	120.5	133.6	103.1	Puckered ring (T form)	48
			137.6			
$(NPCl_2)_5$	1.52	118.4	148.6	102.2	Nearly planar ring	41
$(NPCl_2)_n$	1.60	119	127		Distorted cis–trans planar chain	47
$(NPBr_2)_3$	1.58	118.3	126.8	103.4	Slightly puckered ring	*b*
		115.8	118.4			
$(NPBr_2)_4$	1.58	120.1	131.0	103.9	Puckered ring	43a
$[NP(NCS)_2]_3$	1.58	119	121	100	Slightly puckered ring	65
N_4P_4-1,1-Me_2F_6	1.47–1.58	116.9–126.1	143.3	93.6	Puckered ring	*c*
			146.7	105.7		
N_4P_4-1,1,5,5-Me_4F_4	1.54	117.5	134.6	96.7	Slightly puckered ring	*d*
	1.59	125.9		106.9		
$(NPMe_2)_4$	1.60	119.8	131.9	104	Puckered ring	*e*
$[NP(NMe_2)_2]_4$	1.58	120	133 (ring)	104	Puckered ring	49
$[NP(NMe_2)_2]_6$	1.56	120	147.5 (ring)	102.9	Puckered ring	*f*
$[NP(OMe)_2]_4$	1.57	121	132	105	Puckered ring (saddle)	60
$[NP(OMe)_2]_8$	1.56	116.7	136.7	101.3	Puckered ring	44
		121.2	141.0			
$[NP(OPh)_2]_3$	1.58	117.3	121.9	94.1	Slightly nonplanar ring	*g*
				100.1		
$(NPO_2C_6H_4$-*o*$)_3$	1.58	117.5	122.5	97	Slightly puckered ring	400
$(NPO_2C_{10}H_6$-2,3$)_3$ (dioxynaphthyl)	~1.59	~119	~121	~94		*h*
$(NPO_2C_{12}H_8$-2,2′$)_3$ (dioxybiphenyl)	1.57	118.6	121	102.7	Slightly puckered ring	*i*
$N_3P_3F_4$-1,1-Ph_2	1.56				Slightly puckered	*j*
	1.54					
$N_3P_3Cl_4$-1,1-Ph_2	1.56–1.62	119.8	122	104.4	Slight chair puckering	58
		115.2	119.2	100.4		
N_3P_3-1,1-Cl_2Ph_4	1.56–1.61	120.7	124.9	104.4	Slight boat puckering	*k*
		115.5	121	98.5		
$(NPPh_2)_3$	1.60	117.8	122.1	103.8	Slight chair puckering	57
(NPClPh)$_4$ (*cis*)	1.57	121.2	137.4	102.9	Puckered crown ring	*l*
(NPClPh)$_4$ (*β-trans*)	1.55–1.60	119.5	132.4	102.2	Puckered, chair-shaped ring	*m*
		121.3	138.6	105.1		
[NP(NHMe)Ph]$_4$ (*β-trans*)	1.60	118.2	124.6	106	Puckered, chair-shaped ring	*m*
		121.0	131.2			
$(MeNPCl_3)_2$	1.77	81.1	98.9	~90	Planar four-membered ring	47, 52
	1.64			~110		
$[MeNP(S)Cl]_2$	1.67	84	96	111.5	Four-membered ring	*n*
$(MeNPF_2Ph)_2$	1.78			91.8		
	1.64	80.6	99.4	87.0	Planar four-membered ring	*o*
$[MeNP(O)OMe]_3$	1.66	103.8–106.2	121.7	113.4–117.7	Twisted, boat-shaped ring	61
$[HNP(O)ONa]_3$	1.68	104.5	123	118	Chair-shaped ring	62
$[HNP(O)OH]_4$	1.66	107.3	125.6	116.1	Puckered ring	*p*

[a] Only the most recent values are reported. [b] H. Zoer, D. A. Koster, and A. J. Wagner, *Acta Crystallogr., Sect. A*, **25**, S107 (1969); E. Giglio and R. Puliti, *ibid.*, **22**, 304 (1967). [c] W. C. Marsh and J. Trotter, *J. Chem. Soc. A*, 573 (1971). [d] W. C. Marsh and J. Trotter, *ibid.*, 569 (1971). [e] M. W. Dougill, *J. Chem. Soc.*, 5471 (1961). [f] A. J. Wagner and A. Vos, *Acta Crystallogr., Sect. B*, **27**, 51 (1971). [g] W. C. Marsh and J. Trotter, *J. Chem. Soc. A*, 169 (1971). [h] H. R. Allcock and M. T. Stein, unpublished work. [i] H. R. Allcock, M. T. Stein, and J. A. Stanko, *J. Amer. Chem. Soc.*, **93**, 3173 (1971). [j] C. W. Allen, I. C. Paul, and T. Moeller, *ibid.*, **89**, 6361 (1967). [k] N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Crystallogr., Sect. B*, **25**, 316 (1969). [l] G. J. Bullen and P. A. Tucker, *Chem. Commun.*, 1185 (1970). [m] G. J. Bullen and P. R. Mallinson, *ibid.*, 691 (1969). [n] J. Weiss and G. Hartmann, *Z. Naturforsch.*, **21b**, 891 (1967). [o] J. W. Cox and E. R. Corey, *Chem. Commun.*, 123 (1967). [p] T. Migchelsen, R. Olthof, and A. Vos, *Acta Crystallogr.*, **19**, 603 (1965).

solved by structure factor methods.[45,46] At temperatures below −56° the stretched polymer occupies a cis–trans planar conformation (17), although at higher temperatures a non-



17

planar arrangement predominates. Optical transform analysis of X-ray fiber patterns from $(NPCl_2)_n$ indicated the presence of a slightly distorted cis–trans planar arrangement.[47]

It seems clear that the high polymer conformations are more a response to intra- and intermolecular nonbonding forces than to the restricting effects of phosphorus–nitrogen bonding. For cyclic phosphazenes, the planarity or nonplanarity of the ring depends on the need for the molecule to avoid skeletal angular strain. For example, cyclic tetramers are usually puckered to avoid the excessively wide angles at phosphorus and nitrogen required by the planar arrangement. However, within these limitations, it appears that nonbonding intra- or intermolecular interactions can tip the balance between chair, boat, tub, or saddle conformations. This is illustrated by the data of Wagner and Vos,[48] which indicate that, in the chair form of $(NPCl_2)_4$, some ring distortion results from transannular Cl···Cl interactions. The conformation assumed by $[NP(NMe_2)_2]_4$ also seems to be a response to ligand interactions.[49] However, it has been suggested that the curious "step" conformation of $[NP(OMe)_2]_8$ (Figure 3) may result from a subtle balancing of nonbonding side-group interactions, avoidance of ring strain, and the need for skeletal planarity to permit efficient π-orbital overlap.[44]

2. *Phosphorus–Nitrogen Bond Lengths*

The length of a phosphorus–nitrogen single bond is usually assumed to be in the region of 1.77–1.78 Å.[50–52] As shown in Table I, the bond lengths in cyclo- and polyphosphazenes are in the range of 1.47–1.62 Å, and this represents an appreciable contraction. The shortest skeletal bonds are associated with highly electronegative substituents, and this bond contraction is ascribed to skeletal π-bond influences (see later). A marginal trend also exists toward shorter skeletal bond lengths as the ring size increases for the smallest rings, although this trend does not continue to the high polymers.

Of particular importance is the fact that, if the substituents are symmetrically disposed around the ring, all the phosphorus–nitrogen bond lengths are equal. No separation into alternating long and short, σ and σ–π bonds is observed in the neutral system. This provides a sharp contrast with the situation encountered in cyclooctatetraene and in boron–nitrogen and thiazyl fluoride heterocycles, where a separation

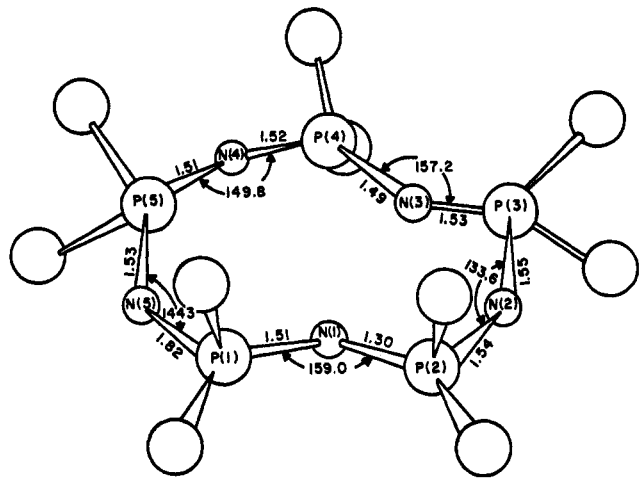


Figure 2. Molecular structure of $(NPCl_2)_5$.[41]

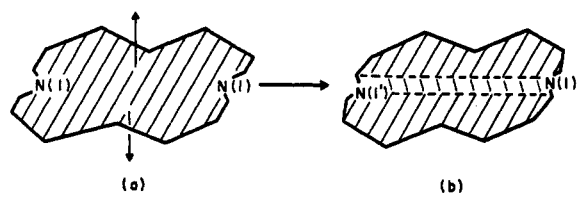
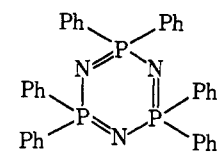
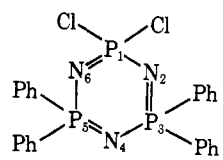


Figure 3. Idealized molecular shape of phosphazene ring in $[NP(OMe)_2]_8$.[44]

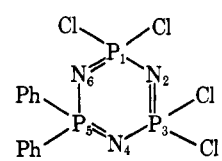
into alternating long and short bonds occurs in the cyclic tetramers.[53,54] However, the protonated phosphazenium cation in $[(NPMe_2)_4H]_2{}^+CoCl_4{}^{2-}$ shows some evidence of bond length alternation.[55,56] It should be noted that asymmetric ligand arrangements lead to the presence of unequal bond lengths around the ring because of the ligand electronegativity influence mentioned above. For example, although the skeletal bonds in octaphenylcyclotriphosphazene (18) are equal (1.60 Å),[57] replacement of two or four phenyl groups by geminally disposed chloro groups destroys this equality. In compound 19 the shortest skeletal bonds flank the phosphorus which bears the chloro groups (P_1–N_2, 1.556 Å; P_3–N_2,



18



19



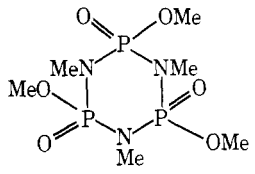
20

(45) H. R. Allcock, G. F. Konopski, R. L. Kugel, and E. G. Stroh, *Chem. Commun.*, 985 (1970).
(46) H. R. Allcock, R. L. Kugel, and E. G. Stroh, *Inorg. Chem.*, **11**, 1120 (1972).
(47) E. Giglio, F. Pompa, and A. Ripamonti, *J. Polym. Sci.*, **59**, 293 (1962).
(48) A. J. Wagner and A. Vos, *Acta Crystallogr., Sect. B*, **24**, 707 (1968).
(49) G. J. Bullen, *J. Chem. Soc.*, 3193 (1962).
(50) E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *Acta Crystallogr.*, **6**, 621 (1953).
(51) L. G. Hoard and R. A. Jacobson, *J. Chem. Soc. A*, 1203 (1966).
(52) H. Hess and D. Forst, *Z. Anorg. Allg. Chem.*, **342**, 240 (1966).
(53) P. T. Clarke, quoted by H. S. Turner and R. J. Warne, *J. Chem. Soc.*, 6421 (1965).
(54) G. A. Wiegers and A. Vos, *Acta Crystallogr.*, **16**, 152 (1963).
(55) J. Trotter, S. H. Whitlow, and N. L. Paddock, *Chem. Commun.*, 695 (1969).
(56) J. Trotter and S. H. Whitlow, *J. Chem. Soc. A*, 460 (1970).
(57) F. R. Ahmed, P. Singh, and W. H. Barnes, *Acta Crystallogr., Sect. B*, **25**, 316 (1969).

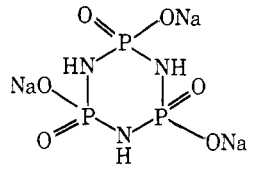
1.609 Å; P_3–N_4, 1.578 Å).[58] Similarly, in compound **20**, the bonds become progressively longer in the sequence P_3–N_2 < P_3–N_4 < P_5–N_4.[58]

Evidence also exists that bonds between skeletal phosphorus and the ligand units can be shorter than predicted. In $[NP(NMe_2)_2]_{4,6}$ the exocyclic P–N bond lengths are near 1.68 Å,[49,59] a 0.09-Å contraction from the σ bond value, and in $[NP(OMe)_2]_{4,8}$[44,60] the P–O bonds are about 0.12 Å shorter than the sum of the covalent radii. These results provide some support for the view that all four bonds to phosphorus are strengthened by π-bonding.

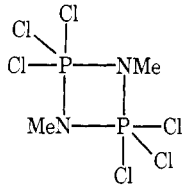
The concept of π-bond contraction in phosphorus–nitrogen compounds is not restricted to cyclo- or polyphosphazenes. Phosphorus–nitrogen bond contractions of ~0.1 Å from the single bond value are found in cyclophosphazanes such as compounds **21**[61] and **22**,[62] while two of the skeletal



21



22

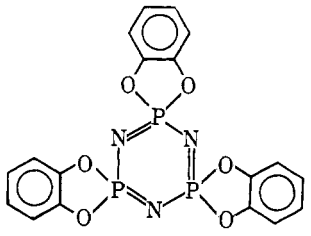


23

bonds in compound **23** show ~0.13-Å contraction.[51,52] These results may reflect coordinate π-bonding involving the nitrogen lone-pair orbitals.

3. *Bond Angles in Phosphazenes*

The N–P–N ring or chain angle in most cyclo- or polyphosphazenes approximates to 120°, irrespective of the degree of polymerization. Thus, the angle is not determined by ring strain influences, although this angular inflexibility precludes the existence of cyclic dimeric phosphazenes. The external angle at phosphorus (Cl–P–Cl, RO–P–OR, RNH–P–NHR, etc.) varies over the range of 95–104.4°, with one of the smallest angles (97°) being associated with the constraints of a five-membered exocyclic ring in **24**.[63] In $(NPF_2)_n$, the F–P–F angle is 95°,[46] and an R–P–R angle of 100° is found in $(NPF_2)_3$,[37] $(NPF_2)_4$,[40] and $[NP(NCS)_2]_3$,[65] but the angle approximates to 103–104° when other substituents are present. A plausible explanation of these values is that the external angle varies between ~95 and ~104° according to the steric restrictions of the exocyclic ligands, but that angles wider than ~104°



24

are not found because of resistance to contraction of the N–P–N ring angle which would be induced by a "scissoring" effect at sp^3-hybridized phosphorus. Presumably, contraction of the N–P–N angle below ~120° is prevented by resistance to interpenetration of the two nitrogen van der Waals boundaries.

The ring angle at nitrogen in phosphazenes is much more flexible. Values from 119.4 to 148.6° have been reported (Table I), and it appears that this angle is determined principally by a response to the requirements of the ring size or conformation. The wider angles are found in five-, six-, and eight-membered rings and in linear high polymers. It will be shown later that a secondary influence may be a hybridization change following delocalization of the nitrogen lone-pair electrons toward phosphorus.

In cyclodiphosphazanes, the ring angles at trigonally connected nitrogen are close to 100° (Table I), but the angle at phosphorus can be in the region of 80–84°. The low angle at phosphorus is particularly evident when the ring forms part of the axial–equatorial components of a trigonal-bipyramidal arrangement.

B. VIBRATIONAL SPECTROSCOPY

Although the structural parameters determined by X-ray diffraction techniques are, in general, the most reliable, the suspicion often exists that the ring or chain conformations deduced by this method are more a reflection of crystal packing forces than of intramolecular influences. For this reason, infrared–Raman studies of simple cyclophosphazenes in the liquid or vapor states allow valuable structural comparisons to be made. Table II lists the results of a number of vibrational spectroscopic studies.

First, it is instructive to compare the ring conformations of the fluorophosphazenes, $(NPF_2)_3$ and $(NPF_2)_4$, as determined by X-ray diffraction and vibrational methods. Both techniques indicate a planar (D_{3h}) model for the trimer but, although X-ray methods indicate a planar structure for the tetramer, vibrational studies suggest the presence of a puckered ring. The pentamer, $(NPF_2)_5$, appears to be planar ($\sim D_{5h}$) in the vapor, liquid, and solid phases.

Some anomalies also exist in the chlorophosphazene series. The trimer, $(NPCl_2)_3$, is planar in the vapor, liquid, and solid phases, but the tetramer, $(NPCl_2)_4$, is planar in the vapor state and puckered in the condensed phases. Specifically, as the tetramer changes from solid to liquid to vapor, the symmetry changes from S_4 or C_{2h} (for different crystallographic forms), through D_{2d} to D_{4h}, changes which cannot reflect bonding influences but which can be ascribed to changes in intramolecular or intermolecular nonbonding forces. It is possible that the planar structure represents the results of rapid conformational averaging between a number of nonplanar forms. Although the X-ray data suggest that $(NPCl_2)_5$ is near planar, the vibrational work excludes a D_{5h} or C_{5v}

(58) N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Crystallogr.*, **19**, 693 (1965).
(59) A. J. Wagner and A. Vos, *Acta Crystallogr., Sect. B*, **24**, 1423 (1968).
(60) G. B. Ansell and G. J. Bullen, *J. Chem. Soc. A*, 2498 (1971).
(61) G. B. Ansell and G. J. Bullen, *J. Chem. Soc. A*, 3026 (1968).
(62) R. Olthof, T. Migchelsen, and A. Vos, *Acta Crystallogr.*, **19**, 596 (1965).
(63) L. A. Siegel and J. H. van den Hende, *J. Chem. Soc. A*, 817 (1967).
(64) Reference deleted in revision.
(65) J. B. Faught, T. Moeller, and I. C. Paul, *Inorg. Chem.*, **9**, 1656 (1970).

Table II

Molecular Structures from Vibrational Spectroscopy

Compound	*Symmetry*	*Skeletal conformation*	*Phase*[i]	*Ref*
$(NPF_2)_3$	D_{3h}	Planar	v, l, s, sln	69, 73, 78
$(NPF_2)_4$	C_{2h} or lower	Nonplanar	v, l, s, sln	69, 73
$(NPF_2)_5$	$\sim D_{5h}$	Slightly nonplanar	v, l, s, sln	73
$(NPCl_2)_3$	D_{3h}	Planar	v, l, s, sln	*a*, 71, 73, 74
	$\sim D_{3h}$	Slightly nonplanar	s	*b*
$(NPCl_2)_4$	D_{4h}	Planar	v	*c*
	D_{2d}	Nonplanar	l, sln	*a*, *c*, 80, 95
	S_4	Nonplanar	s	*c*
	C_{2h}	Nonplanar	s	*c*
$(NPCl_2)_5$	Not D_{5h} or C_{5v}	Nonplanar	v, s, sln	73
$(NPCl_2)_n$	C_2	Distorted cis–trans planar chain	s	99
$(NPBr_2)_3$	D_{3h}	Planar	v, sln	*d*, *e*, 80, 81
	$D_{3h} \rightarrow C_{3v}$	Slightly nonplanar	s	80
$(NPBr_2)_4$	D_{2d}	Nonplanar	s, sln	80
$(NPBr_2)_5$	$\sim D_{5h}$	Slightly nonplanar	s, sln	98
$N_3P_3Cl_{6-n}Br_n$	D_{3h}	Planar	s	*f*, *g*
$[NP(NCS)_2]_3$	D_{3h}	Planar	s, sln	83
$[NP(N_3)_2]_3$	D_{3h}	Planar	s	*h*

[a] L. A. Daasch, *J. Amer. Chem. Soc.*, **76**, 3403 (1954). [b] I. C. Hisatsune, *Spectrochim. Acta*, **21**, 1899 (1965). [c] I. C. Hisatsune, *Spectrochim. Acta, Part A*, **25**, 301 (1969). [d] E. Steger and R. Stahlberg, *Z. Naturforsch. B*, **17**, 780 (1962). [e] E. Steger and R. Stahlberg, *Z. Anorg. Allg. Chem.*, **326**, 243 (1964). [f] E. Steger and R. Stahlberg, *J. Inorg. Nucl. Chem.*, **28**, 688 (1966). [g] E. Steger and R. Stahlberg, *Spectrochim. Acta, Part A*, **23**, 2057 (1967). [h] F. Rauchle and M. Gayoso, *An. Real Soc. Espan. Fis. Quim., Ser. A*, **66**, 241 (1970). [i] v = vapor phase, l = liquid, s = solid, and sln = solution.

form and favors a nonplanar ring. The vibrational data for $(NPCl_2)_n$, for the bromophosphazenes, and for hexakis(isothiocyano)cyclotriphosphazene are either consistent with the X-ray results or are the only data available.

Extensive use has been made of the infrared group frequency concept in phosphazene chemistry. For example, monophosphazenes show characteristic phosphorus–nitrogen vibrational-rotational absorptions in the 1300–1400-cm^{-1} region[66–68] (Table III). Since cyclodiphosphazanes exhibit vibrations in the 820–900-cm^{-1} region, it is often assumed that a shift to higher frequencies can be correlated with an increase in the force constant and with the change from a σ to a σ–π bond. Cyclotriphosphazenes show a strong characteristic absorption in the 1200-cm^{-1} region,[69–92] which corresponds to a P–N–P degenerate ring stretching mode, plus a second band at 700–950 cm^{-1} for solids from a forbidden symmetric stretch.

The 1200-cm^{-1} band usually moves approximately 100 cm^{-1} to higher frequencies in the change from cyclic trimer to cyclic tetramer. This shift is often sufficiently characteristic that it can be used for identification purposes. The available evidence suggests that the change is not a consequence of stronger P–N π-bonding in the tetramer, since the higher cyclic species do not exhibit additional shifts. More likely, the shift represents changes in the ring stretching vibrational mode, which would be expected to change from the rather rigid trimers to the more flexible tetramers, pentamers, and higher species.

Highly electronegative substituents, such as F, Cl, CF_3, or OCH_2CF_3, raise the characteristic stretching frequency, whereas electron-supplying ligands, such as SEt, NH_2, NHMe, or NMe_2, lower it. This effect is ascribed to the fact that electronegative substituent groups facilitate donation of the nitrogen lone-pair electrons to phosphorus, with a resultant strengthening of the P–N bond. At the same time, electron withdrawal by the ligands from phosphorus could permit more effective d_π–p_π bonding around the ring by contraction of the phosphorus 3d orbitals. Some caution should be exer-

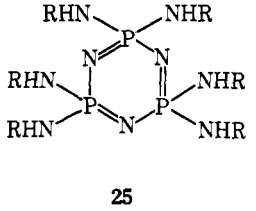
(66) E. S. Kozlov, A. A. Kisilenko, A. I. Sedlov, and A. V. Kirsanov, *Zh. Obshch. Khim.*, **37**, 1611 (1967).
(67) W. Wiegräbe and H. Bock, *Chem. Ber.*, **101**, 1414 (1968).
(68) H. Schmidbaur and W. Wolfsberger, *ibid.*, **100**, 1000 (1967).
(69) H. J. Becher and F. Seel, *Z. Anorg. Allg. Chem.*, **305**, 148 (1960).
(70) A. C. Chapman, N. L. Paddock, D. H. Paine, H. T. Searle, and D. R. Smith, *J. Chem. Soc.*, 3608 (1960).
(71) S. Califano, *J. Inorg. Nucl. Chem.*, **24**, 483 (1962).
(72) R. Stahlberg and E. Steger, *Z. Naturforsch. B*, **17**, 780 (1962).
(73) A. C. Chapman and N. L. Paddock, *J. Chem. Soc.*, 635 (1962).
(74) S. Califano and A. Ripamonti, *J. Inorg. Nucl. Chem.*, **24**, 491 (1962).
(75) H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5**, 1709 (1966).
(76) R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, **22**, 1449 (1966).
(77) R. Stahlberg and E. Steger, *Spectrochim. Acta, Part A*, **23**, 2057 (1967).
(78) T. R. Manley and D. A. Williams, *ibid.*, **23**, 1221 (1967).
(79) J. Emsley, *J. Chem. Soc. A*, 109 (1970).
(80) T. R. Manley and D. A. Williams, *Spectrochim. Acta, Part A*, **23**, 149 (1967).
(81) R. Stahlberg and E. Steger, *ibid.*, **23**, 627 (1967).
(82) P. Pulay, B. Lakatos, G. Toth, H. Hesz, and Z. Vetessy, *Acta Chim. (Budapest)*, **60**, 333 (1969).
(83) R. Stahlberg and E. Steger, *Spectrochim. Acta, Part A*, **23**, 2185 (1967).
(84) G. Tesi and C. M. Douglas, U. S. Patent, 3,065,266 (1962).
(85) A. J. Bilbo, *Z. Naturforsch. B*, **15**, 330 (1960).
(86) D. D. Magnelli, G. Tesi, J. V. Lowe, and W. E. McQuiston, *Inorg. Chem.*, **5**, 457 (1966).
(87) F. Rallo, *Chimica*, **8**, 1134 (1965).
(88) B. W. Fitzsimmons and R. A. Shaw, *J. Chem. Soc.*, 1735 (1964).
(89) H. R. Allcock, *J. Amer. Chem. Soc.*, **86**, 2591 (1964).
(90) A. P. Carroll and R. A. Shaw, *J. Chem. Soc. A*, 914 (1966).
(91) D. B. Sowerby and L. F. Audrieth, *Chem. Ber.*, **94**, 2670 (1961).
(92) C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **4**, 890 (1965).
(93) R. Rätz and C. Grundmann, *J. Inorg. Nucl. Chem.*, **16**, 60 (1960).
(94) T. Chivers and N. L. Paddock, *J. Chem. Soc. A*, 1687 (1969).
(95) T. R. Manley and D. A. Williams, *Spectrochim. Acta, Part A*, **24**, 1661 (1968).
(96) H. R. Allcock, R. Caputo, A. Kalmus, C. W. Roberts, and E. T. McBee, *U. S. Govt. Res. Rep.*, AD 209,669 (1959).
(97) H. R. Allcock and D. P. Mack, unpublished results, 1968.
(98) G. E. Coxon and D. B. Sowerby, *Spectrochim. Acta, Part A*, **24**, 2145 (1968).
(99) T. R. Manley and D. A. Williams, *Polymer*, **10**, 307 (1969).
(100) G. F. Konopski, M. S. Thesis, The Pennsylvania State University, 1970.
(101) G. Tesi and C. M. Douglas, *J. Amer. Chem. Soc.*, **84**, 549 (1962).
(102) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1716 (1966).
(103) M. P. Yagupsky, *ibid.*, **6**, 1770 (1967).
(104) H. G. Horn and M. Becke-Goehring, *Z. Anorg. Allg. Chem.*, **367**, 165 (1969).
(105) A. J. Downs, *Chem. Commun.*, 628 (1967).
(106) R. Schmutzler, *Z. Naturforsch. B*, **19**, 1101 (1964).
(107) M. Green, R. N. Haszeldine, and G. S. A. Hopkins, *J. Chem. Soc. A*, 1766 (1966).

Table III

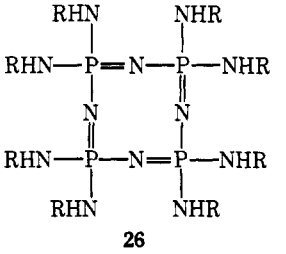
Selected Characteristic P–N "Stretching" Frequencies

Compound	ν (cm^{-1})ref	*Compound*	ν (cm^{-1})ref
$Me_3CN{=}PCl_3$	1370[66]	$[NP(OMe)_2]_4$	1337[76,87,88]
$Cl_3CN{=}PCl_3$	1360 (1450)[66]	$[NP(OEt)_2]_4$	1320[76,88]
$PhN{=}PPh_3$	1344[67]	$[NP(OPr^n)_2]_4$	1323[88]
$PhN{=}P(C_4H_9)_3$	1339[67]	$[NP(OPh)_2]_4$	1330–1350[88]
$Me_3SiN{=}PMe_3$	1287[68]	$[NP(NH_2)_2]_4$	1240[76,91]
$(NPF_2)_3$	1297[69,70]	$[NP(NMe_2)_2]_4$	1265[76,97]
$(NPCl_2)_3$	1218[71,79]		
$(NPBr_2)_3$	1175[72,77,78,80–82]	$(NPF_2)_5$	1405–1450[73,76]
$[NP(NCS)_2]_3$	1218[83]	$(NPCl_2)_5$	1298, 1354[73,76,87]
$[NP(N_3)_2]_3$	1200[82]	$(NPBr_2)_5$	1265–1330[98]
$(NPMe_2)_3$	1180[76,82]	$[NP(OMe)_2]_5$	1340[87]
$[NP(CF_3)_2]_3$	1205, 1300[84]	$(NPF_2)_6$	1408[70]
$(NPEt_2)_3$	(1157), 1225[76,82,85]	$(NPCl_2)_6$	1325[87]
$(NPPh_2)_3$	1190[76,86]	$[NP(OMe)_2]_6$	1335[87]
$[NP(OMe)_2]_3$	1235, 1275[75,76,87]		
$[NP(OEt)_2]_3$	1225–1240[75,76,88]	$(NPF_2)_n$	1290[46]
$[NP(OPr^n)_2]_3$	1225–1240[88]	$(NPCl_2)_n$	1230, 1275[75,99]
$[NP(OCH_2CF_3)_2]_3$	1240, 1280[75]	$[NP(NCS)_2]_n$	1240[100]
$[NP(OPh)_2]_3$	1160–1200, 1250–1280[75,88,89]	$[NP(CF_3)_2]_n$	1335–1430[101]
$[NP(SEt)_2]_3$	1150[90]	$(NPPh_2)_n$	1200[86]
$[NP(NH_2)_2]_3$	1170[76,91]	$[NP(OMe)_2]_n$	1250[75]
$[NP(NHMe)_2]_3$	1180[92]	$[NP(OEt)_2]_n$	1240[75]
$[NP(NMe_2)_2]_3$	1195[76]	$[NP(OCH_2CF_3)_2]_n$	1270[75]
		$[NP(OPh)_2]_n$	1240[75]
$(NPF_2)_4$	1419, 1438[69,72,73,76,93,94]	$[NP(NHMe)_2]_n$	1255, 1200[102]
$(NPCl_2)_4$	1315[69,72,73,76,81,87]	$[NP(NMe_2)_2]_n$	1240, 1280[102]
$(NPBr_2)_4$	1253–1280[72,76,80,81,95]	$[NP(NHPh)_2]_n$	1180–1220[102]
$(NPMe_2)_4$	1180[76]	$(MeN{-}PCl_3)_2$	847[103,104]
$[NP(CF_3)_2]_4$	1216, 1412[84]	$(MeN{-}PF_3)_2$	847[103,105]
$(NPEt_2)_4$	1320[76]	$(NH{-}PFPh_2)_2$	864[106]
$(NPPh_2)_4$	1213[76,86]	$(EtN{-}P(O)Cl)_2$	886[107]

cised in the correlation of stretching frequencies with ligand electronegativity, since combination vibrations involving bulky ligand groups may distort the picture. In this connection, it is of interest that primary alkylaminocyclophosphazenes (**25**, **26**) show small shifts to higher frequencies as the



25



26

dimensions of the group R increase.[34,108,109] For example, $[NP(NH_2)_2]_3$ shows a characteristic vibration at 1170 cm^{-1}, whereas $[NP(NHBu)_2]_3$ shows a shift to 1195 cm^{-1}. It is possible that the bulkier substituents are unable to achieve coplanarity and that this prevents the donation of electrons from exocyclic nitrogen to phosphorus. The phosphorus 3d orbitals are, thus, free to accept electrons from the ring nitrogen atoms with a concurrent strengthening of the ring bonds.

Vibrational frequency data have also been used to calculate the P–N and P–halogen force constants in $(NPCl_2)_3$ and $(NPF_2)_3$.[110] In $(NPCl_2)_3$, the P–N force constant is 8.19 mdyn/Å, and the P–halogen value is 4.38 mdyn/Å, whereas in $(NPF_2)_3$ the corresponding values are 8.95 and 5.79 mdyn/Å. The high values for the P–halogen bonds suggest the presence of exocyclic π character.

C. NUCLEAR MAGNETIC RESONANCE

Nmr spectroscopy has been used extensively in phosphazene chemistry as a structural identification technique and as a means for probing bonding patterns. The investigations have included ^1H, ^{31}P, and ^{19}F studies.

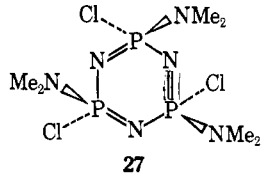
1. Proton Nmr Studies

The chemical shift of a proton located in a substituent group will be influenced by the other nuclei within that same group, by the other group attached to the same phosphorus atom, by the substituent groups attached to nearby phosphorus atoms, and often by the size of the phosphazene ring. However, in general, the proton chemical shifts are comparable to those found in related organic compounds, as illustrated by the following examples (chemical shift in τ *vs.* TMS in parentheses): NMe_2 (7.27–7.79),[111] OCH_3 (6.29–6.46),[75,112]

(108) S. G. Kokalis, K. John, T. Moeller, and L. F. Audrieth, *J. Inorg. Nucl. Chem.*, **19**, 191 (1961).
(109) K. John, T. Moeller, and L. F. Audrieth, *J. Amer. Chem. Soc.*, **83**, 2608 (1961).
(110) A. C. Chapman and D. F. Carroll, *J. Chem. Soc.*, 5005 (1963).
(111) R. Keat, S, K. Ray, and R. A. Shaw, *ibid.*, 7193 (1965).
(112) G. Allen, D. J. Oldfield, N. L. Paddock, F. Rallo, J. Serregi, and S. M. Todd, *Chem. Ind. (London)*, 1032 (1965).

OPh (2.8–3.2),[75,112,113] and Ph (2.2–2.7).[114] Spin–spin coupling effects are also usually present. Thus, proton nmr spectra can be used for "fingerprint"-type identification and for the structure determination of unknown compounds.[115]

The spin–spin coupling behavior in organophosphazenes can be complex. In a structure such as **27**, for example, the methyl protons yield a prominent doublet from coupling



27

with the closest ^{31}P nucleus (J = 17.5 cps), but a striking feature of the spectrum is a broad absorption from longer range couplings.[116] In general, methylene protons that are separated by two or three bonds from the supporting phosphorus atom yield hyperfine spectra, but methyl protons separated by four bonds from phosphorus do not.

2. ^{31}P Nmr Studies

Although ^{31}P nmr spectroscopy is a valuable tool for structural identification, it cannot be used reliably for direct chemical identification by "group shift" methods. Table IV lists ranges for ^{31}P shifts (relative to aqueous 85% H_3PO_4) with different substituent groups attached to phosphorus. It can be seen that appreciable overlap exists between the chemical shift ranges characteristic of most $>PR_2$, $>PR'R''$, or $-PR_3$ units in cyclic trimers and linear species. Cyclic trimers generally yield ^{31}P shifts in the range of 0 to −46 ppm. However, the large positive shift of the PBr_2 unit (+37 to +45 ppm) is characteristic. Furthermore, apart from bromophosphazene trimers, positive shifts appear to be characteristic of cyclic tetramers, pentamers, hexamers, heptamers, octamers, and linear high polymers. Cyclic tetrameric and higher ring systems resemble the high polymers in providing more opportunities for conformational changes than do the rather rigid cyclic trimers. Thus, it is tempting to ascribe the positive shifts to the consequences of skeletal bond torsional mobility. It has, in fact, been observed[75] that the ^{31}P shift of $[NP(OCH_2CF_3)_2]_n$ moves to more positive values (+4.7 to +8.2 ppm) as the solution temperature is raised from −80 to +80°. Presumably the enhanced torsional motions of the chains at elevated temperatures improve the π-bond symmetry around the phosphorus and thereby increase the shielding.

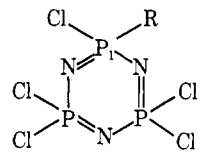
Table IV

^{31}P Nmr Chemical Shift Ranges[a]

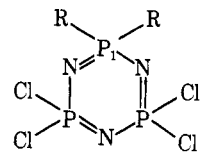
Unit	*^{31}P shift range, ppm*	*Unit*	*^{31}P shift range, ppm*
PMe_2	−45	PF_2	−6 to −14
$-PClPh_2$ (linear)	−40	$PBr(NMe_2)$	−4 to −15
$P(SEt)_2$	−29 to −46	$P(NH_2)_2$	−9 to −19
PFPh	−27 to −38	$P(OAr_2)$ (trimer)	−9 to −12
PClPh	−29 to −33	$P(NHMe)_2$	−12
$-PCl_2Ph$ (linear)	−32	PHR	−6 to −13
P(NCS)	−30	$P(NMe_2)_2$ (polymer)	0 to −5
$P(NMe_2)$ (trimer)	−24	$-PCl_3$ (linear)	−9 to +3
$PCl(NMe_2)$	−23 to −28	$PCl(N{=}PCl_3)$	+2
PPh_2	−14 to −30	$P(NH_2)(N{=}PCl_3)$	+1 to +4
PPh_2 (linear)	−2.4 to −55	P(OAlk) (polymer)	+3 to +8
$-PPh_3$ (linear)	−15 to −24	$P(NC_5H_{10})_2$ (polymer)	+8
PBrPh	−16 to −20	PCl_2 (tetramer)	+7.4
$PCl(NH_2)$	−19	PClBr	+8 to +14
$P(OAlk)_2$ (trimer)	−15 to −22	PCl_2 (pentamer to polymer)	+16 to +18
PCl_2 (trimer)	−14 to −23	$P(NHPh)_2$ (polymer)	+14
PFCl	−14	$P(OAr)_2$ (polymer)	+19
PCl(OAlk)	−13 to −17	PBr_2	+37 to +45

[a] Relative to aqueous 85% H_3PO_4. Values are for cyclic trimers unless otherwise indicated.

Attempts have been made to correlate the ^{31}P chemical shift with the electronegativity of the substituent groups attached to phosphorus.[117] For derivatives with the general structure shown in **28**, the chemical shift of P_1 becomes more



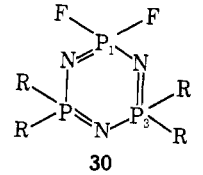
28



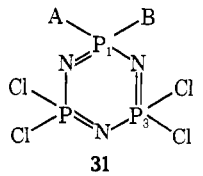
29

negative in the order R = OPr^i > OEt > F > OCH_2CF_3 > OMe > Cl > NMe_2. Thus, there is only a very rough relationship between chemical shift and the ligand electronegativity. The same is true for derivatives of general structure **29**, where the order of chemical shifts is Br > NH_2 > NHMe > Cl ≈ Ph. It appears that the observed chemical shift at phosphorus is a consequence of the ease with which the nitrogen lone-pair electrons can be drawn toward phosphorus. Thus, the shielding at any one phosphorus atom will depend on the ligands attached to the other phosphorus atoms, on the *relative* electronegativities of two different groups attached to each phosphorus, and perhaps even on neighbor-anisotropy effects.

Long-range influences around a phosphazene ring can be detected both by chemical shift effects and by spin–spin coupling. For example, the ^{31}P chemical shift of P_1 in **30** varies from −8.6 ppm if R is fluorine to −13.9 ppm when R



30



31

is phenyl. Replacement of a strongly electron-withdrawing group such as fluorine, by a less electron-withdrawing group, such as phenyl, may allow the ring π electrons to be drawn toward P_1, thus increasing the shielding at that atom. Phosphorus–phosphorus spin coupling within a cyclic trimeric

(113) D. Dell, B. W. Fitzsimmons, R. Keat, and R. A. Shaw, *J. Chem. Soc. A*, 1680 (1966).
(114) C. Hewlett and R. A. Shaw, *ibid.*, 56 (1966).
(115) R. A. Shaw, *Rec. Chem. Progr.*, **28**, 243 (1967).
(116) E. G. Finer, R. K. Harris, M. R. Bond, R. Keat, and R. A. Shaw, *J. Mol. Spectrosc.*, **33**, 72 (1970).
(117) F. Heatley and S. M. Todd, *J. Chem. Soc. A*, 1152 (1966).

ring can be observed in high resolution spectra.[111,117-120] The coupling constant, $J_{P_1P_3}$, generally increases as the electronegativity of the substituents attached to P_1 and P_3 increases. For example, in **31**, when groups A and B are SEt,[118] $J_{P_1P_3}$ is 4.8 cps, whereas the value is 66.2 cps if A is OCH_2CF_3 and B is Cl[117] and 100 cps if A and B are F.[119] These effects may reflect coupling through the σ electrons.

3. ^{19}F Nmr Studies

Fluorine atoms bound directly to the phosphazene ring show ^{19}F spectra which indicate an influence by the supporting phosphorus atom and by nearby ring phosphorus atoms. Fluorine chemical shifts range from 19.6 ppm (relative to $CFCl_3$) for the PFBr unit in $N_3P_3F_5Br$ to 71.9 ppm for the PF_2 group in $(NPF_2)_3$.[121] Typical values are shown in Table V.

Table V

^{19}F Chemical Shift Ranges for Different Phosphazene Substituent Groupings

Group	*Range of chemical shift values*[a]	*Ref*
PF_2	68.6-71.9	45, 121
PFCl	30.7-38.2	121
PFBr	19.6-30.6	121
P(F)NCS	49.6-53.9	121
P(F)Ph	49.3-51.5	124
$P(F)NMe_2$	60.2-62.2	122, *b*
P(F)NSO	70.0	*c*

[a] Values in ppm relative to $CFCl_3$. [b] O. Glemser, E. Niecke, and H. W. Roesky, *Chem. Commun.*, 282 (1969). [c] E. Niecke, O. Glemser, and H. Thamm, *Chem. Ber.*, **103**, 2864 (1970).

The spin–spin coupling between fluorine atoms and the phosphorus to which they are attached is quite strong (J_{FP} = 840–1056 cps).[121-125] The lowest coupling constants are associated with the presence of a highly electronegative substituent, such as fluorine, attached to the same phosphorus atom. Smaller coupling constants ($J_{FP} \approx$ 11–14 cps) are found for fluorine coupled with the ring phosphorus atoms adjacent to the supporting phosphorus.

D. MISCELLANEOUS STRUCTURAL STUDIES

1. Ultraviolet Spectroscopy

Cyclo- and polyphosphazenes show virtually no *skeletal* ultraviolet or visible absorption spectra at wavelengths longer than 220 mμ. The spectra that are observed in the near-ultraviolet or visible regions (for aryl-containing phosphazenes) can be explained in terms of absorptions by the side groups alone.[75,89,126,127] Indeed, the available evidence indicates that the phosphazene ring exerts only a minor perturbation on the spectrum of a phenyl group directly bonded to it in phenylcyclophosphazenes,[128] and this implies that the delocalization interaction between the two cyclic units must be small.

Perhaps even more surprising is the fact that high molecular weight polymers, such as $[NP(OMe_2)_2]_n$,[75] $[NP(OEt)_2]_n$,[75] $[NP(OCH_2CF_3)_2]_n$,[75] $[NP(NHMe)_2]_n$,[102] and $[NP[NMe_2)_2]_n$[102] are as transparent in the 220–700-mμ region as the corresponding cyclic trimers and tetramers. Thus, in cyclo- and polyphosphazenes, there is no evidence for the existence of the delocalization-induced bathochromic shifts that are characteristic of long-chain or polycyclic organic unsaturated species. Indeed, the ultraviolet transparency of many phosphazene high polymers constitutes a valuable attribute for technological applications.

Vacuum ultraviolet work[129] with halogenocyclotri- and tetraphosphazenes has led to the detection of the absorption maxima shown in Table VI. Bathochromic shifts in $(NPX_2)_{3,4}$ are observed in the change from fluoro- to chloro- to bromophosphazene. The low intensities observed are consistent with the belief that these absorption peaks result from n $\rightarrow$ π^* transitions involving either the nitrogen or halogen atoms.

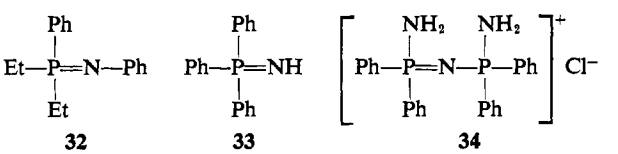
Table VI

Ultraviolet Absorption Maxima of Halocyclophosphazenes[126,129]

Compound	λ_{max}[a] *(log)*	*Compound*	λ_{max}[a] *(log)*
$(NPF_2)_3$	149.4 (4.0)	$(NPBr_2)_3$	200 (4.4)
$(NPF_2)_4$	147.5 (4.0)	$(NPBr_2)_4$	199 (4.5)
$(NPCl_2)_3$	~175 (4.0)	$N_3P_3F_4Ph_2$-*gem*	266 (5.8)[b]
$(NPCl_2)_4$	~175 (4.0)	$N_3P_3F_2Ph_4$-*gem*	266 (11.2)[b]
$(NPCl_2)_n$	<220	$N_3P_3FPh_5$	266 (12.5)[b]
$N_3P_3Cl_5Br$	192 (4.0)	$N_3P_3Cl_4Ph_2$	266 (5.86)[b]
$N_3P_3Cl_4Br_2$	192 (4.0)		

[a] Wavelength in mμ. [b] Phenyl group absorption.

On the other hand, phenyl-substituted monophosphazenes (phosphinimines) and related derivatives show ultraviolet spectra which could be ascribed partly to the excitation of skeletal π electrons. For example, compounds of structure **32** absorb at 243 and 283 mμ,[130] compound **33** absorbs at

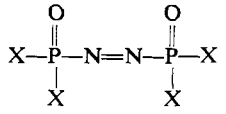


32 **33** **34**

275, 303, 258, and 298 mμ,[131] and derivative **34** absorbs at 225 and 261–273 mμ.[132] However, the compounds, $Ph_2P(O)OH$, $Ph_2P(O)NHP(O)Ph_2$, $Ph_2P(O)N{=}PPh_3$, $Ph_2P(O)N{=}PPh_2NHP(O)Ph_2$, and $Ph_2P(O)[N{=}PPh_2]_2NHP(O)Ph_2$, show

(118) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Chem. Ind. (London)*, 1909 (1962).
(119) M. L. Heffernan and R. F. M. White, *J. Chem. Soc.*, 1382 (1961).
(120) H. Lederle, G. Ottmann, and E. Kober, *Inorg. Chem.*, **5**, 1818 (1966).
(121) T. Chivers, R. T. Oakley, and N. L. Paddock, *J. Chem. Soc. A*, 2324 (1970).
(122) B. Green and D. B. Sowerby, *ibid.*, 987 (1970).
(123) C. W. Allen, F. Y. Tsang, and T. Moeller, *Inorg. Chem.*, 7, 2183 (1968).
(124) C. W. Allen and T. Moeller, *ibid.*, 7, 2177 (1968).
(125) J. Emsley and N. L. Paddock, *J. Chem. Soc. A*, 2590 (1968).
(126) K. L. Paciorek, *Inorg. Chem.*, **3**, 96 (1964).
(127) H. R. Allcock and R. L. Kugel, *ibid.*, **5**, 1016 (1966).
(128) A. J. Wagner and T. Moeller, *J. Inorg. Nucl. Chem.*, **33**, 1307 (1971).
(129) B. Lakatos, A. Hesz, Z. Vetessy, and G. Horvath, *Acta Chim. (Budapest)*, **60**, 309 (1969).
(130) B. J. Stepanov, T. G. Edelman, and I. M. Kolbasova, *Zh. Obshch. Khim.*, **37**, 1883 (1967).
(131) B. I. Stepanov and T. G. Edelman, *ibid.*, **39**, 1549 (1969).
(132) F. G. Sherif and C. D. Schmulbach, *Inorg. Chem.*, **5**, 322 (1966).

strikingly similar spectra in the 260–273-mμ region,[133] and the suspicion remains that phenyl $\pi \rightarrow \pi^*$ or nitrogen n $\rightarrow$ π^* transitions are responsible for these absorptions. Compounds of structure **35**, where X is OPh, Ph, OK, or NR_2,



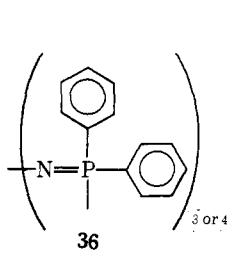
35

are violet colored compounds, the color resulting from an n $\rightarrow$ π^* transition near 500 mμ. This transition and the related $\pi \rightarrow \pi^*$ transition near 300 mμ are derived from the skeletal electrons, including the phosphorus 3d orbitals.[134-137]

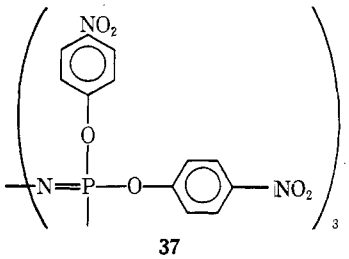
2. *Polarography and Electron Spin Resonance*

Most organic aromatic compounds can be reduced polarographically in nonaqueous media to yield radical anions, which can then be studied by electron spin resonance techniques. Attempts have been made to apply the same type of approach to phosphazene compounds.[138,139] It has been found that cyclotri- and cyclotetraphosphazenes which contain only fluoro, chloro, bromo, trifluoroethoxy, methoxy, phenoxy, *o*-dioxyphenyl, or phenylamino substituents cannot be reduced electrolytically at potentials more positive than −3 V. However, species which contain phenyl (**36**), *p*-nitrophenoxy (**37**), 2,3-dioxynaphthyl (**38**), and 1,8-dioxynaphthyl (**39**) side groups can be reduced in the −1 to −3 V range, and esr spectra can be detected.

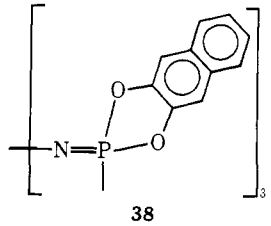
Two types of behavior are observed, depending on the nature of the side group. In the first, if the side group is itself independently reducible (**37**, **38**, **39**), the electron enters the organic aromatic unit, and the esr hyperfine splittings characteristic of the organic radical anion unit can be observed. Electron spin delocalization into the phosphazene ring is not



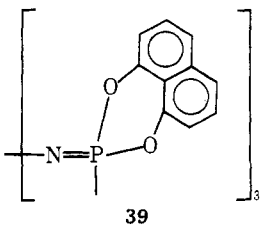
36



37



38



39

detected. In the second case, when phenyl groups are bonded directly to phosphorus (**36**), reduction occurs at −2.65 V (even though benzene or toluene cannot be reduced at this potential), and an unresolved singlet esr spectrum is observed. All attempts to resolve this singlet into a hyperfine spectrum have been unsuccessful, and it is assumed that extensive electron spin delocalization occurs or that rapid electron exchange takes place. However, it is found that the reduction potential and esr spectra of the radicals formed from $(NPPh_2)_3$ and $(NPPh_2)_4$ are identical, and this suggests that the lowest antibonding orbital levels in the phosphazene skeleton are unaffected by the degree of polymerization. Furthermore, long-chain polymers, such as $[NP(OCH_2CF_3)_2]_n$ or $[NP(OPh)_2]_n$, could not be reduced, in spite of the fact that at least 15,000 repeating units are linked end to end. It is also of interest that the trifluoroethoxy groups in $[NP(OCH_2CF_3)Ph]_3$ and *gem*-$N_3P_3Ph_2(OCH_2CF_3)_4$ lower the reduction potential relative to $(NPPh_2)_3$, presumably by an inductive influence on the phenyl and phosphazene π electrons.

3. *Dipole Moments*

The dipole moments of cyclophosphazenes are useful for the study of ring conformations and for distinguishing between different isomers. Some typical dipole moment values are shown in Table VII.

Table VII

Selected Dipole Moments of Cyclophosphazenes

Compound	μ, *D*	*Compound*	μ, *D*
$(NPF_2)_3$	0.10[a]	$N_3P_3Cl_4(NMe_2)_2$ (non-*gem-trans*)	2.61[278]
$(NPCl_2)_3$	0.83–0.98[140]	$N_3P_3Cl_4(NMe_2)_2$ (non-*gem-cis*)	4.3[278]
$(NPCl_2)_4$	0.20[a]	$N_3P_3Cl_3(NMe_2)_3$ (*gem*)	2.01[278]
$[NP(OPh)_2]_3$	2.84–3.00[140]	$N_3P_3Cl_5(NC_2H_4)$[d]	3.07[b]
$[NP(O_2C_6H_4)]_3$[c]	1.9[89]	$N_3P_3Cl_5(NC_4H_8)$[e]	3.74[b]
$(NPBrPh)_3$ (*cis*)	5.27[209]	$N_3P_3Cl_4(NC_4H_8)_2$ (non-*gem-trans*)	3.28[b]
$(NPBrPh)_3$ (*trans*)	2.36[209]	$N_3P_3Cl_4(NC_4H_8)_2$ (non-*gem-cis*)	5.02[b]
$N_4P_4Cl_2Ph_6$ (1,5-*cis*)	3.7[348]	$N_3P_3Cl_3(NC_4H_8)_3$ (*gem*)	1.75[b]
$N_4P_4Cl_2Ph_6$ (1,5-*trans*)	0.2[348]	$N_3P_3Cl_5(NC_5H_{10})$[f]	3.67[b]
$N_3P_3Cl_5(NHMe)$	3.41[295]	$N_3P_3Cl_4(NC_5H_{10})$ (non-*gem-trans*)	3.02[b]
$N_3P_3Cl_4(NHMe)_2$ (*gem*)	4.33[295]	$N_3P_3Cl_4(NC_5H_{10})$ (non-*gem-cis*)	4.61[b]
$N_3P_3Cl_4(NHMe)_2$ (non-*gem-trans*)	2.88[295]	$[NP(NC_5H_{10})_2]_3$	1.16[b]
$N_3P_3Cl_4(NHMe)_2$ (non-*gem-cis*)	4.12[295]		
$N_3P_3Cl_4(NMe_2)_2$ (*gem*)	3.12[278]		

[a] G. Corfield, *J. Chem. Soc.*, 4258 (1962). [b] I. Yu. Kokoreva, Ya. K. Syrkin, A. A. Kropacheva, N. M. Kashnikova, and L. E. Mukhina, *Dokl. Akad. Nauk SSSR*, **166**, 155 (1966). [c] Tris-2,2′-dioxybiphenyl derivative. [d] Ethylenimino derivative. [e] Pyrrolidino derivative. [f] Piperidino derivative.

The compounds $(NPF_2)_3$, and $(NPCl_2)_3$ have the low dipole moments expected of symmetrically substituted planar cyclic trimers, but the low value found for the tetramer, $(NPCl_2)_4$, may reflect conformational averaging in the liquid phase. The fact that $[NP(OPh)_2]_3$ has a dipole moment of 2.84 D implies that the ring is nonplanar, and this is consistent with

(133) K. L. Paciorek, *Inorg. Chem.*, **3**, 96 (1964).
(134) H. Bock and E. Baltin, *Chem. Ber.*, **98**, 2844 (1965).
(135) H. Bock and G. Rudolph, *ibid.*, **98**, 2273 (1965).
(136) H. Bock, *Angew. Chem., Int. Ed. Engl.*, **4**, 457 (1965).
(137) H. Bock, *Chimica*, **21**, 35 (1967).
(138) H. R. Allcock and W. J. Birdsall, *J. Amer. Chem. Soc.*, **91**, 7541 (1969).
(139) H. R. Allcock and W. J. Birdsall, *Inorg. Chem.*, **10**, 2495 (1971).

X-ray diffraction results. The other values listed in Table VII can be rationalized in terms of asymmetrical ligand arrangements.

It should be noted that the capacitance of molten $(NPCl_2)_3$ increases dramatically as the temperature is raised above ~200°, and this has been ascribed to the consequences of polymerization of the trimer.[140] On the other hand, the capacitance of molten $[NP(OPh)_2]_3$ (which does not undergo ring-opening polymerization) varies very little up to 350°.

4. Mass Spectrometry

Mass spectrometric studies of cyclophosphazenes have been used to obtain information about the relative stabilities of different cations and to measure ionization potentials.[141-148a] In particular, studies have been reported of the mass spectrometric behavior of the positive ions formed from $(NPF_2)_{3-16}$, $(NPCl_2)_{3-8}$, $(NPBr_2)_{3-6}$, $N_3P_3Cl_zBr_{6-z}$, and $[NP(NCS)_2]_{3,4}$.

In the fluorophosphazene series, the larger cations break down to smaller rings, but ring contraction apparently does not proceed through monomer formation.[143] Thus, for $(NPF_2)_n^+$, n changes in the pattern $n = 6 \rightarrow 3$, $7 \rightarrow 3 + 4$, $8 \rightarrow 4$, $9 \rightarrow 3$, $11 \rightarrow 3 + 5$, and $12 \rightarrow 3$. However, the higher cyclic fluorophosphazene species $(NPF_2)_n$, where n is greater than 6, yield a surprisingly stable $(NPF_2)_n^+$ parent ion, a result which has been ascribed to greater delocalization stability in the higher ring systems.[143] Chains as well as rings are formed during the breakdown processes. The higher cyclic chlorophosphazene cations, $(NPCl_2)_n^+$, also break down to smaller rings according to the pattern $6 \rightarrow 3$, $7 \rightarrow 3 + 4$, and $8 \rightarrow 3 + 4 + 5$.[142-144] The smaller rings, such as $(NPCl_2)_{3-5}$, retain their ring structure during fragmentation. With bromocyclophosphazenes, $(NPBr_2)_{3-5}$, the strongest mass spectral peaks correspond to $N_3P_3Br_5^+$, $N_4P_4Br_7^+$, and $N_5P_5Br_9^+$, but the hexamer, $(NPBr_2)_6$, undergoes both ring contraction to $N_3P_3Br_3^+$ and $N_6P_6Br_{11}^+$ and condensation to polycyclic species.[141] Bromine atoms are lost 50 times more easily than chlorine atoms from chlorobromocyclotriphosphazenes.[145,146]

The principal breakdown products from $[NP(NCS)_2]_{3,4}$ retain the trimeric and tetrameric phosphazene rings, but ring contraction of tetrameric to trimeric species is evident from an analysis of the metastable ions.[148a] The substituent groups break down by removal of a sulfur atom or an S_2 molecule, or by loss of CS_2.

5. Photoelectron Spectroscopy

Electron impact mass spectrometry and photoelectron spectroscopy have been used to measure the first ionization potentials of cyclophosphazenes.[148] The values obtained reflect the energy required to remove an electron from the cyclophosphazene π system. The first ionization potential for $(NPR_2)_{3,4}$ increases with R in the order $R = NMe_2 < Me < OPh < OMe < Br < Cl < OCH_2CF_3 < F$, a sequence which roughly parallels the increasing electronegativity of the ligands. For cyclic trimers, the potentials cover the range of 8.35–11.4 eV. Cyclic tetramers have *lower* ionization potentials than cyclic trimers. In the fluorophosphazene series, $(NPF_2)_{3-8}$, the ionization potential alternates as the series is ascended: those compounds with n even have higher potentials than those where n is odd. By contrast, in the chlorophosphazene series, no alternation is observed with the compounds of formula $(NPCl_2)_{4-7}$ having similar first ionization potentials, all of which are below that of the trimer.

6. Other Physical Studies

The diamagnetic anisotropy of a crystalline organic aromatic compound can be correlated with the density of delocalized π electrons in a particular crystal plane. Unfortunately, the measured anisotropy value for $(NPCl_2)_3$ is so low (-10.5×10^{-6} cgs unit)[149] compared to benzene (-60×10^{-6} cgs unit) that very little information can be obtained from these data about π-electron ring currents.

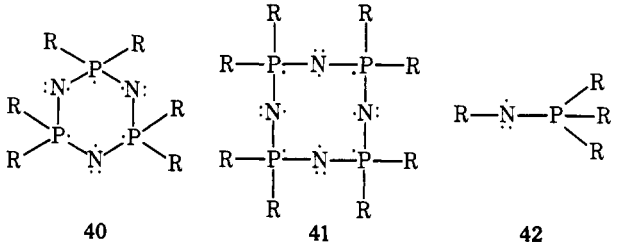
^{35}Cl nuclear quadruple resonance studies have been carried out with $(NPCl_2)_3$ and with the K and T forms of $(NPCl_2)_4$.[150-154] Since the nqr spectrum is sensitive to the chlorine atom environments in the crystalline lattice, the results can be correlated with X-ray crystallographic results. In fact, the four-line spectrum obtained from $(NPCl_2)_3$ (intensities 2:1:1:2) indicate that the 24 chlorine atoms in the cell consist of four sets of 8, 4, 4, and 8, in complete agreement with the X-ray data. Nqr spectra can also be used to follow the change of the K form of $(NPCl_2)_4$ to the T form above 63 ± 1.5° by the conversion of the two-line spectrum (equal intensities) to a four-line spectrum (intensities 2:3:2:3).[152-154]

E. BONDING IN PHOSPHAZENES

The problem of explaining the bonding arrangements in phosphazenes has occupied the attention of a number of investigators.[155-166] Two questions, one practical and the other theoretical, need to be answered. First, why are the phosphorus–nitrogen bonds in phosphazenes shorter, slightly stronger, and more chemically stable than phosphorus–

(140) H. R. Allcock and R. J. Best, *Can. J. Chem.*, **42**, 447 (1964).
(141) G. E. Coxon, T. F. Palmer, and D. B. Sowerby, *J. Chem. Soc. A*, 1568 (1967).
(142) C. E. Brion and N. L. Paddock, *ibid.*, 388 (1968).
(143) C. E. Brion and N. L. Paddock, *ibid.*, 392 (1968).
(144) C. D. Schmulbach, A. G. Cook, and V. R. Miller, *Inorg. Chem.*, 7, 2463 (1968).
(145) G. E. Coxon, T. F. Palmer, and D. B. Sowerby, *Inorg. Nucl. Chem. Lett.*, 2, 215 (1966).
(146) G. E. Coxon, T. F. Palmer, and D. B. Sowerby, *J. Chem. Soc. A*, 358 (1969).
(147) C. E. Brion, D. J. Oldfield, and N. L. Paddock, *Chem. Commun.*, 226 (1966).
(148) G. R. Branton, C. E. Brion, D. C. Frost, K. A. R. Mitchell, and N. L. Paddock, *J. Chem. Soc. A*, 151 (1970).
(148a) A. J. Wagner and T. Moeller, *ibid.*, 596 (1971).
(149) D. P. Craig, N. L. Heffernan, R. Mason, and N. L. Paddock, *J. Chem. Soc.*, 1376 (1961).
(150) H. Negita and S. Satou, *J. Chem. Phys.*, **24**, 621 (1956).
(151) K. Torizuka, *J. Phys. Soc. Jap.*, **11**, 84 (1956).
(152) E. A. C. Lucken, *Proc. Colloq. AMPERE (At. Mol. Etud. Radio Elec.)*, 678 (1962).
(153) M. Kaplansky and M. A. Whitehead, *Can. J. Chem.*, **45**, 1669 (1967).
(154) M. Dixon, H. D. B. Jenkins, J. A. S. Smith, and D. A. Tong, *Trans. Faraday Soc.*, **63**, 2852 (1967).
(155) D. P. Craig, *Chem. Ind. (London)*, 3 (1958).
(156) D. P. Craig, *Chem. Soc., Spec. Publ.*, **No. 12**, 343 (1958).
(157) D. P. Craig and N. L. Paddock, *Nature (London)*, **181**, 1052 (1958).
(158) D. P. Craig, *Theoret. Org. Chem., Pap. Kekule Symp.*, 20 (1959).
(159) D. P. Craig, *J. Chem. Soc.*, 997 (1959).
(160) D. P. Craig and N. L. Paddock, *ibid.*, 4118 (1962).
(161) D. P. Craig and K. A. R. Mitchell, *ibid.*, 4682 (1965).
(162) K. A. R. Mitchell, *J. Chem. Soc. A*, 2683 (1968).
(163) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).
(164) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).
(165) D. A. Brown and C. G. McCormack, *ibid.*, 5385 (1964).
(166) D. W. J. Cruickshank, *ibid.*, 5486 (1961).

nitrogen σ bonds in phosphazanes, phosphinic amides, etc.? Second, how are the electrons distributed in the phosphazene skeleton? This second question revolves around the fact that, after pairs of electrons are assigned to the sigma bond framework, one electron from each phosphorus and three from each nitrogen remain to be accounted for (**40**, **41**, **42**).



40 41 42

It is generally assumed that two of the electrons at each nitrogen atom occupy a lone-pair (sp^2) orbital oriented in the plane of the ring, but the disposition of the remaining electron from each skeletal atom has been the subject of controversy. Nitrogen is more electronegative than phosphorus, but it seems unlikely that all four non-σ electrons are held in lone-pair orbitals at nitrogen. The resultant zwitterion would be unstable, and an abnormally low P–N–P bond angle would be generated. A more plausible explanation is that one electron from each phosphorus and nitrogen atom is involved in some type of skeletal π-bonding which shortens and strengthens the P–N bond.[155–166] In addition, it is assumed that the nitrogen lone-pair electrons can be donated to phosphorus to form a second (in-plane) coordinate π' system, and this exerts a further strengthening influence on the skeleton.

The orbital symmetry arrangement at nitrogen is believed to resemble that shown in Figure 4, with the lone pair directed

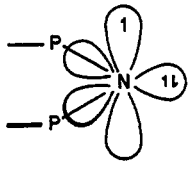


Figure 4. Orbital symmetry arrangement at nitrogen.

radially and with the third electron occupying a p_z orbital. The situation at phosphorus is less clear. With the phosphorus 3s and 3p orbitals filled, the possibility exists that π-bonding could involve the use of 3d orbitals and formation of a stabilized excited state. The arguments in favor of 3d orbital structures for phosphorus have been reviewed in detail elsewhere.[1,163,167] Suffice it to say that it seems highly likely that phosphorus makes use of its 3d orbitals in expanding its coordination number to 6, but it remains to be proved that the 3d orbitals alone are involved in π-bonding in compounds such as phosphazenes.

The problem is one of orbital energies. In the free phosphorus atom, the energy required to promote an electron from the 3p to the 4s level is ~150 kcal, and the promotional energies to the 4p and 3d levels are ~180 and ~200 kcal, respectively.[168] These energies are almost prohibitively high for ground-state molecules. However, it has been pointed out that electronegative ligands attached to phosphorus will bring about contraction of the 3d orbitals and will lower their energy sufficiently to permit π-bonding to occur.[162,163,169–171] It has also been pointed out that the 4s and particularly the 4p orbitals would be lowered in energy as well, and that the 4p orbital could also participate in π-bond formation.[172,173] In fact, the postulate that only the 3d orbitals are involved in π-bonding is probably an oversimplification since 3d–4s mixing is likely, and the concept of discrete Hückel-type σ–π bonds may be invalid for second and later row elements.

Nevertheless, the use of a $3d_\pi$–$2p_\pi$ bonding model is instructive in attempting to explain the physico-chemical facts about phosphazenes, and the following outline is presented with this in mind. First, consider those phosphorus 3d orbitals which have the appropriate symmetry to π-bond with the nitrogen p_z orbitals. These are the phosphorus d_{xz} and d_{yz} orbitals (Figure 5). Different effects are anticipated according

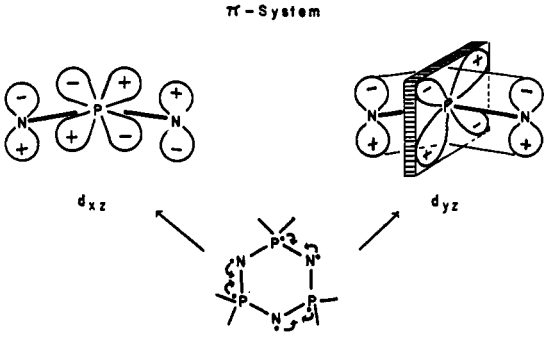


Figure 5. Formation of skeletal d_π–p_π bonds.

to the relative participation of the d_{xz} and d_{yz} orbitals. If only the d_{xz} orbital participates, a broadly delocalized, heteromorphic, "pseudoaromatic" π orbital could be formed.[155–160] Exclusive involvement by d_{yz} would generate a homomorphic π system, perhaps comparable to p_π–p_π aromatic systems. If, on the other hand, both orbitals participate equally, then the π orbitals should separate into islands of π character, interrupted at each phosphorus atom, and broad delocalization effects would not be anticipated.[161,164] The argument hinges on whether or not the d_{xz} orbital can ever be sufficiently electronegative to dominate the bonding pattern.

To date, no unambiguous experimental evidence has appeared to favor one model or another. The ultraviolet and polarographic data discussed earlier provide an argument against a broadly delocalized π system if, as in p_π–p_π delocalized systems, the orbital energies depend on the degree of delocalization. On the other hand, the curious alternation of first ionization potentials as the $(NPF_2)_n$ series is ascended[148] can be understood in terms of a heteromorphic model. The

(167) H. R. Allcock, "Phosphorus-Nitrogen Compounds," Academic Press, New York, N. Y., 1972.

(168) C. E. Moore, "Atomic Energy Levels," Vol. 1, p 163, National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949.

(169) D. P. Craig, A. Maccol, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

(170) D. P. Craig and E. A. Magnusson, *ibid.*, 4895 (1956).

(171) D. P. Craig and C. Zauli, *J. Chem. Phys.*, **37**, 601, 609 (1962).

(172) E. A. C. Lucken, *Struct. Bonding (Berlin)*, **6**, 1 (1969).

(173) C. K. Jørgensen, *ibid.*, **6**, 94 (1969).

singlet esr spectrum observed for radical anions derived from $(NPPh_2)_{3,4}$ is also consistent with delocalization over several skeletal centers.[138,139] What does seem clear is that skeletal π-bonding in phosphazenes imposes virtually no torsional barrier on the P–N bond[46] and that the nitrogen p_z orbital interacts with a diffuse, cylindrically symmetrical orbital arrangement at phosphorus. The composition of the π cloud at phosphorus probably includes 3d contributions, but substantial amounts of L and N level orbitals may also be mixed in.

π-Bonding between phosphorus and the ligand groups is also possible in phosphazenes. The principal contributing orbital would be d_{z^2} (Figure 6a), and, in theory at any rate,

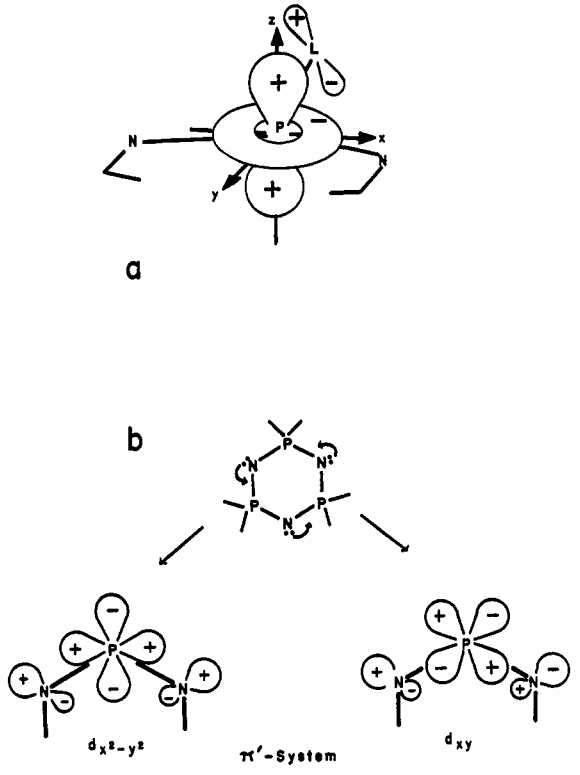


Figure 6. (a) π-Bonding between phosphorus and a ligand group. (b) Formation of the π' system.

the symmetry opportunities exist for delocalization interactions between phosphorus and ligand phenyl groups, halogeno units, and oxygen, nitrogen, or sulfur atoms.

In addition to these π interactions, the possibility exists that the nitrogen lone-pair electrons can be donated to phosphorus to form a coordinate π' bond. The remaining two phosphorus 3d orbitals (d_{xy} and $d_{x^2-y^2}$) are available to accept these electrons (Figure 6b). The experimental evidence in favor of an interaction of this type is quite strong. Those highly electronegative ligands which would be expected to draw the nitrogen lone pair toward phosphorus do indeed shorten and strengthen the phosphorus–nitrogen bonds. Furthermore, the basicity of the skeletal nitrogen atoms decreases as the ligand electronegativity is increased.

III. Synthesis of Phosphazenes

The synthesis of the phosphazene skeleton can be accomplished by a number of routes.[167] The cyclo- or polyphosphazenes formed by these direct synthesis methods are principally chloro, bromo, alkyl, or aryl derivatives. The majority of other phosphazenes are then synthesized by substitution reactions using the halogeno derivatives. This section will review the direct synthesis routes, and the following section will deal with substitution reactions.

A. REACTION OF AMMONIUM CHLORIDE WITH PHOSPHORUS PENTACHLORIDE

1. General Features of the Reaction

Ammonium chloride reacts with phosphorus pentachloride in a boiling solvent, such as *s*-tetrachloroethane, to yield a mixture of cyclic and linear phosphazenes, with the concurrent evolution of hydrogen chloride.[27] This reaction provides the

$$n\mathrm{NH_4Cl} + n\mathrm{PCl_5} \longrightarrow (\mathrm{NPCl_2})_{3\text{ to }>10} + 4n\mathrm{HCl}\uparrow$$

most convenient route for the synthesis of chlorophosphazenes. These are themselves used as precursors for the preparation of nearly all organophosphazenes, and, the importance of this reaction cannot, therefore, be overemphasized. Since the initial report of this process in 1924,[27] a considerable amount of research has been conducted to control the yields of specific chlorophosphazenes, to elucidate the reaction mechanism, and to develop a manufacturing process.[28,29,173a–197] At the present time, several companies produce chlorophosphazenes on a pilot plant or limited commercial basis, and it now seems clear that the technological future of phosphazene chemistry may depend on the efficiency and cost of these manufacturing processes.

The laboratory preparation requires the reaction of approximately equimolar amounts of ammonium chloride and phosphorus pentachloride in boiling tetrachloroethane for ~7.5 hr, followed by filtration to remove unreacted am-

(173a) R. Steinman, F. B. Schirmer, and L. F. Audrieth, *J. Amer. Chem. Soc.*, **64**, 2377 (1942).
(174) L. G. Lund, N. L. Paddock, J. E. Proctor, and H. T. Searle, *J. Chem. Soc.*, 2542 (1960).
(175) Albright and Wilson Mfg. Ltd., British Patents 905,314 and 905,315 (1962); 1,011,237 and 1,017,375 (1966).
(176) Albright and Wilson Mfg. Ltd., Australian Patents 230,487, 233,600 (1958).
(177) Albright and Wilson Mfg. Ltd., U. S. Patent 3,008,799 (1961).
(178) Albright and Wilson Mfg. Ltd., Canadian Patent 614,267 (1961).
(179) Albright and Wilson Mfg. Ltd., and Hooker Chemical Corp., French Patent 1,331,078 (1965).
(180) M. C. Taylor, U. S. Patent 2,872,283 (1959).
(181) Compagnie Francaise de Matieres Colorantes, British Patent 774,694 (1957) and U. S. Patent 2,782,133 (1957).
(182) F. G. R. Gimblett, *Chem. Ind. (London)*, 365 (1958).
(183) M. Becke-Goehring and K. Koch, *Chem. Ber.*, **92**, 1188 (1959).
(184) M. Becke-Goehring and E. Fluck, *Angew. Chem.*, **74**, 382 (1962).
(185) M. Becke-Goehring and W. Lehr, *Z. Anorg. Allg. Chem.*, **327**, 128 (1964).
(186) M. Yokoyama, *J. Chem. Soc. Jap., Pure Chem. Sect.*, **80**, 1189 (1959).
(187) H. Saito and M. Kajiwara, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **66**, 618 (1963).
(188) E. Kobayashi, *ibid.*, **69**, 618 (1966).
(189) E. Kobayashi, *J. Chem. Soc. Jap., Pure Chem. Sect.*, **87**, 135 (1966).
(190) E. Kobayashi, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **70**, 628 (1967).
(191) S. M. Zhivukhin, *Zh. Neorg. Khim.*, **6**, 2414 (1961).
(192) S. M. Zhivukhin, V. B. Tolstoguzov, V. V. Kireev, and K. G. Kuznetsova, *Russ. J. Inorg. Chem.*, **10**, 178 (1965).
(193) M. A. Glushkova, M. M. Ershova, and Yu. A. Buslaev, *ibid.*, **10**, 1060 (1965).
(194) J. Emsley and P. B. Udy, *Chem. Commun.*, 633 (1967).
(195) J. Emsley and P. B. Udy, *J. Chem. Soc. A*, 3025 (1970).
(196) J. Emsley and P. B. Udy, *ibid.*, 768 (1971).
(197) G. Wunsch, R. Schiedermaier, V. Kiener, E. Fluck, and G. Heckmann, *Chem.-Ztg., Chem. App.*, **94**, 832 (1970).

monium chloride. Removal of the solvent from the filtrate leaves an oily mixture of linear and cyclic phosphazenes, and the latter can be selectively removed by extraction with petroleum hydrocarbons. Typically, the cyclic chlorophosphazenes constitute ~60–70% of the total product, and, in this component, approximately 37% is $(NPCl_2)_3$, 28% is $(NPCl_2)_4$, and 35% is a mixture of higher cyclic chlorophosphazenes of formula $(NPCl_2)_n$. Pure trimer can be obtained by several fractional crystallizations from petroleum, by fractional sublimation, or by zone refining.[140] A rapid method for the separation of trimer and tetramer makes use of the fact that the trimer is preferentially extracted from a solution in petroleum or *n*-heptane by concentrated sulfuric acid.[167,174] The composition of chlorophosphazene mixtures can be determined by vapor phase chromatography.[198]

The trimer, $(NPCl_2)_3$, is a white, crystalline solid, mp 114°, which is stable to the atmosphere, can be sublimed at ~50° at reduced pressure, and is soluble in organic liquids. The tetramer, mp 124°, is similar in general properties, but it shows lower solubility in most solvents. The higher cyclic species are low-melting solids or oils. Chlorophosphazenes have a rather pleasant "organic"-type odor, but inhalation of the vapor should be avoided. Temporary eye, nose, and throat irritation has been reported, and precautions should be taken to avoid exposure to the vapor.[199] These responses are not evident with cyclic or polymeric organo phosphazenes, and it appears that hydrolysis of the phosphorus–halogen bond on the mucous membranes is responsible for the irritant properties.

The petroleum-insoluble, linear phosphazenes, which are also formed in the synthesis reaction, are more sensitive than the cyclic species to atmospheric hydrolysis.

2. Factors Which Affect the Reaction

Recent publications[195,196] have emphasized that the course of the reaction between ammonium chloride and phosphorus pentachloride is markedly affected by the reaction conditions.

Although the synthesis can be carried out in the absence of a solvent,[178a,192,200] higher yields of chlorocyclophosphazenes can normally be obtained when a solvent is present. Chlorobenzene can be used as a reaction medium, but inconveniently long reaction times are needed. The preferred solvent for laboratory preparations is boiling *s*-tetrachloroethane. Because this compound undergoes partial reaction during the process, the use of crudely recovered solvent for subsequent reactions is not recommended.[196] The yields of cyclic chlorophosphazenes are increased by a greater dilution of the reactants in *s*-tetrachloroethane and by the use of finely divided ammonium chloride crystals.[196] Since the ammonium chloride is essentially insoluble in the medium, the larger surface area of the more finely divided material facilitates the reaction. It has also been reported that the slow addition of phosphorus pentachloride to a suspension of ammonium chloride in boiling *s*-tetrachloroethane improves the yield of cyclic chlorophosphazenes,[174] but apparently this effect is not observed if finely divided ammonium chloride is used.[196] Catalysis by phosphorus oxychloride has also been observed,[196] and rigorous drying of the reactants and solvents appears to be unnecessary, since this compound is formed by the action of water on phosphorus pentachloride.

3. The Reaction Mechanism

The simplicity of the equation for this reaction disguises an extraordinarily complex sequence of interrelated processes.[174,184,194–196,201] The first sequence of reactions leads to the formation of a linear phosphazene salt of structure, $[Cl_3P{=}N{=}PCl_3]^+PCl_6^-$. This compound is formed in over 80% yield within 1 hr of the start of the reaction.[195] Since it has a low solubility in *s*-tetrachloroethane, it is effectively precipitated from solution and thereby rendered temporarily inactive to further reaction. The mechanism of formation of this species is still somewhat obscure. However, ^{31}P nmr spectroscopy suggests that at least two unidentified compounds are involved and that these contain only one phosphorus atom.[195] Thus, a possible sequence of events is described by the equations[195]

$$PCl_5 + NH_4Cl \longrightarrow Cl_4PNH_2 + 2HCl$$

$$Cl_4PNH_2 \longrightarrow Cl_3P{=}NH + HCl$$

$$Cl_3P{=}NH + PCl_5 \longrightarrow Cl_3P{=}N{-}PCl_4 + HCl$$

$$Cl_3P{=}NPCl_4 + PCl_5 \longrightarrow [Cl_3P{=}N{=}PCl_3]^+PCl_6^-$$

Alternatively, PCl_5 could react initially as $[PCl_4]^+[PCl_6]^-$, with a salt being present at each step.[184,185]

The second sequence of reactions involves chain growth from $[Cl_3P{=}N{=}PCl_3]^+PCl_6^-$, followed by cyclization. Chain growth could occur by reaction of the salt with ammonium chloride

$$[Cl_3P{=}N{=}PCl_3]^+PCl_6^- + NH_4Cl \xrightarrow{-4HCl} [Cl_3P{=}N{=}PCl_2{=}N{=}PCl_3]^+Cl^-$$

or by reaction of this product with the monophosphazene, $Cl_3P{=}NH$

$$[Cl_3P{=}N{=}PCl_2{=}N{=}PCl_3]^+Cl^- + HN{=}PCl_3 \xrightarrow{-HCl} [Cl_3P({=}NPCl_2)_2{=}N{=}PCl_3]^+Cl^-$$

It appears that, when nearly all of the linear dimeric cation has disappeared, the linear trimeric and tetrameric cations are present in nearly equal amounts.[195] Subsequent chain growth then occurs by reactions between ammonium chloride, $[Cl_3PNPCl_3]^+$, $[Cl_3PNPCl_2NPCl_3]^+$, and $[Cl_3PN(NPCl_2)_2PCl_3]^+$ according to the general equation[195]

$$[Cl_3P(NPCl_2)_nNPCl_3]^+Cl^- + [Cl_3P(NPCl_2)_mNPCl_3]^+Cl^- + NH_4Cl \longrightarrow [Cl_3P(NPCl_2)_{n+m+2}NPCl_3]^+Cl^- + 4HCl$$

to yield linear tetramer, pentamer, hexamer, heptamer, and octamer.

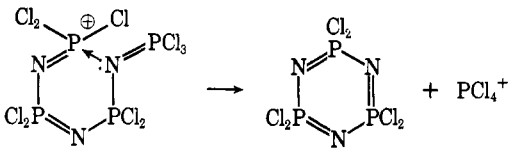
The cyclic species are formed from these linear molecules, but it appears that cyclization may be concurrent with the loss of one phosphorus atom. Cyclic trimer would, therefore, be produced from linear tetramer **43**.[189,195] An alternative mechanism would involve the loss of hydrogen chloride from a mixture of linear trimer and ammonium chloride to give the cyclic trimer.[183,184] The above general description of the mechanism is almost certainly an oversimplification, since it

(198) K. S. Brenner, *J. Chromatogr.*, **57**, 131 (1971).

(199) Experience in the author's laboratory indicates that the handling of solid $(NPCl_2)_3$ and $(NPCl_2)_4$ in the open in a well-ventilated laboratory poses no hazard. However, the trimer or tetramer should not be handled in an unventilated, confined space (*e.g.*, in an unventilated fume hood), and particular care should be exercised to avoid the heating and volatilization of these materials on the open laboratory bench.

(200) S. M. Zhivukhin, V. V. Kireev, G. S. Kolesnikov, V. P. Popilin, and E. A. Filippov, *Russ. J. Inorg. Chem.*, **14**, 548 (1969).

(201) M. Becke-Goehring, *Angew. Chem.*, **73**, 246 (1961).



43

has been shown, for example, that the concentration of $(NPCl_2)_3$ falls as the reaction proceeds. Evidence also exists that $(NPCl_2)_3$ can react with phosphorus pentachloride to form a linear tetramer.[174] Yet there is no question that cyclic phosphazenes can be formed from linear phosphazenes both in the presence of ammonium chloride[185] and in its absence,[189] and the general reaction sequence outlined above explains many of the experimental facts.

B. REACTIONS OF AMMONIUM HALIDES WITH OTHER HALOPHOSPHORANES

1. Synthesis of Bromophosphazenes

Bromophosphazenes are synthesized by the interaction of ammonium bromide with phosphorus pentabromide in hot *s*-tetrabromoethane.[202] Phosphorus pentabromide is unstable, and a mixture of phosphorus tribromide and bromine is employed. Because of the volatility of phosphorus tribromide,

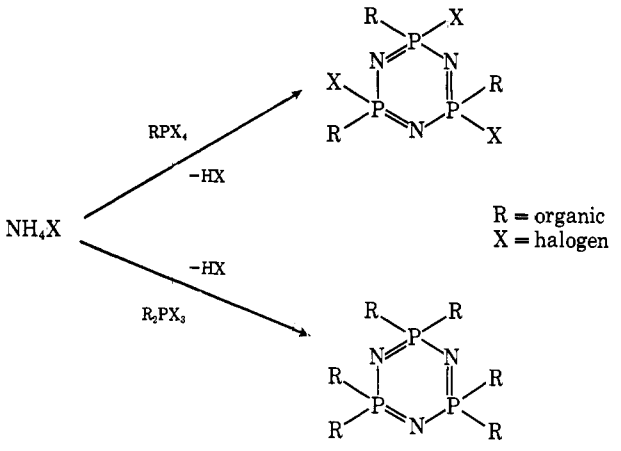
$$n\mathrm{NH_4Br} + n\mathrm{PBr_3} + n\mathrm{Br_2} \longrightarrow (\mathrm{NPBr_2})_n + 4n\mathrm{HBr}$$

the reaction mixture is heated slowly to ~140°. Bromocyclophosphazenes are more susceptible to hydrolysis by atmospheric moisture than are the chloro derivatives. The use of *s*-tetrachloroethane as a solvent leads to the formation of chlorobromophosphazenes.[203] The mixed chloro–bromo derivative, $N_3P_3Cl_2Br_4$, is prepared by the reaction of ammonium bromide with phosphorus trichloride and bromine in *s*-tetrachloroethane, and $N_3P_3Cl_4Br_2$ is formed from phosphorus tribromide, phosphorus pentachloride, and ammonium chloride.[204]

2. Synthesis of Organophosphazenes

Organohalophosphoranes also react with ammonia or ammonium halides to yield organocyclophosphazenes. For the formation of cyclic trimers, the general reactions are shown in Scheme I. For example, $[NP(Cl)Ph]_{3,4}$ are formed when $PhPCl_4$ reacts with ammonium chloride,[205–207] $[NP(Br)Ph]_{3,4}$ are synthesized from $PhPBr_2$, bromine, and ammonium bromide,[208,209] and $[NP(Cl)NMe_2]_3$ is isolated from the reaction of $(Me_2N)PCl_4$ with ammonia.[210] Such nongeminal derivatives are formed as mixtures of cis and trans isomers, which are often difficult to separate by recrystallization techniques. Other examples are the formation of $(NPPh_2)_{3,4}$ from Ph_2PCl_3

Scheme I



and ammonium chloride,[211] the synthesis of $(NPMe_2)_{3,4}$ from Me_2PCl_3 and ammonia or ammonium chloride,[212,212a] and the isolation of $(NPEt_2)_n$ from the reaction of Et_2PCl_3 with ammonia.[85] More recently, the heptafluoropropyl derivative, $[NP(C_3F_7)_2]_3$, has been prepared from $(C_3F_7)_2PCl_3$ and ammonium chloride.[213]

C. SYNTHESIS VIA AZIDE INTERMEDIATES

Organohalophosphines react with sodium or lithium azides to form organoazidophosphines. These latter compounds can be induced to eliminate nitrogen to yield organocyclo- or polyphosphazenes. Azidophosphines can be violent detonators

$$\mathrm{R_2PCl} + \mathrm{NaN_3} \xrightarrow{-\mathrm{NaCl}} \mathrm{R_2PN_3} \xrightarrow[\text{heating}]{\text{gentle}} (\mathrm{R_2PN})_n + n\mathrm{N_2}\uparrow$$

and must be handled with appropriate care. For example, bis(trifluoromethyl)azidophosphine, $(CF_3)_3PN_3$, formed from $(CF_3)_2PCl$ and lithium azide, detonates even at liquid nitrogen temperature.[214] However, slow decomposition of this material at 50–60° (37 mm) has been accomplished to yield a white, waxy polymer of composition $[NP(CF_3)_2]_n$.

In other cases, isolation of the azidophosphine is unnecessary, since addition of sodium azide to the chlorophosphine at elevated temperature results in decomposition of the intermediate as it is formed. In this way, phosphorus tribromide can be converted to $(NPBr_2)_n$,[215] $PhPCl_2$ yields $[NP(Cl)Ph]_n$,[215] Ph_2PCl gives $(NPPh_2)_4$,[215] and a mixture of Ph_2PCl and $PhPCl_2$ gives the nongeminal tetramer $N_4P_4Cl_2Ph_6$.[216] In a related reaction, diphenylchlorophosphine reacts with trimethylsilyl azide to yield hexaphenylcyclotriphosphazene.[217]

$$\mathrm{Ph_2PCl} + \mathrm{Me_3SiN_3} \xrightarrow[-\mathrm{Me_3SiN_3}]{25^\circ} \mathrm{Ph_2PN_3} \longrightarrow (\mathrm{Ph_2PN})_3 + 3\mathrm{N_2}$$

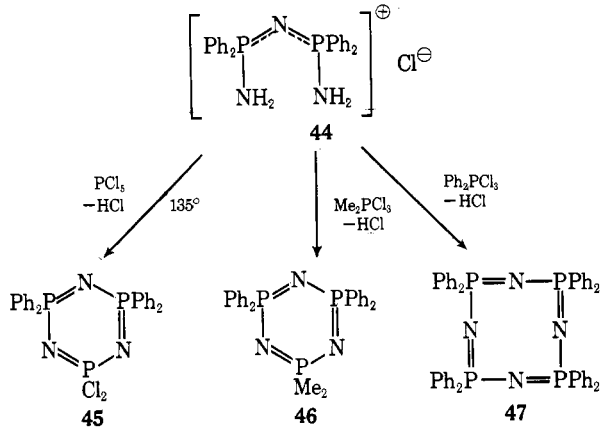
(202) K. John and T. Moeller, *J. Inorg. Nucl. Chem.*, **22**, 199 (1961).
(203) G. E. Coxon and D. B. Sowerby, *J. Chem. Soc. A*, 1566 (1967).
(204) R. G. Rice, L. W. Daasch, J. R. Holden, and E. J. Kohn, *J. Inorg. Nucl. Chem.*, **5**, 190 (1958).
(205) R. A. Shaw and C. Stratton, *J. Chem. Soc.*, 5004 (1962).
(206) F. S. Humiec and I. I. Bezman, *J. Amer. Chem. Soc.*, **83**, 2210 (1961).
(207) B. Grushkin, M. G. Sanchez, and R. G. Rice, *Inorg. Chem.*, **3**, 623 (1964).
(208) T. Moeller and P. Nannelli, *ibid.*, **2**, 659 (1963).
(209) P. Nannelli and T. Moeller, *ibid.*, **2**, 896 (1963).
(210) A. Schmidpeter, C. Weingand, and E. Hafner-Roll, *Z. Naturforsch. B*, **24**, 799 (1969).
(211) C. P. Haber, D. L. Herring, and E. A. Lawton, *J. Amer. Chem. Soc.*, **80**, 2116 (1958).
(212) H. T. Searle, *Proc. Chem. Soc., London*, 7 (1959).
(212a) F. A. Cotton and A. Shaver, *Inorg. Chem.*, **10**, 2362 (1971).
(213) V. N. Prons, M. P. Grinblat, and A. L. Klebanskii, *J. Gen. Chem. USSR*, **40**, 2108 (1970).
(214) G. Tesi, C. P. Haber, and C. M. Douglas, *Proc. Chem. Soc., London*, 219 (1960).
(215) D. L. Herring, *Chem. Ind. (London)*, 717 (1960).
(216) D. L. Herring and C. M. Douglas, *Inorg. Chem.*, **4**, 1012 (1965).
(217) R. H. Kratzer and K. L. Paciorek, *ibid.*, **4**, 1767 (1965).

D. OTHER SYNTHETIC ROUTES TO CYCLOPHOSPHAZENES

The preceding methods are perhaps the most convenient for the synthesis of cyclo- and polyphosphazenes, but a number of other useful synthetic routes are reported below.

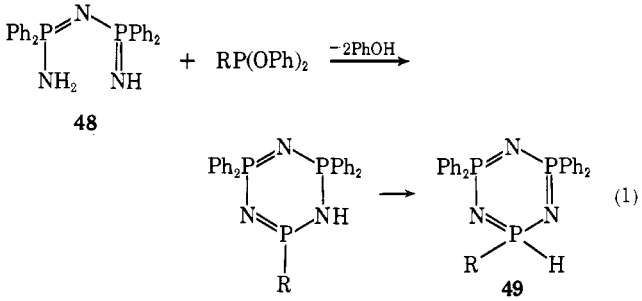
1. Cyclization of Linear Phosphazenes

The linear phosphazene **44** can be prepared by the reaction of



diphenyltrichlorophosphorane, Ph_2PCl_3, with ammonia in chloroform solution.[218,219] Phosphorus pentachloride and dimethyltrichlorophosphorane react with **44** to yield the cyclic trimers **45** and **46** but, surprisingly, the reaction with phosphorus pentachloride also yields a cyclic tetramer, and the tetramer **47** is formed when **44** reacts with diphenyldichlorophosphorane.[218]

A particularly interesting cyclization involves the reaction of the linear phosphazene **48** with a phosphonite according to eq 1.[220] Compound **49** was the first hydrocyclophosphazene to

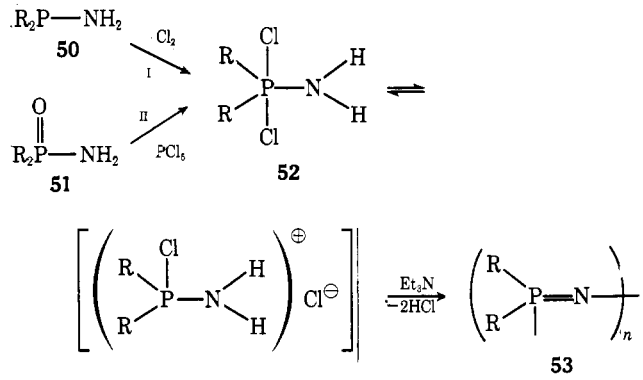


(1)

be reported. Compound **48** also reacts with tris(dimethylamino)phosphine to yield a related hydrophosphazene.[220a]

2. Dehydrohalogenation of Aminochlorophosphoranes

The oxidative chlorination of aminophosphines (**50**) and the chlorination of phosphinic amides (**51**) both yield aminodichlorophosphoranes (**52**). These compounds dehydrohalogenate in the presence of a tertiary amine to yield cyclophos-

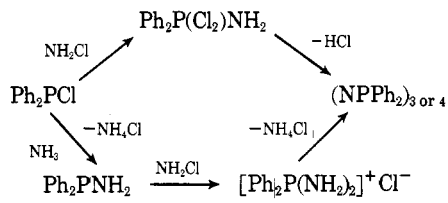


phazenes (**53**).[84,86,101,221,222] For example, reaction route I has been used to prepare $[NP(CF_3)_2]_{3,4,n}$,[84,101] $[NP(C_3F_7)_2]_3$,[84,101] and $(NPPh_2)_3$.[86] Route II has been employed for the synthesis of $(NPPh_2)_{3,4}$.[222]

3. Chloroamination Reactions

Chloroamine, or chloramine and ammonia, reacts with diphenylchlorophosphine to yield phenylcyclophosphazenes.[223-225] Two different reaction mechanisms can be discerned depending on the absence or presence of ammonia, as shown in Scheme II. When ammonia is used, a gaseous mix-

Scheme II



ture of chloramine and ammonia is bubbled through a solution of diphenylchlorophosphine in *s*-tetrachloroethane.

4. Miscellaneous Syntheses

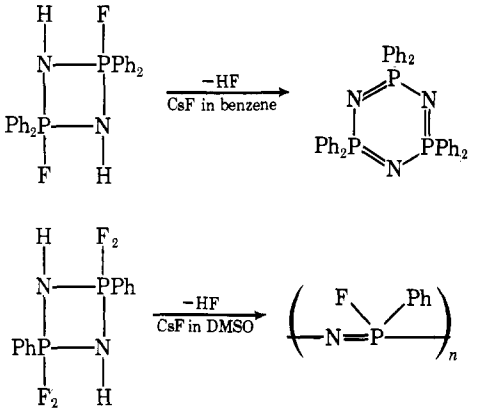
Dimethyldiaminophosphonium chloride, $[Me_2P(NH_2)_2]^+Cl^-$, can be pyrolyzed at 200° to eliminate ammonium chloride and form poly(dimethylphosphazene), $(NPMe_2)_n$. The degree of polymerization is ~120 monomer units.[226]

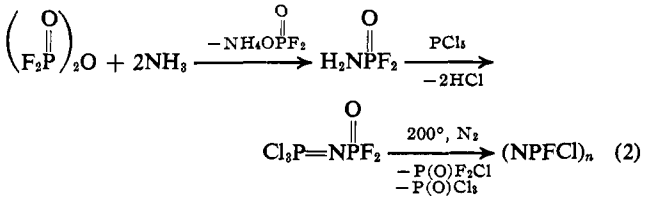
Another synthetic method involves the dehydrohalogenation of fluorocyclodiphosphazanes in the presence of cesium fluoride as a catalyst[227] (Scheme III).

Finally, halogenophosphazene polymers of formula $(NPFCl)_n$ can be prepared by the ammonolysis of $F_2P(O)OP(O)F_2$.[228] The reaction pathway is complex and probably proceeds according to eq 2.

(218) D. L. Herring and C. M. Douglas, *Inorg. Chem.*, **3**, 428 (1964).
(219) I. I. Bezman and J. H. Smalley, *Chem. Ind. (London)*, 839 (1960).
(220) A. Schmidpeter and J. Eberling, *Angew. Chem., Int. Ed. Engl.*, **7**, 209 (1968).
(220a) M. Bermann and J. R. Van Wazer, *Inorg. Chem.*, **11**, 209 (1972).
(221) G. Tesi and C. M. Douglas, *U. S. Govt. Res. Rep.*, AD 236-914 (1961).
(222) M. Becke-Goehring, *U. S. Govt. Res. Rep.*, AD 642-394 (1965).
(223) H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).
(224) I. T. Gibson and H. H. Sisler, *ibid.*, **4**, 273 (1965).
(225) W. R. Grace and Co., German Patent 1,189,077 (1965).
(226) H. H. Sisler, S. E. Frazier, R. G. Rice, and M. G. Sanchez, *Inorg. Chem.*, **5**, 326 (1966).
(227) R. Schmutzler, *Z. Naturforsch. B*, **19**, 1101 (1964).
(228) S. Kongpricha and W. C. Preusse, *Inorg. Chem.*, **6**, 1915 (1967).

Scheme III





E. SYNTHESIS OF MONOPHOSPHAZENES

Monophosphazenes and other linear phosphazenes are synthesized by a variety of routes. This subject has been reviewed elsewhere,[167] and here attention is drawn briefly to only one important type of synthesis, the Kirsanov reaction. The general reaction can be formulated by the equation

$$R_3PCl_2 + R'NH_2 \longrightarrow R_3P{=}NR' + 2HCl$$

in which R can be Cl, F, Ph, etc., and R′ can be a wide variety of groups, including Ph, OH, SO_3H, SO_2Ph, etc. Two points should be noted. First, this reaction is reminiscent of the initial step proposed for the interaction of phosphorus pentachloride with ammonia or ammonium chloride (see section III.A). Second, monophosphazenes in which R′ is aryl show a strong tendency to dimerize to cyclodiphosphazanes, $(R_3P{-}NR')_2$. Cyclic dimers have not been detected in the cyclophosphazene series.

IV. Reactions of Phosphazenes

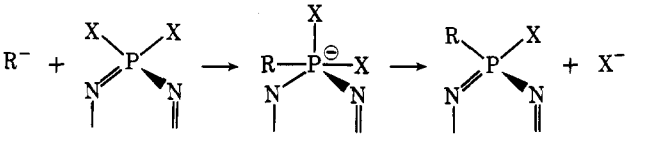
A. NUCLEOPHILIC SUBSTITUTION REACTIONS

1. General Introduction

The largest number of organic substituted cyclo- and polyphosphazenes has been prepared by the nucleophilic replacement of halogen atoms in halogenophosphazenes by organic groupings. Cyclic trimers, higher cyclic oligomers, and high molecular weight polyhalophosphazenes participate in these reactions, and a large part of the literature of phosphazene chemistry is concerned with these processes.

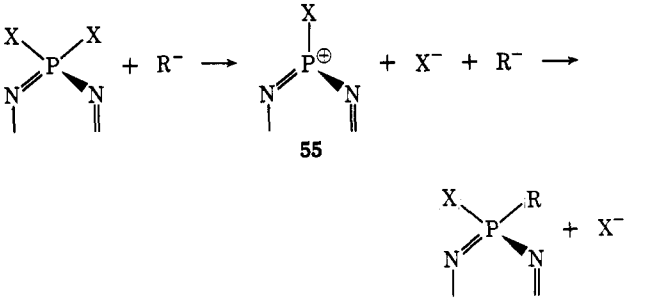
The evidence that is currently available suggests that nucleophilic substitution mechanisms account for a wide variety of different reactions including hydrolysis and aminolysis processes, substitution by alkoxides and aryloxides, metathetical exchange reactions, and substitution by organometallic reagents. All these reactions can be viewed as an attack by a nucleophile R^- at a skeletal phosphorus atom with displacement of one of the original ligands.

If the displacement follows a normal SN2 pattern, a pentacoordinate transition state will be formed (**54**) or a concerted



54

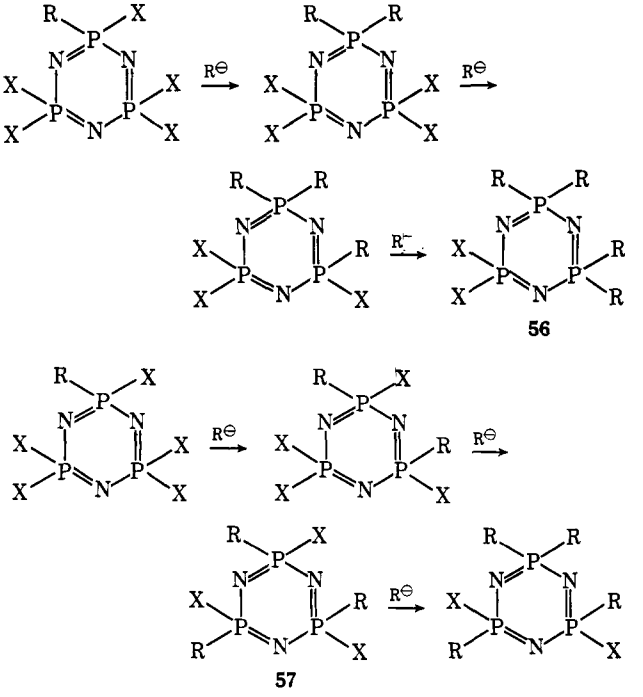
bimolecular pathway will be followed. Inversion of the configuration at phosphorus would also be anticipated unless the nucleophile attacked radially in the plane of the phosphazene ring. However, if the reaction conditions are such that ionization of X^- from phosphorus precedes substitution (**55**), then configurational scrambling would be expected.



55

In addition to this mechanistic variation, it is also necessary to take into account the *site* of substitution, and particularly the influence of substituent groups already present in directing an attacking group to the same phosphorus atom (geminal substitution, **56**) or another phosphorus atom (nongeminal replacement, **57**) (Scheme IV). With nongeminally substituted derivatives, cis and trans isomers may be formed.

Scheme IV



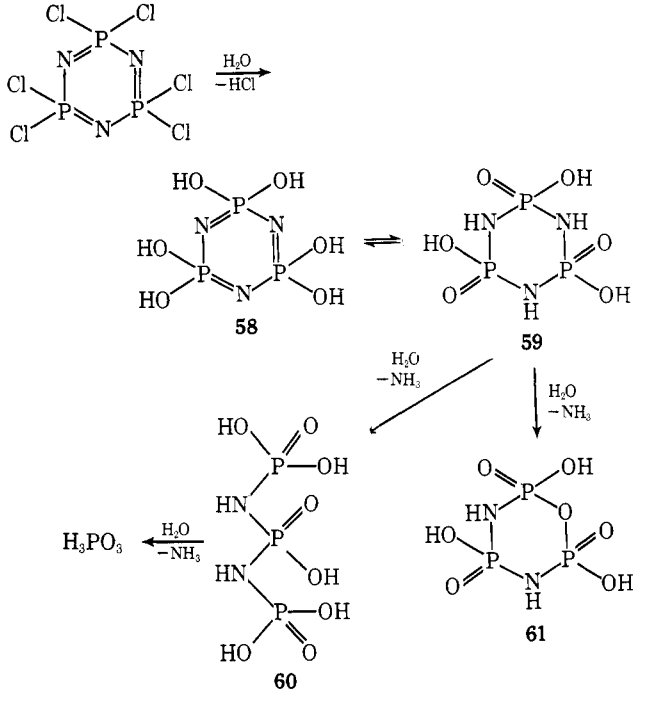
56

57

2. Hydrolysis Reactions

Halocyclophosphazenes, such as $(NPF_2)_{3 \text{ or } 4}$, $(NPCl_2)_{3, 4 \text{ or } n}$, and $(NPBr_2)_{3 \text{ or } 4}$ hydrolyze quite rapidly in acidic or basic homogeneous media. The reaction products are the hydrohalide acid or salt, hydroxyphosphazenes such as $[NP(OH)_2]_{3 \text{ or } 4}$, cyclophosphazanes such as $[HNP(O)OH]_{3 \text{ or } 4}$, and ultimately phosphates and ammonia.[18, 25, 27, 183, 229, 230] In heterogeneous systems, hydrolysis may be very slow.

The hydrolysis of hexachlorocyclotriphosphazene has been examined in some detail.[18, 22–25, 27, 230–232] The initial step is the replacement of chloro by hydroxyl groups to form hexahydroxycyclotriphosphazene (**58**) which, in acidic media, undergoes proton migration to give the cyclotriphosphazane (**59**). Two alternative reaction pathways exist for subsequent



58 59 60 61

hydrolysis. In the first, ring cleavage occurs to give species such as **60**. In acidic media this is a slow process compared with the second alternative, which involves replacement of NH groups by oxygen bridges in the ring (**61**).[233–236] Both processes ultimately yield phosphoric acid and ammonia. Although octachlorocyclotetraphosphazene, $(NPCl_2)_4$, is hydrolyzed faster than the trimer, the initial hydrolysis product, $[NP(OH)_2]_4$, is considerably more stable to subsequent hydrolysis than is **58**.

Organophosphazenes are generally more stable to hydrolysis than are halophosphazenes. When both phenyl and chloro groups are attached to the same ring, the chloro group is removed first in basic media. Hydrolysis of $N_3P_3ClPh_5$ and nongeminal $N_4P_4Cl_2Ph_6$ in pyridine–water mixtures yields the hydroxycyclophosphazenes $N_3P_3(OH)_2Ph_5$ and $N_4P_4(OH)_2Ph_6$.[216, 237]

The hydrolytic behavior of fluoroalkoxy-substituted phosphazenes in basic media has been examined by both product analysis and kinetic techniques.[238, 239] Compounds studied include $[NP(OCH_2CF_3)_2]_{5,4}$, $[NP(OCH_2C_2F_5)_2]_3$, and $[NP(OCH_2C_3F_7)_2]_{3,4}$. The initial steps in the hydrolysis reaction involve cleavage of fluoroalkoxy groups from phosphorus as fluoro alcohol molecules and an introduction of ONa units in their place. The hydrolysis of $[NP(OCH_2CF_3)_2]_3$ proceeds by a nongeminal pathway (**62–68**), and each of the sodium oxophosphazenate salts formed can be converted to the appropriate phosphazane (**64, 66, 68**) by treatment with acid (Scheme V).

Removal of the first fluoroalkoxy group was found to be first order in both phosphazene and hydroxide ion concentrations with the reactivity of the phosphazenes decreasing in the order $[NP(OCH_2CF_3)_2]_4 > [NP(OCH_2C_2F_5)_2]_3 > [NP(OCH_2C_3F_7)_2]_4 \approx [NP(OCH_2CF_3)_2]_3 > [NP(OCH_2C_3F_7)_2]_3$. Thus cyclic tetramers are more reactive than cyclic trimers, and trifluoroethoxy derivatives are slightly more reactive than heptafluorobutoxy compounds. The activation entropies suggested that the cyclic tetramers react faster than the trimers because of their greater flexibility during the approach to the transition state or because of different solvation parameters. $H_2{}^{18}O$ experiments confirmed that the P–OR bond cleaves during hydrolysis rather than the PO–R bond, and an SN2-type mechanism such as **54** is consistent with the data.

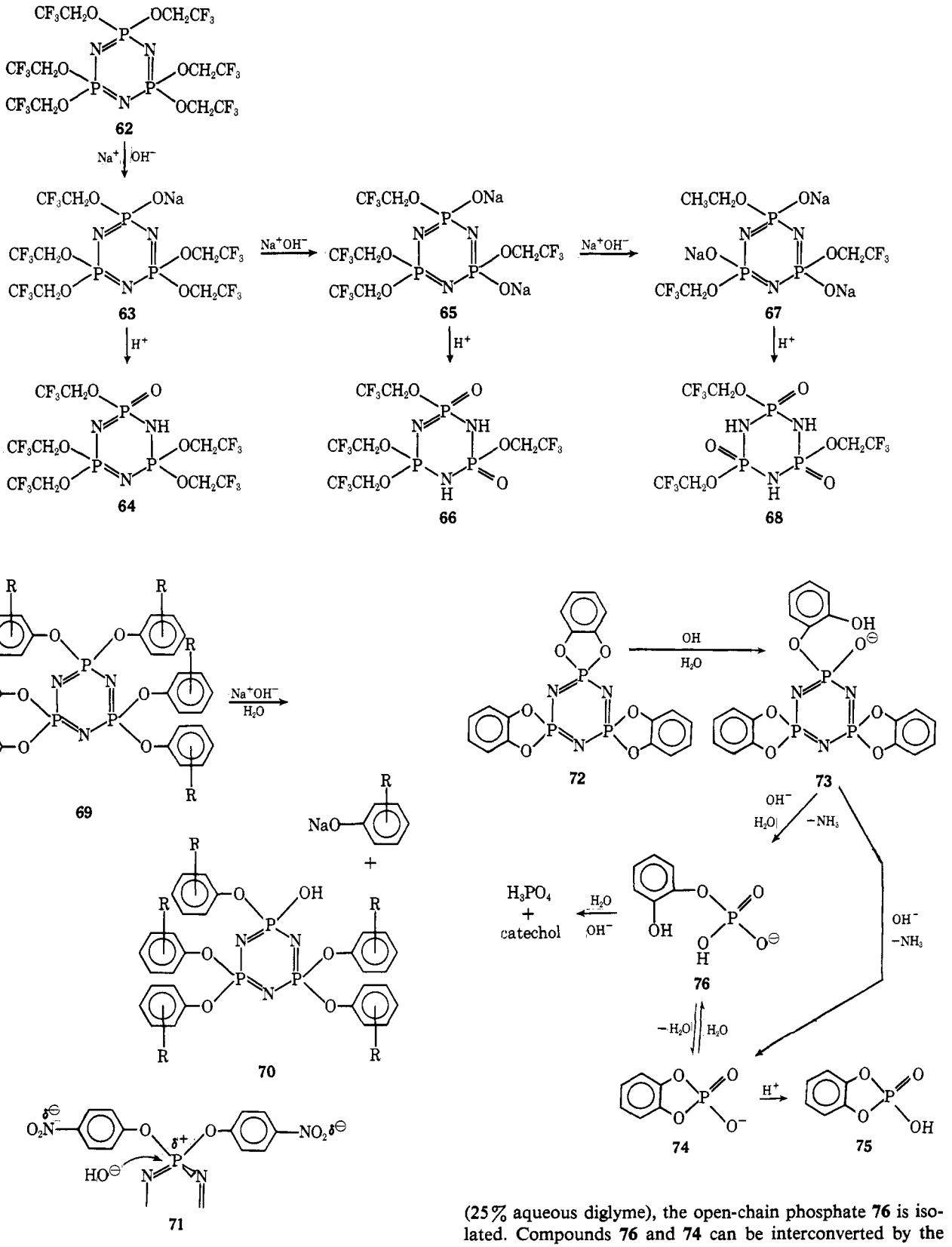
The hydrolytic behavior of aryloxycyclophosphazenes in basic media has also been studied.[240] Aryloxy groups are cleaved from phosphorus and replaced by OH or ONa units. However, the hydrolysis rates are markedly dependent on the nature of the aryloxy substituent. Phenoxy- or *p*-methylphenoxyphosphazenes are exceedingly resistant to hydrolysis. For compounds of structure **69**, the rate of hydrolytic removal of the first aryloxy group to give **70**, in 25 vol % aqueous diglyme, varies with the substituent R in the order R = *p*-NO_2 > *m*-NO_2 > *o*-NO_2 ≫ H > *p*-Me, with the specific rate constants varying over the range of 5.16×10^{-1} to 6.93×10^{-7} M^{-1} sec^{-1}. This behavior is consistent with an SN2-type mechanism in which electron withdrawal by R facilitates attack by OH^- on phosphorus (**71**). Again, $H_2{}^{18}O$ experiments confirm that the P–O bond and not the O–C bond is broken.

The entropy of activation values for this reaction are very negative (−16 to −40 eu), and this is considered to be evidence in favor of a pentacoordinate transition state. Removal of a second aryloxy group from the phosphazene ring is a very slow step, presumably because of the presence of the P–O^-Na^+ unit in basic media.

The presence of a five-membered exocyclic ring at phosphorus, as in compound **72**, induces a striking susceptibility to hydrolysis.[238, 240] Compound **72** hydrolyzes almost instantaneously in basic aqueous–organic media. Even in neutral media the reaction is very rapid. In fact, the hydrolytic behavior of **72** is reminiscent of that of organophosphates which contain a five-membered ring.[241]

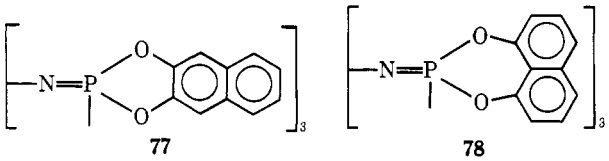
(229) F. Seel and J. Langer, *Z. Anorg. Allg. Chem.*, **295**, 316 (1958).
(230) M. Yokoyama, H. Cho, and M. Sakuma, *Kogyo Kagaku Zasshi*, **66**, 422 (1963).
(231) B. I. Stepanov and G. I. Migachev, *Zavod. Lab.*, **32**, 414 (1966).
(232) U. Einsele, *Melliand Textilber.*, **3**, 299 (1969).
(233) A. Narath, F. H. Lohman, and O. T. Quimby, *J. Amer. Chem. Soc.*, **78**, 4493 (1956).
(234) O. T. Quimby, A. Narath, and F. H. Lohman, *ibid.*, **82**, 1099 (1960).
(235) F. H. Pollard, G. Nickless, and R. W. Warrender, *J. Chromatogr.*, **9**, 493 (1962).
(236) F. H. Pollard, G. Nickless, and A. M. Bigwood, *ibid.*, **11**, 534 (1963).
(237) C. D. Schmulbach and V. R. Miller, *Inorg. Chem.*, **5**, 162 (1966).
(238) H. R. Allcock and E. J. Walsh, *J. Amer. Chem. Soc.*, **91**, 3102 (1969).
(239) H. R. Allcock and E. J. Walsh, *ibid.*, **94**, 119 (1972).
(240) H. R. Allcock and E. J. Walsh, *Chem. Commun.*, 580 (1970); *J. Amer. Chem. Soc.*, **94**, 4538 (1972).
(241) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

Scheme V

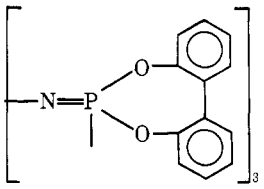


The hydrolysis mechanism appears to involve a prior cleavage of a P–O bond to form the unstable intermediate **73**. This has never been isolated, but in media which have a low water content (2 vol % aqueous diglyme), the cyclic phosphate **74** and, after acidification, the free acid **75** can be isolated. However, in media which contain higher water concentrations (25% aqueous diglyme), the open-chain phosphate **76** is isolated. Compounds **76** and **74** can be interconverted by the addition or removal of water.

It seems clear that the rapid hydrolysis rate of **72** is a consequence of the release of exocyclic ring strain. Compound **77** behaves similarly,[238,240] but **78** and **79** are resistant to hydrolysis. The initial step in the hydrolysis of **72** again appears to be an SN2-type attack by OH^- ion on the phosphorus atom.



77 78



79

3. *Reactions of Halophosphazenes with Alkoxides, Aryloxides, and Thiolates*

A large number of organophosphazenes have been synthesized by the interaction of alkoxides, aryloxides, and thiolates with halophosphazenes. The overall reaction can be described by the equations

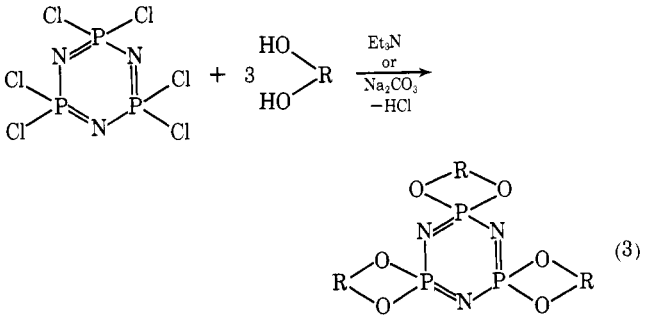
$$2n\text{RONa} + (\text{NPX}_2)_n \longrightarrow [\text{NP(OR)}_2]_n + 2n\text{NaX}$$

$$2n\text{RSH} + (\text{NPX}_2)_n \xrightarrow{\text{base}} [\text{NP(SR)}_2]_n + 2n\text{HX}$$

The reactions are applicable to cyclic trimers (n = 3), tetramers, pentamers, higher cyclic species, and very high molecular weight polymers. Most of the reported reactions have used chlorophosphazenes (X = Cl) as substrates, but fluoro- and bromophosphazenes react similarly.

From an experimental point of view, the reactions are quite straightforward. Sodium alcoholate or phenolate is allowed to react with the halophosphazene in an inert solvent such as ether or tetrahydrofuran, sodium chloride is removed, and the product is isolated from solution. Alternatively, a tertiary amine, such as triethylamine or pyridine, is used together with the alcohol, phenol, or mercaptan to generate the nucleophilic anion, and the amine hydrochloride precipitates from solution. Sodium carbonate has also been used as a base.

Techniques such as these allow a wide variety of different substituents to be attached to the phosphazene ring. The enormous scope of this type of reaction has been detailed in earlier reviews.[1,32,33,167] Here we will restrict ourselves to the observation that most of the available alkoxy,[75,88,112,242-248] fluoroalkoxy,[75,96,245,249-252] phenoxy, methylphenoxy, trifluoromethylphenoxy, methoxyphenoxy, halogenophenoxy, nitrophenoxy,[75,88,140,245,250,252a-256] and mercapto groups[90,246,247] have been incorporated into phosphazene structures. In addition, spirocyclic aryloxyphosphazenes, such as **72**, **77**, **78**, and **79**, can be synthesized by the interaction of chlorocyclophosphazenes with catechol,[89] 2,3-dihydroxynaphthalene,[257] 1,8-dihydroxynaphthalene,[258] or 2,2′-dihydroxybiphenyl,[257] according to eq 3. Toluene-3,4-dithiol reacts similarly,[257] and aliphatic spirophosphazenes can also be prepared.[249,259-262] Many of the substitutions that occur with trimeric chlorocyclophosphazenes are applicable to cyclic tetramers, and some have been carried out with poly(dichlorophosphazene).[75] A noticeable exception is the reaction of $(\text{NPCl}_2)_4$ or $(\text{NPCl}_2)_n$ with *o*-dihydroxybenzene. The tetrameric or polymeric analogs of **72** are not formed, and phosphazene skeletal degradation takes place instead (see section IV.B).[89,258]



(3)

The pattern of halogen replacement in $(\text{NPCl}_2)_3$ by trifluoroethoxide or butoxide ions may be nongeminal,[263,264] but insufficient evidence is available to generalize on this point. However, it seems clear that phenoxy or *p*-bromophenoxy groups are introduced nongeminally,[113,252a,255,265,266] and some evidence exists that inversion of configuration probably does not occur during phenoxide attack.[252a] Ethylthio and phenylthio groups enter in a geminal pattern.[90]

The limited evidence that is available suggests that substitution reactions of this type proceed *via* a nucleophilic attack by RO^- or RS^- on phosphorus, possibly by an S_N2 mechanism of the type discussed earlier (**54**). The nongeminal replacement pattern for phenoxide attack may be a consequence of steric hindrance by phenoxy groups already present, although amino (NH_2) and dimethylamino groups apparently do not noticeably retard chlorine replacement by alkoxide ion at the same

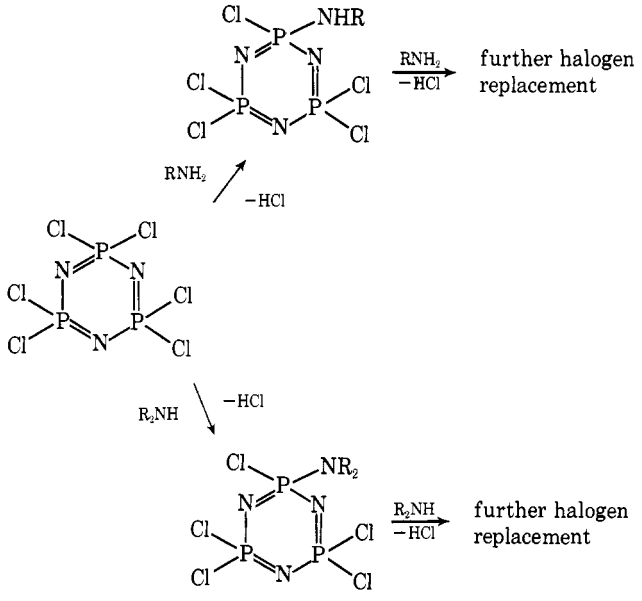
(242) B. Dishon, *J. Amer. Chem. Soc.*, 71, 2251 (1949).
(243) B. W. Fitzsimmons, C. Hewlett, K. Hills, and R. A. Shaw, *J. Chem. Soc. A*, 679 (1967).
(244) S. M. Zhivukhin, V. B. Tolstoguzov, and Z. Lukashevskii, *Russ. J. Inorg. Chem.*, 10, 901 (1965).
(245) H. R. Allcock and R. L. Kugel, *J. Amer. Chem. Soc.*, 87, 4216 (1965).
(246) B. W. Fitzsimmons and R. A. Shaw, *Inorg. Syn.*, 8, 77 (1966).
(247) M. Yokoyama, *J. Chem. Soc. Jap., Pure Chem. Sect.*, 81, 158 (1960).
(248) C. Hamalainen, W. A. Reeves, and J. D. Guthrie, *Text. Res. J.*, 26, 145 (1956).
(249) R. Rätz, H. Schroeder, H. Ulrich, E. Kober, and C. Grundmann, *J. Amer. Chem. Soc.*, 84, 551 (1962).
(250) H. Lederle, E. Kober, and G. Ottmann, *J. Chem. Eng. Data*, 11, 221 (1966).
(251) M. V. Lenton and B. Lewis, *J. Chem. Soc. A*, 665 (1966).
(252) S. H. Rose, *J. Polym. Sci., Part B*, 837 (1968).
(252a) E. T. McBee, K. Okuhara, and C. J. Morton, *Inorg. Chem.*, 5, 450 (1966).
(253) M. Yokoyama and F. Yamada, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, 66, 613 (1963).
(254) D. Dell, B. W. Fitzsimmons, R. Keat, and R. A. Shaw, *J. Chem. Soc. A*, 1680 (1966).
(255) V. B. Tolstoguzov, V. V. Pisarenko, and V. V. Kireev, *Russ. J. Inorg. Chem.*, 10, 382 (1965).
(256) C. T. Ford, J. M. Barr, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 5, 351 (1966).
(257) H. R. Allcock and R. L. Kugel, *ibid.*, 5, 1016 (1966).
(258) H. R. Allcock and E. J. Walsh, *ibid.*, 10, 1643 (1971).
(259) M. S. Chang and A. J. Matuszko, *Chem. Ind. (London)*, 410 (1962).
(260) R. Pornin, *Bull. Soc. Chim. Fr.*, 2861 (1966).
(261) A. J. Matuszko and M. S. Chang, *J. Org. Chem.*, 31, 2004 (1966).
(262) A. Wende and D. Joel, *Z. Chem.*, 3, 467 (1963).
(263) E. T. McBee, L. Brinkmann, and H. P. Braendlin, *U. S. Govt. Res. Rep.*, AD 254,982 (1960).
(264) M. F. Sorokin and V. K. Latov, *Zh. Obshch. Khim.*, 35, 1471 (1965).
(265) D. Dell, B. W. Fitzsimmons, and R. A. Shaw, *J. Chem. Soc.*, 4070 (1965).
(266) C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 4, 419 (1965).

phosphorus atom.[267] The geminal replacement pattern characteristic of phenylthio groups has been ascribed to the high polarizability of the RS–P–Cl unit, compared to that of the Cl–P–Cl moiety.[90] More definitive information about the mechanisms of these reactions will be probably delayed until kinetic data are available.

4. *Aminolysis Reactions*

Primary or secondary amines react with halophosphazenes with the elimination of hydrogen halide and formation of an aminophosphazene (Scheme VI). Excess of the amine may

Scheme VI

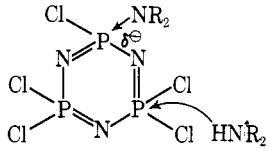


function as a hydrohalide acceptor. A considerable number of cyclic and polymeric compounds are accessible by this route. Aminophosphazenes constitute the largest single class of phosphazene derivatives, and comprehensive listings of these compounds have been compiled.[32,33,167] Here we will examine the ease of substitution with different amines, the pattern of halogen replacement, and the reaction mechanism.

Ammonia reacts with $(NPCl_2)_3$ under mild conditions to give bis- and hexakisaminophosphazenes, $N_3P_3Cl_4(NH_2)_2$ and $[NP(NH_2)_2]_3$.[268,269] The tetrameric chloride, $(NPCl_2)_4$, yields bis, tetrakis, and octakis derivatives.[269] The fully ammonolyzed derivatives dissolve in water and decompose in solution. Unbranched primary alkylamines also react readily to replace all the halogen atoms, and very mild conditions are required if partially substituted derivatives are to be isolated.[102,270–273] Total halogen replacement is more difficult when branched primary alkyl amines are employed. For example, isopropylamine, isobutylamine, *sec*-butylamine, and cyclohexylamine replace all the halogen atoms in $(NPCl_2)_3$ only after reaction in boiling benzene or at 140–180° under pressure.[270] Partial substitution occurs at 25°. Both partially and fully substituted products are obtained with aniline and substituted anilines using only mild conditions,[27,102,120,274–276] and amino acid esters behave similarly.[277]

Total substitution is generally more difficult with secondary amines. Dimethylamine reacts with $(NPCl_2)_3$ to give mono-,[273,278,279] bis-,[278,280,281] tris-,[278,281] tetrakis-,[281,281a] and hexakis(dimethylamino)[281] derivatives, but formation of the latter compound requires the use of excess amine in boiling xylene. Analogous derivatives are formed with diethylamine,[270,273] but di-*sec*-butylamine is virtually unreactive with $(NPCl_2)_3$, even after drastic treatment.[270] Steric factors may be responsible for these differences, although the strong electron supply to phosphorus from the amino unit may also retard attack by a second nucleophile. Diphenylamine and *N*-methylaniline are similarly unreactive.[102] Piperidine reacts with $(NPCl_2)_3$ to yield mono, bis, tris, tetrakis, and hexakis derivatives,[282] and morpholine and pyrrolidine yield the complete range of derivatives, from mono- to hexakismorpholino under relatively mild conditions.[283–288] All degrees of replacement of chlorine in $(NPCl_2)_3$ by ethylenimine have also been reported.[289–291] Table VIII illustrates the substitution pattern found for different amines.

Three factors appear to influence the pattern of aminolysis. The first of these is the ability of a strongly electron-supplying substituent to generate a partial negative charge at phosphorus and thereby to direct a second nucleophile to a nongeminal position (**80**). Such a mechanism could explain



80

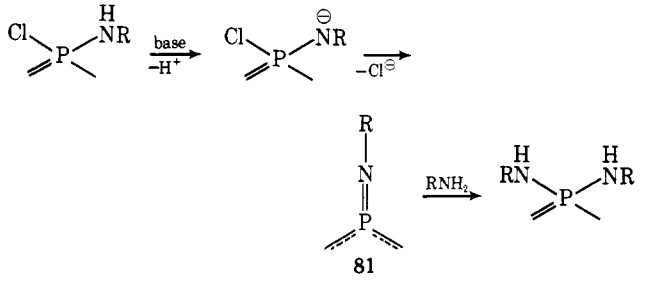
(267) M. R. Pitina and N. I. Shvetsov-Shilovskii, *J. Gen. Chem. USSR*, **36**, 517 (1966).
(268) L. F. Audrieth and D. B. Sowerby, *Chem. Ber.*, **94**, 2670 (1961).
(269) A. M. de Ficquelmont, *C. R. Acad. Sci.*, **199**, 1045 (1935); *Ann. Chim.*, **12**, 169 (1939).
(270) S. K. Ray and R. A. Shaw, *J. Chem. Soc.*, 872 (1961).
(271) S. K. Ray, R. A. Shaw, and B. C. Smith, *ibid.*, 3236 (1963).
(272) T. Moeller and S. Lanoux, *J. Inorg. Nucl. Chem.*, **25**, 229 (1963).
(273) T. Moeller and S. Lanoux, *Inorg. Chem.*, **2**, 1061 (1963).
(274) H. Bode, K. Butow, and G. Lienau, *Chem. Ber.*, **81**, 547 (1948).
(275) E. T. McBee, H. R. Allcock, R. Caputo, A. Kalmus, and C. W. Roberts, *U. S. Govt. Res. Rep.*, AD 209,666 (1958).
(276) K. John, T. Moeller, and L. F. Audrieth, *J. Amer. Chem. Soc.*, **82**, 5616 (1960).
(277) A. A. Kropavheva, N. M. Kashnikova, and V. A. Parshina, *J. Gen. Chem. USSR*, **34**, 532 (1964).
(278) H. Koopman, F. J. Spruit, F. van Deursen, and J. Bakker, *Recl. Trav. Chim. Pays-Bas*, **84**, 341 (1965).
(279) J. M. E. Goldschmidt and J. Weiss, *J. Inorg. Nucl. Chem.*, **26**, 2023 (1964).
(280) M. Becke-Goehring, K. John, and E. Fluck, *Z. Anorg. Allg. Chem.*, **302**, 103 (1959).
(281) R. Keat and R. A. Shaw, *J. Chem. Soc.*, 2215 (1965).
(281a) B. Green and D. B. Sowerby, *J. Inorg. Nucl. Chem.*, **33**, 3687 (1971).
(282) R. Keat and R. A. Shaw, *J. Chem. Soc. A*, 908 (1966).
(283) A. A. Kropacheva and L. E. Mukhina, *J. Gen. Chem. USSR*, **32**, 512 (1962).
(284) A. A. Kropacheva and L. E. Mukhina, *ibid.*, **33**, 699 (1963).
(285) L. E. Mukhina and A. A. Kropacheva, *ibid.*, **38**, 314 (1966).
(286) A. A. Kropacheva and N. M. Kashnikova, *ibid.*, **32**, 645 (1962).
(287) A. A. Kropacheva and N. M. Kashnikova, *ibid.*, **33**, 1036 (1963).
(288) A. A. Kropacheva and N. M. Kashnikova, *ibid.*, **35**, 1978 (1965).
(289) Y. Kobayashi, L. A. Chasin, and L. B. Clapp, *Inorg. Chem.*, **2**, 212 (1963).
(290) G. Ottmann, H. Agahigian, H. Hooks, G. D. Vickers, E. Kober, and R. Rätz, *ibid.*, **3**, 753 (1964).
(291) R. Rätz, C. Grundmann, and G. Ottmann, *ibid.*, **3**, 757 (1964).

Table VIII

Substitution Patterns for Halogen Replacement in $(NPCl_2)_{3,4}$ by Amines

Amine	*Phosphazene*	*Substitution pattern*	*Ref*
NH_3	$(NPCl_2)_3$	Gem	292, 293
NH_3	$(NPCl_2)_4$	Non-gem	294
CH_3NH_2	$(NPCl_2)_3$	Gem and non-gem	280, 295
$C_2H_5NH_2$	$(NPCl_2)_3$	Non-gem	296
i-$C_3H_7NH_2$	$(NPCl_2)_3$	Gem and non-gem	297
tert-$C_4H_9NH_2$	$(NPCl_2)_3$	Gem	298
$C_6H_5NH_2$	$(NPCl_2)_3$	Gem	120, 299
$C_6H_5NH_2$	$(NPCl_2)_4$	Non-gem (trans)	276
$(CH_3)_2NH$	$(NPCl_2)_3$	Mainly non-gem	281
$(C_2H_5)_2NH$	$(NPCl_2)_n$	Non-gem	97
$C_6H_{11}N(CH_3)H$	$(NPCl_2)_4$	Non-gem (β-trans)	300
$C_5H_{10}NH$	$(NPCl_2)_3$	Mainly non-gem	282
OC_4H_8NH	$(NPCl_2)_3$	Non-gem	283–285
C_4H_8NH	$(NPCl_2)_3$	Mainly non-gem	286–288
C_2H_4NH	$(NPCl_2)_3$	Gem	289, 290

the nongeminal preference of dimethylamine,[281] diethylamine,[97] *N*-methylaniline,[300] piperidine,[282] morpholine,[283–285] and pyrrolidine.[286–288] A second likely influence is steric retardation by the bulky substituent already present, which inhibits attack at the phosphorus atom and induces a nongeminal substitution pattern. Bulky secondary amino groups, such as dimethylamino, diethylamino, *N*-methylanilino, or piperidino, would be expected to behave in this manner. Finally, geminal substitution by ammonia or *tert*-butylamine may be a consequence of the loss of a proton from the substituent amino group and the formation of an imino intermediate (**81**).[292, 298]

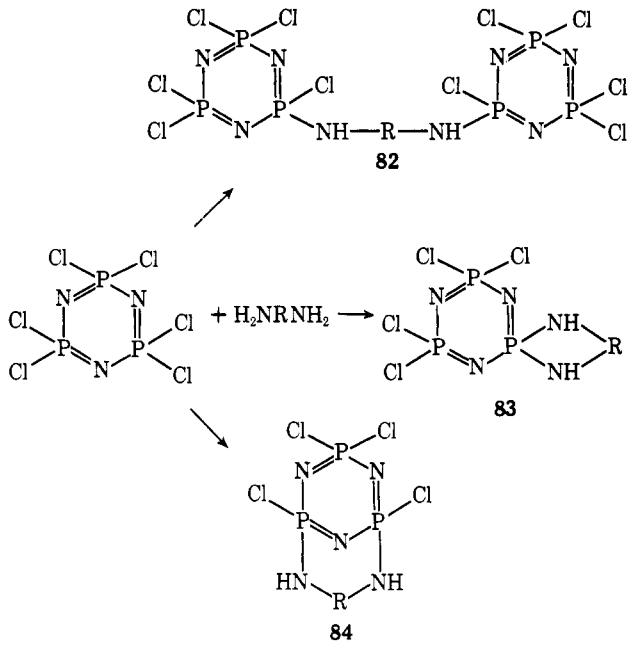


81

Hydrogen bonding between the incoming amine and the substituent primary amino group could also favor geminal substitution. The geminal mechanism followed by ethylenimine is difficult to explain in terms of the above factors.

An analysis of the mechanisms of aminolysis in terms of the formation of cis or trans nongeminal isomers is a complex problem, particularly since aminochlorocyclophosphazenes can undergo cis–trans isomerization in the presence of amine hydrochlorides.[301]

The reaction of chlorocyclophosphazenes with diamines can lead to the coupling of two or more phosphazene rings (**82**) or to cyclization reactions (**83**, **84**). Ring coupling reactions occur with meta and para aromatic diamines, 4,4′-diaminobiphenyl, 1,5-pentamethylenediamine, 1,6-hexamethylenediamine, 1,8-octamethylenediamine, and 4,4-′diaminodicyclohexylmethane.[302, 303] Cyclomatrix polymers are the ultimate products. *o*-Phenylenediamine forms spirocyclic derivatives such as **85**,[257] but ethylenediamine, 1,3-propylenediamine, and 1,4-butylenediamine yield products of the type depicted as **84**.[304, 305] Thiourea and *N*,*N*′-dimethylethylenediamine form spiro compounds analogous to **85**.[306, 306a]

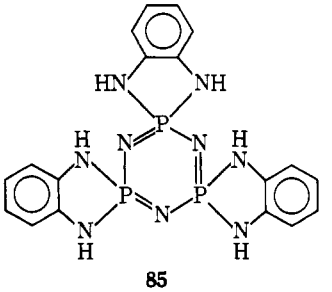


82

83

84

Although there is some ambiguity on this point, a synchronous bimolecular (SN2) mechanism for aminolysis is



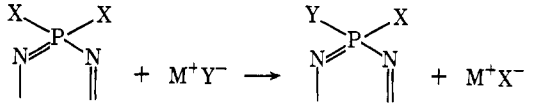
85

(292) G. R. Feistel and T. Moeller, *J. Inorg. Nucl. Chem.*, **20**, 2731 (1967).
(293) W. Lehr, *Z. Anorg. Allg. Chem.*, **350**, 18 (1967).
(294) W. Lehr and J. Pietschmann, *Chem. Ztg.*, **94**, 362 (1970).
(295) W. Lehr, *Z. Anorg. Allg. Chem.*, **352**, 27 (1967).
(296) R. Keat and R. A. Shaw, *Angew. Chem., Int. Ed. Engl.*, **7**, 212 (1968).
(297) S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc. A*, 1677 (1966).
(298) S. K. Das, R. Keat, R. A. Shaw, and D. C. Smith, *J. Chem. Soc.*, 5032 (1965).
(299) V. B. Desai, R. A. Shaw, and B. C. Smith, *J. Chem. Soc. A*, 1977 (1969); 2023 (1970).
(300) A. J. Berlin, B. Grushkin, and L. R. Moffett, *Inorg. Chem.*, **7**, 589 (1968).
(301) R. Keat and R. A. Shaw, *J. Chem. Soc.*, 4067 (1965).
(302) M. Becke-Goehring and D. Neubauer, German Patent 1,143,027 (1963) (to Olin Mathieson Chem. Corp.).
(303) M. Yokoyama and S. Konya, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **68**, 2444 (1965).
(304) M. Becke-Goehring and B. Boppel, *Z. Anorg. Allg. Chem.*, **322**, 239 (1963).
(305) B. Cardillo, G. Mattogno, A. Melera, and F. Tarli, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, **35**, 328 (1963); **37**, 194 (1964).
(306) A. V. Babaeva and G. V. Derbisher, *Russ. J. Inorg. Chem.*, **10**, 156 (1965).
(306a) T. Chivers and R. Hedgeland, *Inorg. Nucl. Chem. Lett.*, **7**, 767 (1971).

consistent with many of the experimental facts. A kinetic study of the reaction between *n*-propylamine and $(NPF_2)_{3,4}$, $(NPCl_2)_{3,4}$ and $(NPBr_2)_{3,4}$ in acetonitrile at 25° indicated that the rate-determining step was second order,[307] and mixed second- and third-order kinetics were observed for replacement of the first chlorine in $(NPCl_2)_3$ by piperidine.[308] However, a number of experimental facts are difficult to explain in terms of a simple SN2 process. For example, the results of competition reactions between aniline and ethanol for reaction with $(NPCl_2)_3$ suggested some SN1 character to the reaction.[309] Furthermore, the rate of the reaction of *n*-propylamine with $(NPX_2)_{3,4}$ varies with the ligand in the order X = Br > Cl > F,[307] the opposite order to that expected on the basis of the magnitude of the positive charge on phosphorus. More recently, kinetic studies have suggested that aminolysis of chlorocyclophosphazenes by methylamine or dimethylamine involves the prior formation of a chlorophosphazene–amine addition complex which subsequently decomposes by loss of hydrogen chloride.[309]

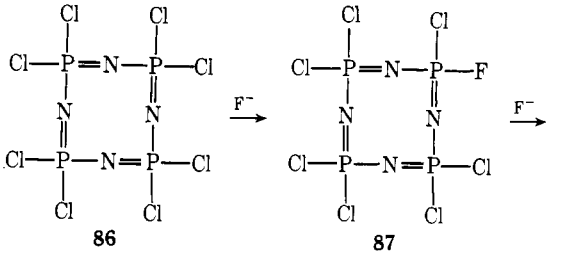
5. *Metathetical Exchange Reactions*

It has been known for a number of years that the chlorine atoms in $(NPCl_2)_{3,4}$ can be replaced by other halogen or pseudohalogen groups. The initial reaction can be summarized by the equation

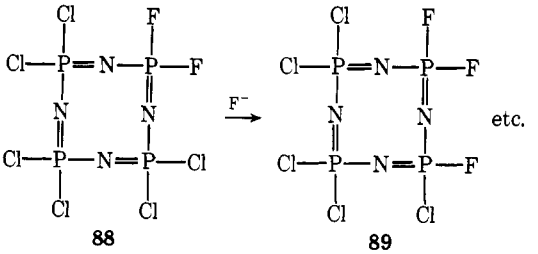


Reactions are known in which X is chloro or bromo and Y is chloro, fluoro, cyano, isothiocyano, and azido. M^+ can be a metal cation or an organic cation. In addition to these "inorganic" metatheses, exchange reactions are known in which the groups X and Y are both organic units.

The most extensively studied of these reactions is the replacement of chloro in $(NPCl_2)_{3,4,n}$ by fluoro. A variety of reagents have been employed for this process, including sodium fluoride,[125,310-312] antimony trifluoride,[122,313] potassium fluorosulfite, or potassium fluoride in sulfur dioxide,[122,125,229,314-318] lead difluoride,[319,320] and silver monofluoride.[93,320] The use of sodium fluoride in acetonitrile is particularly convenient for the preparation of $(NPF_2)_3$ and $(NPF_2)_4$. It is possible that the replacement sequence differs with different reagents, but fluorination with potassium fluorosulfite or potassium fluoride in sulfur dioxide takes place by a geminal pathway.[125,315,316] This is true for the reactions of both $(NPCl_2)_3$ and $(NPCl_2)_4$. With $(NPCl_2)_4$ (**86**), the third and fourth fluorine atoms introduced are closest to the site of original fluorination (**86**–**89**).[125,315] This pattern reflects the greater inductive electron withdrawal by fluorine than chlorine. Thus, the electrophilicity of a phosphorus atom in a PClF group will be greater than in a PCl_2 unit, and fluoride ion will attack the former preferentially. A similar inductive process causes a phosphorus atom adjacent to the PF_2 group to be substituted in



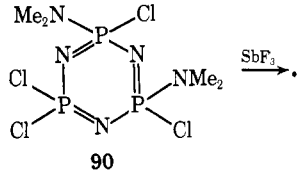
86 **87**



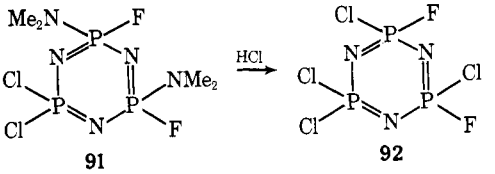
88 **89**

preference to the distant phosphorus atom. Thus, fluorination reactions of this type show the characteristics expected of an SN2-type replacement.

Nongeminal fluorination of $(NPCl_2)_3$ can be accomplished by the use of dimethylamino blocking groups.[122,320a] Thus, dimethylaminolysis of $(NPCl_2)_3$ yields **90**, and treatment of this compound with antimony trifluoride induces nongeminal fluorination (**91**). The dimethylamino groups can then be removed with hydrogen chloride to yield **92**. Fluorination probably takes place geminal to the dimethylamino unit because of coordination between that group and the antimony trifluoride.



90



91 **92**

Experiments have been conducted to follow the rate of exchange of chlorine in $(NPCl_2)_3$, $(NPCl_2)_4$, $(NPCl_2)_5$, and $(NPCl_2)_6$ by radioactive chlorine from tetraethylammonium chloride in acetonitrile.[321] In each case, the exchange rates

(307) T. Moeller and S. G. Kokalis, *J. Inorg. Nucl. Chem.*, **25**, 1397 (1963).
(308) B. Capon, K. Hills, and R. A. Shaw, *J. Chem. Soc.*, 4059 (1965).
(309) J. V. Bailey and R. E. Parker, *Chem. Ind. (London)*, 1823 (1962).
(309a) J. M. E. Goldschmidt and E. Licht, *J. Chem. Soc. A*, 2429 (1971); *Dalton Trans.*, 728, 732 (1972).
(310) T. Moeller, K. John, and F. Tsang, *ibid.*, 347 (1961).
(311) T. Moeller and F. Tsang, *Inorg. Syn.*, **9**, 78 (1967).
(312) R. Schmutzler, *ibid.*, **9**, 75 (1967).
(313) B. Green and D. B. Sowerby, *Inorg. Nucl. Chem. Lett.*, **5**, 989 (1969).
(314) F. Seel and J. Langer, *Angew. Chem.*, **68**, 461 (1956).
(315) A. C. Chapman, D. H. Paine, H. T. Searle, D. R. Smith, and R. F. M. White, *J. Chem. Soc.*, 1768 (1961).
(316) G. Allen, M. Barnard, J. Emsley, N. L. Paddock, and R. F. M. White, *Chem. Ind. (London)*, 952 (1963).
(317) A. C. Chapman, N. L. Paddock, D. H. Paine, H. T. Searle, and D. R. Smith, *J. Chem. Soc.*, 3608 (1960).
(318) C. P. Haber and R. K. Uenishi, *Ind. Eng. Chem., Chem. Eng. Data Ser.*, **3**, 323 (1958).
(319) O. Schmitz-DuMont and M. Walther, *Z. Anorg. Allg. Chem.*, **298**, 193 (1959).
(320) O. Schmitz-DuMont and A. Braschos, *ibid.*, **243**, 113 (1939).
(320a) B. Green, D. B. Sowerby, and P. Clare, *J. Chem. Soc. A*, 3487 (1971).
(321) D. B. Sowerby, *J. Chem. Soc.*, 1396 (1965).

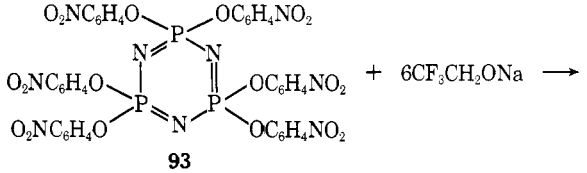
were overall second order (first order in phosphazene and in alkylammonium chloride), and this was taken as evidence for an SN2-type mechanism. The exchange rates for the different cyclophosphazenes decreased in the order $(NPCl_2)_4$ > $(NPCl_2)_5$ > $(NPCl_2)_6$ > $(NPCl_2)_3$. The lower reactivity of the trimer may reflect the greater rigidity of this molecule, which inhibits the conformational changes required during formation of a pentacoordinate transition state. However, the different reactivities of the tetramer, pentamer, and hexamer are difficult to explain in terms of differing molecular flexibilities.

Other inorganic metatheses include the fluorination of hexabromocyclotriphosphazene, $(NPBr_2)_3$, by silver monofluoride,[322] the chlorination of $(NPBr_2)_3$ with mercuric chloride,[323] and the introduction of nitrile groups into $(NPCl_2)_3$ with the use of potassium cyanide in tetrahydrofuran or acetonitrile.[324] Isothiocyano groups can be introduced into chlorophosphazenes by ammonium or potassium thiocyanate, according to the equation[325,326,326a]

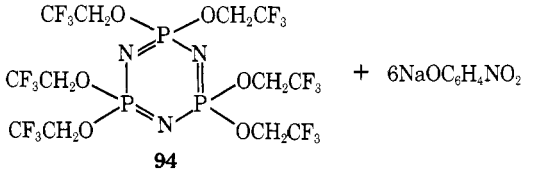
$$(NPCl_2)_n + 2n\text{KSCN} \longrightarrow [NP(NCS)_2]_n + 2n\text{KCl} \quad (n = 3 \text{ or } 4)$$

and organo chlorocyclotriphosphazenes, such as $N_3P_3Ph_2Cl_4$ and $N_3P_3(OCH_2C_3F_7)_4Cl_2$, undergo similar reactions.[327,328] Hexachlorocyclotriphosphazene reacts with sodium azide in acetone to form hexakis(azido)cyclotriphosphazene, $[NP(N_3)_2]_3$, which is a violent detonator,[329] and 1,5-dichlorohexaphenylcyclotetraphosphazene yields *cis*- and *trans*-bisazido derivatives with lithium azide.[330]

A logical extension of these inorganic metatheses is the replacement of organic ligands by organic anions, and these reactions have recently been investigated.[331] For example, hexakis(*p*-nitrophenoxy)cyclotriphosphazene (**93**) reacts with sodium trifluoroethoxide to give hexakis(trifluoroethoxy)-cyclotriphosphazene (**94**) in 70% yield.[331] Similar displacements occur between nitrophenoxyphosphazenes, such as **93** and sodium phenoxide or ethoxide, amide or anilide ions, and

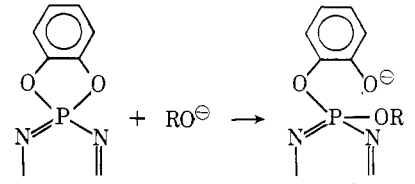


93



94

Grignard or organolithium reagents. Fluoroalkoxyphosphazenes, such as **94** or the tetramer, $[NP(OCH_2CF_3)_2]_4$, undergo ligand exchange with phenoxide, ethoxide, or anilide ions, and with Grignard or organolithium reagents. Hexaphenoxycyclotriphosphazene, $[NP(OC_6H_5)_2]_3$, undergoes ligand displacement with methyllithium or anilide ion. Grignard and organolithium reagents also cleave the phosphazene ring. The general sequence of displacements is such that a particular ligand can only be displaced by a less electron-withdrawing group. Thus, the relative nucleophilicities of the two groups determine the displacement pattern. It has also been observed that a wide variety of nucleophiles ranging from alkoxide ion to amines react with tris(*o*-phenylenedioxy)cyclotriphosphazene (**72**) to cleave one P–O–C bond per phosphorus (**95**),



95

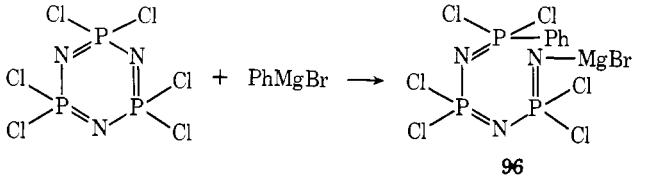
and this can be viewed as ligand exchange process facilitated by the release of exocyclic ring strain.

6. *Reactions of Halophosphazenes with Organometallic Reagents*

Although the early literature in this field implied that the reactions between chlorophosphazenes and Gignard reagents could be employed to prepare aryl- and alkylphosphazenes by reactions such as

$$(NPCl_2)_3 + 6\text{PhMgBr} \longrightarrow (NPPh_2)_3 + 6\text{MgClBr}$$

the most recent work has shown that simple substitution of halogen by phenyl is not the predominant reaction.[332] Instead, replacement of the first chlorine atom by phenyl is accompanied by phosphazene ring cleavage to yield **96**. The

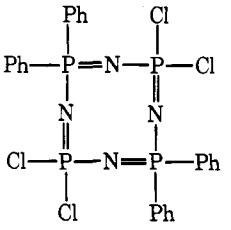


96

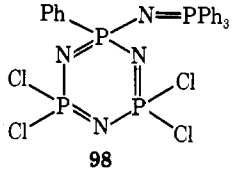
remaining chlorine atoms are then replaced by phenyl groups to yield $Ph_3P{=}NPPh_2{=}NPPh_2{=}NMgBr$, which is a principal reaction product. The very low yield (~5%) of $(NPPh_2)_3$ which is formed appears to result from cyclization of a linear phenylated precursor.[332]

A similar ring cleavage–recyclization reaction is believed to take place when octachlorocyclotetraphosphazene, $(NPCl_2)_4$, reacts with phenylmagnesium bromide in boiling ether.[333] The products include octaphenylcyclotetraphosphazene, $(NPPh_2)_4$, open-chain phenylphosphazenes, and the tetraphenyltetrachlorocyclotetraphosphazene and cyclotriphosphazene shown in **97** and **98**. Compound **98** can also be prepared by the interaction of derivative **99** with phenylmagnesium bromide.[334] Diphenylmagnesium also reacts with

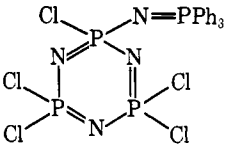
(322) E. Steger and D. Klemm, *J. Inorg. Nucl. Chem.*, **29**, 1812 (1967).
(323) G. E. Coxon and D. B. Sowerby, *Inorg. Chim. Acta*, **1**, 381 (1967).
(324) D. L. Herring, *U. S. Govt. Research Rep.*, AD 276-920 (1962).
(325) R. J. A. Otto and L. F. Audrieth, *J. Amer. Chem. Soc.*, **80**, 5894 (1958).
(326) G. Tesi, R. J. A. Otto, F. G. Sherif, and L. F. Audrieth, *J. Amer. Chem. Soc.*, **82**, 528 (1960).
(326a) T. Moeller and R. L. Dieck, *Syn. Inorg. Metal-Org. Chem.*, **2**, 19 (1972).
(327) L. F. Audrieth, T. Moeller, G. Tesi, A. F. Vandi, and K. O. John, *WADC Tech. Rep.*, (III) 58-51 (1960).
(328) R. F. W. Rätz, U. S. Patent 3,074,989 (1963) (to Olin Mathieson).
(329) C. Grundmann and R. Rätz, *Z. Naturforsch. B*, **10**, 116 (1955).
(330) C. M. Sharts, A. J. Bilbo, and D. R. Gentry, *Inorg. Chem.*, **5**, 2140 (1966).
(331) H. R. Allcock, R. L. Kugel, and E. J. Walsh, *Chem. Commun.*, 1283 (1970).
(332) M. Biddlestone and R. A. Shaw, *J. Chem. Soc. A*, 178 (1969).
(333) R. A. Shaw and M. Biddlestone, *J. Chem. Soc.*, 1750 (1970).



97



98



99

chlorophosphazenes to yield a mixture of cyclic and linear derivatives.[334a]

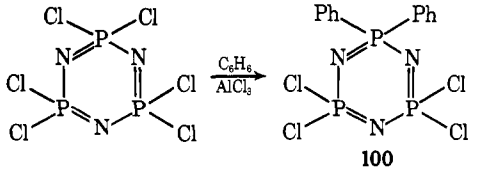
The reactions of fluorocyclophosphazenes with organolithium reagents appear to be more straightforward.[123,124,335-338] Hexafluorocyclotriphosphazene, $(NPF_2)_3$, reacts with phenyllithium to yield mono-, tri-, tetra-, and pentaphenylfluorocyclotriphosphazenes,[123,124,335] and with *m*- and *p*-tolyllithium to yield monoaryl derivatives.[335] With phenyllithium, there appears to be no clear-cut preference for geminal, nongeminal, cis, or trans replacement, and the degree of substitution is controlled by the molar ratio of the reactants.[123,124] However, bisarylation favors the nongeminal cis derivative, and it has been suggested that this is a consequence of a cis-labilizing effect by the fluorine atom of the PFPh unit.[124]

However, methyllithium reacts with $(NPF_2)_{3-5}$ by a predominantly geminal pathway.[338] With the tetramer, total substitution gives $(NPMe_2)_4$ in ~70% yield, but a competitive addition reaction with $(NPF_2)_5$ reduces the yield of $(NPMe_2)_5$ and prevents the conversion of $(NPF_2)_3$ to derivatives with more than two methyl groups. *n*-Butyllithium reacts with $(NPF_2)_{3,4}$ to yield mainly monosubstituted products.[336]

B. OTHER SUBSTITUTION REACTIONS

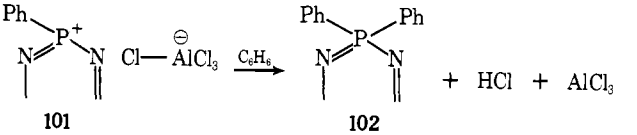
1. Friedel–Crafts Reactions

Halocyclophosphazenes can be arylated in the presence of aluminum chloride. Hexachlorocyclotriphosphazene, for example, interacts with boiling benzene and aluminum chloride to yield the geminal diphenyl derivative **100**.[339,340] Prolonged reaction times (6 weeks) are required before substantial amounts of the geminal tetraphenyl derivative are formed, and even longer times before very small amounts of hexaphenylcyclotriphosphazene can be isolated. Bistolyl, bisxylyl, tetrakisxylyl, and *p*-chlorophenyl compounds can also be prepared by similar techniques.[340] Phenylation of phenylpentafluorocyclotriphosphazene and nongeminal diphenyltetrachlorocyclotriphosphazene in the presence of boiling benzene, aluminum chloride, and triethylamine takes place geminally to the phenyl group already present.[123] Nongeminal phenylation occurs only when nongeminal electron-supplying groups, such as the dimethylamino groups, are present.[341] In such cases the secondary amino groups direct phenylation geminal to themselves.



100

Any postulated mechanism for these reactions must take into account the striking tendency for an incoming phenyl group to substitute in the position geminal to a phenyl or dimethylamino group already present. It must also explain why subsequent arylation is strongly retarded when two or four phenyl groups are present. A plausible mechanistic explanation is that arylation is preceded by ionization of halogen from phosphorus under the influence of aluminum chloride (**101**) and that the cationic center then attacks the aromatic molecule (**102**). Separation of the halide ion (as in **101**) would be facilitated by electron-supplying groups such



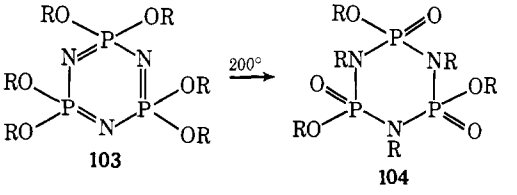
101 102

as phenyl or dimethylamino on the same phosphorus atom, and geminal substitution would be favored. The slowness of the reaction when two or four phenyl groups are already present can be ascribed to the fact that the nitrogen lone-pair electrons are now more available to partly neutralize the positive charge at phosphorus.

2. Rearrangement Reactions

Two types of rearrangement reactions will be considered here—reactions in which ligand groups migrate from one site on the ring to another and cis–trans isomerization reactions.

The thermal rearrangements of alkoxycyclophosphazenes (**103**) to *N*-alkylcyclophosphazanes (**104**) are examples of the first type of rearrangement.[342,343] Alkyl group migration

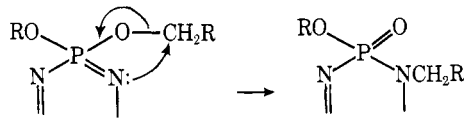


103 104

occurs from oxygen to skeletal nitrogen, in many cases when the alkoxyphosphazene is heated at ~200° for 1–6 hr.[342] The rearrangement has been observed when R is methyl, ethyl, *n*-propyl, isopropyl, and benzyl, and for cyclic trimers

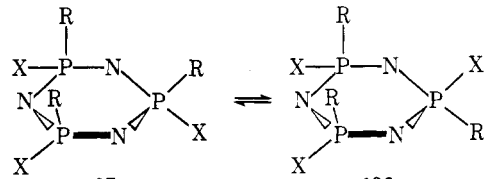
(334) M. K. Feldt and T. Moeller, *J. Inorg. Nucl. Chem.*, **30**, 2351 (1968).
(334a) M. Biddlestone and R. A. Shaw, *ibid.*, 2715 (1971).
(335) T. Moeller and F. Tsang, *Chem. Ind. (London)*, 361 (1962).
(336) T. Moeller, A. Failli, and F. Y. Tsang, *Inorg. Nucl. Chem. Lett.*, **1**, 49 (1965).
(337) C. W. Allen and T. Moeller, *Inorg. Syn.*, **12**, 293 (1970).
(338) N. L. Paddock, T. N. Ranganathan, and S. M. Todd, *Can. J. Chem.*, **49**, 164 (1971).
(339) H. Bode and H. Bach, *Chem. Ber.*, **75**, 215 (1942).
(340) K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J. Chem. Soc.*, 121 (1964).
(341) I. I. Bezman and C. T. Ford, *Chem. Ind. (London)*, 163 (1963).
(342) B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *J. Chem. Soc.*, 4459 (1964).
(343) B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *ibid.*, 7432 (1965).

and tetramers. Alkyl halides are catalysts for these transformations[343] and alkyl groups from the catalyst may become attached to the skeletal nitrogen atoms. From a mechanistic point of view, it is significant that the rearrangement does not take place when trifluoroethoxy or phenoxy groups are the ligands in the original cyclophosphazene. This suggests that the rearrangement takes place by attack of a skeletal nitrogen atom on the α-carbon atom of an alkoxy group, as shown in **105** and **106**. Presumably, electron withdrawal by trifluoroethoxy reduces the availability of the nitrogen lone-pair electrons, and this inhibits nucleophilic attack by that atom.



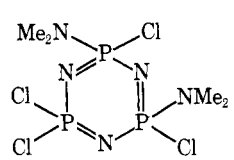
105 **106**

In the second category of rearrangements are those which constitute cis–trans isomerizations, of the type depicted in the conversion of **107** to **108**. Nearly all the cis–trans isom-



107 **108**

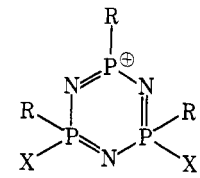
erizations reported to date have involved compounds which contain a halogen atom as one of the isomerized units. For example, nongeminal *trans*-tribromotriphenylcyclotriphosphazene (**108**, R = phenyl; X=Br) is converted to the cis isomer (**107**) simply by heating in boiling acetonitrile, whereas in bromobenzene at 175–180° the reverse transformation occurs.[344] Nongeminal tris(dimethylamino)trichlorocyclotriphosphazene (**107** and **108**, R = NMe_2, X = Cl) undergoes cis–trans isomerization in the presence of hydrogen chloride[345] or alkylammonium halides.[301] Piperidinochlorophosphazenes rearrange with alkylammonium halides.[301] The trisbromo analog behaves similarly in the presence of hydrogen bromide.[345] Treatment of the trans isomer of nongeminal bis(dimethylamino)tetrachlorocyclotriphosphazene (**109**) with aluminum chloride in *sym*-tetrachloroethane at 100° yields



109

a mixture of cis and trans isomers,[346] and aluminum chloride also induces the cis–trans isomerization of nongeminal triphenyltrichlorocyclotriphosphazene (**107** and **108**, R = phenyl; X = Cl).[347]

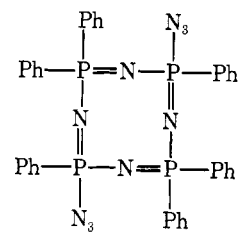
It appears possible that all of these rearrangements have a mechanistic feature in common—the ability of a halogen atom to ionize from phosphorus to yield a planar quasiphosphonium ion (**110**), which can then be attacked by the halide



110

ion to yield both cis and trans isomers. Unless the opportunities exist for preferential attack by halogen ion from one particular side of the molecule, the ratio of the cis and trans isomers formed will be determined by thermodynamic factors. Presumably, the catalytic effect of hydrogen halide, alkylammonium halide, or aluminum chloride is to facilitate the removal of halide ion from phosphorus, although evidence exists that hydrogen halide can also labilize dimethylamino groups.[122]

An example also exists of the cis–trans rearrangement of an azido phosphazene (**111**) in boiling acetonitrile in the presence of lithium azide.[348] Since azido groups often function as



111

pseudohalogeno units, the possibility exists that the rearrangement could proceed *via* reversible ionization of these units from phosphorus.

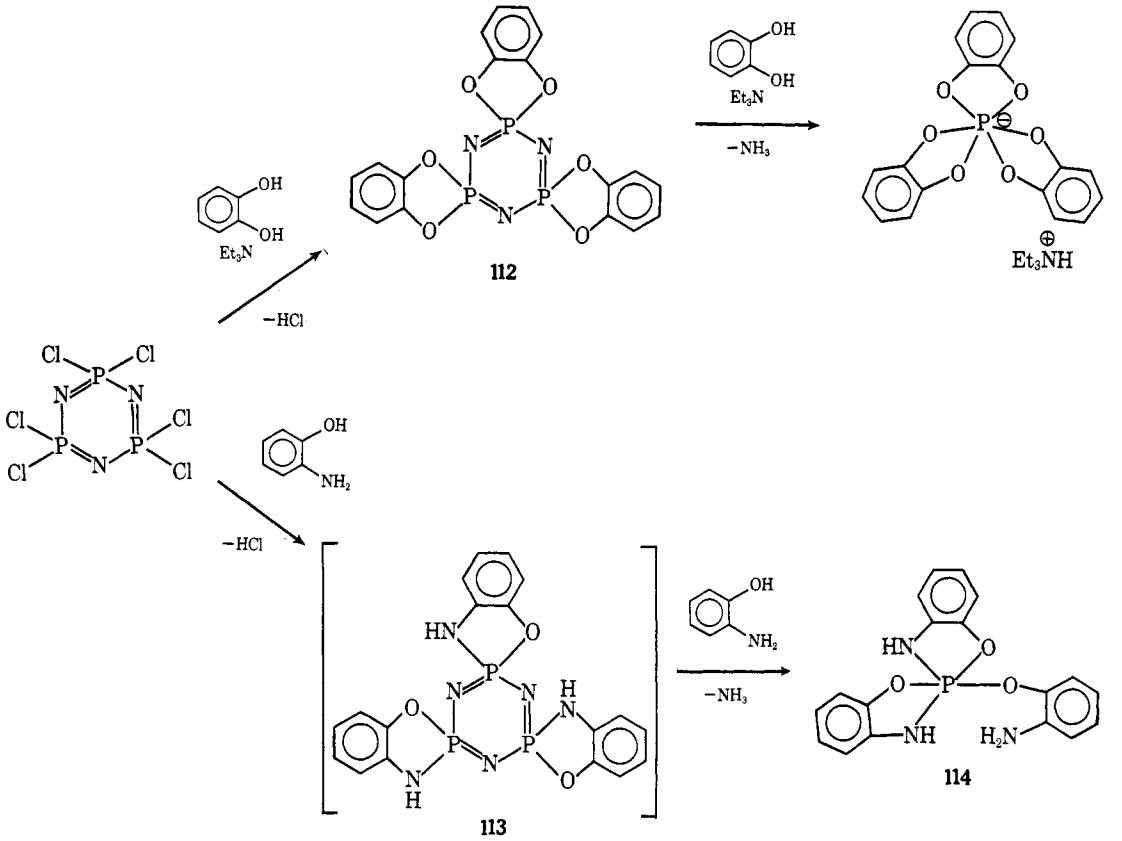
3. Ring Degradation Reactions

At least four different types of reaction are known to lead to breakdown of the phosphorus–nitrogen skeleton. The first of these, hydrolysis, has been discussed earlier. Secondly, it has recently been shown that the reactions of halophosphazenes or some organophosphazenes with ortho-substituted aromatic dinucleophiles lead to the formation of phosphoranes.[89,349–352] Thirdly, chlorophosphazenes react with carboxylic acids or their salts with decomposition of the ring,[353–355] and, lastly, alkoxyphosphazenes react with benzoyl chloride in a ring degradation reaction.[356] These processes will be considered in turn.

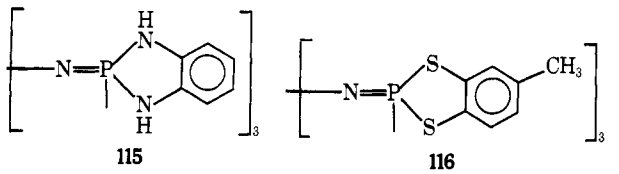
Hexachlorocyclotriphosphazene reacts with catechol and

(344) B. S. Manhas, S. K. Chu, and T. Moeller, *J. Inorg. Nucl. Chem.*, **30**, 322 (1968).
(345) S. N. Nabi, R. A. Shaw, and C. Stratton, *Chem. Ind. (London)*, 166 (1969).
(346) R. Keat, R. A. Shaw, and C. Stratton, *J. Chem. Soc.*, 2223 (1965).
(347) B. Grushkin, M. G. Sanchez, M. V. Ernest, J. L. McClanahan, G. E. Ashby, and R. G. Rice, *Inorg. Chem.*, **4**, 1538 (1965).
(348) C. M. Sharts, A. J. Bilbo, and D. R. Gentry, *ibid.*, **5**, 2140 (1966).
(349) H. R. Allcock, *J. Amer. Chem. Soc.*, **85**, 4050 (1963).
(350) H. R. Allcock and R. L. Kugel, *Chem. Commun.*, 1606 (1968).
(351) H. R. Allcock and R. L. Kugel, *J. Amer. Chem. Soc.*, **91**, 5452 (1969).
(352) H. R. Allcock, R. L. Kugel, and G. Moore, unpublished work.
(353) I. I. Bezman and W. R. Reed, *J. Amer. Chem. Soc.*, **82**, 2167 (1960).
(354) A. B. Burg, "Inorganic Polymers Involving Phosphorus, Nitrogen, and Boron," presented at the 134th National Meeting of the American Society, Chicago, Ill., Sept 7–12, 1958.
(355) M. Yokoyama, H. Cho, and F. Aida, *Kogyo Kagaku Zasshi*, **66**, 609 (1963).
(356) F. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *J. Chem. Soc.*, 4799 (1965).

Scheme VII



tertiary amines or with *o*-aminophenol to yield phosphoranes, as shown Scheme VII.[89,349-352] With catechol and $(NPCl_2)_3$, the spirocyclophosphazene (**112**) can be isolated, but the presumed intermediate formed with *o*-aminophenol (**113**) has not yet been observed. Cyclic tetrameric and polymeric chlorophosphazenes react similarly, and the reaction with *o*-aminophenol takes place with fluoro-, bromo-, and spirocyclic aryloxyphosphazenes, such as **112**, as the substrate. Specifically, the degradation reaction with *o*-aminophenol requires an organophosphazene that has a five-membered arylenedioxy, arylenedithio, or arylenediamino group at phosphorus. Compounds such as **112**, **115**, **116**, and **77** yield

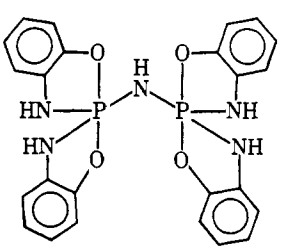


115 **116**

phosphoranes, but those with six- and seven-membered rings at phosphorus, such as **78** and **79**, or those with two independent organic substituents at phosphorus do not.

The mechanism of these degradations is rather unusual. Phosphorane formation will not occur unless the organophosphazene contains five-membered exocyclic units or unless the halophosphazene can react with the reagent to form a spirocyclic compound (**112** or **113**) with the required five-membered ring. The driving force for the degradation of the spirocyclophosphazene to phosphorane is the release of exocyclic ring strain. In a spirophosphazene, such as **113**, the O–P–N angle is constrained below the preferred ~103° angle found in most cyclo- and polyphosphazenes, whereas in phosphoranes an O–P–N angle near 90° is required by the trigonal-bipyramidal geometry. Thus, a marked enthalpy decrease is to be expected during breakdown of the phosphazene skeleton.

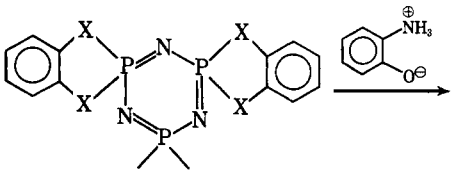
The mechanism of phosphorane formation has been studied by product analysis techniques.[349-352] First, it is known that an ortho dinucleophile is required before phosphoranes are formed. Mononucleophiles, such as aryloxide ion, alkoxide ion, or primary amines will cleave only *one* P–O–C bond per phosphorus in **112**, but phosphazene skeletal cleavage does not take place. Secondly, *o*-aminophenol displaces the other organic ligands from phosphorus, and the final product is **114** in each case. Thirdly, compound **117** can be isolated as a reaction intermediate.



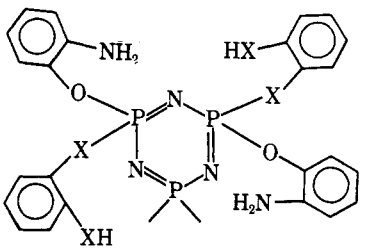
117

Starting from a spirocyclic phosphazene, the mechanism appears to follow the initial pathway shown in **118** → **119**, and this is followed by a chelate type attack on the backbone, with further ligand scrambling to yield **117**. Subsequent further attack by *o*-aminophenol cleaves **117** to give **114**.

Chlorophosphazenes are degraded by carboxylic acids or their salts to yield the nitrile of the acid, the carboxylic acid



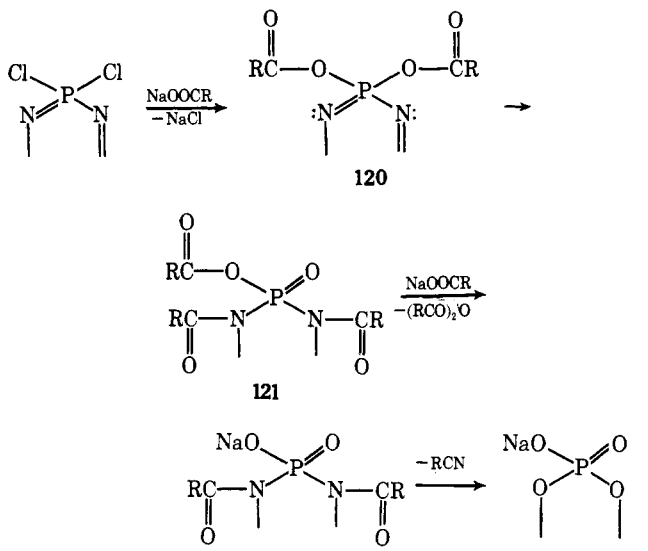
118



119

anhydride, and a precursor of a cyclic metaphosphate.[353-355] The sodium salt of benzoic, *p*-chlorobenzoic, *p*-methoxybenzoic, lauric, and acetic acids, silver trifluoroacetate, and pyridinium acetate yield similar types of products. The reaction mechanism may be as shown in Scheme VIII. The conversion

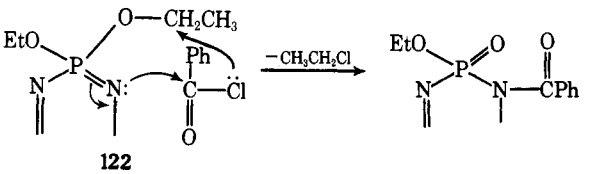
Scheme VIII



of **120** to **121** is plausible in view of the known rearrangements of alkoxyphosphazenes to *N*-alkylphosphazanes (see earlier). It is possible that an intermediate such as **120** also participates in the conversion of primary or secondary amines to amides or hydrazides in the presence of $(NPCl_2)_3$ and a carboxylic acid or carboxylate salt.[357]

Alkoxyphosphazenes, such as $[NP(OEt)_2]_{3 \text{ or } 4}$, react with benzoyl chloride on heating to yield ethyl choride, ethyl phosphates, and triphenyl-*s*-triazine.[356] The reaction mechanism is believed to involve nucleophilic attack by a skeletal nitrogen atom on the carbonyl carbon atom of benzoyl chloride (**122**). Evidence in favor of this mechanism is the observation that the *N*-ethylcyclophosphazane, $[EtNP(O)OEt]_3$, does not

(357) L. Caglioti, M. Poloni, and G. Rosini, *J. Org. Chem.*, 33, 2979 (1968).



122

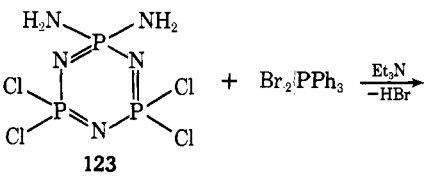
undergo this reaction. Subsequent insertion of the carbonyl oxygen into the skeleton causes elimination of benzonitrile, which then trimerizes to triphenyl-*s*-triazine.

4. *Miscellaneous Reactions*

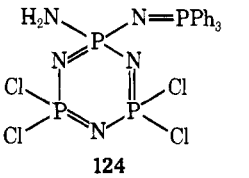
In addition to the foregoing reactions of phosphazenes, a variety of miscellaneous reactions have been observed. These range from straightforward substitution reactions on organophosphazene side groups to the use of phosphazenes to induce unusual organic transformations.

Many organic ligands attached to a phosphazene ring are sufficiently stable to permit reactions of the ligands without decomposition of the skeleton. For example, fluoroalkoxyphosphazenes, such as $[NP(OCH_2(CF_2)_nCF_3)_2]_{3 \text{ or } 4}$ or $[NP(OCH_2(CF_2)_nH)_2]_{3 \text{ or } 4}$, can be chlorinated photochemically to yield derivatives such as $[NP(OCCl_2(CF_2)_nCF_3)_2]_{3 \text{ or } 4}$ or $[NP(OCCl_2(CF_2)_nCl)_2]_{3 \text{ or } 4}$.[358] Allyloxycyclophosphazenes, such as $[NP(OCH_2CH{=}CH_2)_2]_3$, can be brominated in benzene solution.[359] Hexakis(*p*-nitrophenoxy)cyclotriphosphazene, $[NP(OC_6H_4NO_2\text{-}p)_2]_3$, is catalytically reduced over Raney nickel in aniline solution to yield the aminophenoxy derivative, $[NP(OC_6H_4NH_2\text{-}p)_2]_3$.[360] This compound reacts with phosgene to yield a *p*-isocyanatophenoxyphosphazene, and this can be converted to the carbamate with methanol or 1-butanol.[360] Aminocyclophosphazenes, such as $N_3P_3Cl_4(NH_2)_2$, react with phosgene to yield carbamyl chloride and isocyano derivatives,[361] and $N_3P_3(NMe_2)_4(NH_2)_2$ reacts with phenyl isothiocyanate to give a monothiourea compound, $N_3P_3(NMe_2)_4(NH_2)(NHC(S)NHC_6H_5)$.[362]

Phosphazenyl units can be introduced as ligands attached to phosphazene rings by several reactions. For example, *gem*-diaminotetrachlorocyclotriphosphazene (**123**) reacts



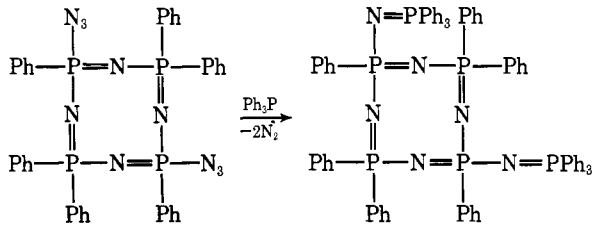
123



124

with triphenyldibromophosphorane to yield compound **124**.[363] Only one amine group undergoes reaction. A bis(phosphazenyl)cyclophosphazene (**126**) is formed when 1,5-bis(azido)-

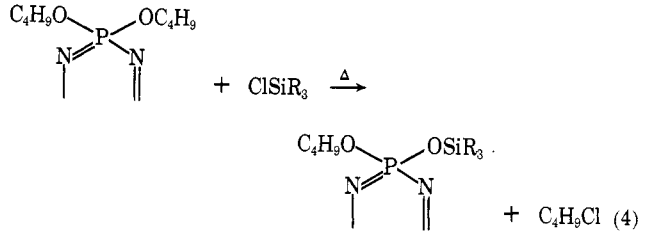
(358) R. F. W. Rätz, U. S. Patent 2,876,248 (1959) (to Olin Mathieson).
(359) C. Hamalainen and J. D. Guthrie, *Text. Res. J.*, 26, 141 (1956).
(360) G. Ottman, H. Lederle, H. Hooks, and E. Kober, *Inorg. Chem.*, 6, 394 (1967).
(361) G. Tesi and R. Zimmer-Galler, *Chem. Ind. (London)*, 1916 (1964).
(362) G. Tesi, A. J. Matuszko, R. Zimmer-Galler, and M. S. Chang, *ibid.*, 623 (1964).
(363) R. Keat, M. C. Miller, and R. A. Shaw, *J. Chem. Soc. A*, 1404 (1967).



125 126

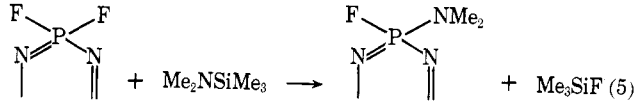
hexaphenylcyclotetraphosphazene (**125**) reacts with triphenylphosphine.[348] Cage-type compounds can be formed with diphosphines.[348]

A number of other miscellaneous reactions of phosphazenes have been reported, most of which have not been studied in detail. For example, hexachlorocyclotriphosphazene reacts with dimethyl sulfoxide to give chloromethyl methyl sulfide and a hydroxyphosphazane,[364] and with dimethylformamide to form phosphazenes with $OCH{=}N^{+}Me_2Cl^{-}$ ligand groups.[365] Transesterification reactions take place between alkoxyphosphazenes and triorganochlorosilanes[366] (eq 4). Organosilicon compounds have also been used to



(4)

prepare dimethylamino-substituted fluorophosphazenes (**127**) by process 5.[367] The reaction is applicable to compounds



(5)

127

of formula $(NPF_2)_{3-6}$. The trimer yields mono- to trisdimethylamino derivatives, and the tetramer through the hexamer gives mono- and bisdimethylamino compounds. A nongeminal pathway is apparently followed.

In other reactions, chlorocyclophosphazenes have been described as amino acid coupling reagents,[368] aromatic coupling agents,[369] substrates for photochemical and electron-induced alkylation and arylation reactions,[370,371] and reagents for the cleavage of trimethylamine.[372]

C. SALTS, COMPLEXES, AND INCLUSION ADDUCTS

As discussed earlier, the phosphazene skeleton is characterized by the presence of a lone pair of electrons on each nitrogen atom. These electrons are available to bind a proton or to complex with electron-acceptor molecules. In addition, specific phosphazenes have the ability to form an unusual series of crystalline inclusion adducts with a variety of guest molecules. These three types of behavior will be discussed in the following sections.

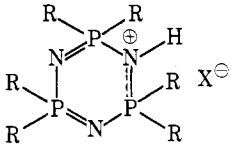
1. Phosphazenes as Brønsted–Lowry Bases

The ability of certain cyclophosphazenes to form stable salt-like adducts with acids has been known for a number of years.[91,274,373] Examples include the perchlorate salts, $(NPCl_2)_3 \cdot HClO_4$, $(NPCl_2)_3 \cdot 2HClO_4$, $[NP(NHPh)_2]_3 \cdot HClO_4$, and $N_3P_3Cl_4(NHMe)_2 \cdot HClO_4$,[274] the acetate salts, $[NP(NH_2)_2]_{3\text{ or }4} \cdot HOOCCH_3$,[91] and hydrohalide salts such as $(NPF_2)_3 \cdot 2HF \cdot 2H_2O$,[373] $[NP(NHPh)_2]_3 \cdot HCl$,[274] $N_3P_3Cl_4(NHC_2H_4NH_2)_2 \cdot 2HCl$,[274] $[NP(NHPr^n)_2]_3 \cdot HCl$,[374] and $[NP(NHBu^n)_2]_3 \cdot HCl$.[374] Many of these adducts have characteristic melting points. They can be converted to the free phosphazene by treatment with organic base, dimethylformamide, or, in some cases, simply by washing with water. The salts are formed by mixing of the components in nonaqueous media or inadvertently during the synthesis of an aminophosphazene from a halophosphazene and an amine.[91,274,373–375]

$$(NPCl_2)_3 + 6RNH_2 \longrightarrow [NP(NHR)_2]_3 \cdot HCl + 5HCl$$

Strong evidence exists that the acidic components are chemically bound to the phosphazene and not simply physically trapped in the crystal lattice. For example, the adducts can often be recrystallized repeatedly without undergoing a change in composition.[374] The salt-like characteristics of hydrohalide adducts can be demonstrated by their ability to react instantly with silver perchlorate to precipitate silver halide.[374] It seems clear, therefore, that the adducts are formed by protonation of the phosphazene to yield a "phosphazenium" cation and a counteranion, $[(NPR_2)_{3\text{ or }4}H]^{+}\ X^{-}$.

The site of the first protonation is a ring nitrogen atom



128

(**128**). This is true even when the substituent groups themselves are strongly basic amino units. Single-crystal X-ray studies with $N_3P_3Cl_2(NHPr)_4 \cdot HCl$ indicate that the skeletal bonds to the protonated nitrogen atom are longer than expected,[376] and infrared spectra of this and other hydrohalide adducts show marked skeletal vibrational shifts compared to the free phosphazenes.[374]

The *degree* of protonation appears to depend on the elec-

(364) S. K. Ray, R. A. Shaw, and B. C. Smith, *Nature (London)*, **196**, 372 (1962).
(365) B. I. Stepanov and G. I. Migachev, *J. Gen. Chem. USSR*, **38**, 195 (1968).
(366) S. I. Belykh, S. M. Zhivukhin, V. V. Kireev, and G. S. Kolesnikov, *Russ. J. Inorg. Chem.*, **14**, 668 (1969).
(367) T. Chivers and N. L. Paddock, *Chem. Commun.*, 337 (1969).
(368) K. C. Das, Y. Y. Lin, and B. Weinstein, *Experientia*, **25**, 1238 (1969).
(369) B. I. Stepanov and G. I. Migachev, *J. Gen. Chem. USSR*, **35**, 2245 (1965).
(370) B. R. Dishon and Y. Hirshberg, *J. Polym. Sci.*, **4**, 75 (1949).
(371) V. I. Spitsyn, N. A. Afanas'eva, A. K. Pikaev, I. D. Kolli, and P. Ya. Glazunov, *Proc. Acad. Sci. USSR*, **131**, 387 (1960).
(372) A. B. Burg and A. P. Caron, *J. Amer. Chem. Soc.*, **81**, 836 (1959).
(373) O. Schmitz-DuMont and H. Kulkens, *Z. Anorg. Allg. Chem.*, **238**, 189 (1938).
(374) T. Moeller and S. G. Kokalis, *J. Inorg. Nucl. Chem.*, **25**, 875 (1963).
(375) K. Denny and S. Lanoux, *ibid.*, **31**, 1531 (1969).
(376) N. V. Mani and A. J. Wagner, *Chem. Commun.*, 658 (1968); *Acta Crystallogr., Sect. B*, **27**, 51 (1971).

tron-supplying characteristics of the ligands attached to the phosphazene ring and on the strength of the acid. Although the formation of mono-acid adducts can be accomplished with many phosphazenes, bis-acid adducts have been isolated only when an *amino*phosphazene is used as a substrate for treatment with hydrogen chloride or when halophosphazenes are treated with hydrogen fluoride or perchloric acid.[274,373] A tris-hydrochloride salt is formed when the pentylaminophosphazene $[NP(NHC_5H_{11})_2]_3$ is treated with hydrogen chloride in benzene.[375] It seems clear from base strength measurements[297] that the introduction of one proton into a phosphazene molecule lowers the pK_a value considerably. Thus, the addition of a second proton is more difficult, and the formation of stable bis-acid adducts requires the presence of strong electron-supplying substituents around the ring to favor utilization of the lone-pair electrons of the second skeletal nitrogen atom. In the event that substituents with different electronegativities are arrayed around the ring, the most basic skeletal nitrogen atoms will be those adjacent to the most strongly electron-supplying substituents.

Shaw and coworkers[297,377-382] have measured the pK_a' values of a large number of different cyclophosphazenes in nitrobenzene medium with the use of perchloric acid as a reagent. In some cases, both pK_{a_1} and pK_{a_2} values could be determined for the introduction of both the first and second protons. A number of representative pK_a values are listed in Table IX.

The data in Table IX illustrate how the pK_a' values vary with the electron-withdrawing or -supplying characteristics of the ligands. Chlorophosphazenes have very low base strengths, presumably because the chloro groups withdraw electrons from the ring and reduce the availability of the nitrogen lone-pair electrons. For alkyl- and arylphosphazenes, $(NPR_2)_{3 \text{ or } 4}$, the base strength increases in the order R = CF_3 < *p*-ClPh < Ph < Et, a series which again reflects the relative electron-withdrawing or -supplying characteristics of the ligands. The same is true for alkoxy- and aryloxyphosphazenes. Aminophosphazenes have the highest pK_{a_1}' base strengths, higher in fact than the parent amines.[377] However, the differences between the base strengths of different aminophosphazenes cannot be rationalized in terms of the expected electron-supplying properties of the ligands, and a saturation effect has been proposed to explain why the individual values are relatively insensitive to subtle ligand effects. Some cyclic tetramers have slightly higher base strengths than the analogous trimers, but this is not a general rule, and the reverse is often true when strongly electron-supplying substituents are present.

Base strength measurements can be used to distinguish between geminal and nongeminal isomers, but the method is insufficiently sensitive for the identification of cis or trans derivatives. If the assumption is made that the electronic effects of various substituents are additive, it is possible to calculate the expected pK_{a_1} value for a compound using substituent constants derived from known derivatives.[381,382] In this way a comparison between the calculated and observed values can distinguish between alternative structures.[381,382]

Table IX

Representative pK_a' Values for Cyclophosphazenes in Nitrobenzene at 25°

Compound	pK_{a_1}'	pK_{a_2}'	*Ref*
$(NPCl_2)_{3 \text{ or } 4}$	<-6.0		383
$[NP(CF_3)_2]_{3 \text{ or } 4}$	<-6.0		378, 383
$(NPPh_2)_3$	1.50		378
$(NPPh_2)_4$	2.20	−5.80	378
$[NP(C_6H_4Cl\text{-}p)_2]_3$	−1.4		378
$(NPEt_2)_3$	6.40		378
$(NPEt_2)_4$	7.60	0.20	378
$[NP(OCH_2CF_3)_2]_{3 \text{ or } 4}$	<-6.0		378
$[NP(OMe)_2]_3$	−1.9		378
$[NP(OMe)_2]_4$	−1.0		378
$[NP(OEt)_2]_3$	0.2		378
$[NP(OEt)_2]_4$	0.6		378
$[NP(OPr^i)_2]_3$	1.4		378
$[NP(OPr^i)_2]_4$	2.1		378
$[NP(OBu^n)_2]_3$	0.1		378
$[NP(OBu^n)_2]_4$	0.7		378
$[NP(OCH_2Ph)_2]_3$	−2.1		378
$[NP(OCH_2Ph)_2]_4$	−1.6		378
$[NP(OPh)_2]_3$	−5.8		378
$[NP(OPh)_2]_4$	−6.0		378
$[NP(SEt)_2]_4$	−2.8		378
$[NP(SPh)_2]_3$	−4.8		378
$[NP(NHMe)_2]_3$	8.8 ± 0.6	−2.0 ± 0.4	377
$[NP(NHMe)_2]_4$	8.2	3.4	377
$[NP(NHEt)_2]_3$	8.2	−1.3	377
$[NP(NHEt)_2]_4$	8.1	3.8	377
$[NP(NHBu^n)_2]_3$	7.9	−1.8	377
$[NP(NHBu^n)_2]_n$	7.6	3.1	377
$[NP(NMe_2)_2]_3$	7.6	−3.3	377
$[NP(NMe_2)_2]_4$	8.3	0.6	377
$[NP(NEt_2)_2]_3$	8.5	−3.9	377
$[NP(NEt_2)_2]_4$	8.3	−0.9	377
$[NP(NMePh)_2]_3$	3.5		382
$N_3P_3Cl_3(NC_5H_{10})_3$ (*gem*)	−3.9		379
$N_3P_3Cl_3(NC_5H_{10})_3$ (*trans*)	−5.3		379
$N_3P_3Cl_3(NMe_2)_3$ (*gem*)	−4.4		379
$N_3P_3Cl_3(NMe_2)_3$ (*trans*)	−5.4		379
$N_3P_3Ph_3(NHMe)_3$ (*cis*)	5.7	−5.2	382
$N_3P_3Ph_3(NHMe)_3$ (*trans*)	5.8	−5.2	382
$N_3P_3Ph_3(NHEt)_3$ (*cis*)	6.0	−4.8	382
$N_3P_3Ph_3(NHEt)_3$ (*trans*)	6.0	−4.7	382
$N_3P_3(NHEt)_4(OCH_2CF_3)_2$ (*gem*)	3.7		381
$N_3P_3(NHEt)_4(OCH_2CF_3)_2$ (non-*gem*)	2.7		381

2. *Coordination Complexes and Related Derivatives*

Metal halides, metal carbonyls, alkyl halides, and tetrafluoroborate salts form complexes with cyclophosphazenes, although several different types of complex can be identified.

Many products have been reported from the interactions of cyclophosphazenes with metal halides. In some cases, the

(377) D. Feakins, W. A. Last, and R. A. Shaw, *J. Chem. Soc.*, 4464 (1964).
(378) D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Shaw, *ibid.*, 2804 (1965).
(379) D. Feakins, W. A. Last, S. N. Nabi, and R. A. Shaw, *J. Chem. Soc. A*, 1831 (1966).
(380) D. Feakins, S. N. Nabi, R. A. Shaw, and P. Watson, *ibid.*, 10 (1968).
(381) D. Feakins, W. A. Last, S. N. Nabi, R. A. Shaw, and P. Watson, *ibid.*, 196 (1969).
(382) D. Feakins, R. A. Shaw, P. Watson, and S. N. Nabi, *ibid.*, 2468 (1969).
(383) D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Shaw, *Chem. Ind. (London)*, 164 (1963).

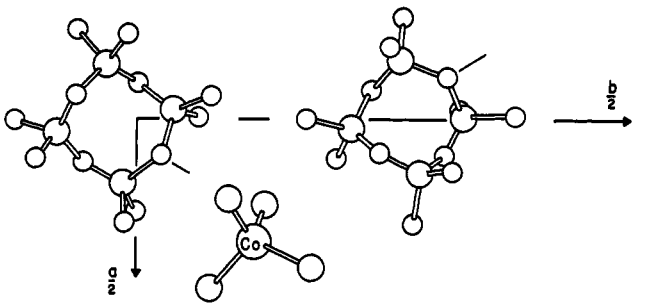
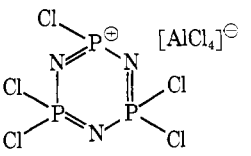


Figure 7. Structural arrangement in the complex, $[(NPMe_2)_4H^+]_2[CoCl_4]^{2-}$ (ref 56).

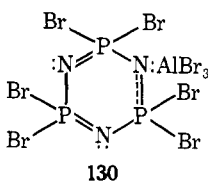
structures of the adducts are not known, but at least two different classes appear to exist. In the first group, a complex is formed by ionization of a halide ion from phosphorus and complexation of it to a metal halide. The complex of formula $N_3P_3Cl_6 \cdot AlCl_3$, formed from $(NPCl_2)_3$ and aluminum chloride,[389] may have this type of structure (**129**). The complexes



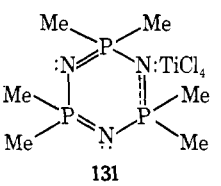
129

formed between $(NPCl_2)_3$·pyridine adducts and stannic chloride,[384] aluminum chloride, cuprous chloride and bromide, ferric chloride, and titanium tetrachloride are believed to contain polymeric ionic complexes similar in structure to compound **129**.[385] A related series of complexes is formed between fluorocyclophosphazenes, $(NPF_2)_{3-6}$, and antimony pentafluoride.[94] These white, crystalline adducts have the formula $(NPF_2)_n \cdot 2SnF_5$, and they can be vacuum sublimed without decomposition at temperatures below 110°. A nonionic, fluorine-bridged structure, has been proposed for these adducts.[94]

A second group of metal halide–phosphazene complexes includes those compounds which are formed by coordination of the metal to a skeletal nitrogen atom. Aluminum bromide reacts with $(NPBr_2)_3$ to form 1:1 and 2:1 adducts and with $(NPCl_2)_3$ to form a 1:1 adduct.[386] Infrared spectral evidence favors the structure shown in **130**.



130



131

Similarly, hexamethylcyclotriphosphazene reacts with titanium tetrachloride or stannic chloride to form stable, crystalline, 1:1 adducts (**131**).[387] Some evidence exists that phosphazenes which contain strongly electron-withdrawing groups, such as chloro ligands, form σ complexes only with the strongest Lewis acids, whereas compounds with strongly electron-supplying ligands can form complexes with the weaker Lewis acids. It seems clear that the availability of the nitrogen lone-pair electrons is the critical factor in complex formation.

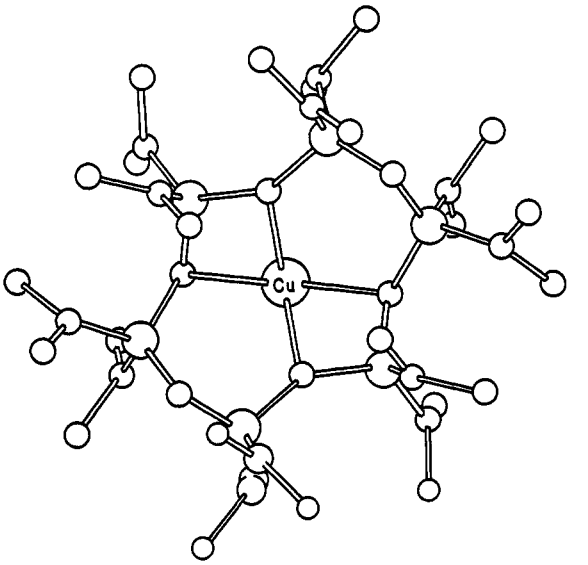
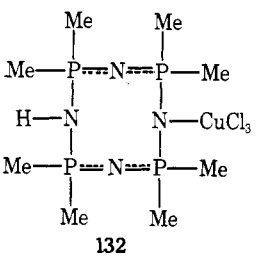


Figure 8. Molecular structure of $[N_6P_6(NMe_2)_{12}CuCl]^+[CuCl_2]^-$ (ref 389).

Several other interesting metal halide complexes have also been reported. Octamethylcyclotetraphosphazene reacts with anhydrous copper(II) chloride in methyl ethyl ketone to form an unusual σ complex in which a $CuCl_3^-$ unit is coordinated to one nitrogen atom and a proton is attached to the most distant nitrogen (**132**).[388] However, metal–nitrogen σ-bonding



132

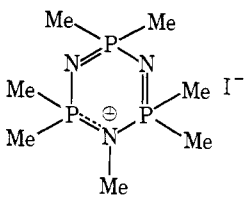
does not occur in the related complex, $[(NPMe_2)_4H^+]_2[CoCl_4]^{2-}$, in which two protonated cyclotetraphosphazene rings are associated ionically with one $CoCl_4^{2-}$ unit (Figure 7).[56] This complex is formed when anhydrous cobalt(II) chloride reacts with $(NPMe_2)_4$ in methyl ethyl ketone. Dodeca(dimethylamino)cyclohexaphosphazene, $[NP(NMe_2)_2]_6$, reacts with copper(II) chloride to form a complex with the formula $[N_6P_6(NMe_2)_{12}CuCl]^+[CuCl_2]^-$, in which a copper atom is coordinated to four of the six skeletal nitrogen atoms (Figure 8).[389]

Other complexes are formed between primary aminophosphazenes and Co^{2+}, Ni^{2+}, or Cu^{2+} salts,[874] between $(NPCl_2)_3$ or $[NP(NCS)_2]_3$ and sodium hexachloroplatinate,[390] between $[NP(OEt)_2]_3$ and titanium or zirconium tetrachlorides,[391] and

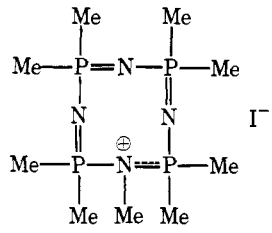
(384) S. M. Zhivukhin and V. V. Kireev, *Russ. J. Inorg. Chem.*, **9**, 1439 (1966).
(385) G. I. Migachev and B. I. Stepanov, *ibid.*, **11**, 929 (1966).
(386) G. E. Coxon and D. B. Sowerby, *J. Chem. Soc. A*, 3012 (1969).
(387) M. F. Lappert and G. Srivastava, *ibid.*, 210 (1966).
(388) J. Trotter and S. H. Whitlow, *ibid.*, 455 (1970).
(389) W. C. Marsh, N. L. Paddock, C. J. Stewart, and J. Trotter, *Chem. Commun.*, 1190 (1970).
(390) G. V. Derbisher and A. V. Babaeva, *Russ. J. Inorg. Chem.*, **10**, 1194 (1965).
(391) U. A. Buslaev, B. V. Levin, Z. G. Rumyantseva, S. P. Petrosants, and V. V. Mironova, *Zh. Neorg. Khim.*, **14**, 3245 (1969).

between metal ions and an *s*-thiosemicarbazido phosphazene,[392] but, in most cases, the structures are unknown. Octamethylcyclotetraphosphazene forms a yellow, solid complex with molybdenum carbonyl which has the composition, $(NPMe_2)_4Mo(CO)_4$.[393] It is believed that this is a σ complex in which two skeletal nitrogen atoms are coordinated to molybdenum.[393] Hexachlorocyclotriphosphazene reacts with $Cr(CO)_3$–$(CH_3CN)_3$ to yield a complex of formula $(NPCl_2)_3Cr(CO)_3$.[393a] The possibility that this is a π complex has been suggested.

Methyl or ethyl iodide reacts with methylcyclophosphazene trimer or tetramer to form *N*-alkylphosphazenium iodides (**133** and **134**).[394] The tetrameric methiodide salt (**134**) reacts

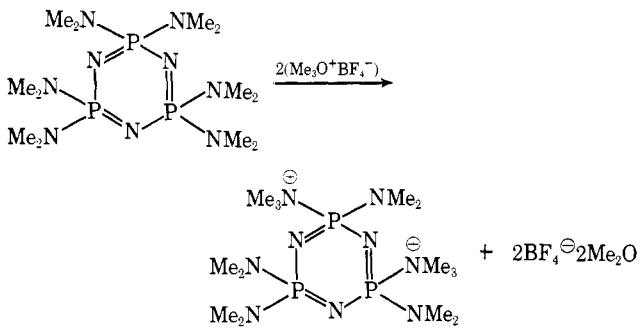


133



134

with chromium or molybdenum hexacarbonyl to displace one molecule of carbon monoxide with the formation of complexes, such as $[N_4P_4Me_9]^+[Cr(CO)_5I]^-$.[393] Onium ions are also formed when trimethyloxonium tetrafluoroborate reacts with amines such as $[NP(NMe_2)_2]_3$, but in this case the exocyclic nitrogen atoms are methylated.[395] Exocyclic mono-

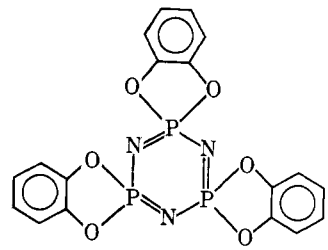


alkylation takes place with $N_3P_3Cl_{6-n}(NMe_2)_n$, where n is 1, 2, 3, 4, and 6, but alkylation of geminal $N_3P_3Cl_2(NHPr^i)_4$ or $(NPPh_2)_3$ occurs at a ring nitrogen atom.

A number of attempts have been made to detect charge-transfer or π complexes formed between cyclophosphazenes and classical donor–acceptor molecules such as tetracyanoethylene, hexamethylbenzene, or iodine. Although phase diagrams suggest that solid-state interactions occur between a variety of cyclophosphazenes and tetracyanoethylene or hexamethylbenzene,[396] infrared spectra of solid solutions of $(NPCl_2)_3$ with hexamethylbenzene show no evidence of complex formation.[397] Similarly, no ultraviolet spectral shifts can be detected when hexane solutions of $(NPCl_2)_3$ and tetracyanoethylene or hexamethylbenzene, or solutions of $(NPF_2)_3$ and hexamethylbenzene are mixed.[397] However, electronic spectral shifts are detected when $[NP(NMe_2)_2]_{3 \text{ or } 4}$ interacts with iodine in nonpolar solvents.[374,398] The overall picture is one in which charge-transfer or π-complex formation with organic molecules, if it occurs at all, is too weak to be detected by conventional spectroscopic techniques. The nature of the interaction with iodine is still not fully understood.

3. Inclusion Adducts

A number of cyclotriphosphazenes participate in the formation of crystalline inclusion adducts with organic compounds. Tris(*o*-phenylenedioxy)cyclotriphosphazene (**135**) is an unusual clathration substrate, as indicated by the following



135

behavior.[399] Compound **135** forms white monoclinic or triclinic crystals, mp 244–245°, when isolated and purified by sublimation. However, recrystallization of the compound from organic media or mere contact with the liquid or vapor of benzene, heptane, or other organic compounds induces a crystal structure change to hexagonal (space group $P6_3$), with the concurrent incorporation of the organic component into the crystal lattice.

An X-ray single crystal study of the clathrates indicated that the guest molecules are mechanically retained in channels which exist between the *o*-phenylenedioxy side groups.[400] As shown in Figure 9, the crystal structure consists of layers of host molecules separated by nearly 5 Å, with an alternating sequence of two different layer types.[399,400] Both types of layer consist of structurally equivalent host molecules centered on the *a*-axis hexagonal net, with the phosphazene rings in the *a*–*a* plane, but with molecules in adjacent layers displaced along *a*–*a* and differing by a 180° rotation in the *a*–*a* plane.[399] This arrangement leads to the formation of 4.5-Å diameter pseudocylindrical channels along the *c* axis of the cell (Figure 9).

Although the guest components are lodged within these channels, they retain appreciable mobility. For example, the X-ray data show no diffuse scattering from molecules held in the channels, and the guest components can be exchanged simply by contact of the crystallites with an excess of a second guest component. The evidence favors the view that the adducts are formed because the guest molecules can "cushion" the side group units and stabilize the channel structure by van der Waals interactions. Differential thermal

(392) B. Janik, W. Ryeszotko, and T. Pelczar, *Zh. Anal. Khim.*, 22, 930 (1967).
(393) J. Dyson and N. L. Paddock, *Chem. Commun.*, 191 (1966).
(393a) N. K. Hota and R. O. Harris, *ibid.*, 407 (1972).
(394) G. Allen, J. Dyson, and N. L. Paddock, *Chem. Ind. (London)*, 1832 (1964).
(395) J. N. Rapko and G. R. Feistel, *Inorg. Chem.*, 9, 1401 (1970).
(396) S. K. Das, D. Feakins, W. A. Last, S. N. Nabi, S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc. A*, 616 (1970).
(397) H. R. Allcock and P. C. Ostrowski, unpublished results, 1968.
(398) S. K. Das, R. A. Shaw, B. C. Smith, W. A. Last, and F. B. G. Wells, *Chem. Ind. (London)*, 866 (1963).
(399) H. R. Allcock and L. A. Siegel, *J. Amer. Chem. Soc.*, 86, 5140 (1964).
(400) L. A. Siegel and J. H. van den Hende, *J. Chem. Soc. A*, 817 (1967).

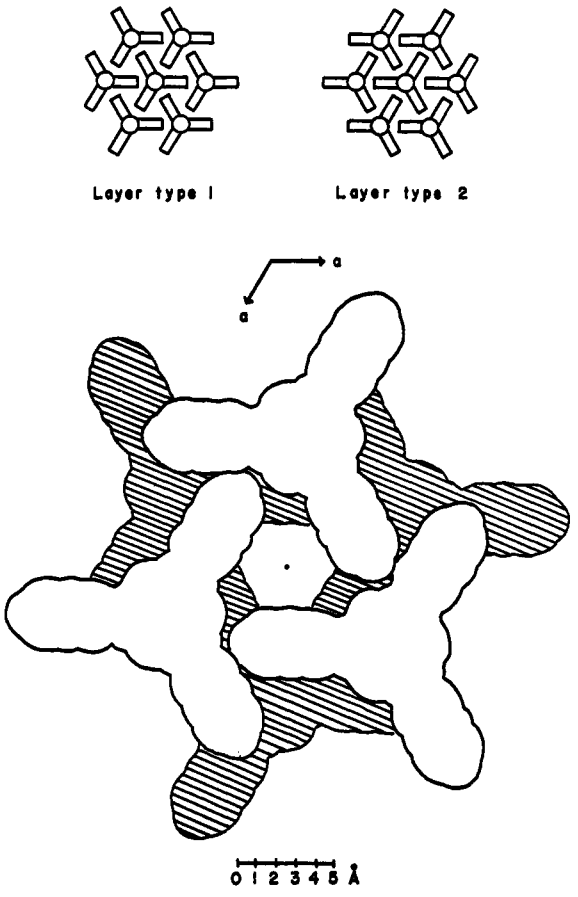


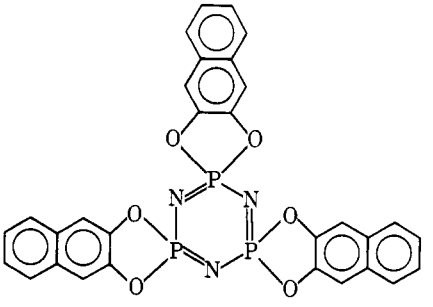
Figure 9. Packing arrangement of molecules of tris(*o*-phenylenedioxy)cyclotriphosphazene in the hexagonal clathrate form.

analysis experiments indicate that the uptake of the guest is a highly exothermic process.[399] Removal of the guest compound under vacuum leads to a collapse of the structure and reversion to the original monoclinic or triclinic modification. However, above 170° the hexagonal modification appears to be stable even in the absence of a guest. Presumably the side-group thermal motions of the host are sufficiently large at this temperature that a guest component is not required to cushion the structure. Thus, the clathration is a response to crystalline packing forces generated by the unusual, paddle-wheel-like shape of the host molecules.

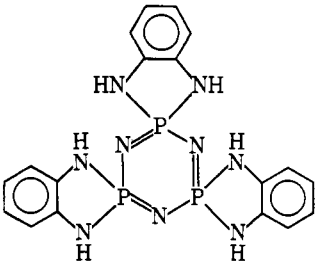
The stability of the clathrates and the ratio of guest compound retained by the lattice depend on the dimensions of the guest molecules. Small molecules, such as carbon disulfide or methanol, are lost slowly from the lattice at 25°, but the clathrates formed with larger guest molecules are stable at ambient conditions. A wide variety of guest compounds have been retained including ethanol, acrylonitrile, acetone, benzene, toluene, diethyl ether, ethyl acetate, methyl methacrylate, chloroform, carbon tetrachloride, tetrahydrofuran, styrene, *n*-heptane, cyclohexane, cumene, xylenes, *trans*-decalin, tetralin, isooctane, and norbornadiene. Many of these adducts have compositions which approximate to one guest molecule to two host molecules.

Competition experiments between two guest compounds for positions in the lattice show that the process can be used to separate the components of a mixture.[399] For example, when heptane–cyclohexane, hexane–benzene, or carbon tetrachloride–benzene mixtures are used, the noncyclic component is incorporated into the clathrate with the almost total exclusion of the cyclic component. Subtle separations of closely related components, such as ethylbenzene and xylenes, and saturated hydrocarbons from olefins can also be achieved. These results may have important technological ramifications in the separation of organic mixtures and particularly in hydrocarbon separations.[401–404]

Tris(2,3-dioxynaphthyl)cyclotriphosphazene (**136**) forms clathrate adducts which are comparable to those of **135**. The



136



137

channels are larger, since benzene molecules are released from the adduct quite rapidly at 25°, but the crystal transformation pattern is similar to that described for **135**. Tris(*o*-phenylenediamino)cyclotriphosphazene (**137**) specifically retains ketones and esters during recrystallization, and it appears possible that hydrogen bonding forces may serve to stabilize the adducts. Other cyclophosphazenes are also known to retain solvent molecules after crystallization. Geminal dichlorotetraphenylcyclotriphosphazene forms a 1:1 adduct with acetonitrile after crystallization from that solvent,[405,406] cis nongeminal trichlorotriphenylcyclotriphosphazene retains benzene,[207] and hexaphenylcyclotriphosphazene retains tetrachloroethane in a 1:3 molar ratio.[228,407] This latter adduct has been examined by means of vapor pressure–composition curves, and it appears that the removal of the guest component is not stepwise and that the binding energy per mole of guest in the adduct is only ~8.7 kcal.[407] This is consistent with a clathration phenomenon.

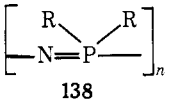
(401) H. R. Allcock and L. A. Siegel, U. S. Patent 3,356,768 (1967) (to American Cyanamid Co.).
(402) A. Goldup and M. T. Westaway, U. S. Patent 3,472,762 (1969) (to British Petroleum Co.).
(403) A. Goldup and M. T. Westaway, U. S. Patent 3,499,944 (1970) (to British Petroleum Co.).
(404) J. M. Haresnape, U. S. Patent 3,504,047 (1970) (to British Petroleum Co.).
(405) C. D. Schmulbach and C. Derderian, *J. Inorg. Nucl. Chem.*, **25**, 1395 (1963).
(406) R. D. Whitaker and W. C. Guida, *ibid.*, **31**, 875 (1969).
(407) R. D. Whitaker, A. J. Barreiro, P. A. Furman, W. C. Guida, and E. S. Stallings, *ibid.*, **30**, 2921 (1968).

V. Phosphazene High Polymer Chemistry

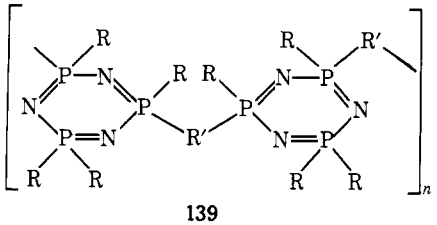
Phosphazenes occupy a strategic place in inorganic polymer chemistry. The rubbery chlorophosphazene high polymer, $(NPCl_2)_n$, was one of the first inorganic materials to be recognized as a linear macromolecule, and the development of applicable phosphazene polymers in recent years has proceeded at a faster pace than for almost any other inorganic-based system except the polysiloxanes. In many respects, phosphazene polymers epitomize the peculiarities, drawbacks, and advantages of other quasi-inorganic polymer systems. At the same time, this research demonstrates clearly the problems to be expected as inorganic polymer chemists attempt to synthesize new materials which blend the properties of organic polymers with those of the inorganic minerals and glasses.

There are a number of reasons why phosphazenes have generated interest as polymer systems. First, the early discovery that the rubbery elastomer, poly(dichlorophosphazene), was thermally stable at temperatures up to 350° generated intriguing possibilities for the synthesis of heat-stable elastomers. Second, the striking chemical and thermal stability of cyclotri- and cyclotetraphosphazene rings suggested the possibility of linking ring systems together to form stable polymers. Third, the wide synthetic versatility in phosphazene chemistry offered the promise of an unusual diversity of polymeric structures.

Three types of phosphazene polymers are known: linear type macromolecules, cyclolinear polymers, and cyclomatrix resins. The *linear* polymers have the general structure shown in **138**, in which R is a halogen, pseudohalogen, alkyl, aryl,

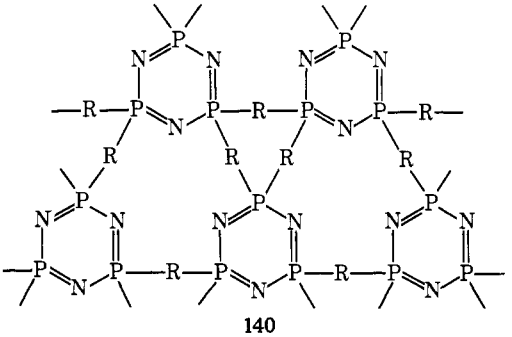


138



139

alkoxy, aryloxy, or amino group, and *n* may be greater than 15,000–20,000. Polymers of this type are elastomers, flexible thermoplastics, or glasses according to the nature of the substituent groups, R. *Cyclolinear* polymers are formed by the linking together of phosphazene ring systems, as in **139**. The synthesis of such materials depends on the presence of



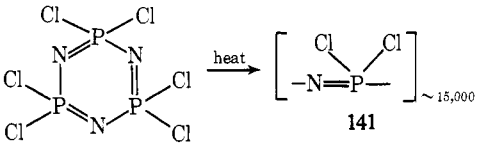
140

blocking groups, R, which limit the functionality and prevent excessive crosslinking. The properties of such polymers depend on the flexibility of the linking group, R′, and these materials range in properties from elastomers to thermoplastic glasses. *Cyclomatrix* polymers, on the other hand, are formed by the extensive crosslinking of multifunctional ring systems to yield structures such as **140**. When crosslinking is complete, these polymers are hard, tough, high-melting resins. Each of these three types of polymer will be considered in turn.

A. POLYMERIZATION AND DEPOLYMERIZATION OF HALOPHOSPHAZENES

1. Polymerization of Chlorophosphazenes

Molten hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene polymerize to a linear-type high polymer (**141**) when heated at 230–300°. In practice, the polymeriza-



141

tion is carried out by the heating of purified hexachlorocyclotriphosphazene in an evacuated sealed tube for 24 to 48 hr at 250°.[75,167] The polymer formed initially is a benzene- or tetrahydrofuran-soluble material (**141**), but prolonged reaction times lead to the formation of a crosslinked polymer.[75,167] This latter material is swelled by organic solvents, but it does not dissolve.

Both modifications of the polymer are transparent, rubbery elastomers which are stable indefinitely in a dry atmosphere but which hydrolyze slowly to phosphate, ammonia, and hydrochloric acid when exposed to moisture. At temperatures above 350° under vacuum, the polymer depolymerizes to cyclic trimer, tetramer, and other oligomers.

The rate of polymerization (and the rate of crosslinking) increases as the temperature is raised, but the polymerization is exceedingly slow at temperatures below 230°. A number of investigators have examined the polymerization kinetics,[408–416] but the results have often been contradictory because trace impurities functioned as powerful polymerization catalysts.[75,167] For example, it has been shown that rigorously purified hexachlorocyclotriphosphazene polymerizes at a slower rate than the vacuum-sublimed material used by most investigators.[416] Traces of dry oxygen gas may function as a catalyst, and a catalytic species may even be formed *in situ* as the polymerization proceeds.[416] Second-order polymerization kinetics are generally observed with activation energies in the region of 42–57 kcal/mol.[410,414,415]

(408) F. Patat and F. Kollinsky, *Makromol. Chem.*, **6**, 292 (1951).
(409) F. Patat, *Angew. Chem.*, **65**, 173 (1953).
(410) F. Patat and K. Frömbling, *Monatsh. Chem.*, **86**, 718 (1955).
(411) M. Yokoyama, *Chem. High Polym.*, **17**, 651 (1960); see *Chem. Abstr.*, **55**, 24354 (1961).
(412) J. O. Konecny and C. M. Douglas, *J. Polym. Sci.*, **36**, 195 (1959).
(413) J. O. Konecny, C. M. Douglas, and M. Y. Gray, *ibid.*, **42**, 383 (1960).
(414) D. Chakrabartty and B. N. Ghosh, *ibid.*, **62**, 5130 (1962).
(415) J. R. MacCallum and A. Werninck, *J. Polym. Sci., Part A-1*, **5**, 3061 (1967).
(416) R. O. Colclough and G. Gee, *J. Polym. Sci., Part C*, **No. 16**, 3639 (1968).

The deliberate introduction of catalysts enables polymerization to be carried out at temperatures below 250°. Carboxylic acids and their salts, ethers, ketones, alcohols, nitromethane, metals such as zinc, tin, or sodium,[412,413,417] 2,6-di-*tert*-butyl-*p*-cresol,[418,419] and sulfur[420] function as catalysts. Virtually the only feature that most of these catalysts have in common is their presumed ability to facilitate removal of a chloride ion from phosphorus. Hexachlorocyclotriphosphazene also polymerizes in the crystalline state when irradiated with 50-kV X-rays, but the polymerization rate falls to zero when the trimer is heated above its melting point.[421] Solution polymerizations have also been investigated. Medium molecular weight polymers (mol wt 130,000) are formed when chloroform solutions of $(NPCl_2)_{3 \text{ or } 4}$ are heated at 270–300° for up to 36 hr.[408] However, in hydrocarbon solvents at 300°, chlorophosphazenes react with the organic media to form substitution products.[408] At lower temperatures (210°), catalyzed reactions take place in benzene solution to yield poly(dichlorophosphazene).[413] Under these conditions the reaction is first order with respect to $(NPCl_2)_3$ but much slower than reactions in the molten phase.

The trimer, $(NPCl_2)_3$, polymerizes at a much faster rate than the tetramer, $(NPCl_2)_4$, in both uncatalyzed and catalyzed reactions.[97,412,422] This effect is sufficiently marked that low polymerization rates are observed when the trimer is contaminated by tetramer.[97] It is possible that the higher reactivity of the trimer reflects a release of ring strain. Certainly the heat of polymerization of the trimer (1.39 kcal/monomer unit) is higher than that of the tetramer (0.86 kcal/monomer unit), and the values for the pentamer (0.80 kcal) and hexamer (0.26 kcal) are lower still.[422] The heptamer, $(NPCl_2)_7$, apparently has a heat of polymerization close to 0 kcal/monomer unit.[422]

The depolymerization of poly(dichlorophosphazene) at elevated temperatures yields cyclic oligomers, such as the trimer, tetramer, pentamer, and higher homologs[26,27,410,423–429] (eq 6). The temperature at which depolymerization be-

$$\left[\begin{array}{c} Cl \quad Cl \\ \diagdown \quad \diagup \\ -N{=}P- \end{array}\right]_n \longrightarrow (NPCl_2)_3 + (NPCl_2)_4 + (NPCl_2)_5 \quad (6)$$

comes evident depends on the experimental conditions. Under nonequilibrium conditions, cyclic oligomers can be sublimed from the polymer under vacuum at 300° or above,[410,423] and the cyclic tetramer predominates in the product mixture.[423] At atmospheric pressure, rapid depolymerization and volatilization of the products become evident above 350°, and a nonvolatile, phospham-type product usually remains when all the volatile products have been removed.[427] The depolymerization is a first-order process with an activation energy of 22.5 ± 2 kcal/mol.[429]

When poly(dichlorophosphazene) or the cyclic trimer or tetramer are heated in a closed system, equilibrium can be established between the polymerization and depolymerization processes. As early as 1939 it was shown that the same mixture of trimer, tetramer, and polymer was formed in a closed quartz tube at 600° irrespective of whether the trimer, tetramer, or polymer was used as the starting material.[430,431] Increases in overall pressure or increases in trimer or tetramer concentration changed the equilibrium to favor the polymer, but elevation of the temperature decreased the concentration of high polymer. More recently, the equilibrium behavior at pressures of 10–70 kbars and temperatures up to 1200° has been studied.[432] Under these conditions, increased pressure again favors the formation of high polymer in the equilibrate but retards its *rate* of formation. Higher temperatures favor the formation of cyclic oligomers at the expense of the high polymer under these conditions.[432] Thus, for the conversion of oligomers to polymer, ΔH_{polym} is negative. Thermochemical measurements of the heat evolved during the zinc-catalyzed polymerization confirm this fact.[422] The interpretation of ring–polymer equilibria for multicomponent systems such as this is a complex process, and much more experimental data will be required before this equilibration system can be fully understood.

2. *Polymerization of Fluoro-, Bromo-, and Isothiocyanophosphazenes*

Cyclophosphazenes which contain fluoro, bromo, and isothiocyano substituent groups also polymerize at elevated temperatures. Hexafluorocyclotriphosphazene, $(NPF_2)_3$, yields a colorless or amber-colored elastomer when heated for 15 hr in a sealed system at 350°.[46,229,314] The high vapor pressure of this compound at elevated pressures poses an explosion hazard unless an autoclave is used for the reaction. The tetramer, $(NPF_2)_4$, polymerizes at a slower rate than the trimer at 350°,[433] and it has been reported that the pentamer, $(NPF_2)_5$, polymerizes very slowly at 250°.[434] Poly(difluorophosphazene), $(NPF_2)_n$, depolymerizes under vacuum at 180° and above to yield principally the cyclic tetramer.[46] The mixed chlorofluorocyclotetraphosphazenes, $N_4P_4Cl_4F_4$ and $N_4P_4Cl_2F_6$, yield rubbery polymers at 300°.[320,373]

Molten hexabromocyclotriphosphazene, $(NPBr_2)_3$, yields a rubbery elastomer when heated at temperatures between 200 and 250°,[433,435,436] and the crystalline solid polymerizes at 80–150° when subjected to γ-ray irradiation.[436] Solid solutions of $(NPBr_2)_3$ and $(NPCl_2)_3$ copolymerize during γ irradiation.[436] Rubbery polymers can also be formed from hexakis(isothiocyano)cyclotriphosphazene, $[NP(NCS)_2]_3$, at temperatures between 145 and 210°.[325,326] These materials appear to be linear species of formula $[NP(NCS)_2]_n$ rather than cyclolinear compounds linked through the substituent groups.

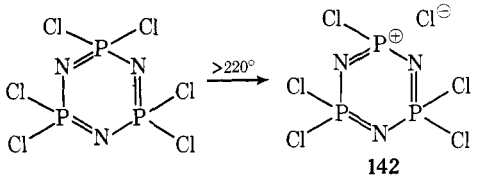
(417) F. G. R. Gimblett, *Polymer*, **1**, 418 (1960).
(418) M. Kajiwara and H. Saito, *Kogyo Kagaku Zasshi*, **66**, 621 (1963).
(419) M. Kajiwara and H. Saito, *ibid.*, **67**, 1002 (1964).
(420) J. R. MacCallum and J. Tanner, *Polym. Lett.*, 7, 743 (1969).
(421) V. Caglioti, D. Cordischi, and A. Mele, *Nature (London)*, **195**, 491 (1962).
(422) J. K. Jacques, M. L. Mole, and N. L. Paddock, *J. Chem. Soc.*, 2112 (1965).
(423) H. R. Allcock and W. J. Cook, unpublished work (1970).
(424) A. M. de Ficquelmont, *C. R. Acad. Sci.*, **204**, 689, 867 (1937).
(425) F. Patat and P. Derst, *Angew. Chem.*, **71**, 105 (1959).
(426) F. G. R. Gimblett, *Trans. Plast. Inst.*, **28**, 65 (1960).
(427) M. Yokoyama and S. Konya, *Kogyo Kagaku Zasshi*, **69**, 1835 (1966).
(428) J. R. MacCallum and J. Tanner, *J. Macromol. Sci., Part A*, **4**, 481 (1970).
(429) J. R. MacCallum and A. R. S. Werninck, *ibid.*, **5**, 653 (1971).
(430) O. Schmitz-DuMont, *Z. Electrochem.*, **45**, 651 (1939).
(431) O. Schmitz-DuMont, *Angew. Chem.*, **52**, 498 (1939).
(432) J. R. Soulen and M. S. Silverman, *J. Polym. Sci., Part A*, 823 (1963).
(433) H. R. Allcock, R. L. Kugel, D. P. Mack, C. W. Cameron, and W. J. Cook, unpublished results, 1967–1970.
(434) G. Allen, C. J. Lewis, and S. M. Todd, *Polymer*, **11**, 31 (1970).
(435) N. E. Bean and R. A. Shaw, *Chem. Ind. (London)*, 1189 (1960).
(436) D. Cordischi, A. D. Site, and A. Mele, *J. Macromol. Chem.*, **1**, 219 (1966).

With very few exceptions (to be mentioned below), this completes the list of cyclophosphazenes that are known to yield linear high polymers by ring-opening type reactions. The polymerization process appears to be principally confined to those derivatives which contain fluoro, chloro, bromo, and isothiocyano substituent groups. Most organo-substituted cyclophosphazenes do not polymerize, and the reasons for this will be examined below (section V.B).

3. The Polymerization Mechanism

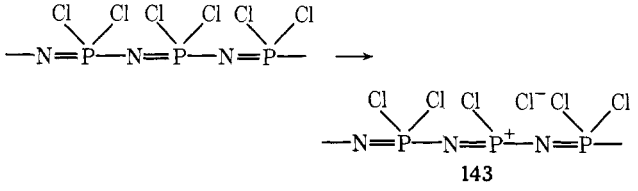
Although the experimental evidence pertaining to the polymerization mechanism is still very incomplete, some useful clues are available. First, it is known that conventional free radical initiators have little effect on the rate of $(NPCl_2)_3$ polymerization[412] and that attempts to detect free radicals by electron spin resonance examination of the polymerizing melt have been unsuccessful.[140] Second, it has been shown that molten $(NPCl_2)_3$ has a low conductance and a low capacitance at temperatures below 210° but that both the conductance and the capacitance rise sharply as the temperature is raised into the range where polymerization occurs.[140] Third, the reaction is catalyzed by those reagents, such as metals, carboxylic acids, and their salts, which would reasonably be expected to induce removal of chloride ion from phosphorus.[412, 413, 437] These three items support an ionic polymerization mechanism rather than a free radical process.

The simplest ionic mechanism that is consistent with the data is one which requires ionization of halogen (or pseudohalogen) from phosphorus (**142**). Such a process would



142

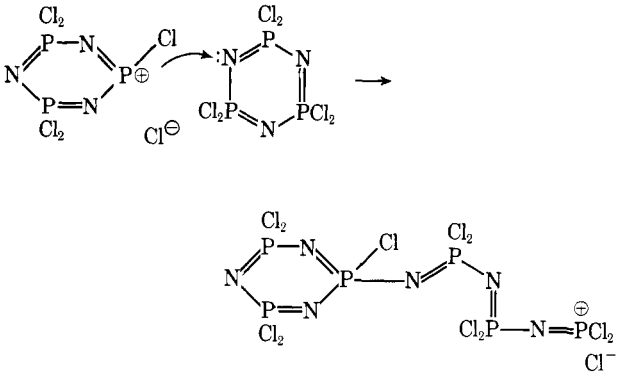
account for the fact that progressively higher temperatures are required to initiate polymerization along the series, $(NPBr_2)_3$, $(NPCl_2)_3$, $(NPF_2)_3$, because this order parallels an increase in P–halogen bond strength. A mechanism for chain branching follows naturally from this initiation scheme, since ionization of chloride ion could also occur from polymer middle units (**143**). The cationic center formed in this way would then



143

initiate the growth of a branch by the same mechanism as in linear chain propagation.

The mechanism of chain propagation is not fully understood. One plausible possibility is the attack by the cation (**142**) at the electron-rich skeletal nitrogen atom of a second trimer molecule to break the ring and commence a conventional cationic-type chain reaction (**144**). Further propagation steps would constitute an insertion of trimer molecules into the



144

terminal $-PCl_2{}^+Cl^-$ ionic complex. The transition state for this propagation would certainly have a higher molecular volume than the precursors, and the rate-retarding effect of high pressures would be consistent with this scheme. Presumably the polymerization rate differences observed between cyclic trimers, tetramers, and higher homologs reflect an influence on the propagation sequence. For example, the fact that $(NPCl_2)_4$ polymerizes less rapidly than $(NPCl_2)_3$ may be a consequence of the fact that the skeletal nitrogen atoms are more shielded in the puckered tetramer. However, other propagation mechanisms have also been proposed,[408, 410, 415, 420, 425, 437] and a clearer understanding of this process must await more definitive experimental work. Virtually no firm evidence is available about the mechanism of thermal crosslinking or spontaneous termination.

B. ORGANIC SUBSTITUENTS AND THE THERMODYNAMIC PROBLEM

1. The Experimental Facts

The polymerization of a cyclophosphazene is usually inhibited when the halogen ligands are replaced by organic units. For example, the phenylcyclophosphazenes, $[NP(C_6H_5)_2]_{3,4}$, the phenoxycyclophosphazenes, $[NP(OC_6H_5)_2]_{3,4}$, and fluoroalkoxycyclophosphazenes such as $[NP(OCH_2CF_3)_2]_{3,4}$ or $[NP(OCH_2C_3F_7)_2]_{3,4}$ do not yield polymers when heated at high temperatures, even in the presence of potential catalysts. Other organocyclophosphazenes, which contain methyl, ethyl, methoxy, ethoxy, or amino substituents, usually decompose at high temperatures rather than polymerize. One of the few organocyclophosphazenes which appear to polymerize thermally is the spiro derivative, tris(*o*-phenylenedioxy)cyclotriphosphazene (**135**).[89]

At first sight, a mechanistic explanation can be formulated to explain the differences between halogeno- and organophosphazenes. It could be argued that halogen (or pseudohalogen) groups can ionize more readily from phosphorus than can organic units. Thus, for organocyclophosphazenes, the initiation step would be inhibited. On closer examination, this argument is seen to be weak. At 350°, ionization of phenoxide ion from molten $[NP(OC_6H_4)_2]_3$ can be detected, and yet the trimer does not polymerize at this temperature.[140] Furthermore, certain organocyclophosphazenes can undergo ring-enlargement or ring-contraction reactions at high temperatures, but high polymers are not formed under these conditions. For example, octaphenylcyclotriphosphazene equilibrates to a mixture of cyclic trimer, tetramer, pentamer, hexamer, and higher oligomers in the 320–500° temperature

(437) F. G. R. Gimblett, *J. Polym. Sci.*, **60**, 529 (1962).

range,[438,439] but conversion of the oligomers to high polymer apparently does not take place. Similarly, the trimer, $[NP(OCH_2C_3F_7)_2]_3$, is partly converted at 340° to the tetramer, but no high polymer is formed. A further argument against this viewpoint is provided by the fact that many poly(organophosphazenes) prepared by alternative routes (see section V.C) depolymerize to cyclic oligomers at moderate temperatures. If the reasonable assumption is made that the mechanisms of polymerization and depolymerization are similar, then the mechanistic argument for inhibition of polymerization is not convincing. Thus, in these examples, the polymerization mechanism must be accessible but high polymer formation is inhibited by other factors. These factors are believed to be thermodynamic in origin.

2. *Ring-Chain Equilibria*

The general polymerization of cyclic compounds to linear high polymers has been treated theoretically by a number of authors.[167,440-446] Basically, three different approaches to the problem have been investigated: classical thermodynamic-kinetic treatments,[440-442] approaches based on the statistics of chain cyclization,[443] and use of the concept of scrambling of end groups and middle units to yield rings and chains.[444,445] For phosphazene equilibrations, insufficient experimental data are available to enable the system to be analyzed in terms of one approach or another, and only a qualitative approach is possible.

Bulky organic substituents attached to a phosphorus skeleton are believed to affect the position of the ring–polymer equilibrium.[167,446] The conversion of a cyclic trimer or tetramer to a linear polymer has the effect of shortening the intramolecular distances between the side groups on nearby phosphorus atoms and between side groups and nearby chain atoms (Figure 10). If the substituent groups are small, such as fluoro, chloro, or bromo, these reduced intramolecular distances will not lead to significantly larger intramolecular repulsions in the polymer than in the cyclic species. But, if bulky substituents are present, conversion of a cyclic phosphazene to a linear polymer will result in a marked increase in intramolecular repulsions. The polymer will, therefore, be thermodynamically destabilized relative to the trimer or tetramer and, statistically also, rings will be favored over chains. The overall consequence is that cyclic trimers or tetramers with bulky substituent groups cannot be polymerized, whereas high polymers with the same side groups, synthesized by other techniques, should depolymerize to cyclic oligomers at moderate temperatures. This agrees with the experimental facts known at the present time. The apparently anomalous polymerization of tris(*o*-phenylenedioxy)cyclotriphosphazene (**135**) is no exception to this principle since this is one of the few compounds in which the substituent structure is "pinned back" by the exocyclic ring and which does not, therefore, suffer steric hindrance during phosphazene ring cleavage.

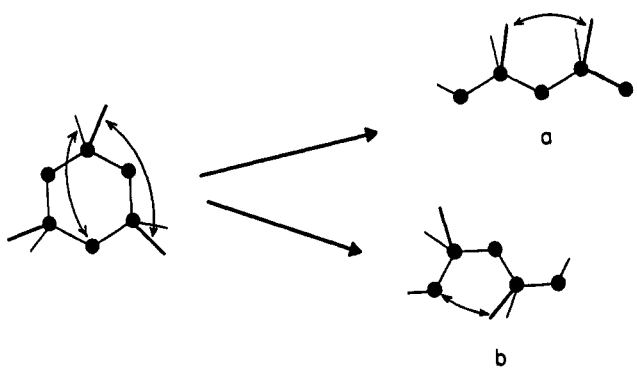


Figure 10. Influence of polymerization on nonbonding intramolecular distances.

C. SYNTHESIS OF OPEN-CHAIN POLY(ORGANOPHOSPHAZENES)

1. *General Synthesis Route*

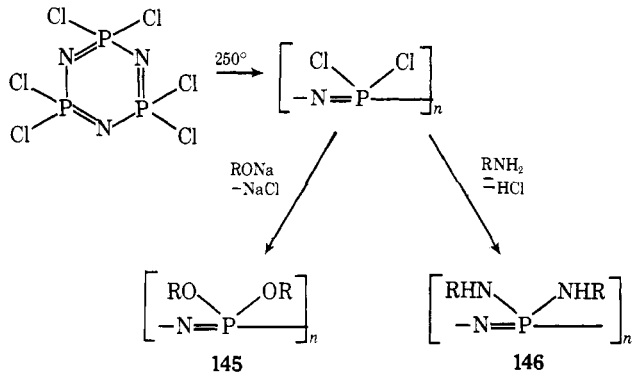
Interest in the synthesis of high molecular weight poly(organophosphazenes) has developed from the knowledge that the elastomeric poly(dichlorophosphazene), $(NPCl_2)_n$, has no practical value because of the hydrolytic instability of the phosphorus–chlorine bonds. Replacement of the halogen atoms by nonhydrolyzable organic groups was expected to give rise to an unusual new series of water-stable polymers. These predictions have been largely fulfilled.

Because organocyclophosphazenes cannot generally be polymerized, and because most direct synthesis routes (see section III) yield cyclic oligomers rather than high polymers, an alternative synthesis scheme for the high polymers has been developed.[75,102,245,447] This process requires the polymerization of hexachlorocyclotriphosphazene to uncrosslinked poly(dichlorophosphazene) followed by nucleophilic replacement of the halogen atoms in the polymer by organic units. Typically, alkoxide or aryloxide ions or primary or secondary amines can be used as the nucleophiles (**145** and **146**). It is important to note that the earliest attempts to achieve such syntheses yielded unstable materials because crosslinked poly(dichlorophosphazene) was used as a substrate, and total halogen replacement was not effected.[448-451] The more recent work has yielded chlorine-free polymers which show a variety of unusual and useful properties.[75,102,167,245,447]

2. *Synthesis of Poly(alkoxy- and aryloxyphosphazenes)*

Alkoxides and aryloxides react with poly(dichlorophosphazene) in organic media (tetrahydrofuran, benzene, toluene etc.) to yield poly(alkoxy- and aryloxyphosphazenes), $[NP(OR)_2]_n$.[74,245] In practice, hexachlorocyclotriphosphazene is allowed to polymerize at 250° until a mixture of ~70% high

(438) V. V. Korshak, I. A. Gribova, T. V. Artamonova, and A. N. Bushmarina, *Vysokomol. Soedin.*, 2, 377 (1960).
(439) H. Bode and R. Thamer, *Chem. Ber.*, 76B, 121 (1943).
(440) A. V. Tobolsky and A. Eisenberg, *J. Amer. Chem. Soc.*, 82, 289 (1960).
(441) A. V. Tobolsky, "Properties and Structure of Polymers," Wiley, New York, N. Y. (1960).
(442) G. Gee, *Chem. Soc., Spec. Publ.*, No. 15, 67 (1961).
(443) H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, 18, 1600 (1950).
(444) J. R. Van Wazer, *J. Macromol. Sci., Part A-1*, 29 (1967).
(445) K. Moedritzer, *Organometal. Chem. Rev.*, 2, 1 (1967).
(446) H. R. Allcock, *J. Macromol. Sci., Rev. Macromol. Chem.*, 4, 3 (1970).
(447) H. R. Allcock and D. P. Mack, *Chem. Commun.*, 685 (1970).
(448) G. Goldschmidt and B. Dishon, *J. Polym. Sci.*, 3, 481 (1948).
(449) M. V. Lenton, B. Lewis, and C. A. Pearce, *Chem. Ind. (London)*, 1387 (1964).
(450) M. E. Mirhej and J. F. Henderson, *J. Macromol. Chem.*, 1, 187 (1966).
(451) R. L. Evans, U. S. Patent 3,271,330 (1966) (to 3M Company).

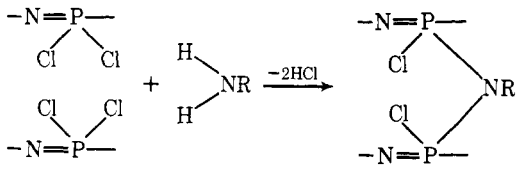


145 146

polymer and ~30% cyclic oligomers is formed. Further polymerization frequently leads to crosslinking. Either the total mixture can be dissolved in a solvent and subjected to substitution, followed by subsequent removal of the substituted cyclic compounds, or the $(NPCl_2)_n$ high polymer can be separated first, and then allowed to react with the nucleophile. Using these techniques, polymers have been prepared which contain the following substituent groups: OCH_3,[75,245] OC_2H_5,[75,245] OCH_2CF_3,[75,245] $OCH_2C_2F_5$,[100] $OCH_2C_3F_7$,[75,100] $OCH_2CF_2CF_2H$,[100,452] OC_6H_5,[75,245] $OC_6H_4CF_3$-*m*,[434,453] OC_6H_4Cl-*p*,[434,453] OC_6H_4F-*p*,[434,453] $OC_6H_3Cl_2$-2,4,[434,453] $OC_6H_4C_6H_5$-*p*.[434,453] The use of two nucleophiles in the reaction mixture allows copolymers such as $[NP(OCH_2CF_3)(OCH_2C_3F_7)]_n$ and $[NP(OCH_2CF_2CF_2H)(OCH_2C_6F_{12}H)]_n$ to be prepared.[252,452] The properties of these materials will be reviewed in section V.D.

3. *Synthesis of Poly(aminophosphazenes)*

The reactions between chlorocyclophosphazenes and primary or secondary amines were reviewed earlier in section IV.A. Similar reactions take place between amines and poly(dichlorophosphazene) but with several important differences. With primary amines, such as methylamine, ethylamine, *n*-propylamine, *n*-butylamine, or aniline as reagents, total replacement of chlorine occurs to give poly(bisaminophosphazenes) by the route shown in the formation of **146**.[97,102,447] However, an alternative reaction is possible with methylamine or ammonia which leads to crosslinking of the chains to form **147**.[102] Methylamine functions as a crosslinking re-



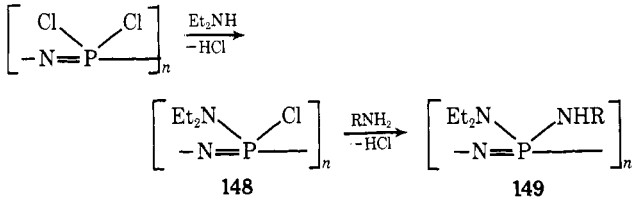
147

agent at room temperature or above and ammonia crosslinks the chains even at low temperatures.[97] Primary amines with bulkier alkyl or aryl groups do not participate in this reaction, and it appears that crosslinking is inhibited by steric hindrance in the amine. However, excessive steric hindrance, as in isopropylamine, prevents total replacement of the halogen. This sensitivity of the reaction to steric factors is consistent with an SN2-type process.[97]

With secondary amines, steric inhibition of the bis-substitution reaction is more serious. Total replacement of halogen takes place with dimethylamine, piperidine, and pyrrolidine by the reaction[97,102,447]

$$(NPCl_2)_n + 4nHNR_2 \longrightarrow [NP(NR_2)_2]_n + 2nR_2NH\cdot HCl$$

but incomplete substitution only occurs with diethylamine, or *N*-methylaniline, and no evidence of any substitution was found with diphenylamine. Diethylamine replaces approximately one-half of the total chlorine to yield a nongeminal chlorodiethylamino derivative (**148**), and this compound can be used as a precursor for the synthesis of copolymers (**149**).[44]



148 149

Use of this technique has permitted the synthesis of copolymers of formula **149** in which NHR is NH_2, NHMe, NHEt, NHPr^n, and NHBu^n. Aminofluoroalkoxy copolymers, such as $[NP(NEt_2)(OCH_2CF_3)]_n$, have also been prepared, and terpolymers containing diethylamino, trifluoroethoxy, and methylamino groups can be synthesized.[447]

4. *Synthesis of Poly(alkyl- and arylphosphazenes)*

Several attempts have been made to prepare poly(alkyl- and arylphosphazenes) by substitution and direct synthesis routes, but evidence is lacking that *high molecular weight* compounds of formula, $(NPR_2)_n$, have yet been synthesized. In general, direct synthesis routes yield low or medium molecular weight polymers, while the interaction of organometallic reagents with poly(dichlorophosphazene) usually gives incompletely substituted or degraded products.

Pyrolysis of dimethyldiaminophosphonium chloride yields a polymer of formula $(NPMe_2)_n$, in which $n \approx 120$.[226] Poly[bis(trifluoromethyl)phosphazene] of unknown molecular weight is prepared by denitrogenation of bis(trifluoromethyl)azidophosphine[214] or by the dehydrohalogenation of bis(trifluoromethyl)dichlorophosphonic amide[101] (see sections III.C and III.D), and the thermal decomposition of phenylchloroazidophosphine yields the polymer, $(NPClPh)_n$, where $n \approx 31$.[215] Poly(dichlorophosphazene) reacts with phenyllithium to give a phenylphosphazene polymer, but the elemental composition differs from that expected.[454]

D. PROPERTIES OF OPEN-CHAIN POLYPHOSPHAZENES

1. *Physical Properties and Transitions*

The physical properties of open-chain polymers can generally be summarized in terms of a glass transition temperature (T_g) and crystalline melting temperatures (T_m). Below the T_g, a polymer will exist as a rigid glass. Above this temperature, if the polymer is amorphous, it will be a rubbery elastomer which slowly liquifies to a gum as the temperature is raised. If the polymer is crystalline, the T_g may represent a change from a

(452) S. H. Rose, J. Cable, and K. A. Reynard U. S. Army Materials and Mechanics Research Report, AD 693-289, 1969; AD 704-332, AD 720-215, 1970; AD 734-347, 1971.

(453) G. Allen, C. L. Lewis, and S. M. Todd, *Polymer*, **11**, 44 (1970).

(454) J. R. MacCallum and J. Tanner, *J. Polym. Sci., Part A-1*, **6**, 3163 (1968).

Table X

Physical Characteristics of Polyphosphazenes

Compound	T_g °C	T_m °C	*Physical form at 25°*	*Solvent*	*Ref*
$(NPF_2)_n$	−96	−68, −40	Elastomer		45, 46
$(NPCl_2)_n$	−63	−30	Elastomer	Benzene	75
$(NPBr_2)_n$	−15	270	Rubbery thermoplastic		45
$[NP(NCS)_2]_n$			Elastomer		45
$[NP(OMe)_2]_n$	−76		Elastomer	Methanol	75, 245
$[NP(OEt)_2]_n$	−84		Elastomer	Alcohols	75, 245
$[NP(OCH_2CF_3)_2]_n$	−66	242	Flexible thermoplastic	Acetone	75, 245
$[NP(OCH_2C_2F_5)_2]_n$	(−25)		Flexible thermoplastic	Ethyl trifluoroacetate	100, 423
$[NP(OCH_2CF_2CF_2H)_2]_n$			Flexible thermoplastic	THF	100, 423
$[NP(OCH_2C_3H_7)_2]_n$	(14)		Thermoplastic	Fluorocarbons	100, 423
$[NP(OCH_2CF_3)(OCH_2C_3F_7)]_n$	−77		Elastomer	$C_2F_3Cl_3$–acetone	252, 452
$[NP(OCH_2(CF_2)_6CF_3)_2]_n$	−40				434, 453
$[NP(OCH_2C_2F_5)(OCH_2C_3F_7)]_n$			Flexible thermoplastic		452
$[NP(OCH_2CF_2CF_2H)(OCH_2C_6F_{12}H)]_n$	−60		Elastomer	$C_2F_3Cl_3$–acetone	452
$[NP(OPh)_2]_n$	−8		Flexible thermoplastic	Benzene	75, 245
$[NP(OC_6H_4F\text{-}p)_2]_n$	−14			THF	434, 453
$[NP(OC_6H_4CF_3\text{-}m)_2]_n$	−35	330		THF	434, 453
$[NP(OC_6H_4Cl\text{-}p)_2]_n$	−12	>350	Flexible thermoplastic	THF	434, 453
$[NP(OC_6H_3Cl_2\text{-}2,4)_2]_n$	2	210		THF	434, 453
$[NP(OC_6H_4C_6H_5\text{-}p)_2]_n$	43	>350		DMF	434, 453
$[NP(NHMe)_2]_n$	14		Flexible thermoplastic	Water	97
$[NP(NHEt)_2]_n$	30		Thermoplastic	Aqueous acid	102
$(NP(NHPr^n)_2]_n$	−92		Flexible thermoplastic	Trifluoroethanol	97
$[NP(NHBu^n)_2]_n$			Flexible thermoplastic	Trifluoroethanol	423
$[NP(NHPh)_2]_n$	91		Brittle glass	Benzene	102
$[NP(NMe_2)_2]_n$	−4		Flexible thermoplastic	Aqueous acid	102
$[NP(NC_5H_{10})_2]_n$	19		Flexible thermoplastic	Benzene	102
$[NP(NEt_2)Cl]_n$			Elastomer	Benzene	447
$[NP(NEt_2)(NH_2)]_n$			Glass	THF	447
$[NP(NEt_2)(NHMe)]_n$	−106		Flexible thermoplastic	THF	447
$(NP(NEt_2)(NHEt)]_n$	−100		Flexible thermoplastic	Benzene	447
$[NP(NEt_2)(NHPr^n)]_n$	<−120		Flexible thermoplastic	Benzene	447
$[NP(NEt_2)(NHBu^n)]_n$	<−120		Flexible thermoplastic	Benzene	447

glass to a flexible thermoplastic. As the temperature is raised, melting of the thermoplastic occurs sharply at T_m to give an elastomer or a liquid. Thus, whether a polymer is a glass, elastomer, thermoplastic, or gum at room temperature depends on the position of T_g and T_m on the temperature scale. Low T_g values generally reflect a high torsional mobility of the backbone.

Table X lists T_g and T_m values for a number of polyphosphazenes, together with their physical form at 25° and solubility. The molecular weights of these poly(organophosphazenes) depend, of course, on the degree of polymerization of the precursor poly(dichlorophosphazene) used for their synthesis. Light scattering molecular weight measurements suggest that the chain lengths of these polymers are often in excess of 15,000 repeating units.[75, 455] However, poly(aminophosphazenes) often show lower degrees of polymerization, in the range of 1000–5000 repeating units.

2. Thermal Behavior

As discussed earlier, in section V.B, polyphosphazenes are prone to depolymerize to cyclic oligomers at elevated temperatures. This fact places an upper limit on the thermal stability of many uncompounded polymers. A variety of methods have been used to study the high-temperature thermal behavior of polyphosphazenes. Of these, thermogravimetric analysis is at once the most convenient and the least reliable method. For most of these polymers, a plot of weight loss against temperature simply identifies the boiling points of the oligomers formed by depolymerization at lower temperatures. Studies of the change in molecular weight distribution with time at different temperatures provides the most satisfactory analysis of thermal behavior. In these terms, it can be shown that, whereas poly(dichlorophosphazene) is stable at least up to 350° at atmospheric pressure, poly[bis(trifluoroethoxy)-phosphazene] and poly[bis(phenoxy)phosphazene] undergo depolymerization in the solid state between 150 and 200°. However, at these temperatures, an equilibrium is established between oligomers and high polymer in such a way that the solids retain most of their thermoplastic physical properties.[75, 423] Only when the oligomers are removed continuously under vacuum at elevated temperature does the polymer lose its physical integrity. Polymeric methoxy-, ethoxy-, and many aminophosphazenes appear to decompose thermally by fragmentation reactions rather than by depolymerization.[75] Some evidence exists that fragmentation reactions also account for the breakdown of trifluoroethoxy-, phenoxy-, and phenylphosphazene polymers at temperatures above 400°.[428] The mechanisms of these high-temperature fragmentation reactions are not fully understood.

It should be noted that the thermal stability of a "raw"

(455) G. L. Hagnauer, N. S. Schneider, and R. E. Singler, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **12**, 525 (1971); G. L. Hagnauer and N. S. Schneider, *J. Polym. Sci. Part A-2*, **10**, 699 (1972).

polymer often bears little resemblance to that of the same material when compounded for specific applications. In these terms it is reasonable to anticipate the development of polyphosphazene compositions with prolonged useful stabilities above 200°.

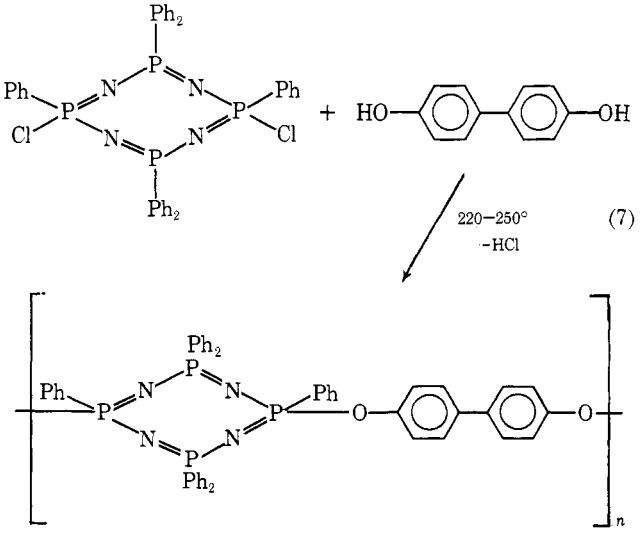
3. *Special Properties of Open-Chain Poly(organophosphazenes)*

One of the unusual features displayed by several poly(organophosphazenes) is their low-temperature flexibility and elasticity. For example, poly[bis(ethoxy)phosphazene], $[NP(OEt)_2]_n$, is elastomeric at temperatures near −84°. The copolymer, $[NP(OCH_2CF_3)(OCH_2C_3F_7)]_n$, is elastomeric at temperatures above −77°. The polymer, $[NP(OCH_2CF_3)_2]_n$, remains flexible at −60°. Few unplasticized organic backbone polymers have these properties, and polyphosphazenes may be useful as low temperature wire insulators, seals, and fuel lines for arctic environments. This latter application seems particularly promising for poly(fluoroalkoxyphosphazenes) which are especially resistant to liquid hydrocarbons.

Poly(fluoroalkoxyphosphazenes) are also useful as water and soil-repellent agents for the treatment of textiles.[456] The same polymers are transparent to visible and ultraviolet light down to wavelengths near 220 mμ and are unaffected by long exposure to ultraviolet irradiation. This property suggests that the polymers may prove useful for outdoor surface coating applications. Finally, the hydrophilicity of specific aminophosphazene polymers may prove useful in biomedical applications.

E. CYCLOLINEAR POLYMERS

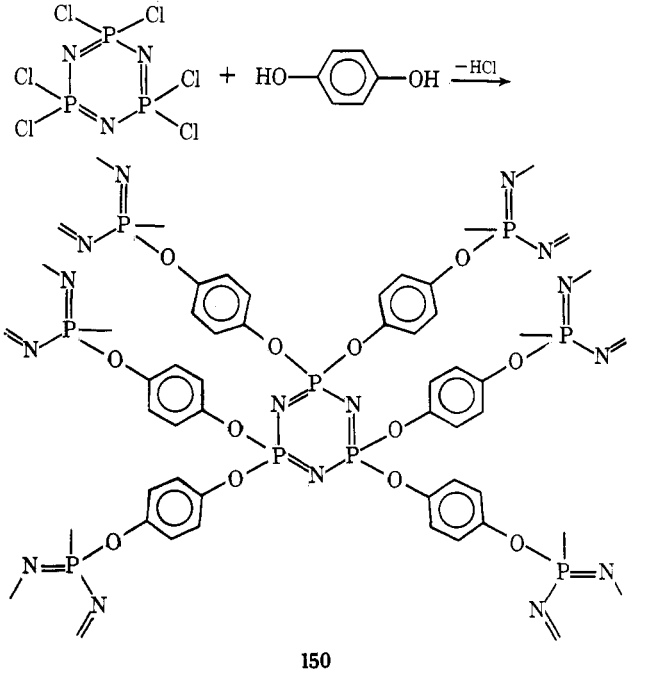
A variety of different reactions have been utilized to link phosphazene ring systems together to form cyclolinear polymers, and a substantial number of patent claims have appeared in this area. In principle, any reaction which has been used to effect substitution at a phosphazene ring can be applied to the synthesis of a cyclolinear polymer. The main requirements are the presence of only two reactive sites on the phosphazene ring to ensure that crosslinking does not occur and the use of a difunctional reagent. For example, the interaction of 1,5-dichloro-1,3,3,5,6,6-hexaphenylcyclotetraphosphazene with 4,4′-dihydroxybiphenyl leads to polymer formation by the process[457] in eq 7. The molecular weight of the product is near 500,000. Other processes which lead to polymer formation include the reactions of hydroxyphosphazenes with diphenyldichlorosilane,[458] the condensation of diaminophosphazenes with diols,[251] transesterifications between alkoxyphosphazenes and aromatic diols,[459] and reactions between bisazidophosphazenes and diphosphines.[460] Polymers made by these methods range from elastomers to glasses according to the flexibility of the linkage groups.



(7)

F. CYCLOMATRIX POLYMERS

Much of the work discussed elsewhere in this review illustrates the inherent stability of the cyclotriphosphazene ring. Attempts have been made to utilize this stability by incorporation of the ring into three-dimensional crosslinked polymers. The fully crosslinked polymers so formed are usually rigid, high-melting, resinous compositions which have good stability at high temperatures. Uses for these materials as wire enamels and surface coatings have been proposed. Typical of these compositions are the polymers formed by the interaction of hexachlorocyclotriphosphazene with aromatic diols (**150**).[461–465]



150

(456) American Cyanamid Co., Netherlands Patent Appl., 6,512,493 (1966); *Chem. Abstr.*, **65**, 3997b (1966).

(457) A. J. Bilbo, C. M. Douglas, N. R. Fetter, and D. L. Herring, *J. Polym. Sci., Part A-1*, **6**, 1671 (1968).

(458) S. I. Belkyh, S. M. Zhivukhin, V. V. Kireyev, and H. S. Kolesnikov, *Vysokomol. Soedin., Ser. A*, **11**, 625 (1969).

(459) S. M. Zhivukhin, V. B. Tolstoguzov, and F. J. Yakobson, *Vysokomol. Soedin.*, **8**, 727 (1966).

(460) A. J. Bilbo and C. M. Sharts, *J. Polym. Sci., Part A-1*, **5**, 2891 (1967).

(461) C. A. Redfarn, U. S. Patent 2,866,773 (1958) (to Walker Extract and Chemical Co.).

(462) R. G. Rice, B. H. Geib, and L. A. Kaplan, U. S. Patent 3,121,704 (1964) (to General Dynamics Corp.).

(463) S. M. Zhivukhin, B. V. Tolstoguzov, and V. V. Kireev, *Sov. Plast.*, 24 (1963).

(464) S. M. Zhivukhin, V. V. Kireev, and A. N. Zelenskii, *Zh. Prikl. Khim. (Leningrad)*, **39**, 234 (1966).

(465) M. Yokoyama, H. Cho, and K. Kono, *Kogyo Kagaku Zasshi*, **67**, 1378 (1964).

Cyclomatrix polymers are also formed when the aminophenylcyclophosphazene, $[NP(NH_2)Ph]_3$, is pyrolyzed,[466] when hexachlorocyclotriphosphazene reacts with hexaethyldisiloxane,[467] and by transesterification reactions.[468] Methylolated aminophosphazenes crosslink when heated,[469] and allyloxy- and allylaminocyclophosphazenes form crosslinked resins when heated with free radical catalysts.[359, 470]

VI. Applications of Phosphazenes

A substantial part of the current research effort in phosphazene chemistry involves a search for uses for the many derivatives now known. As discussed in the foregoing sections, the incorporation of phosphazenes into polymeric compositions is one of the most active areas in this field. Other research has been directed to the study of ethyleniminocyclophosphazenes as chemosterilant insecticides[471] and as cancer chemotherapeutic agents.[472] Hexakis(amino)cyclotriphosphazene has been proposed as a high capacity fertilizer.[473] Alkoxyphosphazenes have proved to be valuable as flame retardants for textiles.[474] Hexabromocyclotriphosphazene is used as a "getter" and bromine source in halogen lamps,[475] and the investigation of phosphazene clathrates as substrates for the separation of organic compounds continues. At the present time, the technological opportunities in phosphazene chemistry appear to be expanding, and this field remains a fertile area for both fundamental and applied research.

(466) W. R. Grace & Co., British Patent 981,821 (1965).
(467) S. M. Zhivukhin, V. B. Tolstoguzov, and A. I. Ivanov, *Russ. J. Inorg. Chem.*, 7, 1134 (1962).
(468) M. Apley and J. R. Alexander, U. S. Patent, 3,164,556 (1965) (to Walker Chemical Co.).
(469) R. J. Irving and J. Dewing, British Patent 903,046 (1962) (to Imperial Chemical Industries).
(470) H. R. Allcock, P. S. Forgione, and K. J. Valan, *J. Org. Chem.*, **30**, 947 (1965).
(471) R. Rätz, E. Kober, C. Grundmann, and G. Ottmann, *Inorg. Chem.*, **3**, 757 (1964).
(472) V. A. Chernov, V. B. Lytkina, S. I. Sergievskaya, A. A. Kropacheva, V. A. Parshina, and L. E. Sventsitkaya, *Farmakol. Toksikol. (Moscow)*, **22**, 365 (1959); *Chem. Abstr.*, **54**, 7900 (1960).
(473) Z. T. Wakefield, B. B. Luff, and J. J. Kohler, *J. Chem. Eng. Data*, **15**, 314 (1970).
(474) L. E. A. Godfrey and J. W. Schappel, *Ind. Eng. Chem., Prod. Res. Develop.*, **9**, 426 (1970).
(475) J. M. Rees, *Lighting Res. Technol.*, **2**, 257 (1970).