factors that most affect shielding and thus chemical shift are oxidation state, coordination symmetry, and ligand substitution.[34] Since our comparisons are among atoms of the same oxidation state (-1 for metal bound; 0 for ring; -2 for "terminal" or "bridging") and the coordination symmetry of these Se atoms is low, the largest contribution may arise from ligand substitution. Although it is a reversal of customary coordination chemistry to regard metals as ligands, for the ^{77}Se NMR chemical shifts it is the effect of metals as ligands that seems to have the greatest contribution.

Note Added in Proof. New syntheses and some crystal structures have been reported for $[PPh_4]_2[M(Se_4)_2]$, M = Mn,[35] Pd,[36] and Pt.[36] Huang et al.[37] have synthesized and determined the crystal structure of $[PPh_4]_3[Sn(Se_4)_3]$, whose synthesis and structure were reported earlier.[38] Huang et al.[37] also provide ^{77}Se NMR data for $M(Se_4)_2^{2-}$ species, M = Zn, Cd, Hg, and Ni. The resonances they report are about 10 ppm downfield from those reported here. Their assignment of resonances to ring and metal-bound Se centers in M = Zn, Cd, and Hg is opposite to our assignment reported here. They report no coupling data.

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Supplementary Material Available: Additional crystallographic details (Table SI) and anisotropic thermal parameters for the Ni structure (Table SII) (2 pages); observed and calculated structure amplitudes (×10) for the Ni (Table SIII) and Zn (Table SIV) structures (51 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Ring Expansion and Equilibration in Organophosphazenes and the Relationship to Polymerization

Harry R. Allcock,* Gayann S. McDonnell, and James L. Desorcie

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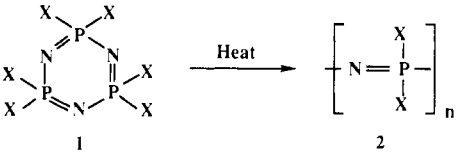
A series of cyclic trimeric phosphazenes that bear both halogen and organic side groups have been found to undergo ring expansion-equilibration reactions at elevated temperatures. Compounds $N_3P_3F_5CMe_3$, $N_3P_3F_5Ph$, *non-gem*-$N_3P_3F_4(CMe_3)_2$, $N_3P_3F_4Ph_2$, $N_3P_3Cl_4Me_2$, $N_3P_3Cl_4Et_2$, $N_3P_3Cl_3Me_3$, and $N_3P_3Cl_3Et_3$ yield cyclic tetramers, pentamers, hexamers, and, in some cases, heptamers, octamers, and nonamers when heated. The cyclic tetramers $(NPClMe)_4$ and $(NPClEt)_4$ also equilibrate to a range of cyclic species that range from trimer to hexamer. Several of these equilibrations also lead to the formation of high polymers. The results are discussed in terms of possible mechanisms for ring-ring equilibration and polymerization.

It is known that certain cyclophosphazenes such as $(NPF_2)_3$ or $(NPCl_2)_3$ (**1**) polymerize to high polymers (**2**) when heated at temperatures between 250 and 350 °C (Scheme I). This is the starting point for the synthesis of a wide range of stable and useful organophosphazene high polymers.[1-7] On the other hand, cyclophosphazenes such as $(NPMe_2)_3$, $(NPPh_2)_3$, or $[NP(OCH_2CF_3)_2]_3$ (**3**)[8-11] undergo thermal ring-expansion reactions but do not give high polymers (Scheme II). This is a mechanistic anomaly that has an important bearing on attempts to synthesize new classes of phosphazene high polymers.

In the present work, we have selected a number of cyclophosphazenes that occupy an intermediate position: they contain both halogeno and organic side groups. When heated they can yield both small-molecule ring expansion products *and* high polymers. Seemingly minor changes within these structures can tip the balance in favor of either of the two extremes. By studying such systems, we hoped to understand the relationship between side group structure in polyphosphazenes and their ability to polymerize.

Scheme I



1 2

X = F or Cl n ~ 15,000

The compounds studied are shown as **7-16**. These were synthesized by methods described previously.[10,12-16] The high polymers obtained from these cyclophosphazenes have been described in another paper.[17] Here we discuss the macromolecules only with respect to their coexistence with the ring-ring equilibration products. Thus, the focus of this paper is on the small-molecule reaction products and on the relationship between the mechanisms of ring-ring equilibration and polymerization. This topic is of practical importance for three reasons. First, it is related to the choice of monomers for conversion to high polymers. Second, it provides information that may allow an understanding of the high-temperature thermal stabilities of phosphazene high

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(18) It was recognized that a potential error in the analysis was the possible equilibration of chloro- or fluorophosphazene small molecules in the mass spectrometer. However, no evidence was found for equilibration when pure trimers or tetramers, **7-16**, were injected into the instrument as controls.

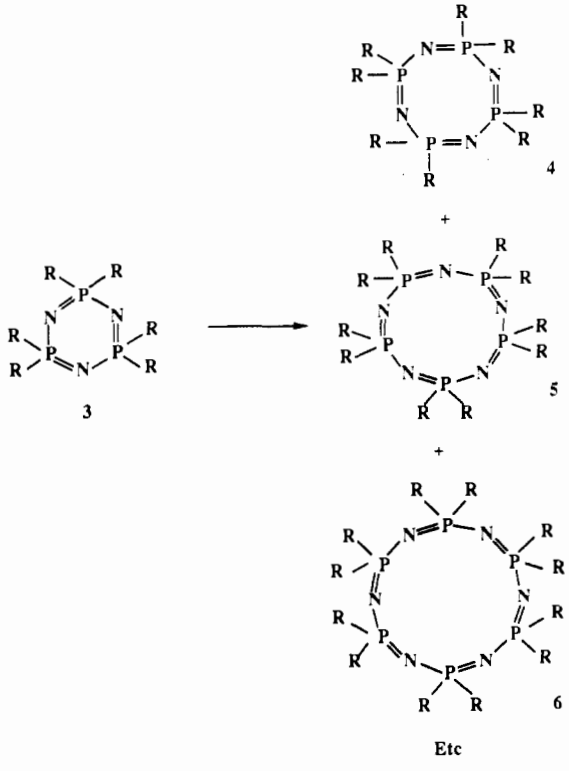
0020-1669/90/1329-3839$02.50/0

Table I. Polymerization and Ring Expansion Reactions of Cyclotriphosphazenes **7–12**

	starting trimers					
	7	**8**	**9**	**10**	**11**	**12**
temp, °C	300	300	300	300	250	250
time	4–6 days	4–6 days	14 days	14 days	6–50 h	6–50 h
yield of polymer, %	49	59	0	0	46	42
yield of oligomers, %	15	13	100	100	30	23
	Detected Oligomers[a]					
$N_3P_3X_5R$	<10	<10	<10	<10	<10	<10
$N_3P_3X_4R_2$	<10	<10	*10–19*	<10	40–49	20–29
$(NPXR)_3$	<10	<10	10–19	<10	<10	10–19
$N_4P_4X_7R$	<10	10–19	<10	<10		<10
$N_4P_4X_6R_2$	30–39	<10	20–29	<10	<10	10–19
$N_4P_4X_5R_3$	<10	<10	30–39	30–39	<10	20–29
$(NPXR)_4$			<10	<10	<10	<10
$N_5P_5X_9R$	<10	<10	<10	<10		
$N_5P_5X_8R_2$	<10	<10	<10	<10	<10	<10
$N_5P_5X_7R_3$	<10	<10	<10	<10	<10	<10
$N_5P_5X_6R_4$			<10	<10	<10	<10
$(NPXR)_5$			<10		<10	<10
$N_6P_6X_{11}R$	20–29	<10	<10	<10		
$N_6P_6X_{10}R_2$	<10	<10	<10	<10		
$N_6P_6X_9R_3$	<10	<10	<10			
$N_6P_6X_8R_4$				<10		
$N_7P_7X_{13}R$		<10				
$N_7P_7X_{12}R_2$	<10	<10	<10			
$N_7P_7X_{11}R_3$		<10				
$N_8P_8X_{15}R$		<10				
$N_8P_8X_{14}R_2$		<10				

[a] X = fluorine or chlorine.

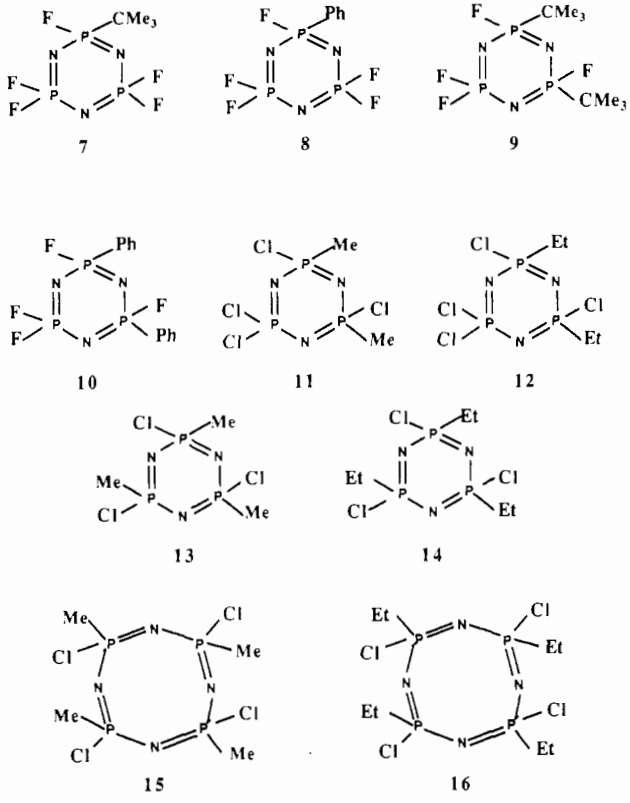
Scheme II



polymers. Third, the ring expansion reactions provide a route to cyclic phosphazenes that are at present inaccessible by any other method.

Results and Discussion

Method of Study. Multiple samples of each compound **7–16** were heated at temperatures in the range of *210–300* °C in evacuated sealed tubes for periods of time that ranged from 1 h to 30 days. When high polymers were formed, the viscosity of



the molten mixtures increased significantly. Otherwise the contents of the heated tubes remained fluid.

The main experimental problem in this work was to identify the various cyclic phosphazenes formed by ring–ring equilibration. An obvious technique, the use of ^{31}P NMR spectroscopy, could not be used to analyze all the mixtures because the chemical shifts were indistinguishable once the ring size exceeded five or six repeating units. However, cyclic trimers could be distinguished from tetramers, and the ^{31}P NMR spectra of these species were used to provide confirmatory evidence. The NMR spectra did not allow information to be obtained about cis–trans configurational changes during ring expansion or polymerization.

Vapor-phase chromatography/mass spectrometry (VPC/MS) proved to be the most useful method of analysis. Two different approaches were employed. In the first, the cyclic oligomers formed by equilibration were solvent extracted from any high polymer present and were then subjected to VPC/MS analysis. The separation from the high polymer was necessary because of the extreme tendency of the polymer to cross-link when exposed to atmospheric moisture[17] and the possibility that any high polymer present would depolymerize in the VPC inlet and thus distort the analysis. However, this approach made it exceedingly difficult to compare the yields of cyclic oligomers and high polymer. The alternative approach involved an intermediate step to replace the halogen atoms in the equilibrated molecules by trifluoroethoxy groups, separation of the derivative cyclic oligomers from the high polymer, and analysis of the cyclic oligomers by VPC/MS techniques. This method had serious limitations because of the relatively high molecular weights of the trifluoroethoxy-substituted oligomeric products, which complicated both the VPC separations and the MS analysis. The only cases in which the oligomer ratios could be monitored by VPC/MS analysis of both the chloro- and trifluoroethoxy derivatives was for the products derived from **13–16** where only one type of repeating unit was incorporated into the products. In these cases a clean VPC separation and an accurate MS analysis of the trifluoroethoxy derivatives were possible.

In all these equilibration reactions, the total percentages of recovered cyclic oligomers and high polymers rarely exceeded 75% and, in a few experiments, was as low as 46%. This was attributed to losses incurred during extraction and recovery of the products and, in specific cases where long reaction times were employed, to side reactions that consumed equilibration products by cross-

Table II. Polymerization and Ring Expansion and Contraction Reactions of Cyclophosphazenes **13–15**

	starting material								
	13	**13**	**13**	**13**	**14**	**14**	**15**	**15**	**15**
temp, °C	210	250	250	250	210	250	210	250	250
time	6–7 days	1 h	4–20 h	20 days	25 days	25 days	15 days	25 h	20 days
yield of polymer, %	9	6	31	32	0	0	18	25	32
yield of oligomers, %	68	68	44	16	91	95	52	42	14
	Detected Oligomers[a,b]								
$(NPXR)_3$	51	53	45	10	93	21	10	14	12
$(NPXR)_4$	20	17	40	77	2	69	82	76	75
$(NPXR)_5$	4	4	5	10	1	9	6	8	10
$(NPXR)_6$	22	23	10	3	4	1	2	2	3
$(NPXR)_7$	3	3							

[a] Percentages based on monomer units. [b] X = OCH_2CF_3.

linking or side group transformations. Thus, the ratios of total cyclic oligomers to high polymers are less meaningful than the relative ratios of the various cyclic oligomers in the reaction mixtures. These values were reasonably reproducible and reflect the relative stabilities of the various cyclic phosphazenes in the equilibrate. However, the experimental difficulties were such that we prefer to compare most of the product ratios in terms of concentration zones—for example, "detected but <10%, 10–19%, 20–29%," etc.—rather than by drawing finer distinctions.

An exception is the case of products derived from $(NPClR)_{3\text{ or }4}$ where more precision was possible. Only one type of monomer unit is present in these systems, and this results in a considerable improvement in chromatographic resolution. As a result, relative concentrations could be estimated without the need to consider detector response factors.[19] In addition, cross-correlation was possible between chromatographic data for the chloro- and trifluoroethoxy derivatives. Authentic samples of specific trifluoroethoxy-substituted cyclic trimers were easily prepared as controls via the reactions of **13–16** with sodium trifluoroethoxide. For these reasons, most of the mechanistic and thermodynamic arguments in this paper are based on these data.

General Behavior of Compounds 7–16. Compounds **7**, **8**, **11–13**, and **15** underwent both ring expansion and polymerization reactions when heated. Species **9**, **10**, **14**, and **16** yielded mainly small-molecule ring expansion (or contraction) products. No high polymers were formed. The reaction conditions employed and the relative yields of cyclic oligomers and high polymers are listed in Tables I and II.

The presence of one bulky organic side group per trimeric ring, together with five fluorine atoms (**7** or **8**), allows ring expansion reactions to occur, together with 50% conversion to high polymers. This is similar to results obtained earlier for a number of cyclotriphosphazenes with one organic group and five chlorine atoms per ring.[20-24] However, when *two tert*-butyl or phenyl groups are present at different phosphorus atoms (non-geminal), together with four fluorine atoms (**9** or **10**), high polymer formation is eliminated in favor of small-molecule ring-expansion products. This effect was not detected if two *non-gem*-methyl or ethyl groups are present, together with four chlorine atoms (**11** or **12**). A third *non-gem*-methyl group (**13**) allows both polymerization and ring expansion, but a third ethyl group (**14**) blocks polymerization in favor of ring expansion. A similar effect is seen in the cyclic tetrameric series (**15** and **16**). One methyl group on every phosphorus allows both ring–ring equilibration and polymerization, but one ethyl group per phosphorus inhibits polymerization. These results illustrate the powerful role played by the organic side groups in directing the reaction pathway in one direction or another.

In the following sections the ring–ring equilibrations will be discussed according to the structural type of the starting material. Reactions that originate from species with one organic group and five fluorine atoms per trimer ring will be described first. These will be followed by systems that contain progressively higher ratios of organic to halogen side groups. A summary of the data is given in Tables I and II.

Behavior of Systems with One Organic Unit Per Ring. In the following discussion, the numbers in parentheses represent the percentage of different cyclic phosphazenes in the oligomeric component detected by VPC/MS.

First, when compound **7** was heated at 300 °C for 4–6 days, an extensive redistribution of repeating units occurred to give different cyclic trimers, tetramers, pentamers, hexamers, and at least one cyclic heptamer. A total of 13 species were detected of which the starting material comprised less than 10% of the small-molecule mixture. The products can be understood in terms of a redistribution of NPF_2 and $NPFCMe_3$ units between the products. The principal products were $N_4P_4F_6(CMe_3)_2$ (30–39%) and $N_6P_6F_{11}CMe_3$ (20–29%), together with $N_3P_3F_5CMe_3$, $N_3P_3F_4(CMe_3)_2$, $N_3P_3F_3(CMe_3)_3$, $N_4P_4F_7CMe_3$, $N_4P_4F_5(CMe_3)_3$, $N_5P_5F_9CMe_3$, $N_5P_5F_8(CMe_3)_2$, $N_5P_5F_7(CMe)_3$, $N_6P_6F_{10}(CMe_3)_2$, $N_6P_6F_9(CMe_3)_3$, and $N_7P_7F_{12}(CMe_3)_2$, each present at a level of less than 10% concentration. No evidence was found for the presence of even traces of $(NPF_2)_{3-8}$, which is surprising. It is speculated that these species, if formed in trace amounts, may be preferentially polymerized rather than oligomerized.

The evidence suggests that in this system each $NPF(CMe_3)$ unit retains its integrity—i.e. that exchange of *side groups at phosphorus* does not occur and that only redistribution of repeating units takes place. This is consistent with the detection of products that mainly reflect the 2:1 ratio of NPF_2–$NPFCMe_3$ in the starting material.

For **8**, with a phenyl group in place of *tert*-butyl, the distribution of products is very similar. Again, <10% of starting material (**8**) was detected, with the major product being the cyclic tetramer $N_4P_4F_7Ph$ (10–19%). All the other species (in the <10% concentration range) matched those derived from the *tert*-butyl analogue, with the addition of the cyclic heptamers $N_7P_7F_{13}Ph$ and $N_7P_7F_{11}Ph_3$ (both <10%), and the octamers $N_8P_8F_{15}Ph$ and $N_8P_8F_{14}Ph_2$ (again <10%). Thus, here too the pattern indicates a very broad distribution of ring–ring equilibration products generated by the redistribution of a 2:1 ratio of NPF_2–NPFPh repeating units.

This does not imply that *free* monomer units are undergoing statistical redistribution but rather that the conversion of rings to other rings allows the redistribution to take place. This is a similar situation to the one found in organocyclosiloxane equilibrations.

It should be noted that for compounds **7** and **8**, the principal reaction product in each case is the high polymer, with the cyclic oligomers constituting only 15% of the isolated products from **7** and 13% from **8**. It seems reasonable to suppose that the cyclic oligomers formed by redistribution are themselves capable of polymerizing to higher cyclic species or high polymers.

Compounds with Two Non-Geminal Organic Groups per Ring. (a) Fluorophosphazenes. Fluorophosphazenes **9** and **10**, with two *tert*-butyl or phenyl side groups, gave no high polymers when

(19) A flame ionization detector was used for these measurements.
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Table III. $(NPCl_2C_2H_5)_x$ Product Ratios at Equilibrium for $(NPClC_2H_5)_3$ and $(NPCl_2C_2H_5)_4$[a]

starting material	temp, °C	time	$[NPCl(C_2H_5)]_x$ rel % of products			
			$x = 3$	$x = 4$	$x = 5$	$x = 6$
$(NPClC_2H_5)_3$	248	30 days	21	68	9	2
$(NPClC_2H_5)_4$	248	30 days	21	69	9	1
$(NPClC_2H_5)_3$	300	36 h	29	55	14	2
$(NPClC_2H_5)_4$	300	36 h	29	55	13	3

[a] Percentages based on $(NPClC_2H_5)$ monomer units, determined by VPC techniques.

heated at 300 °C. Instead, the products consisted of a series of ring-expansion products. Species identified for the *tert*-butyl system included cyclic trimers through heptamers, and for the phenyl system, trimers through hexamers. Again, the complex mixture of cyclophosphazenes was indicative of a broad redistribution reaction in which many of the possible combinations of NPF_2 and NPFR repeating units are represented.

For the *tert*-butyl system, the trimeric species included $N_3P_3F_5CMe_3$ (<10%), $N_3P_3F_4(CMe_3)_2$ (starting material, 10–19%), and $[NPF(CMe_3)]_3$ (10–19%). Four tetramers were detected—$N_4P_4F_7CMe_3$ (<10%), $N_4P_4F_6(CMe_3)_2$ (20–29%), $N_4P_4F_5(CMe_3)_3$ (30–39%), and $[NPF(CMe_3)_4]$ (<10%). Pentamers $N_5P_5F_9CMe_3$, $N_5P_5F_8(CMe_3)_2$, $N_5P_5F_7(CMe_3)_3$, $N_5P_5F_6(CMe_3)_4$, and $[NPF(CMe_3)]_5$, as well as hexamers $N_6P_6F_{11}CMe_3$, $N_6P_6F_{10}(CMe_3)_2$, and $N_6P_6F_9(CMe_3)_3$ and heptamer $N_7P_7F_{12}(CMe_3)_2$ were detected, all at concentrations below 10%. No species of type $(NPF_2)_x$ were detected. For the phenyl system derived from **10**, a similar pattern of products was formed (Table I) but with only one species $N_4P_4F_5Ph_3$ (30–39%) present at levels above 10%.

Again, it appears that the cyclic products represent the results of a scrambling of NPF_2 and NPFR repeating units as extensive ring–ring equilibration reactions occur. The absence of high polymers from these two systems is interesting, since the related *chloro*phosphazenes, **11** and **12**, with smaller methyl or ethyl side groups generate substantial amounts of high polymer.

(b) Chlorophosphazenes. Chlorophosphazenes **11** and **12**, with two *non-gem*-methyl or -ethyl groups per ring underwent equilibration at 250 °C to give polymers (42–46%) and a mixture of ring-expansion oligomers (23–30%). For both systems, the cyclic products consisted of trimers through pentamers (Table I). For the methyl system, the main component of the oligomeric mixture was the starting material (**11**) (40–49%), together with less than 10% each of $N_3P_3Cl_5Me$ and $(NPClMe)_3$; $N_4P_4Cl_6Me_2$, $N_4P_4Cl_5Me_3$, and $(NPClMe)_4$; and $N_5P_5Cl_8Me_2$, $N_5P_5Cl_7Me_3$, $N_5P_5Cl_6Me_4$, and $(NPClMe)_5$. The products obtained from the ethyl system (**12**) were identical with those from **11** with the exception that species $N_3P_3Cl_4Et_2$ (**12**) (20–29%), $(NPClEt)_3$ (10–19%), $N_4P_4Cl_6Et_2$ (10–19%), and $N_4P_4Cl_5Et_3$ (20–29%) were present in the largest amounts. In addition, **12** gave $N_4P_4Cl_7Et$ and $N_5P_5Cl_9Et$. Once again, no cyclic species of type $(NPCl_2)_x$ were detected.

In these two methyl or ethyl chlorophosphazene systems, no cyclic hexamers, heptamers, or octamers were detected. This could be due to the ability of these species to readily polymerize or depolymerize to smaller rings. Direct comparisons with compounds *non-gem*-$N_3P_3F_4Me_2$ or *non-gem*-$N_3P_3F_4Et_2$ could not be made because, to our knowledge, synthetic routes to these species are not yet available. However, comparisons of **11** and **12** with the more highly organosubstituted species **13–16** are possible, and these are discussed in the following sections.

Compounds of Formula $(NPClMe)_3$ and $(NPClEt)_3$. As discussed earlier, the equilibration reactions from species of type $(NPClR)_x$ are simpler than those discussed in previous sections, since only one type of repeating unit is involved in the interchanges. Hence, a more detailed analysis was possible.

We first consider the situation for $(NPClMe)_3$ (**13**). When heated at 210 or 250 °C, this compound was converted to a mixture of cyclic oligomers and high polymer. Typical reaction conditions and results are shown in Table II.

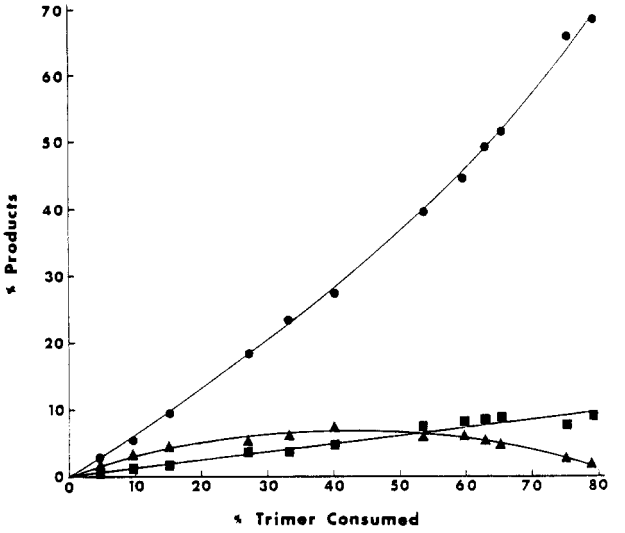


Figure 1. Changes in the relative concentrations of cyclic phosphazenes as $(NPClC_2H_5)_3$ is heated at 250 °C: ●, $(NPClC_2H_5)_4$; ■, $(NPClC_2H_5)_5$; ▲, $(NPClC_2H_5)_6$.

For this system, the equilibration reaction was a slow and somewhat unpredictable process. However, a tendency was detected for the molecular weights of the isolated polymers to *decrease* if the equilibration reactions were allowed to continue for long periods of time. This suggests the presence of a general oligomer–polymer redistribution equilibrium in which the rates of redistribution are slow. However, it should be noted that, at very long reaction times (20–40 days at 250 °C), side reactions occur that remove both oligomers and polymers from the system (perhaps by cross-linking), and this undoubtedly interferes with the analysis. Perhaps the most important result from this section of the work was the detection of the early formation of the cyclic hexamer $(NPClMe)_6$ (22%) and nonamer $(NPClMe)_9$ (3%) in the slower reactions carried out at 210 °C (Table II). As the reaction progressed (or the temperature was raised), the hexamer decreased in concentration as the percentage of tetramer increased. This is strong evidence that the initial step during equilibration is a fusion of two trimer rings to form hexamer. Tetramer may then be formed by ring contraction from the hexamer. If this ring fusion process applies to the whole equilibration process, it implies that the high polymers may be macrocyclic rather than linear species.

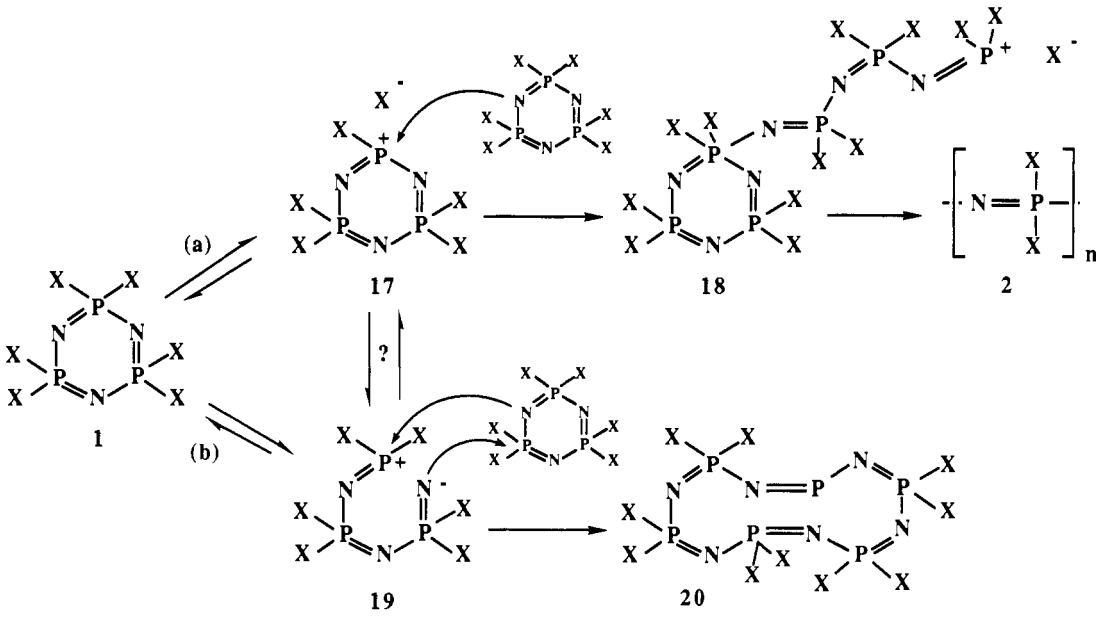
When $(NPClEt)_3$ (**14**) was heated at 210–250 °C, no high polymer was formed at all. Ring expansion reactions accounted for all the products. This provided an added simplification and allowed a more detailed examination of the ring–ring equilibration reactions without the complexity of a possible preferential loss of certain cyclic species to the polymerization process.

At 210 °C the equilibration reaction was slow (Table II). After 25 days at this temperature the product mixture consisted of 93% trimer **14** and only trace amounts of tetramer, pentamer, and hexamer (Table II). At 250 °C the equilibration rate increased markedly, with the principal product after 25 days being the cyclic tetramer (69%). Indeed, this provides the only route known at the present time for the preparation of $(NPClEt)_4$. However, if the temperature was raised to 300 °C the concentration of trimer increased at the expense of the tetramer (Table III).

On the basis of the concentration of trimer and tetramer in the equilibria at 248 and 300 °C (Table III), it was calculated that $\Delta H = -22.1$ kcal and $\Delta S = -36.7$ eu. Thus, the trimer is destabilized by about 1.8 kcal/monomer unit relative to the tetramer. This probably reflects the existence of ring strain in the trimer.

Careful monitoring of the reaction products as a function of consumed trimer indicated that the relative concentrations of cyclic oligomers is dependent on the extent to which the ring-expansion reaction has progressed. As shown in Figure 1, the concentrations of cyclic tetramer and pentamer increased steadily throughout the course of the reaction, but the concentration of cyclic hexamer first increased to a maximum and then decreased. This suggests

Scheme III



Pathway (a) would be favored if X is a readily ionizable group such as Cl, F, or perhaps OCH_2CF_3

Pathway (b) would be preferred if X is alkyl, aryl, or perhaps OCH_2CF_3

that, in the $(NPClEt)_x$ system also, the cyclic hexamer may be an initial reaction intermediate from which trimer, tetramer, and pentamer can be formed.

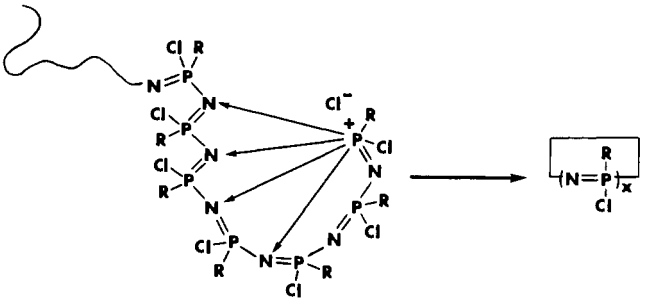
Cyclic Tetramers of Formula $(NPClMe)_4$ and $(NPClEt)_4$. The cyclic tetramer, $(NPClMe)_4$, (**15**), polymerized at a slightly lower rate than did the trimer, $(NPClMe)_3$. However, the polymers formed from the two cyclic species were essentially identical in molecular weight and molecular-weight-distribution. The distribution of cyclic oligomers, $(NPClMe)_{3,4,5,and6}$, at equilibrium (20 days at 250 °C) was virtually identical irrespective of whether the trimer or tetramer was used as the starting material. The cyclic hexamer appeared to play a lesser role in the early stages of this equilibration than was the case in the system that originated from the trimer. This would tend to confirm an initial mechanism that involves trimer ring fusion in the $(NPClMe)_3$ system. However, no octamer was detected from the reactions of $(NPClMe)_4$. As discussed, the $(NPClEt)_4$ system yielded the same mixture of oligomers at equilibrium as was formed from the trimer.

Reaction Mechanisms. Three questions are of special interest: (1) What is the overall pathway by which ring expansion or contraction or polymerization occurs? (2) What is the initiation step and the detailed reaction pathway for ring–ring or ring–polymer interconversions? (3) Why do changes in side group structure allow polymerization in some cases but favor small-molecule ring expansions or contractions in others?

It appears unlikely that ring-expansion or polymerization proceeds via a mechanism that involves breakdown of the initial cyclophosphazenes into NPXR and/or NPX_2 monomer molecules, followed by subsequent recombination. If this occurred, detectable amounts of $(NPF_2)_{3,4,...}$ or $(NPCl_2)_{3,4,...}$ would be expected from species **7–12**. No products of this type were found. Hence, unless species such as these are formed in substantial quantities but are rapidly and preferentially incorporated into the high polymer, it must be assumed that the initial steps involve the incorporation of trimer (or tetramer) molecules directly into larger rings or into a growing polymer chain. The formation of cyclic oligomers such as tetramer or pentamer from the trimer would then be a consequence of ring contraction reactions or depolymerization of the high polymer.

The generally accepted mechanism for polymerization of halogenocyclophosphazenes involves an ionization of a Cl^- or F^- group from phosphorus to generate a cyclic phosphazenium ion

Scheme IV



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(**17** in Scheme III), which then attacks another trimer molecule to cleave its ring (**18**) and begin a cationic linear chain propagation reaction (Scheme III, pathway a).[25] This mechanism explains why species such as $(NPCl_2)_3$ or $(NPF_2)_3$ polymerize to give high yields of very high molecular weight polymer, whereas compounds such as $(NPMe_2)_3$, $(NPPh_2)_3$, or $[NP(OCH_2CF_3)_2]_n$ give no high polymers. However, it does *not* explain why the hexaorgano-substituted trimers undergo ring expansion reactions. Neither does it explain why compounds **9**, **10**, **14**, and **16** undergo ring expansion rather than polymerization.

With these facts in mind, we propose the existence of two closely related mechanisms, as shown in Scheme III. Pathway a is the classical mechanism[25] that can lead to high polymer formation. It is favored when most of the side units are ionizable halogen atoms. The failure of ^{31}P NMR spectroscopy to detect the cyclophosphazene end groups may reflect the low concentration of these units in a polymer that has 15 000 or more repeating units. However, progressive replacement of chlorine or fluorine side units in **1** by organic residues will have two polymerization-inhibiting effects. First, it will reduce the probability of initiation, since there are now fewer initiation sites (P–Cl or P–F units) in the system. Second, organic groups, especially bulky units, at the growing chain end, will sterically retard an attack by the active end on another trimer molecule. Finally, if the organic groups are bulky enough,

(25) Allcock, H. R.; Best, R. J. *Can. J. Chem.* **1964**, *42*, 447.

they may force the chain component of species such as **18** into a bent conformation that would bury the active chain end within the molecular coil and favor "backbiting" to split out a ring.

The alternative pathway (Scheme III, pathway b) involves heterolytic cleavage of a P–N bond rather than a P–halogen bond. The electronegativity difference within the P–N bond is sufficiently high to permit this step, especially if the side groups are electron-supplying (Me, Et, *t*-Bu, or Ph) rather than electron-withdrawing units. Thus, heterolytic ring cleavage would allow attack by the zwitterion on another ring (**19**) to generate expanded ring **20**. The mutual attraction between the chain ends would favor cyclization at every step.

Both mechanisms could also provide a pathway for chain or ring contraction. Backbiting as shown in Scheme IV, structure **21**, could yield small-molecule rings.[22] Heterolytic cleavage of any ring or chain formed by pathway b could lead to ring contraction or depolymerization.

The main point to be made is this. An increased loading of organic side groups will favor mechanism b, which provides a bias in favor of small-molecule rings. An increased loading of P–halogen bonds favors mechanism a, which provides a more efficient pathway for high polymer formation.

This interpretation explains two other facts discovered in previous studies. First, it explains why phosphazene cyclic trimers (such as **14** or **16**), which ring-equilibrate but do not polymerize on their own, nevertheless give high polymers when copolymerized with $(NPCl_2)_3$. Second, it explains why phosphazene cyclic trimers that bear transannular ferrocenyl groups[26] and no halogen cosubstituents polymerize in the presence of traces of $(NPCl_2)_3$. Presumably even small amounts of $(NPCl_2)_3$ are sufficient to initiate polymerization via mechanism a if sufficient ring strain exists in the cyclophosphazene to escape from the manifold provided by pathway b. However, when very bulky organic or organometallic side groups are the main side units present, pathway b is preferred, and small-molecule equilibration will be favored over polymerization.

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, was supplied by Ethyl Corp. Tetrahydrofuran (THF) was distilled into the reaction flask under an atmosphere of dry argon from a sodium benzophenone ketyl drying agent. Hexane was distilled from calcium hydride before use. Trifluoroethanol (Halocarbon Products) was distilled and then dried over 3-Å molecular sieves. Sodium stick (Aldrich) was stored, cut, and weighed in a nitrogen-filled drybox equipped with a recirculating atmosphere system to remove oxygen and water.

Analytical Equipment and Techniques. ^{31}P NMR spectra were recorded with the use of a JEOL FX-90Q spectrometer operated at 36 MHz. Positive chemical shifts are downfield from external phosphoric acid. Vapor phase chromatography was carried out by use of a Varian 3700 gas chromatograph equipped with a flame ionization detector and a 2-m SP2100 (3%) column. Relative peak areas were determined with a Hewlett-Packard 3392A integrator. VPC/MS data were obtained with the use of a Finnigan 3200 gas chromatograph/mass spectrometer. The thermodynamic data given in Table III were obtained from experiments in which the oven temperature was measured by means of a platinum thermocouple. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

Synthesis of Starting Materials, 7–16. Compounds **7–15** were prepared by methods in the literature (**7**, **8**)[15,16] or reported by us previously (**10–15**).[10–14] Species $(NPClEt)_4$ (**16**) was prepared by the thermal ring expansion of $(NPClEt)_3$ (**14**) (3.0 g, 0.027 mol) in an evacuated sealed Pyrex glass tube at 250 °C for 25 days. The product mixture consisted of 69% of **16**. It was isolated by column chromatography over silica gel, with hexane/methylene chloride (60/40) as eluent. Pure tetramer eluted first, followed by mixtures of tetramer, pentamer, and hexamer. The trimer was eluted last. The tetramer was further purified by sublimation at 0.05 Torr: isolated yield, 1.3 g, 43%; mp 65–67 °C. ^{31}P NMR: 25.7, 19.8 ppm. ^1H NMR: CH_2, δ 2.09, CH_3, δ 1.22. IR: ν_{PN} 1305 cm^{-1}. Anal. Calcd for $C_8H_{20}N_4P_4Cl$: C, 21.92; H, 4.57; N, 12.79; MW, 435.9393. Found: C, 22.02; H, 4.34; N, 13.02; MW, 435.9417.

All the starting materials used in this work were purified by vacuum distillation (**7–10**) or by two recrystallizations from heptane or hexane, followed by three vacuum sublimations at 0.05 Torr (**11–16**). These procedures yielded material that gave only one peak in the VPC analysis. The purified compounds were then stored in an inert-atmosphere drybox.

Preparation of Trifluoroethoxy-Substituted Cyclic Phosphazenes. These compounds were used for ^{31}P NMR monitoring of ring–ring equilibrates and as controls for establishing the reaction conditions needed for halogen replacement of the equilibrate mixtures. The following example is typical.

A solution of $N_3P_3F_4(CMe_3)_2$ (**9**) (2.0 g, 6.2 mmol) in THF (30 mL) was added to a solution of $NaOCH_2CF_3$, prepared from Na (2.1 g, 0.091 mol) and $HOCH_2CF_3$ (9.0 mL, 0.124 mol) in THF (200 mL) at −78 °C. The mixture was warmed to 25 °C and was stirred at 25 °C for 24 h before deactivation with $ClSiMe_3$. The product was isolated by addition to distilled water (200 mL), extraction with diethyl ether (three 150-mL portions), drying over $MgSO_4$, solvent removal, and recrystallization from heptane and sublimation (0.05 mmHg, 25 °C). Yield: 1.8 g, 58%, mp 66–67 °C. ^{31}P NMR: 15.3 (d) ppm, $P(OCH_2CF_3)_2$; 53.9 (d,t) ppm, PF^{t}Bu; J_{PNP} = 33.2 Hz, J_{PF} = 1026.8 Hz. ^1H NMR: δ 4.3 (p) OCH_2CF_3; δ 1.2 (d) ^{t}Bu; J_{PH} = 19.0 Hz. IR (KBr): ν_{CH} 2960 cm^{-1}; ν_{PN} 1165 cm^{-1}, 1205, 1250, 1290 cm^{-1}. Anal. Calcd for $C_{12}H_{22}N_3P_3OF_8$: C, 29.7; H, 4.5; N, 8.6; F, 31.3. Found: C, 29.82; H, 4.42; N, 8.76; F, 31.61. Derivatives of **7**, **8**, and **10–16** were prepared in a similar way.

The same procedures were employed for replacement of fluorine or chlorine in the mixtures of cyclic oligomers (and polymers) formed by the thermal equilibration reactions.

Equilibration Reactions (Tables I and II). The equilibrations were carried out in Pyrex glass tubes, 220 mm long, 12 mm o.d., and 10 mm i.d. with a constriction 100 mm from the open end. The tubes were soaked in ethanolic KOH for 24 h, followed by five washings each with tap water, 2% aqueous HCl solution, distilled water, and distilled/deionized water. The tubes were then dried at 140 °C for 48 h. The tubes were charged with the appropriate cyclophosphazenes (~3.0 g) in a drybox and were then connected to a vacuum line and evacuated for 30 min at 0.05 Torr. The tubes were then sealed at the constriction, wrapped in aluminum gauze, and placed on a rocking device in a Freas thermoregulated oven preheated to the desired temperature. The viscosity of the molten reaction mixture increased significantly when high polymer was formed (i.e. during the equilibration of **7**, **8**, **11–13**, and **15**). No viscosity increase was detected during the ring expansion reactions of **9**, **10**, **14**, and **16**.

The polymerization tubes were opened in a nitrogen-filled glovebag, and the contents were Soxhlet extracted with dry hexane for 48 h. The hexane was then removed from the extract under reduced pressure, and the recovered cyclic oligomers were subjected to VPC/MS analysis.

Alternatively, the contents of the polymerization tube were dissolved in dry THF and were treated with a solution of sodium trifluoroethoxide as described earlier.[17] The product mixture was extracted with pentane to remove the cyclic oligomers which were then subjected to VPC analysis.

For the experiments summarized in Table III and Figure 1, Pyrex glass tubes (20 mm × 6 mm o.d.) were charged with **14** or **16** (0.05 g), and were sealed and heated as described above. When removed from the oven, the tubes were allowed to cool to room temperature and were then opened. The contents were dissolved in CH_2Cl_2 and were subjected to VPC analysis.

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