Article

Novel Approach for the Synthesis of Chlorophosphazene Cycles with a Defined Size via Controlled Cyclization of Linear Oligodichlorophosphazenes [Cl(PCl2=N)n–PCl3]+[PCl6]−

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Abstract: Despite a significant number of investigations in the field of phosphazene chemistry, the mechanism of this class cyclic compounds formation is still poorly studied. At the same time, a thorough understanding of this process is necessary both for the direct production of phosphazene rings with a given size, and for the controlled cyclization reaction when it is secondary and undesirable. Here we have synthesized a series of short linear phosphazene oligomers with the general formula Cl[PCl2=N]n–PCl3+PCl6− and studied their tendency to form cyclic structures under the influence of elevated temperature or in the presence of nitrogen-containing agents, such as hexamethyldisilazane (HMDS) or ammonium chloride. It was established that linear oligophosphazenes are inert when heated in the absence of the mentioned cyclization agents, and the formation of cyclic products occurs only when these agents are involved in the process. It is for the first time shown the ability to obtain the desired size phosphazene cycle from corresponding linear chain. Known obstacles like side interaction with the PCl6− counterion and a tendency of longer chains to undergo crosslinking elongation instead of cyclization are still relevant and ways to overcome them are being discussed.

Keywords: phosphazenes; cyclization; controlled cycle size; living cationic polymerization; hexamethyldisilazane

1. Introduction

Linear high-molecular weight phosphazenes are of a great interest due to their unique properties such as high flexibility of the polymer chain, low glass transition temperature, high thermal stability and high values of quadratic electro-optic effect [1,2] Thereby, these polymers find applications as elastomers [3], solid polyelectrolytes [4], photosensitive materials [5], gas separation membranes [6], liquid crystals [7,8], non-linear optic materials [9], sensors and actuators [10], and etc.

Phosphazene structures and their properties can be easily tuned due to the ease of backbone derivatization by the nucleophilic substitution of chlorine atoms with various organic groups [4,11] (Figure 1).
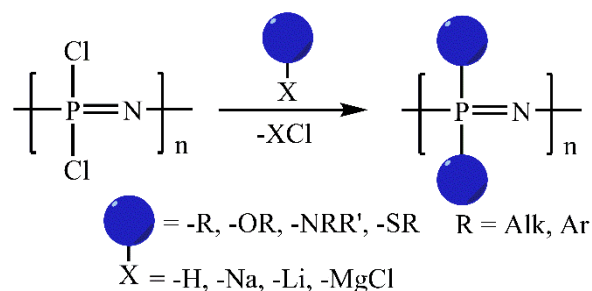
Figure 1. Nucleophilic substitution of chlorine atoms in dichlorophosphazenes.

Since the synthesis of high polyphosphazenes is quite complicated, it is a common approach to use cyclic compounds, mainly hexachlorocyclotriphosphazene (HCP), as the relevant models [12] suitable for extrapolation of functional properties and reaction activity to linear polymers. Of course, cyclophosphazenes are in demand as self-sufficient materials as well: for example, as curing agents for polymer resins [13–15]; as modifiers for polymers to improve their inflammability [16,17] and mechanical characteristics [16,18]; as building blocks for porous materials [19,20]; as cores of star-shaped polymers [21–24] and dendrimers [25–27] and much more. The size of a cycle plays an important role when phosphazenes are used as coordination ligands for metal ions [2,28,29] or as building blocks in preparation of porous materials [30].

The most comprehensively studied HCP was first obtained as a side compound in very low yield in 1843 by von Liebig by the interaction of phosphorus pentachloride with ammonia [31]. In 1896 Stokes [32], by reaction of NH_4Cl with PCl_5 in a sealed vessel at 150–200 °C, he obtained HCP as the target product in 27% yield, isolated and identified it. Since the work of Schenk and Romer [33], the interaction of phosphorus pentachloride and ammonium chloride was usually carried out in a solvent, usually sim-tetrachloroethane and, later, less toxic and cheaper chlorobenzene. The rate of the ammonolysis reaction is highly temperature dependent. For the complete completion of the interaction of PCl_5 and NH_4Cl in boiling chlorobenzene (b.p. 131 ° C), 25-30 hours are required, and in the case of using *sym*-tetrachloroethane (b.p. 147 °C) – only 7-8 hours [34]. Carrying out the reaction in anhydrous pyridine, which acts simultaneously as a solvent and an acceptor of the hydrogen chloride formed during the reaction, makes it possible to reduce the reaction time to 1 hour with the yield of the target HCP of 80%. As ammonium chloride is practically insoluble in organic solvents; its solution interacts with PCl_5 at the phase boundary. Therefore, in the case of using finely dispersed NH_4Cl, the reaction rate increases and the yield of cyclic chlorophosphazenes increases due to a local increase in the concentration of ammonium chloride [34].

Becke-Goehring et al. were the first to propose a probable mechanism for the formation and growth of the phosphazene chain [35]. According to their theory, phosphorus pentachloride is present in the system in the form of an ion pair, while ammonium chloride dissociates into NH_3 and HCl (**Figure 1 a, b**). In the first stage of the reaction, a nucleophilic attack of a positively charged phosphorus atom with an ammonia molecule occurs (**Figure 1c**). The result is a highly reactive trichlorophosphoraneimine $Cl_3P=NH$, which interacts with the next ion pair $[PCl_4]^+[PCl_6]^-$ (**Figure 1d**). Trichlorophosphazotrichlorophosphonium hexachlorophosphate $[Cl_3P=N-PCl_3]^+[PCl_6]^-$ is an intermediate product formed at the initial stage of the process, but it is stable in anhydrous medium and was isolated in pure form [43]. $[Cl_3P=N-PCl_3]^+[PCl_6]^-$ is poorly soluble in non-polar solvents, as a result of which the growth process of the phosphazene chain becomes heterophase and slows down after the **Figure 1d** stage. As the chain grows according to a scheme similar to Figure 1d and the length of the cation increases, its solubility increases, and further interaction with ammonia occurs in solution. Cyclic products are formed during the cyclization of linear oligophosphazenes under the action of ammonium chloride (**Figure 1e**).
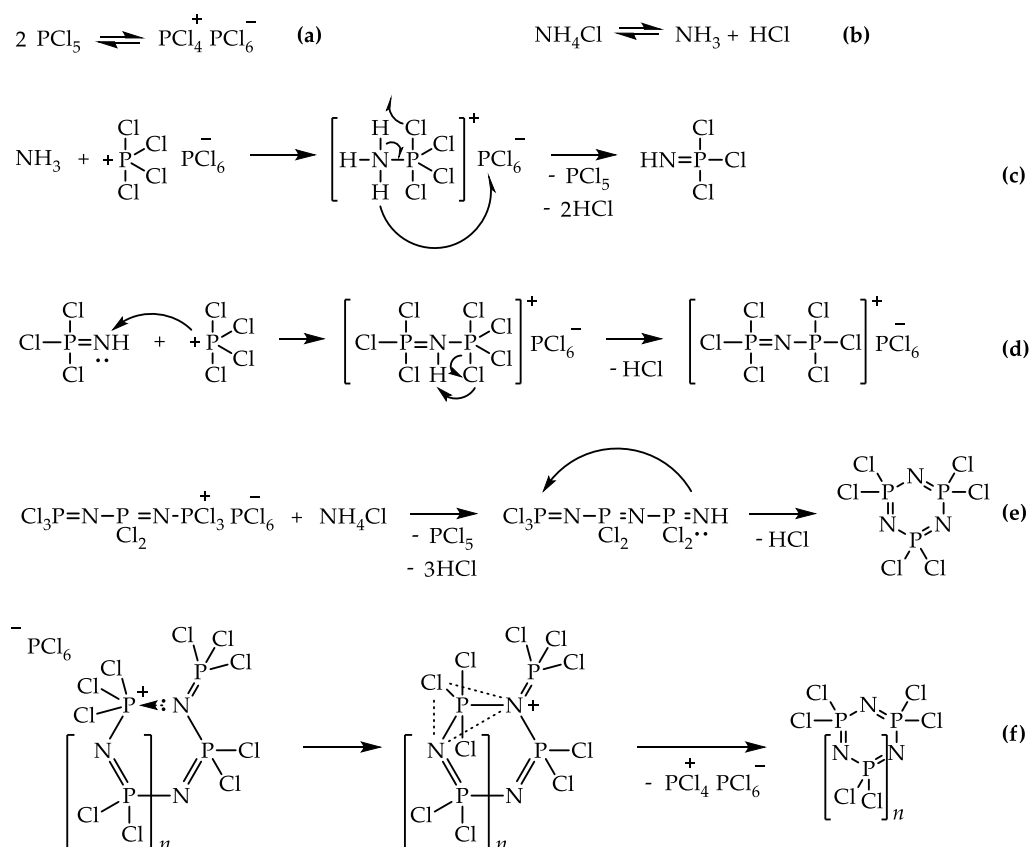
Figure 2. The mechanism of the formation of cyclic chlorophosphazenes proposed by Becke-Goehring et al. [35] (a-e) and alternative cyclization mechanism proposed by Emsley al. (f) [36].

Emsley et al. [36] presented an alternative scheme for the cyclization of growing phosphazene chains (**Figure 1f**), which does not require the participation of NH$_4$Cl and is accompanied by the elimination of the [PCl$_4$]$^+$ cation. The Emsley's scheme is in poor agreement with the results of Paddock's studies, which indicate a strict dependence of the yield of cyclic reaction products on the presence of an excess of ammonium chloride in the system [37]. Thus, it has been shown that the yield of a mixture of cyclophosphazenes can be increased from 67%, typical for the classical reaction of partial ammonolysis of PCl$_5$, to 93% by maintaining an excess of NH$_4$Cl in the reaction medium due to the gradual introduction of phosphorus pentachloride. Emsley [36] also found that the formation of the hexamer (N=PCl$_2$)$_6$ occurs before the appearance of a pentamer in the system, and suggested that the formation of higher cyclic phosphazenes at high temperatures occurs not through intramolecular cyclization, but as a result of the intermolecular interaction of two smaller cycles 2 (N=PCl$_2$)$_3$ → (N=PCl$_2$)$_6$.

In 2014 Bowers et al. [38] separated the products of the ammonolysis reaction by liquid chromatography, which made it possible to isolate the cycles (NPCl$_2$)$_{n = 5\text{-}9}$ and identify them separately from each other using ^{31}P NMR spectroscopy and mass spectrometry. The obtained values of chemical shifts on ^{31}P nuclei are given in **Table 1**, which contradicted the generally accepted data, in particular, the fact that the hexamer signal turns out to be shifted to the region of a weaker field relative to the pentamer singlet. Taking these data into account, the results obtained by Emsley indicate a gradual increase in the size of the formed cycles with an increase in the duration of the reaction. Thus, cyclophosphazenes are most likely formed by intramolecular cyclization.

Table 1. ^{31}P NMR chemical shifts of chlorocyclophazenes.

Value of ^{31}P NMR chemical shift of chlorophosphazenes [Cl$_2$P=N]$_n$				Reference
5	**6**	**7**	**≥8**	
− 17.0	− 16.0	− 18.0	-	[34] (1972)
− 15.1	− 15.3	− 17.0	− 17.7	[38] (2014)

A significant step in the development of the chemistry of phosphazenes was the discovery of the method of living cationic polymerization of phosphoraneimine in presence of Lewis acids, which made it possible to controllably obtain linear compounds of a given length with a narrow molecular weight distribution at ambient temperature [39]. Later Allcock showed [40] that HCP may also be obtained by the interaction of PCl$_5$ with tris-(trimethylsilyl)amine N (SiMe$_3$)$_3$ (Figure 3a) with a yield of up to 70%, which is comparable to the yield of the classical reaction, but the process proceeds under milder conditions.

De Jaeger et al. [41] investigated the possibility of obtaining cyclic and linear phosphazenes by interaction of salts [Cl$_3$P=N−PCl$_3$][+][PCl$_6$][−] and [Cl$_3$P=N−PCl$_3$][+]Cl^{−} with hexamethyldisilazane (HMDS). The authors assumed that the process of phosphazene chain growth begins with the replacement of the terminal −PCl$_3$[+] cation of the growing chain with the =N−SiMe$_3$ group. Subsequent condensation of the formed linear oligomers can occur both intermolecularly and intramolecularly with the formation of linear polyphosphazenes and cyclic compounds, respectively. In this way, with an excess of HMDS, a cyclic trimer can be obtained with a yield of up to 50%.

Thus, at present, no methods are known that allow achieving the predominant content of higher cyclic homologues of a given structure in the product and excluding the formation of (N=PCl$_2$)$_3$ and (N=PCl$_2$)$_4$. It is only possible to slightly increase the yield of cyclic homologues of a certain size in the presence of some catalysts for the ammonolysis reaction (mainly anhydrous chlorides of metals such as magnesium, tin (IV), titanium (IV), molybdenum (V), zinc and cobalt [34,42–44]).

All the above-mentioned shows that the development of the novel methods for controlled synthesis of linear and cyclic phosphazenes still remains as an actual challenge and is necessary for both fundamental and applied aspects. Although the synthesis of HCP is not a technologically difficult task, and a lot of synthetic routes – traditional from PCl$_5$ and NH$_4$Cl and modern ones, based on the reaction of PCl$_5$ with N(SiMe$_3$)$_3$ [40] are known, – the final product usually contains impurities of side products and demands a multistep purification.

On the contrary, the higher phosphazene cycles nowadays can be obtained only by poorly controlled methods which in turn lead to irreproducible results and impossibility for quantitative yields.

Despite the large number of works, dedicated to phosphazene chemistry, the mechanism of cyclic compounds formation is still not unequivocally approved. Meanwhile, the complete understanding of this process is vital for producing the cycles with a defined size on the one hand, and for the prevention of the undesired cyclization, on the other. Here we report the synthesis of the short linear phosphazene oligomers Cl[PCl$_2$=N]$_n$–PCl$_3$[+]PCl$_6$[−] via living cationic polymerization of Cl$_3$P=NSiMe$_3$ and the investigation of their ability for intramolecular cyclization under the thermal treatment or by the reaction with hexamethyldisilazane (HMDS) HN(SiMe$_3$)$_2$ or ammonium chloride NH$_4$Cl. A possible scheme for the formation of cyclic and linear phosphazenes was proposed and discussed in comparison with the known literature data.

2. Experimental

2.1 Materials

Phosphorus pentachloride, hexamethyldisilazane (HMDS) were purchased from Sigma-Aldrich (St. Louis, MI, USA) and used as received. Solvents were purified according to known methods, their physical characteristics corresponded to the literature data [45].

2.2 Syntesis

2.2.1 General procedure of synthesis of linear oligodichlorophosphazenes

100 mL of dichloromethane and HMDS under argon flow were placed into three-necked flask, equipped with magnetic stirrer, reflux condenser. The solution was stirred for 15 min at -55 °C and then 5 g (0.024 mol) of PCl_5 were added in one portion. The reaction mixture after that was stirred for another 15 min at -55 °C and then the temperature was raised during 2 h till 0 °C and mixture was stirred at this temperature for another 1 h. After that the mixture was naturally heated till room temperature and stirred for 2 h. After ending of reaction, the mixture was filtered under argon flow from the precipitated NH_4C and all volatile products were removed by vacuum rotary evaporation. The resulted product looks like viscous transparent greenish liquid. Loadings of HMDS and yields of products are given in **Table 2.**

Table 2. Amounts of HMDS for synthesis of linear oligodichlorophosphazenes with general formula $[Cl(PCl_2=N)_nPCl_3]^+[PCl_6]^-$.

n	Weight (g)	mol	Yield of product (%)
2	2.58	0.016	75
6	3.88	0.024	82
7	4.03	0.025	84
9	4.23	0.027	88

2.2.2 General procedure for cyclization reaction

The calculated amount of HMDS was added under argon flow to reaction mixture, containing 2 g of linear oligodichlorophosphazene with specified chain length. After stirring at room temperature for 1.5 h, the mixture was filtered and all volatile compounds were removed by rotary evaporation. Loadings of HMDS and yields of products are given in **Table 3.**

Table 3. Amounts of HMDS for cyclization of linear oligodichlorophosphazenes with general formula $[Cl(PCl_2=N)_nPCl_3]^+[PCl_6]^-$

n	Weight (g)	mol	Yield of product (%)
2	1.49	0.00923	130[1]
6	0.87	0.00539	80
7	0.79	0.00488	78
9	0.66	0.00410	71

[1] The formation of hexachlorocyclotriphosphazene is resulted not only after reaction of HDMS with $[Cl(PCl_2=N)_nPCl_3]^+[PCl_6]^-$ but also after its reaction with $[PCl_6]^-$ ion.

2.2.3 Synthesis of phenoxycyclotriphosphazenes

In three-necked flask with reflux condenser and magnetic stirrer were added under argon flow 100 mL of dioxane, 3.89 (0.0414 mol) of phenol and 0.95 (0.0414 mol) of sodium. After full sodium dissolution to resulted mixture were added dropwise 30 mL of solution of 2 g of cyclic chlorophosphazene in dioxane. Then the mixture was stirred for 48 h at 100 °C. After that the mixture was cooled to room temperature and poured to water. The precipitated product was dissolved in chloroform and washed subsequently with 3% alkaline solution, 10% $NaHCO_3$ solution and water till neutral medium. Then the chloroform solution was dried with Na_2SO_4 and the solvent was removed by rotary evaporation. Yield of product after drying was 74-83 %, depending of chain length.
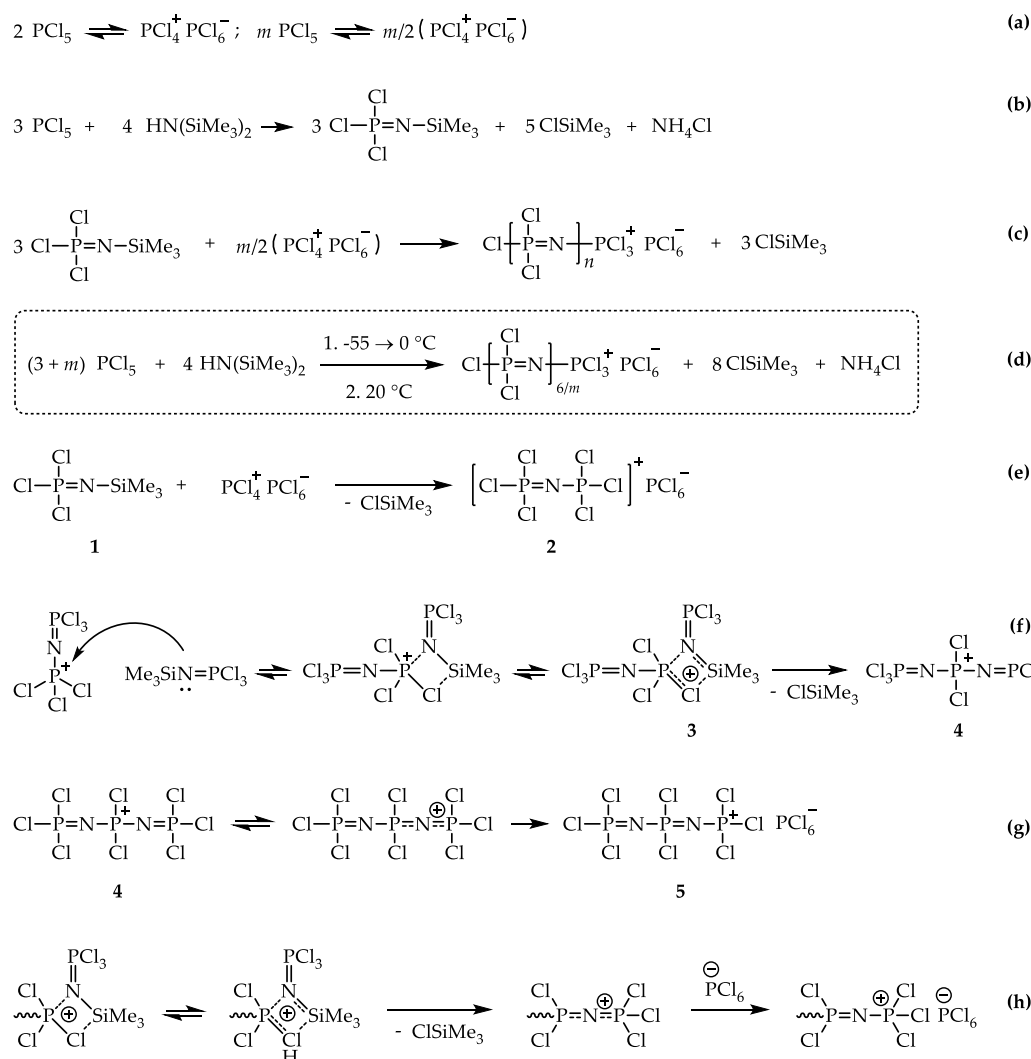
2.3 Characterization

^{31}P NMR spectra were recorded on "Bruker AMX-360" spectrometer (145.7 MHz) with the use of solvents $CDCl_3$ and acetone-d_6 and with the use of 80 % H_3PO_4 as internal standard. MALDI-TOF spectra were recorded on "Bruker Auto Flex II" spectrometer.

3. Linear chains preparation.

Significant move in phosphazene chemistry was reached with the development of Lewis acid catalyzed living cationic polymerization of phosphoranimines, usually N-(trimethylsilyl)trichlorophosphoranimine $Cl_3P=NSiMe_3$, which allows to obtain at room temperature linear compounds with the defined length and narrow molecular weight distribution [39]. $Cl_3P=NSiMe_3$ preparation is complicated by its instability, ability to spontaneous polymerization and complex purification procedure.

Within this work, based on previously developed method [46], one-pot approach for the preparation of linear phosphazenes by direct reaction of PCl_5 with HMDS was utilized. This allowed to escape the necessity of pure phosphoranimine isolation. The presence of unreacted excess of PCl_5 during the synthesis of monomer leads to spontaneous growth of phosphazene chain when the reaction mixture is heated up to the room temperature. The polymerization degree was controlled by changing of molar ratio between initial reagents PCl_5 and HMDS. Hence, this one-pot synthesis can be divided into two stages: the formation of monomer $Cl_3P=NSiMe_3$ at –55 °C and its further living cationic polymerization initiated by the residual unreacted PCl_5 and activated when temperature is naturally increased up to 20 °C. The analogous method was described in work [47] where the monomer $Cl_3P=NSiMe_3$ was at first obtained from PCl_3 [48] and then initiator PCl_5 was added to reaction mixture to start polymerization process. In the present work PCl_5 was added in one portion and its initiation ability was regulated only by temperature of the process.

$$2\ PCl_5 \rightleftharpoons PCl_4^+\,PCl_6^-\ ;\quad m\ PCl_5 \rightleftharpoons m/2\left(PCl_4^+\,PCl_6^-\right) \tag{a}$$

$$3\ PCl_5\ +\ 4\ HN(SiMe_3)_2 \rightarrow 3\ Cl-\underset{Cl}{\overset{Cl}{P}}=N-SiMe_3\ +\ 5\ ClSiMe_3\ +\ NH_4Cl \tag{b}$$

$$3\ Cl-\underset{Cl}{\overset{Cl}{P}}=N-SiMe_3\ +\ m/2\left(PCl_4^+\,PCl_6^-\right) \longrightarrow Cl\left[\underset{Cl}{\overset{Cl}{P}}=N\right]_n PCl_3^+\,PCl_6^-\ +\ 3\ ClSiMe_3 \tag{c}$$

$$(3+m)\ PCl_5\ +\ 4\ HN(SiMe_3)_2 \xrightarrow[\ 2.\ 20\,°C\ ]{1.\ -55\to 0\,°C} Cl\left[\underset{Cl}{\overset{Cl}{P}}=N\right]_{6/m} PCl_3^+\,PCl_6^-\ +\ 8\ ClSiMe_3\ +\ NH_4Cl \tag{d}$$

$$Cl-\underset{Cl}{\overset{Cl}{P}}=N-SiMe_3\ +\ PCl_4^+\,PCl_6^- \xrightarrow[-\ ClSiMe_3]{} \left[Cl-\underset{Cl}{\overset{Cl}{P}}=N-\underset{Cl}{\overset{Cl}{P}}-Cl\right]^+\,PCl_6^- \tag{e}$$

$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

(f) $\mathbf{3}$ $\mathbf{4}$

$Cl_3P=N-\overset{+}{\underset{Cl}{P}}-N=PCl_3$

(g) $\mathbf{4}$ $\mathbf{5}$

(h)

Figure 3. One-pot synthesis of oligodichlorophosphazene from PCl_5 and HMDS via living cationic process and its mechanism.

As the polymerization is initiated by the ionic form of PCl_5, built by two molecules, in case of m moles of added PCl_5 as an initiator the m/2 of active centers for polymerization will be formed (Figure 3a). In general, the formation of monomer $Cl_3P=NSiMe_3$ can be demonstrated by scheme Figure 3b. If m moles of PCl_5 or $m/2$ moles of $[PCl_4]^+[PCl_6]^-$ will be taken, the polymerization degree n of final linear product will be as follows:

$$n= 3/(m/2)= 6/m, \tag{1}$$

where 3 – total molar amount of $Cl_3P=NSiMe_3$ monomer, $m/2$ – the number of polymerization active centers (Figure 3c).

The general scheme of polymerization is shown in Figure 2d and represents combination of Figure 2b and 2c.

It seems to be an important challenge to postulate the mechanism of phosphazene chain growth when $Cl_3P=NSiMe_3$ is polymerized by the initiation with PCl_5 ($[PCl_4^+][PCl_6^-]$) (Figure 3e). Probably it starts with nitrogen atom of compound 1 coordination with phosphonium cation 2 and the formation of intermediate structure 3 (Figure 3f). This intermediate structure is stabilized due to the delocalization of positive charge within four atoms of the formed cyclic structure. When this cycle collapses, Me_3SiCl evolves and new intermediate 4 with positively charged tetracoordinated phosphorus atom is obtained.

This compound quickly transforms to more stable form with terminal trichlorophosphonium cation, stabilized with PCl_6^- (Figure 3g). This compound and its higher homologues react in analogous manner with compound 1 and continue the chain growth (Figure 3e).

As the terminal trichlorophosphonium cations are the active centers of polymerization, the molecular weight of the formed polymer can be regulated by the amount of the initial PCl_5. The dependence of molecular weight of linear polyphosphazene from amount of initial PCl_5 used for initiation ($n = f(m)$) has a hyperbolic character and shown in Figure 4. In order to obtain a number of phosphazene compounds $[Cl(Cl_2P=N)_nPCl_3]^+[PCl_6]^-$ of various chain length we repeatedly conducted the reaction between PCl_5 and HMDS with various molar ratios (Table 3). The average degree of polymerization was determined by ratio of integral intensities for signals of terminal and backbone phosphorus atoms in ^{31}P NMR spectra and the results were in a good agreement with the theoretical calculations. The proposed in the presented work one-pot synthesis is promising for preparation of linear phosphazenes with define chain length and polymerization degree not higher than 20. It can be explained probably by decreasing of chain growth rate due to the decrease of electrophilicity and activity of the growing macrocation [49].
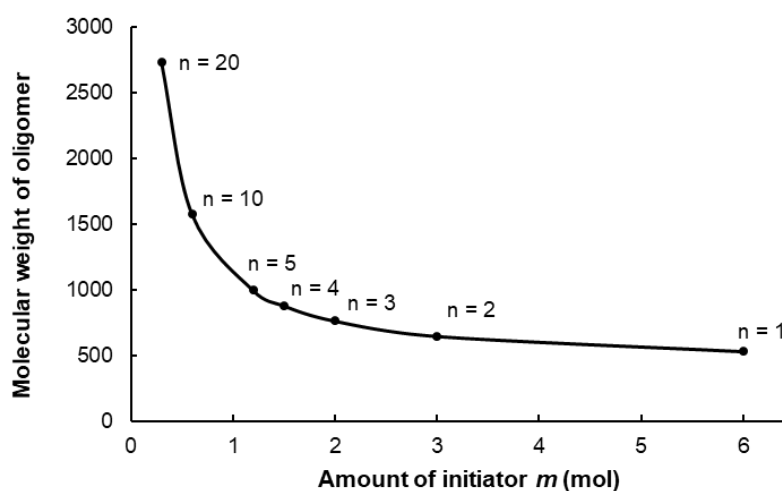
Figure 4. Dependence of molecular weight of linear oligodichlorophosphazene $[Cl(PCl_2=N)_nPCl_3]^+[PCl_6]^-$ from amount of initiator PCl_5.

Nowadays there is no effective method, which allows to obtain predominantly higher cyclic homologues and exclude formation of low cycles $(N=PCl_2)_3$ and $(N=PCl_2)_4$. Some catalysts, as usual anhydrous chlorides of such metals as Mg, Sn (IV), Ti (IV), Mo (V), Zn [34,42,43] and Co [44] definitely have some influence and variation of their amount can a little bit increase the yield of cyclic products with the defined size. That's why it was interesting to evaluate the ability of compounds $[Cl(PCl_2=N)_nPCl_3]^+[PCl_6]^-$ (where n=2-7) to spontaneous cyclization under various conditions.

4. Thermal cyclization.

Emsley and coworkers [36] proposed a scheme for phosphazene chains cyclization which includes the elimination of terminal $[PCl]^{4+}$ cation. However, Allcock showed that $[Cl(PCl_2=N)_4PCl_3]^+[PCl]^{6-}$ does not form cyclic product under refluxing in dichloromethane for 24 h [40].

In current work the linear phosphazene compounds with various chain lengths were refluxed at 131 °C for 4 h in chlorobenzene and the formation of cyclic product was not observed in any case. So, the scheme proposed by Emsley is highly doubtful and cyclization with the elimination of terminal $-PCl_3^+$ group does not occur. Nevertheless, the possibility of the reaction of two cycles with the formation of the bigger cycle still cannot be excluded especially in light of work by Sirotin [42], where such reactions as 2 $(N=PCl_2)_3 \rightarrow$

$(N=PCl_2)_6$ and $2 (N=PCl_2)_4 \rightarrow (N=PCl_2)_8$ were observed in mass-spectra after electron beam ionization.

## 5. Cyclization in the presence of N-containing agents.

The cyclic products were obtained according to Figure 5a from preliminary synthesized oligodichlorophosphazenes with various chain length by addition of stoichiometric amount of HMDS (Table 3). NMR data showed the complete cyclization of all phosphazene chains.
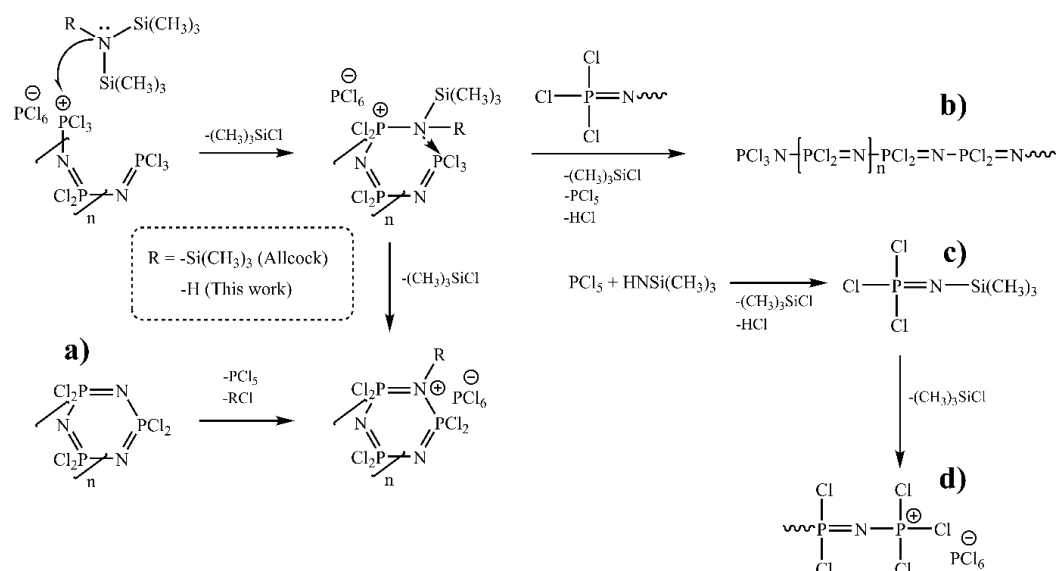
Figure 5. The formation of various-sized cyclophosphazenes via short-chain linear oligodichlorophosphazenes $[Cl(PCl_2=N)_n–PCl_3]^+[PCl_6]^-$ cyclization and possible side reactions.

According to the following scheme the formation of cycles is accompanied by the enlargement of chain length on one $-PCl_2=N-$ unit due to the introduction of nitrogen atom from HMDS.

Hence, in case of $[Cl(PCl_2=N)_2–PCl_3]^+[PCl_6]^-$ the cyclization leads to the targeted HCP quantitatively with a small content of cyclic tetramer and pentamer impurities (Figure 6a). Due to the fact that not only the target interaction of the linear cation $[Cl(PCl_2=N)_2–PCl_3]^+$ with HMDS (or NH_4Cl) leads to the formation of HCP, but also the side reaction of HMDS with the PCl_5 molecule from the $[PCl_6]^-$ counterion leads first to the formation of a $Cl_3P=NSiMe_3$ monomer and its further spontaneous growth with immediate cyclization in the presence of HMDS excess, the total yield of HCP turns out to be even more than the theoretical 100%. For the higher cycles the experimental data of cyclization product composition always have some deviation from the theoretical calculation and so the broadening of molecular weight distribution occurs (Table 4). That is most probably caused by the side reactions including partial intermolecular cross-linking (Figure 5b), HMDS interaction with PCl_5 from counterion leading to spontaneous formation of phosphoraninime $Cl_3P=NSiMe_3$ (Figure 5c) with the following polymerization and increasing of chain length (Figure 5d). For example, in case of the expected final product with five $-PCl_2=N-$ units one can see the predominant content of tetramer and high content of cyclophosphazenes with 9 and 10 units (Figure 6b).

(a)

(b)
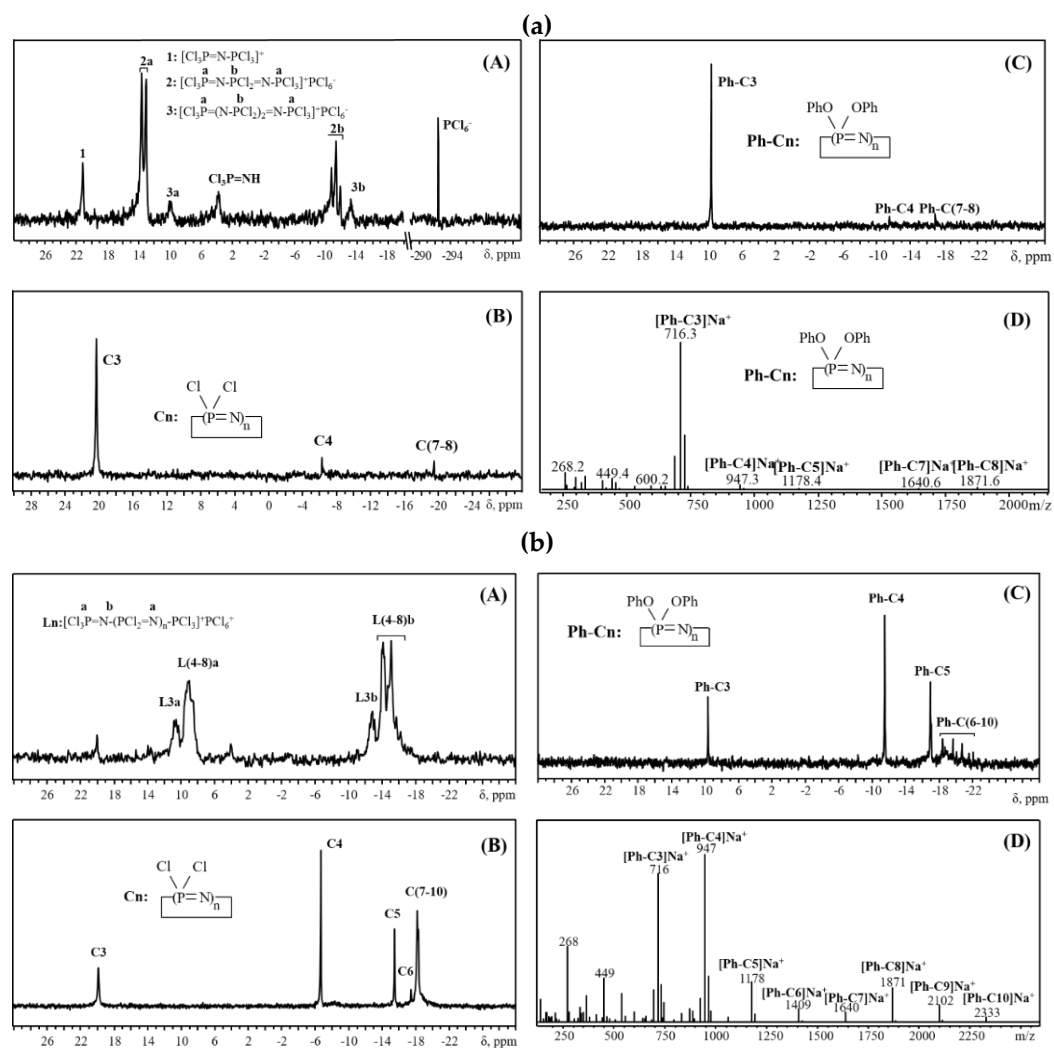
Figure 6. ^{31}P NMR spectra (A) of linear oligophosphazene: [Cl(PCl$_2$=N)$_2$PCl$_3$]$^+$[PCl$_6$]$^-$ **(a)** and [Cl(PCl$_2$=N)$_4$PCl$_3$]$^+$[PCl]$^{6-}$ **(b)**, product after their cyclization (B), phenoxylated derivatives of cyclization products (C) and MALDI-TOF spectrum of phenoxylated products (D).

This is due to the fact that part of reagent molecules with four units took participation in formation of longer chains, which resulted in decreasing of pentamer yield. Similar behavior is observed in case of the use of [Cl(PCl$_2$=N)$_7$PCl$_3$]$^+$[PCl]$^{6-}$ for preparation of cyclooctaphosphazene (Figure 7).
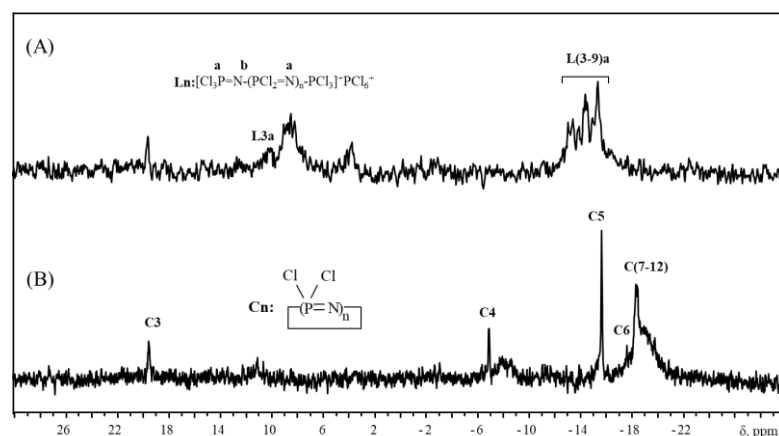
Figure 7. ^{31}P NMR spectra of linear oligophosphazene [Cl(PCl$_2$=N)$_7$PCl$_3$]$^+$[PCl$_6$]$^-$ (A) and its cyclization product (B).

In sum, the linear phosphazenes with number of chain units higher than 5 are more disposed to intermolecular reactions than short linear oligomers. With the increasing of chain length, the cyclization becomes more hindered and the yield of cyclic product decreases. In case of cyclic product with calculated chain length of 8 units, the broadened signal in range of -19 ppm, characteristic for backbone units of linear phosphazenes with polymerization degree about 10-20, is observed.

Table 4. The composition of cyclic phopshazenes obtained by cyclization of linear oligomers.

Cycle size k of the cyclic homologue in the product	m/z of phenoxylated derivatives $[N=P(OPh)_2]_k$	PCl$_5$: HMDS ratio used to obtain linear chlorophosphazene oligomer/calculated average number of P=N-links in the product after cyclization		
		2:3/k = 3	8:9/k = 5	1.04:1/k = 8
		composition of the cyclic product, determined by MALDI-TOF[a)]		
3	694	95.00	38.40	0.7
4	925	3.00	40.30	0.8
5	1156	-	7.81	3.4
6	1387	0.50	2.32	47.9
7	1618	0.50	1.69	31.7
8	1849	1.00	5.70[)]	7.4[)]
9	2080	-	2.95	3.1
10	2311	-	0.84	2.7
11	2541	-	-	1.7
12	2773	-	-	0.5

a) Determined from absolute intensities of the oligomer species on the MALDI-TOF spectra of phenoxy-derivatized cyclophosphazenes $[N=P(OPh)_2]_k$

It indicates the increasing of intermolecular reactions between oligomers $[Cl(PCl_2=N)_n–PCl_3]^+[PCl]^{6-}$ (where n ≥ 5) in comparison with cyclization reaction. According to MALDI-TOF data of phenoxy derivatized compounds, the product contains cyclic oligomers with the number of chain units up to 12. On the other hand, the linear phosphazenes were not observed on spectra which indicates about their too high molecular weight.

6. Conclusion

A new method of synthesis of cyclic phosphazenes via the interaction of corresponding linear chains with HMDS or NH$_4$Cl was developed. HCP can be obtained in a yield, higher than 100% of theoretical. At the same time, higher cycles with 4-7 units can be prepared as dominant products with neighbor homologues as the main side-products.

Author Contributions: Conceptualization, M. Gorlov and V. Oberemok; methodology, N. Bredov and A. Esin; writing—original draft preparation, M. Soldatov; writing—review and editing, M. Gorlov; supervision, V. Kireev; project administration, I. Sirotin. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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