INORGANIC CHEMISTRY

Silicones and Phosphazenes

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Introduction
Polymers have revolutionized human civilization. Carbon forms polymers most extensively on account of its unparalleled catenation property (tendency to form chains). Although to a limited extent, catenation is exhibited by some other elements in Group 14 and Group 15. For example, in Group 14, the catenation tendency follows the sequence C >> Si > Ge ~ Sn >>Pb. In Group 15, the $\overset{-}{N}N$ single bond is so weak that its chain length does not go beyond 3 (in N_3ion). The chain length in case of phosphorus is up to 2 (e.g. in P_2H_4). Silicon in Group 14 forms polymeric silanes with difficulty. In conjugation with oxygen however, it makes extensive Si$\overset{-}{O}$Si linkages forming silicones. Similarly, in conjugation with nitrogen, phosphorus shows unique capability of forming extensive — N = P — bonds in what are called phosphazenes. These two classes of polymers established Si and P as the second and the third most extensively polymer- forming elements, respectively and, have revolutionized polymer science on account of their oxidative, thermal and radiation stabilities. The C = C and C – H bonds in C-based polymers are susceptible to oxidation and the C-C bonds are prone to cleavage, but these two classes of silicones and phosphazenes are free from these lacunae. Their good dielectric properties, excellent water repellency, antistick & antifoam properties, solvent resistance, flame resistance, sometimes physiological inertness and similar other properties have brought out remarkable versatility in their applications from engineering goods to items in medical sciences.

Silicones

General introduction
Originally this word was coined by F. S. Kipping to mean a silicon atom substituting carbon in a ketone (>C=O). But it was soon found that even the first such compound Ph_2SiO was a polymer and it had no chemical resemblance with ketones. Today silicones are well known polymers having extensive Si-O-Si linkages similar to those in silicates. Silicon is sp^3 hybridized and the tetrahedra undergo permutations and combinations to give large variety of polymeric structures. But unlike silicates, in which there are terminal oxygens, silicones contain organic moieties (e. g. CH_3, C_6H_5) attached to silicon and hence Si-C bonds. For this reason they are also called organosilicon polymers. Such polymeric structures are formed in many ways *viz.*, linear and cyclic; chains and cross-linked. Depending upon the degree of polymerization the polymer formed may be a liquid (oils), semisolid (greases), rubber like solid (elastomers) or hard solid (resins). They are often classified on the basis of physical state as

   (a)   Linear silicones (silicone oils)
   (b)   Silicone elastomers
   (c)   Silicone resins

Some are also called silicone greases.

Structural features and synthesis
Silicones contain Si–O–Si linkages and Si–C bonds. Naturally, the synthetic routes involve formation of one or both of the two. Formation of Si–O–Si linkage is simple and is achieved through condensation of two Si–OH bonds (as in the case of formation of silicates from hydrolysis product of $SiCl_4$). The first step in synthesis of silicones naturally, involves putting 'R' groups (R = – CH_3, –C_6H_5) on the tetrahedral Si atom. Care is taken to have at least one 'X'
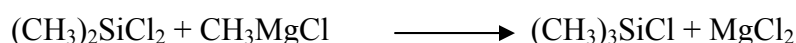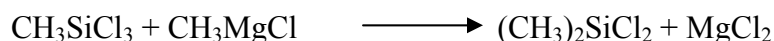
(X = Cl) on this atom so that it could be substituted by hydrolysis. Subsequent condensation through Si–OH bonds generate Si–O–Si linkage.

Step 1 - Introduction of Si–C bonds: Preparation of alkyl (or aryl) substituted chlorosilanes:
i)   Treating $SiCl_4$ with a Grignard reagent in laboratory gives organosilanes:

$$SiCl_4 + CH_3MgCl \longrightarrow CH_3SiCl_3 + MgCl_2$$
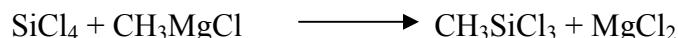
Further alkylation will depend upon the molar ratio of the two reactants:

$$CH_3SiCl_3 + CH_3MgCl \longrightarrow (CH_3)_2SiCl_2 + MgCl_2$$

$$(CH_3)_2SiCl_2 + CH_3MgCl \longrightarrow (CH_3)_3SiCl + MgCl_2$$

ii)   Industrially, such organosilanes are prepared by direct reaction of alkyl or aryl halides with Si. A fluidized silicon bed is used in presence of copper catalyst (90% Si ; 10% Cu metal by weight) :

$$2CH_3Cl + Si \xrightarrow[300^0C]{Cu \ powder} (CH_3)_2 \ SiCl_2$$
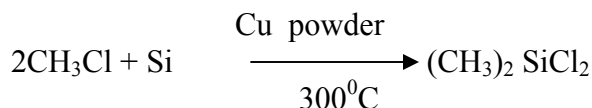
The reaction proceeds via free radical mechanism and the role of Cu is to form free radical intermediates such as {CuCl} and {CuCH$_3$}. CuCl halogenates Si and CuCH$_3$ dissociates to give CH$_3$ · radical. Some mono and trimethyl derivatives are also formed. Adding HCl increases the yield of the monoderivative and reduces that of the dimethlyl derivative. The reactions in both the cases are exothermic. Naturally, the heat generated has to be removed. The product is always a mixture which has to be fractionated to bring desired perfection in polymerization ahead.

Step 2 – Hydrolysis of alkyl / aryl halosilanes :
The substituted halosilanes undergo hydrolysis to corresponding substituted silanols, which on condensation produce silicones. The properties of these silicones depend upon the degree of polymerization and stereochemistry. More – OH groups in the silanols naturally, lead to condensations in more directions. The silanol is usually acidic so it is easily converted to its sodium salt using a 12 M solution of NaOH:
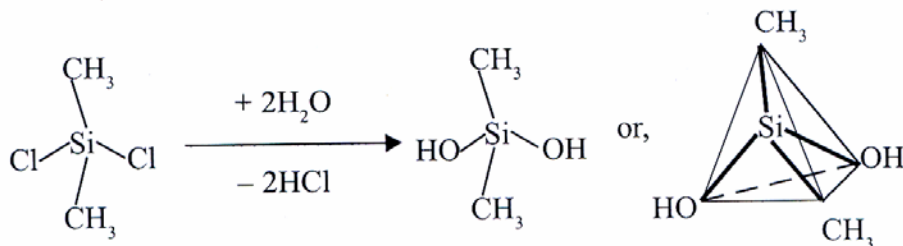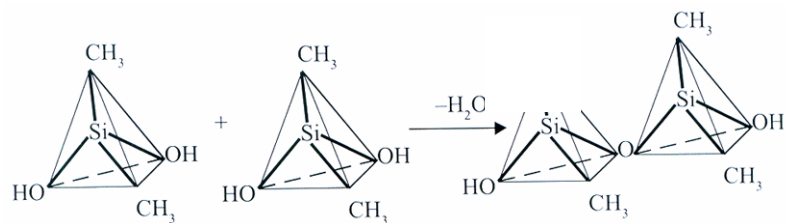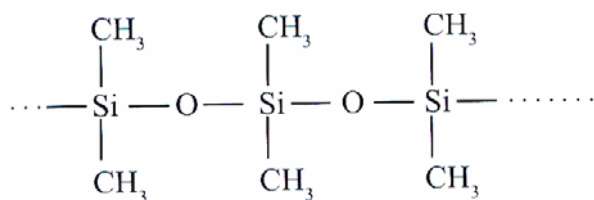
Similar condensations may go on.

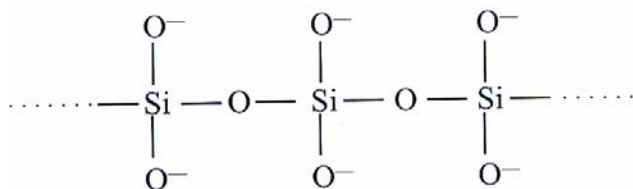In place of $-CH_3$, there could be a $-C_6H_5$. Further condensations lead to higher polymers.

As we have seen, the reaction represented by equation (1) gives linear silicones:
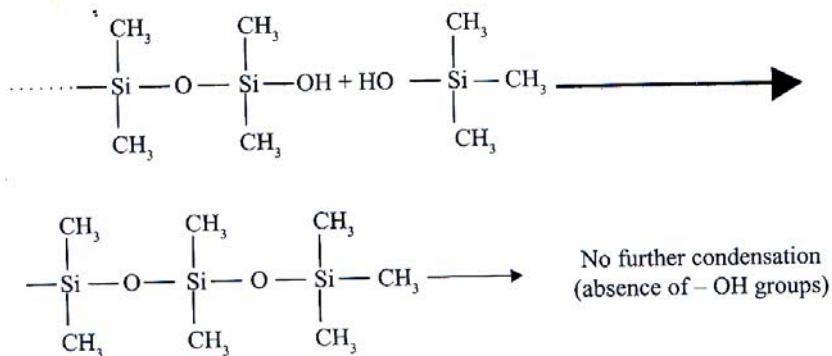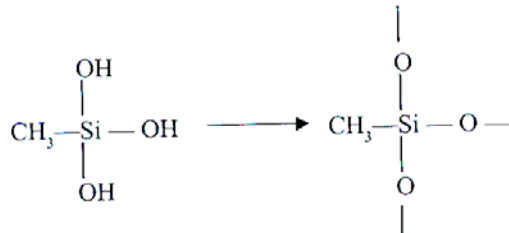

(Polydimethylsiloxane)

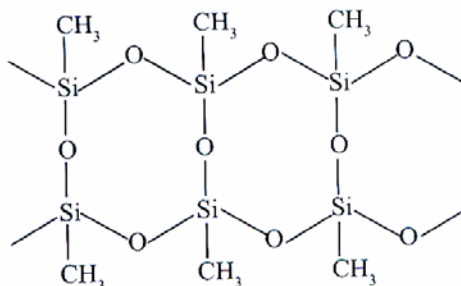It has structural resemblance with silicates:

To terminate the process of polymerization, appropriate amounts of trimethyl silanols are used:

No further condensation
(absence of – OH groups)

Monoalkyl silanols are used to incorporate in order to achieve desired branching and bridging groups,


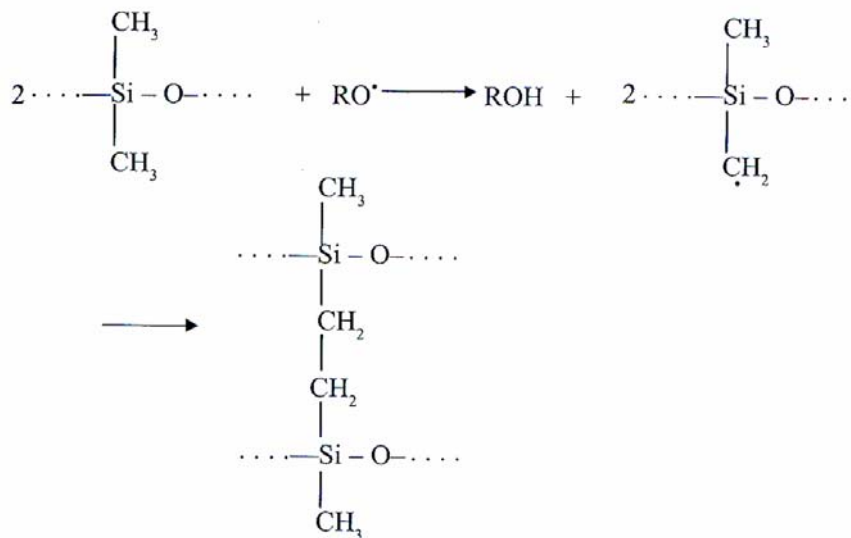These may give siloxenes (silicone resins)

Thus, for getting a desired variety of silicone, calculated amounts of the mono -, di- and trihalosubstituted versions of alkyl silanes are used. The following examples may be given as illustration:

Silicone oils: These are prepared by stirring hexamethyl disiloxane and the cyclo tetramer, tetrakis*cyclo*-dimethyl siloxane in suitable ratio with a little of conc. H_2SO_4. The Si–O bonds are broken to form esters with H_2SO_4 :

$$>Si-O-Si< \xrightarrow{H_2SO_4} > Si-O-SO_3H + HO-Si <$$
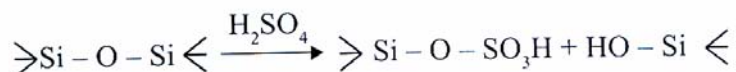
Thereafter, hydrolysis gives new Si – O bonds and this brings randomness in the Si–O–Si linkages. The molecular weight, viscosity etc. depend on the initial ratio.

Silicone elastomers: These are prepared by taking the dihaloderivatives only. The dimethyl polysiloxanes thus obtained are reinforced using fumed silica. The chain blocking precursors [monohalo derivative which gives $(CH_3)_3Si–O–$] and the precursors causing cross-linking are totally avoided. KOH is used and the linear polymer thus produced is in form of a viscous gum. For effective use, vulcanization is carried out using benzoyl peroxide etc. This brings about cross-linking in the polymer:

$$2\cdots-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\cdots \quad + \quad RO^{\bullet} \longrightarrow ROH \quad + \quad 2\cdots-\underset{\underset{CH_2^{\bullet}}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\cdots$$

$$\longrightarrow \quad \cdots-\underset{\underset{\underset{\underset{\underset{\underset{CH_3}{|}}{Si-O-\cdots}}{|}}{CH_2}}{\overset{\overset{CH_3}{|}}{Si}}}{}-O-\cdots$$

Using catalytic techniques, vulcanization is also effected by introducing acetoxy groups in the side chain:

$$-O-\underset{\underset{OCOCH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-OCOCH_3 \quad \xrightarrow[\text{room temperature}]{\text{Moisture}} \quad -O-\underset{\underset{OCOCH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-OH + CH_3COOH$$

$$-O-\underset{\underset{OCOCH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-OH + \quad -O-\underset{\underset{CH_3}{|}}{\overset{\overset{OCOCH_3}{|}}{Si}}-OH \quad \longrightarrow \quad -O-\underset{\underset{\underset{\underset{\underset{CH_3}{|}}{Si-OH}}{|}}{O}}{\overset{\overset{CH_3}{|}}{Si}}-OH$$
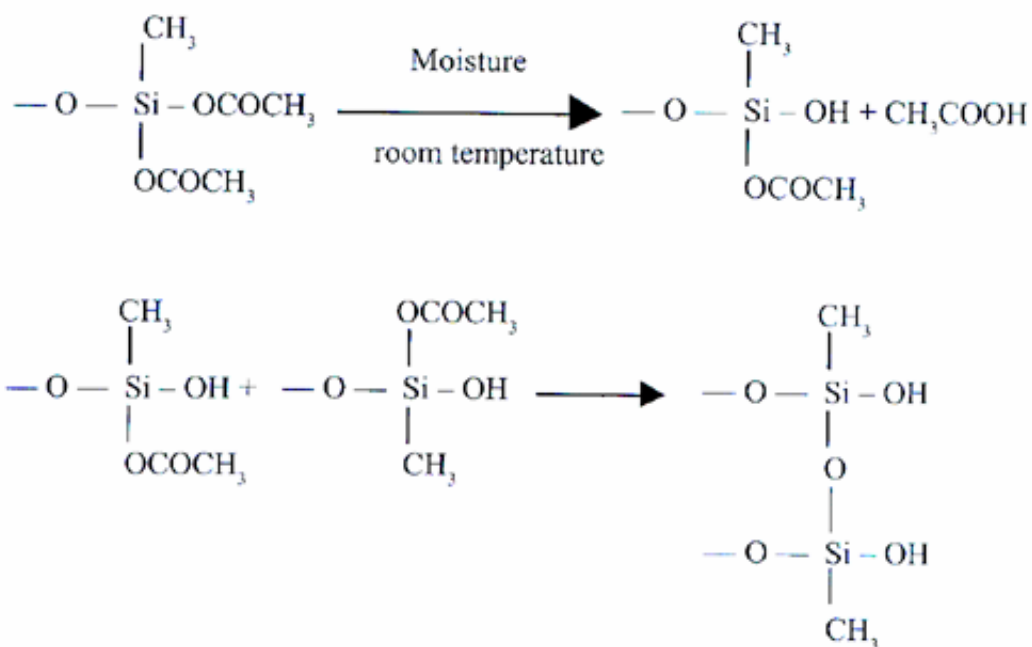
Simultaneous condensation through hydroxyl group brings out desired, cross-linking. This controlled cross-linking (1 in every 100-1000 Si units) brings about unusual flexibility, elasticity, strength and capacity to bear temperature as high as 250^0C and as low as -100^0C.

Silicone resins: These are prepared by hydrolyzing methyl and phenyl substituted dichloro and trichloro silanes in toluene. Introduction of phenyl groups in place of methyl brings about further heat stability and flexibility. Extensive cross-linking makes them look like bakelite but with better dielectric properties suitable for use as insulators.

The nature of the polymer is determined by the extent of cross-linking and the nature of the alkyl/aryl substituent.

Interesting properties and uses
All silicones are excellent water repellent, thermally and electrically insulating and chemically inert. They exhibit antistick, antifoam and flame resistance properties. As such, they have brought out technological revolutions in all walks of life. A few of their applications are given below:

(i) Silicone oils: They have extremely high viscosity (*ca.* 50,000 to 3,00,000 times that of water depending upon the chain length) which does not change appreciably with temperature. Their surface tension is low. Chemical inertness and presence non-polar groups make them non-toxic. They are used:

- As dielectric insulating media e.g. in transformer oils.
- As hydraulic oils
- As compressible fluids for liquid springs
- As antifoaming agents in sewage disposal plants, textile dyeing, cooking oil etc. (ppm quantities do wonder!)
- As an additive in cosmetics (lipsticks, sun tan lotion, hair oil etc.)

(ii) Silicone greases: Silicone oils are thickened to make silicone greases for use in heavy-duty steel gears and shafts. For this purpose, methyl phenyl silicone oils are thickened by Li-soaps.

(iii) Silicone rubber: Silicon rubbers are used in making

- Cable insulation
- Static and rotary seals
- Gaskets
- Diaphragms
- Electric tape insulation
- Industrial sealants and adhesives
- Heart valves
- Space suits
- Accurate impressions for dentures
- Masks in cinema.

(iv)Silicone resins: Silicone resins are used in making

- Insulations in electrical equipments
- Laminates and printed circuit boards for electronic equipments
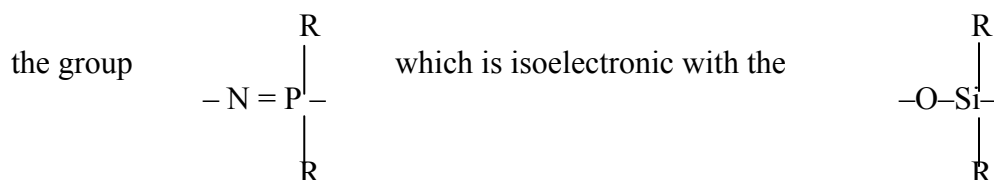- High temperature paints and coatings on cooking utensils.

Phosphazenes

General introduction
Phosphazenes were initially termed phosphonitrilic polymers. Later on, the new term was used to represent **phosph**orus, nitrogen (=**az**o) and P = N double bonds (=**ene**) which are always present in these polymers. They are thus 'unsaturated PN compounds' containing phosphorus, mostly in +V state. As is usual with polymers, they may have cyclic or chain structure. The nitrogen in
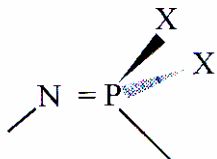

groups is in 2-coordination and phosphorus in 4-coordination. They contain

the group $-N=\overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle R}{|}}{P}}-$ which is isoelectronic with the $-O-\overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle R}{|}}{Si}}-$

groups of silicones. Their polymers differ in substitution on phosphorus and on the nature of those substitutents besides the way and the extent, to which polymerization has taken place. Their water repellent, solvent resistant and flame resistant properties have found new applications and these have led to many technological innovations during the last few decades. They are usually classified on the basis of number of phosphazene units that are incorporated in the structure:

Monophosphazenes: Monophosphazenes are compounds of the type $X_3P = NR$, (X and R = Cl, OR, NR_2, Ar etc.). These are unsaturated compounds and can be prepared as follows:

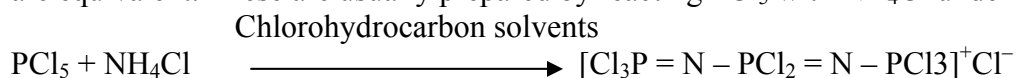(a) Reacting an azide $(R - N_3)$ with PR_3 (R = Ar, OR, Cl, NR_2) :

$$P\,(C_6H_5)_3 \quad + \quad C_6H_5\text{–}N_3 \quad \xrightarrow[-N_2]{} \quad (C_6H_5)_3 - P = N - C_6H_5$$
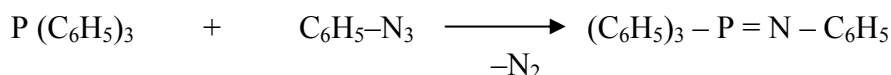
(b)   Reacting dihalotriphenylphosphenes with aromatic amines :-

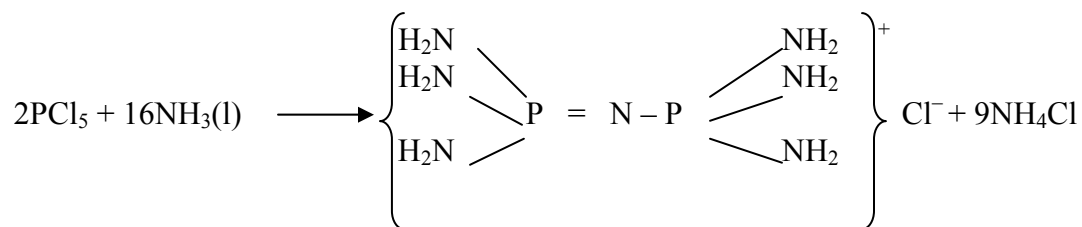$$(C_6H_5)_3PCl_2 \quad + \quad C_6H_5\text{–}NH_2 \quad \xrightarrow[-2HCl]{} (C_6H_5)_3 - P = N - C_6H_5$$
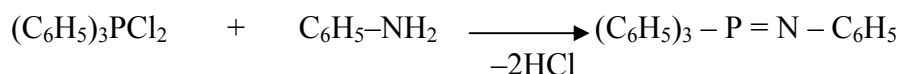
Diphosphazenes: These contain two $>P = N-$ groups and the P = N and the P – N bonds are equivalent. These are usually prepared by reacting PCl_5 with NH_4Cl under mild conditions:

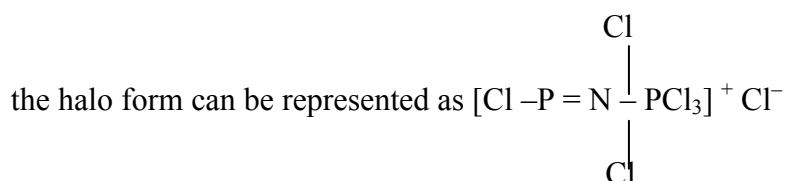$$PCl_5 + NH_4Cl \quad \xrightarrow{\text{Chlorohydrocarbon solvents}} \quad [Cl_3P = N - PCl_2 = N - PCl3]^+Cl^-$$

However, PCl_5 undergoes ammonolysis in liq. NH_3 :

$$2PCl_5 + 16NH_3(l) \longrightarrow \left\{ \begin{array}{c} H_2N \\ H_2N \\ H_2N \end{array} \!\!\!\!\! P = N - P \!\!\!\!\! \begin{array}{c} NH_2 \\ NH_2 \\ NH_2 \end{array} \right\}^{+} Cl^{-} + 9NH_4Cl$$

The disphosphazenes exist both in covalent and ionic forms . Thus

the halo form can be represented as $[Cl - P = N - \overset{\displaystyle Cl}{\underset{\displaystyle Cl}{|}} PCl_3]^{+} Cl^{-}$

**Polyphosphazenes:**

These contain more than two $>P = N -$ groups. Polymeric phosphazene dichlorides are formed when further halogen or halophosphorus substitutions of $- NH_2$ groups in P takes place. The polymeric phosphazene dichlorides can be represented as

$$[Cl \!\!- \!\!\left[\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{| \atop |}} P = N - \right] \!\! PCl_3]^{+} PCl_6^{-}$$
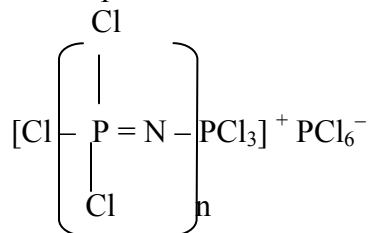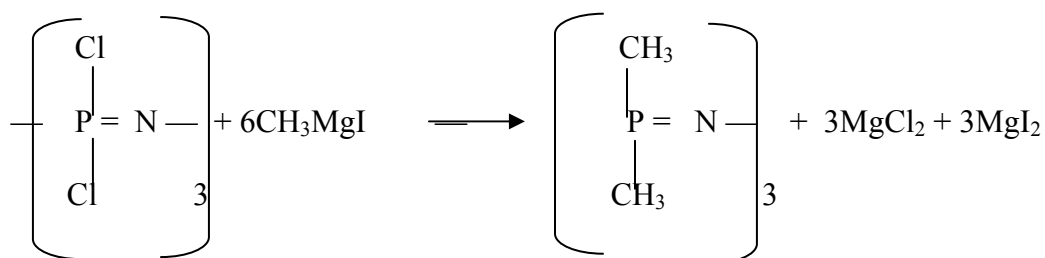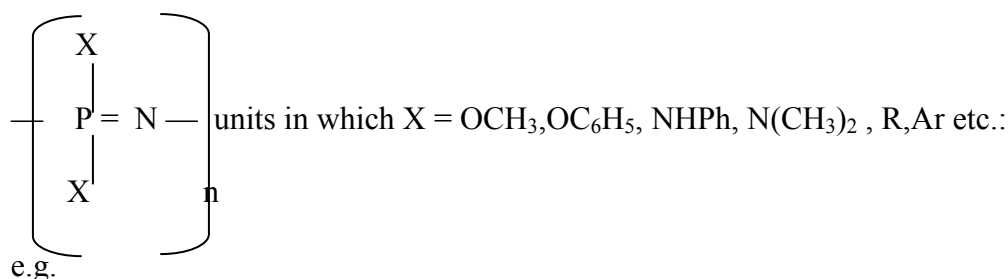
These form chains and cyclic structures having 'n' value upto 10^4. The simple representation of polyphosphazene dichlorides is made as $(NPCl_2)_n$. These are prepared as follows:

$$nPCl_5 + nNH_4Cl \xrightarrow[120 - 150^0C]{\text{Solvent (a halo hydrocarbon)}} [NPCl_2)_n] + 4n\ HCl$$
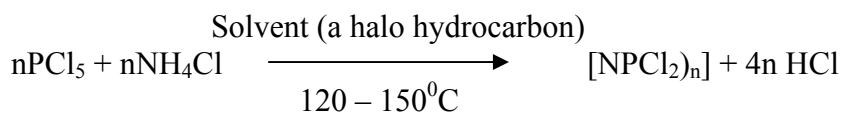
Cyclic trimer, tetramer etc. are prepared by using different conditions. Separation is done through fractionation. The cyclic trimer, $cyclo - [NPCl_2]_3$ on heating at $150 - 300^0C$ furnishes polymeric products. But heating at a higher temperature $(350 - 360^0C)$ causes cleavage and depolymerization.

The chlorines in the product may be substituted by nucleophiles and varieties of substituted polyphosphazenes are obtained having

$$\left[\begin{array}{c} X \\ | \\ -\!\!-\ P = N -\!\!- \\ | \\ X \end{array}\right]_n \text{ units in which } X = OCH_3, OC_6H_5, NHPh, N(CH_3)_2 , R, Ar \text{ etc.:}$$

e.g.

$$\left[\begin{array}{c} Cl \\ | \\ -\!\!-\ P = N -\!\!- \\ | \\ Cl \end{array}\right]_3 + 6CH_3MgI \longrightarrow \left[\begin{array}{c} CH_3 \\ | \\ -\!\!-\ P = N -\!\!- \\ | \\ CH_3 \end{array}\right]_3 + 3MgCl_2 + 3MgI_2$$

Nature of bonding in triphosphazenes

Bonding in phosphazenes is quite interesting. Diphosphazene contains one $P = N$ and one $P - N$ bonds both of which are equivalent and the bond length is shorter than single bond. This is easily explained by resonance

$$\left[\begin{array}{c} \diagdown \quad\quad\quad\quad\quad\quad \diagup \\ P \cdots N \cdots P \\ \diagup \quad\quad\quad\quad\quad\quad \diagdown \end{array}\right]$$
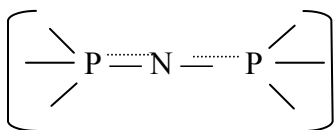
In case of trimer and higher phosphazenes however, things are complex. At first sight, there seems to be alternate single and double bond conjugate systems through out $P - N - P$ skeleton. Such conjugate systems are expected to lead to delocalization of the sort of benzene. The cyclic trimer has an accurately planar 6-membered ring structure but, unlike aromatic systems, it is difficult to reduce it electrochemically. Also, the spectral evidence of delocalized system (bathochromic ultraviolet shift) is not found. This is explained by the unique and interesting structure that triphosphazenes possess.

As in other phosphazenes, triphosphazenes have

  (i)   Very stable ring
  (ii)   All the skeletal interatomic distances are equal if all the six substituent groups on phosphorus are identical.
  (iii) A shorter $P - N$ bond length ($\sim$ 158 pm) than single bond ($\sim$177 pm)
  (iv)   All the nitrogen atoms weakly basic hence protonable (more so if substituents on P are electron releasing).

The symmetry of the molecule is like that of benzene. It has planar structure with three nitrogen and three phosphorus atoms situated on alternate corners of the hexagon. The substitutents (X) on P are placed above and below the plane. If all the substituents are identical then three of them form together one plane above and three form one plane below the molecular plane.
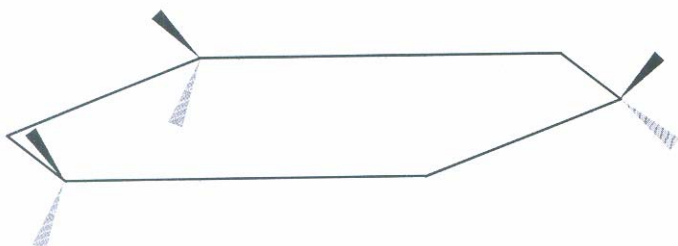
Some more features are mentioned below:

- Nitrogen atoms are sp^2 hybridized:

$2p_z$

sp^2 hybridization
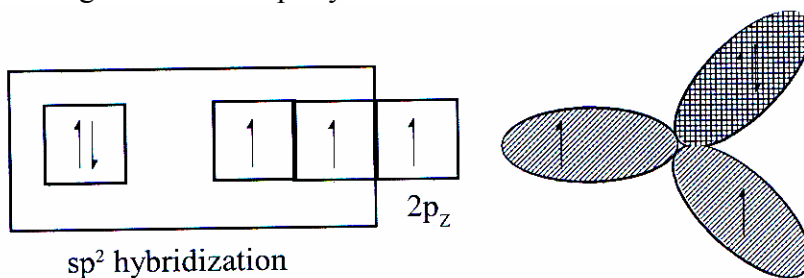
Two such hybrid orbitals are involved in σ-bonding
- Similarly, each phosphorus is sp^3 hybridized

Three such hybrid orbitals are involved in σ- bonding.

- There is then one 'in plane' π-bonding involving the lone pair of N (sp^2 orbital) in xy plane and the vacant d_{xy} or $d_{x^2-y^2}$ orbital of the P — atom.
- There are two 'out of plane' interactions:
  (i)   Heteromorphic interactions: The singly occupied p_z^1 orbital on the nitrogen overlaps with the d_{xz}^o or d_{yz}^O orbital of phosphorus ($p\pi$ – $d\pi$ bonding).
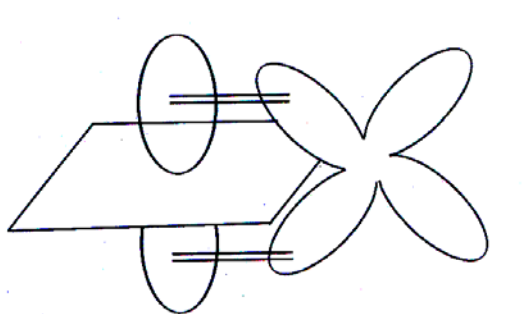
(ii) Homomorphic interactions: There is a $p\pi - p\pi$ interaction of p_z orbitals of two nitrogens through the d_{yz} orbital of the phosphorus in between.
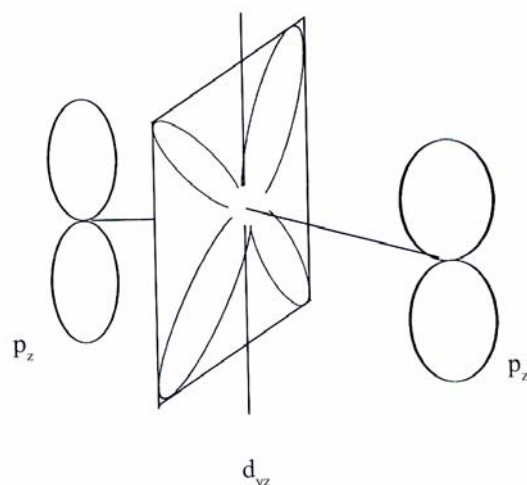
- It is believed that the two contributions *viz.* heteromorphic and homomorphic are equal. This results in separation of the π orbitals into localized 3-centre orbital islands. There are 3 such islands with interruptions at the three phosphorus atoms. These interruptions in the M. O's. prevent the systems from exhibiting delocalization of the π-electron.

Uses

Both the cyclic and non-cyclic polyphosphazenes have great oxidative, thermal & radiative stabilities. Substituents such as $-NH_2$, $-OR$, $-OC_6H_5$ or fluorinated derivatives bring about further stabilities. Their water repellency, solvent resistance, flame resistance, retention of flexibility at low temperatures and their dielectric properties make them very useful for a variety of modern technological purposes. These are used for making:

i) rigid plastics, plastic films, expanded foams
ii) fuel hoses, gaskets
iii) O-ring seals for use in extremely cold climate (e.g. in high flying aircrafts or in vehicles for Arctic type climate)
iv) metal coatings & wire insulation
v) composite materials together with asbestos, glass or with ordinary phenolic resins.

Suggested Readings
1. N.N.Greenwood and A.Earnshaw, *Chemistry of the Elements*, Pergamon
2. J.D.Lee, *Concise Inorganic Chemistry*, Chapman and Hall
3. S.S. Krisnamurthy, A.C. Sau and M.Woods, "Cyclophosphazenes" in *Adv. Inorg. Chem. Radiochem.*, **21**,41- 112(1978)