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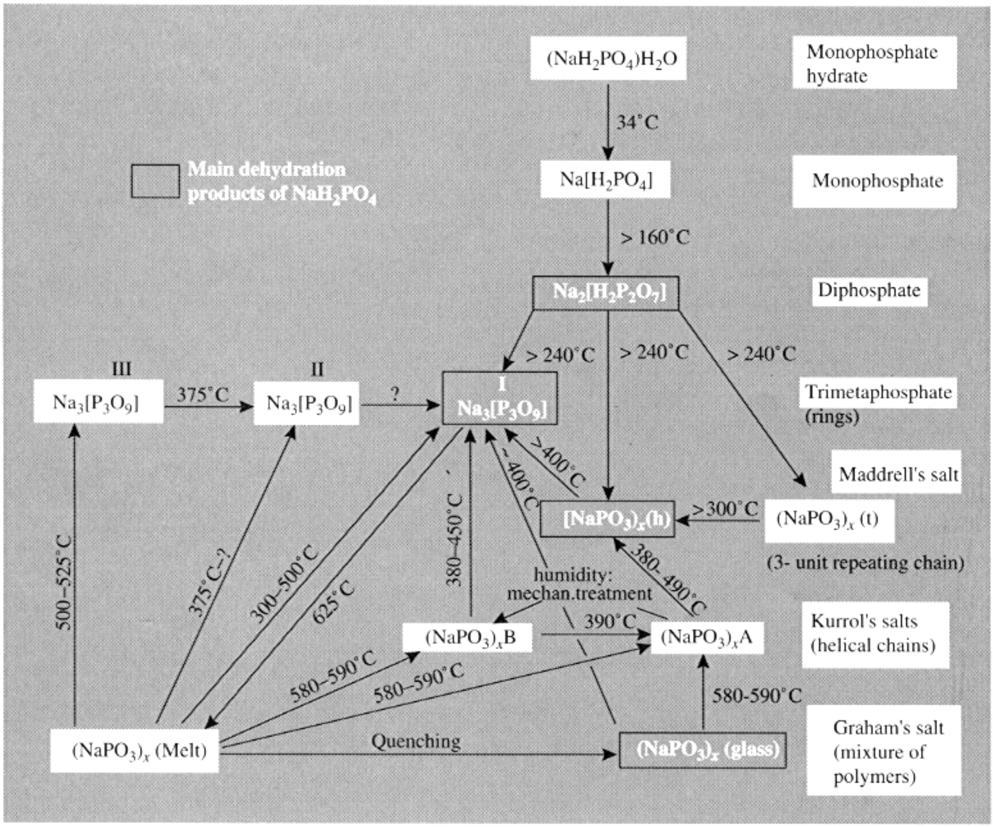
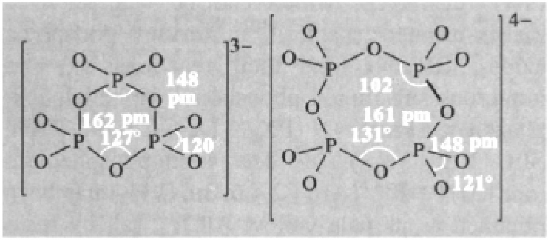


Figure 12.21 Interrelationship of metaphosphates. (From CIC, Vol. 2, p. 521.)



chromatographic separation from Graham's salt in which they are present to the extent of ~1%.

12.3.7 Phosphorus–nitrogen compounds

The P–N bond is one of the most intriguing in chemistry and many of its more subtle aspects still elude a detailed and satisfactory description. It occurs in innumerable compounds, frequently of great stability, and in many of these the strength of the bond and the shortness of the interatomic distance have been interpreted in terms of "partial double-bond character". In fact, the conventional symbols P–N and P=N are more an aid to electron counting than a description of the bond in any given compound (see p. 538).

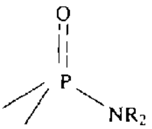
Many compounds containing the P–N link can be considered formally as derivatives of the oxoacids of phosphorus and their salts (pp. 510–31) in which there has been isoelectronic replacement of:

PH [or P(OH)] by $P(NH_2)$ or $P(NR_2)$;
P=O [or P=S] by P=NH or P=NR;

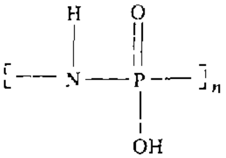
P–O–P by P–NH–P or P–NR–P,

etc.$^{(148,149)}$

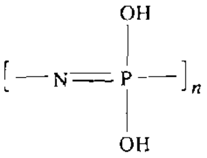
Examples are phosphoramidic acid, $H_2NP(O)(OH)_2$; phosphordiamidic acid, $(H_2N)_2P(O)(OH)$; phosphoric triamide, $(H_2N)_3PO$; and their derivatives. There are an enormous number of compounds featuring the 4-coordinate group shown in structure (1) including the versatile nonaqueous solvent hexamethylphosphoramide $(Me_2N)_3PO$; this is readily made by reacting $POCl_3$ with $6Me_2NH$, and dissolves metallic Na to give paramagnetic blue solutions similar to those in liquid NH_3 (p. 77).



(1)



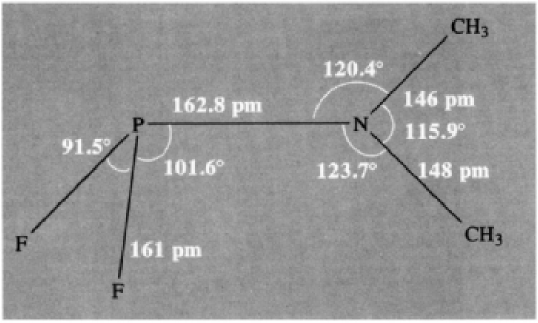
(2)



(3)

Another series includes the *cyclo*-metaphosphimic acids, which are tautomers of the *cyclo*-polyphosphazene hydroxides (p. 541). Similarly, halogen atoms in PX_3 or other P–X compounds can be successively replaced by the isoelectronic groups $-NH_2$, $-NHR$, $-NR_2$, etc., and sometimes a pair of halogens can be replaced by =NH or =NR. These, in turn, can be used to prepare a large number of other derivatives as indicated schematically opposite for $P(NMe_2)_3$$^{(2)}$.

Although such compounds all formally contain P–N single bonds, they frequently display properties consistent with more extensive bonding. A particularly clear example is $PF_2(NMe_2)$ which features a short interatomic P–N distance and a *planar* N atom as indicated in the diagram below. (In the absence of this additional π bonding the P^{III}–N single-bond distance is close to 177 pm.) Again, the proton nmr of such compounds sometimes reveals restricted rotation about P–N at low temperatures and typical energy barriers to rotation (and coalescence temperatures of the non-equivalent methyl proton signals) are $PCl_2(NMe_2)$ 35 kJ mol^{-1} (−120°), $P(CF_3)_2(NMe_2)$ 38 kJ mol^{-1} (−120°), $PClPh(NMe_2)$ 50 kJ mol^{-1} (−50°).



Other unusual P/N systems which have recently been investigated include the crystalline compound HPN_2, i.e. PN(NH), which is formed by ammonolysis of P_3N_5 at 580°C and which has a β-cristobalite (SiO_2) type structure;$^{(150)}$ PNO (cf. N_2O), which can be studied as a matrix-isolated species;$^{(151)}$ various phosphine azides, $RR'PN_3$, and their reactions;$^{(152)}$ and numerous substituted phosphonyl triphenylphosphazenes, $Ph_3P{=}N{-}PX_2$, (X=Cl, F, OPh, SEt, NEt_2, etc.).$^{(153)}$ The iminophosphenium ion, $[ArN{\equiv}P]^+$ (Ar = $2,4,6\text{-}Bu^t_3C_6H_2$) has been obtained as its pale yellow $AlCl_4^-$ salt by reaction of the corresponding covalently bonded chloride, ArN=PCl, with $AlCl_3$; the ion is notable

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[148] D. A. Palgrave, Section 28, pp. 760–815, in ref. 26

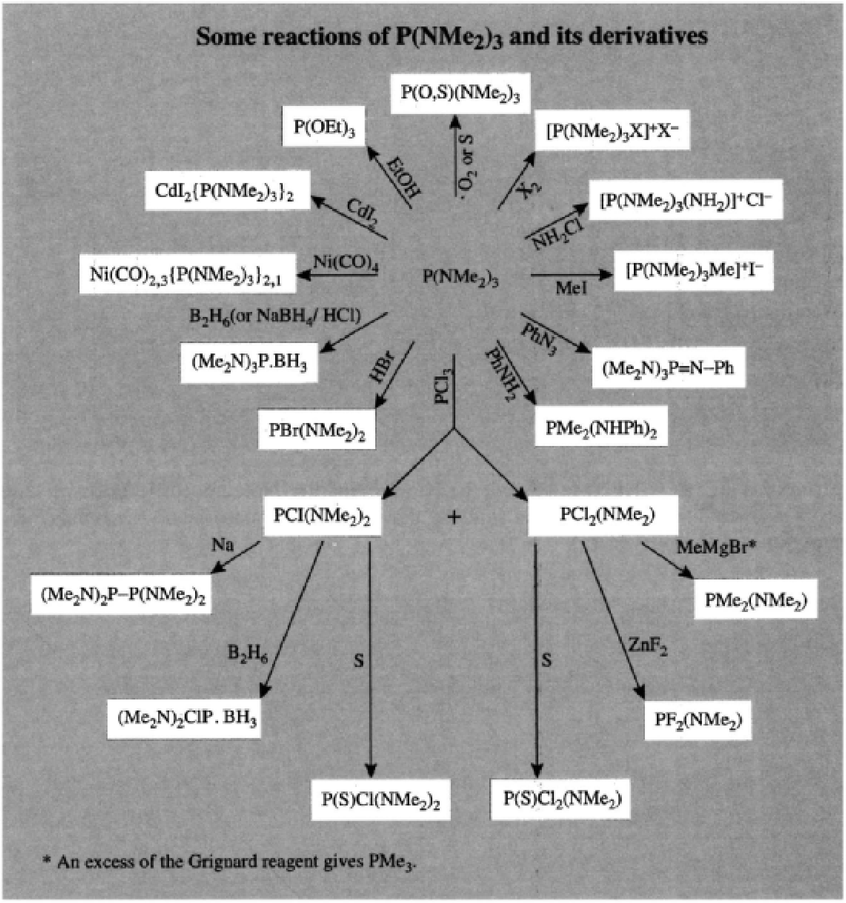
[149] M. L. Nielsen, Chap. 5 in C. B. Colburn (ed.), *Developments in Inorganic Nitrogen Chemistry*, Vol. 1, pp. 307–469, Elsevier, Amsterdam, 1966.

[150] W. Schnick and J. Lücke, *Z. anorg. allg. Chem.* **610**, 121–6 (1992).

[151] R. Ahlrichs, S. Schunk and H.-G. Schnöckel, *Angew. Chem. Int. Edn. Engl.* **27**, 421–2 (1988).

[152] J. Boske, E. Niecke, E. Ocando-Maverez, J.-P. Majoral and G. Bertand, *Inorg. Chem.* **25**, 2695–8 (1986).

[153] L. Riesel and R. Friebe, *Z. anorg. allg. Chem.* **604**, 85–91 (1991).


Some reactions of $P(NMe_2)_3$ and its derivatives

* An excess of the Grignard reagent gives PMe_3.

as the first stable species having a P≡N triple bond (P–N 148 pm, angle C–N–P 177°).[154] The coordination chemistry of phosphorane iminato complexes (containing the R_3PN^- ligand) of transition metals has been reviewed.[155]

Cyclophosphazanes

Many heterocyclic compounds contain formally single-bonded P–N groups, the simplest being the *cyclo*-diphosphazanes $(X_3PNR)_2$ and $\{X(O,S)PNR\}_2$. These contain P^V and have the structures shown in Fig. 12.22. A few phosph(III)azane dimers are also known, e.g. $(RPNR')_2$. A more complex example, containing fused heterocycles of alternating P^{III} and N atoms, is the interesting hexamethyl derivative $P_4(NMe)_6$ mp 122°. This stable compound (Fig. 12.23a) is readily obtained by reacting PCl_3 with $6MeNH_2$; it is isoelectronic with and isostructural with P_4O_6 (p. 504) and undergoes many similar reactions. The stoichiometrically similar compound $P_4(NPr^i)_6$ can be prepared in the non-adamantane-type structure shown in Fig. 12.23b, though it converts to structure-type a on being heated at 157° for 12 days.[156] A different sequence of atoms occurs in $P_2(NMe)_6$

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[154] E. Niecke, M. Nieger and F. Reichert *Angew. Chem. Int. Edn. Engl.* **27**, 1715–6 (1988).

[155] K. Dehnicke and J. Strähle, *Polyhedron* **8**, 707–26 (1989).

[156] O. J. Scherer, K. Andres, C. Krüger, Y.-H. Tsay and G. Wolmershäuser, *Angew. Chem. Int. Edn. Engl.* **19**, 571–2 (1980).

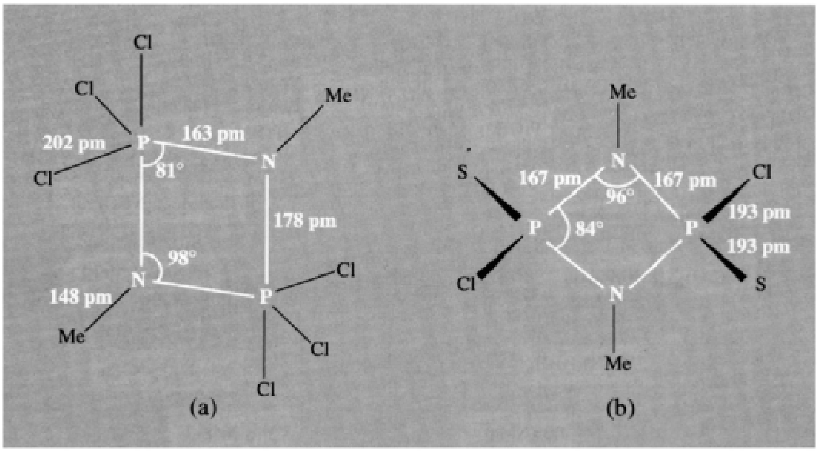


Figure 12.22 Structures of (a) $(Cl_3PNMe)_2$, and (b) $\{Cl(S)PNMe\}_2$. Note the difference in length of the axial P–N and equatorial P–N bonds (and of the axial and equatorial P–Cl bonds) about the trigonal bipyramidal P atoms in (a).

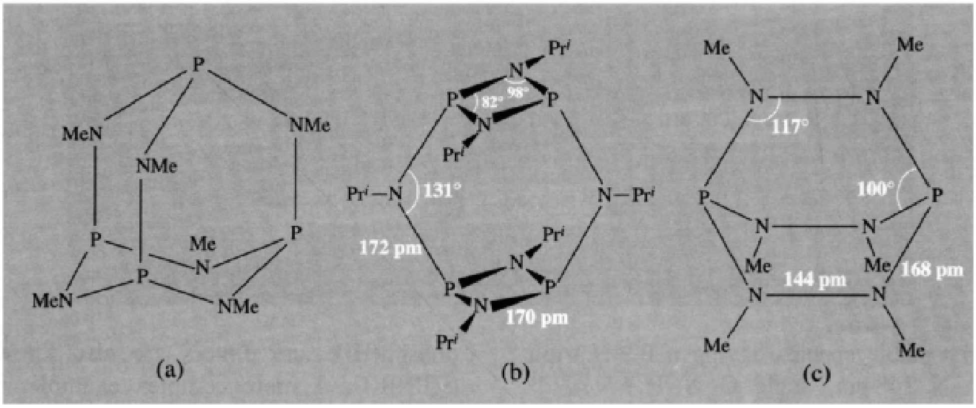
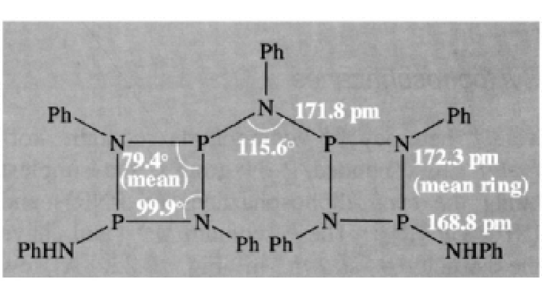


Figure 12.23 Structures of (a) $P_4(NMe)_6$, (b) $P_4(NPr^i)_6$, and (c) $P_2(NMe)_6$ (see text).

(Fig. 12.23c) and many other "saturated" heterocycles featuring either P^{III} or P^{V} have been made. A typical example, made by slow addition of PCl_3 to $PhNH_2$ in toluene at 0°, is $[PhNHP_2(NPh)_2]_2NPh$; the crystal structure of the 1:1 solvate of this compound with CH_2Cl_2 (mp 250°) reveals that all N atoms are essentially planar with distances to P as indicated in the following diagram.[157]



Phosphazenes

Formally "unsaturated" PN compounds are called phosphazenes and contain P^{V} in the

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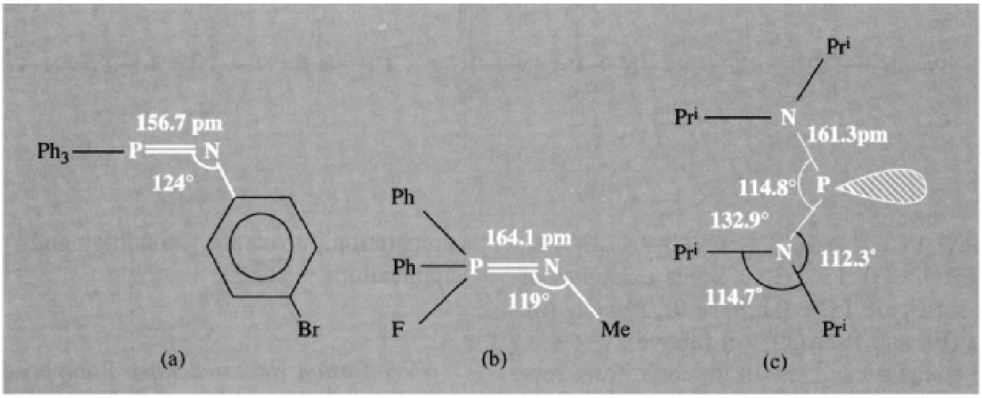
[157] M. L. THOMPSON, R. C. HALTIWANGER, and A. D. NORMAN, *J. Chem. Soc., Chem. Commun.*, 647–8 (1979).



grouping $\gt P{=}N-$. A few phosph(III)azenes are also known. Phosphazenes can be classified into monophosphazenes (e.g. $X_3P{=}NR$), diphosphazenes (e.g. $X_3P{=}N{-}P(O)X_2$), polyphosphazenes containing 2,3,4,...∞ $-X_2P{=}N-$ units, and the *cyclo*-polyphosphazenes $[-X_2P{=}N-]_n$, $n = 3,4,5 \ldots 17$.

Monophosphazenes, particularly those with organic substituents, $R_3P{=}NR'$, derive great interest from being the N analogues of phosphorus ylides $R_3P{=}CR_2$ (p. 545). They were first made by H. Staudinger in 1919 by reacting an organic azide such as PhN_3 with PR_3 ($R = Cl$, OR, NR_2, Ar, etc.), e.g.:

$$PPh_3 + PhN_3 \longrightarrow N_2 + Ph_3P{=}NPh;\ \text{mp } 132^\circ$$

More recently they have been made via a reaction associated with the name of A. V. Kirsanov (1962), e.g.:

$$Ph_3PCl_2 + PhNH_2 \longrightarrow Ph_3P{=}NPh + 2HCl$$

As expected, the P–N distance is short and the angle at N is ~120°, e.g. (a) and (b) above. Over 600 such compounds are now known, especially those with the $Cl_3P{=}N-$ group.[158]

Diphosphazenes can be made by reacting PCl_5 with NH_4Cl in a chlorohydrocarbon solvent under mild conditions:

$$3PCl_5 + NH_4Cl \xrightarrow{\text{solvent}} 4HCl + [Cl_3P{=}N{-}PCl_3]^+PCl_6^-;\quad \text{mp } 310^\circ$$

$$\downarrow NH_4Cl$$

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

The inverse of these compounds are the phosphadiazene cations, prepared by halide ion abstraction from diaminohalophosphoranes in CH_2Cl_2 or SO_2 solution, e.g.:

$$(R_2N)_2PCl + AlCl_3 \longrightarrow [(R_2N)_2P]^+[AlCl_4]$$

An X-ray crystal structure of the Pr^i_2N-derivative shows the presence of a bent, 2-coordinate P atom, equal P–N distances, and accurately planar 3-coordinate N atoms as in (c) above.[159] In liquid ammonia ammonolysis also occurs:

$$2PCl_5 + 16NH_3(\text{liq.}) \longrightarrow [(H_2N)_3P{=}N{-}P(NH_2)_3]^+Cl^- + 9NH_4Cl$$

The P=N and P–N bonds are equivalent in these compounds and they could perhaps better be written as $[X_3P{\cdots}N{\cdots}PX_3]^+$, etc. Like the parent phosphorus pentahalides (p. 498), these diphosphazenes can often exist in ionic and covalent forms and they are part of a more extended group of compounds which can be classified into several general series $Cl(Cl_2PN)_nPCl_4$, $[Cl(Cl_2PN)_nPCl_3]^+Cl^-$,

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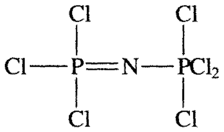
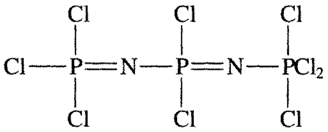
[158] M. Bermann, *Topics in Phosphorus Chemistry* **7**, 311–78, 1972.

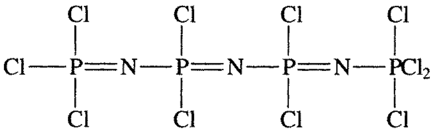
[159] A. H. Cowley, M. C. Cashner and J. S. Szobota, *J. Am. Chem. Soc.* **100**, 7784–6 (1978).


$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{P}}{=}N{-}\overset{Cl}{\underset{Cl}{P}}Cl_2}$$

(a)


$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{P}}{=}N{-}\overset{Cl}{\underset{Cl}{P}}{=}N{-}\overset{Cl}{\underset{Cl}{P}}Cl_2}$$

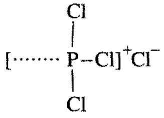
(b)


$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{P}}{=}N{-}\overset{Cl}{\underset{Cl}{P}}{=}N{-}\overset{Cl}{\underset{Cl}{P}}{=}N{-}\overset{Cl}{\underset{Cl}{P}}Cl_2}$$

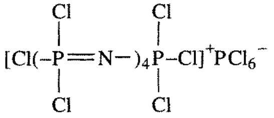
(c)

$[Cl(Cl_2PN)_nPCl_3]^+PCl_6^-$, $Cl(Cl_2PN)_nPOCl_2$, etc., where $n = 0, 1, 2, 3\ldots$. Some examples of the first series are PCl_5 (i.e. $n = 0$), P_2NCl_7 (a), $P_3N_2Cl_9$ (b), and $P_4N_3Cl_{11}$ (c) (above).

Some of these can exist in the ionic form represented by the second series (d):


$$\mathrm{[\cdots\cdots\overset{Cl}{\underset{Cl}{P}}{-}Cl]^+Cl^-}$$

(d)

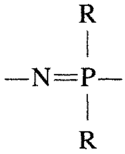

$$\mathrm{[Cl({-}\overset{Cl}{\underset{Cl}{P}}{=}N{-})_4\overset{Cl}{\underset{Cl}{P}}{-}Cl]^+PCl_6^-}$$

(e)

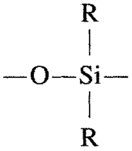
Likewise, the third series runs from $n = 0$ (i.e. $PCl_4^+PCl_6^-$) through P_3NCl_{12}, $P_4N_2Cl_{14}$, and $P_5N_3Cl_{16}$ to $P_6N_4Cl_{18}$ (e). In the limit, polymeric phosphazene dichlorides are formed $(-NPCl_2-)_n$, where n can exceed 10^4 and these polyphosphazenes and their *cyclo*-analogues form by far the most extensive range PN compounds.

Polyphosphazenes

The grouping


$$\mathrm{{-}N{=}\overset{R}{\underset{R}{P}}{-}}$$

is isoelectronic with the


silicone grouping $\mathrm{{-}O{-}\overset{R}{\underset{R}{Si}}{-}}$ (p. 364)

and, after the silicones, the polyphosphazenes form the most extensive series of covalently bonded polymers with a non-carbon skeleton. This section will describe their preparation, structure, bonding and potential applications.[2,8,160,161]

Preparation and structure. Polyphosphazenes have a venerable history. $(NPCl_2)_n$ oligomers were first made in 1834 by J. von Liebig and F. Wöhler who reacted PCl_5 with NH_3, but their stoichiometry and structure were not elucidated until much later. The fluoro analogues $(NPF_2)_n$ were first made in 1956 and the bromo compounds $(NPBr_2)_n$ in 1960. The synthesis of $(NPCl_2)_n$ was much improved by R. Schenk and G. Römer in 1924 and their method remains the basis for present-day production on both the laboratory and industrial scales:

$$n\mathrm{PCl_5} + n\mathrm{NH_4Cl} \xrightarrow[120-150^\circ]{\text{solvent}} (\mathrm{NPCl_2})_n + 4n\mathrm{HCl}$$

Appropriate solvents are 1,1,2,2-tetrachloroethane (bp 146°), PhCl (bp 132°) and 1,2-dichlorobenzene (bp 179°). By varying the conditions, yields of the cyclic trimer or tetramer and other oligomers can be optimized and the compounds then separated by fractionation. Highly polymeric $(NPCl_2)_\infty$ can be made by heating *cyclo*-$(NPCl_2)_3$ to 150–300°, though heating to 350° induces depolymerization. Polycyclic compounds are rarely obtained in

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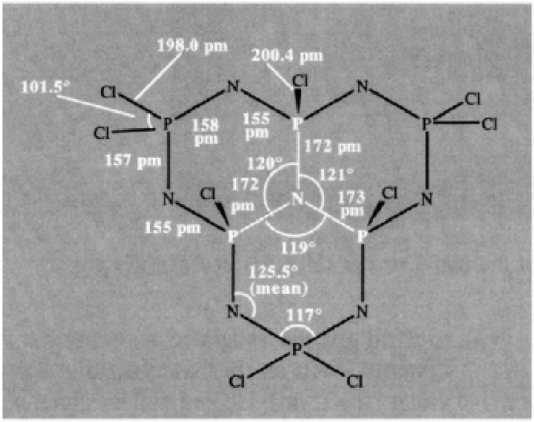
[160] H. R. ALLCOCK, *Phosphorus Nitrogen Compounds*, Academic Press, New York, 1972, 498 pp.; H. R. ALLCOCK, *Chem. Rev.* **72**, 315–56 (1972) (475 refs.). H. R. ALLCOCK, Chap. 3 in A. H. COWLEY (ed.) *Rings, Clusters and Polymers of the Main Group Elements*, ACS Symposium Series No. **282**, Washington, DC, 49–67 (1982). H. R. ALLCOCK in J. E. MARK, R. WEST and H. R. ALLCOCK, *Inorganic Polymers*, Prentice Hall, 1991, 304 pp. H. R. ALLCOCK, Chap. 9 in R. STEUDEL (ed.) *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, 145–69 (1992).

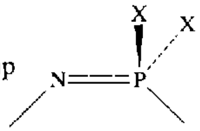
[161] S. S. KRISNAMURTHY, A. C. SAU and M. WOODS, *Adv. Inorg. Chem. Radiochem.* **21**, 41–112 (1978) (499 refs.).

these preparations, one exception being $N_7P_6Cl_9$, mp 237.5°, which can be obtained in modest yields from the direct thermolytic reaction of PCl_5 and NH_4Cl. The tricyclic structure is strongly distorted from planarity though the central NP_3 group features an accurately planar 3-coordinate N atom with much longer N–P bonds than those in the peripheral macrocycle. The 2 sorts of P–Cl bonds are also noticeably different in length and the 3 central Cl atoms are all on one side of the NP_3 plane with ∠NPCl 104°.



Many details of the preparative reaction mechanism remain unclear but it is thought that NH_4Cl partly dissociates into NH_3 and HCl, and that PCl_5 reacts in its ionic form $PCl_4^+PCl_6^-$ (p. 499). Nucleophilic attack by NH_3 on PCl_4^+ then occurs with elimination of HCl and the $\{HN{=}PCl_3\}$ attacks a second PCl_4^+ to give $[Cl_3P{=}N{-}PCl_3]^+$ and HCl. After 1 h the major (insoluble) intermediate product is $[Cl_3P{=}N{-}PCl_3]^+PCl_6^-$ (i.e. P_3NCl_{12}, p. 536) and this then slowly reacts with more NH_3 to give HCl and $\{Cl_3P{=}N{-}PCl_2{=}NH\}$, etc. It is probable that NH_4Br and $PBr_4^+Br^-$ react similarly to give $(NPBr_2)_n$ but NH_4F fluorinates PCl_5 to NH_4PF_4 and the fluoroanalogues $(NPF_2)_n$ are best prepared by fluorinating $(NPCl_2)_n$ with KSO_2F/SO_2 (i.e. KF in liquid SO_2). Similarly, standard substitution reactions lead to many derivatives in which all (or some) of the Cl atoms are replaced by OMe, OEt, OCH_2CF_3, OPh, NHPh, NMe_2, NR_2, R, Ar, etc. Partial replacement leads to geminal derivatives (in which both Cl atoms on 1 P atom are replaced) and to non-geminal derivatives which, in turn, can exist as *cis*- or *trans*- isomers.

The cyclic trimer $(NPF_2)_3$, mp 28°, has an accurately planar 6-membered ring (D_{3h} symmetry) in which all 6 P–N distances are equal (156 pm) and the angles NPN and PNP are all 120 ±1°. Most other trimers are also more-or-less planar with equal P–N distances: for example, $(NPCl_2)_3$ is almost planar (pseudo-chair with P–N 158 pm, P–Cl 197 pm, ∠NPN 118.4°, ∠PNP 121.4°, ∠ClPCl 102°. Perhaps surprisingly, the cyclic tetramer $(NPF_2)_4$, mp 30.4°, is also a planar heterocycle (D_{4h} symmetry) with even shorter P–N bonds (151 pm) and with ring angles of 122.7° and 147.4° at P and N respectively. However, other conformations are found in other derivatives, e.g. chair (C_{2h}), saddle (D_{2d}), boat (S_4), crown tetrameric (C_{4v}) and hybrid. Thus $(NPCl_2)_4$ exists in the metastable K form (in which it has the boat conformation) and the stable T form (chair configuration) as shown in Fig. 12.24. The remarkable diversity of molecular conformations observed for the 8-membered heterocycle $\{P_4N_4\}$ suggests that the particular structure adopted in each case results from a delicate balance of intra- and intermolecular forces including the details of skeletal bonding, the orientation of substituents and their polar and steric nature, crystal-packing effects, etc. The mps for various series of *cyclo*-$(NPX_2)_n$ frequently show an alternation, with values for *n* even being greater than those for adjacent *n* odd. Some examples are in Fig. 12.25. The crystal structures of the four compounds $(NPMe_2)_{9-12}$ have recently been determined.[162]

Bonding. All phosphazenes, whether cyclic or chain, contain the formally unsaturated group  with 2-coordinate N and

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[162] R. T. OAKLEY, S. J. RETTIG, N. L. PADDOCK and J. TROTTER, *J. Am. Chem. Soc.* **107**, 6923–36 (1985).

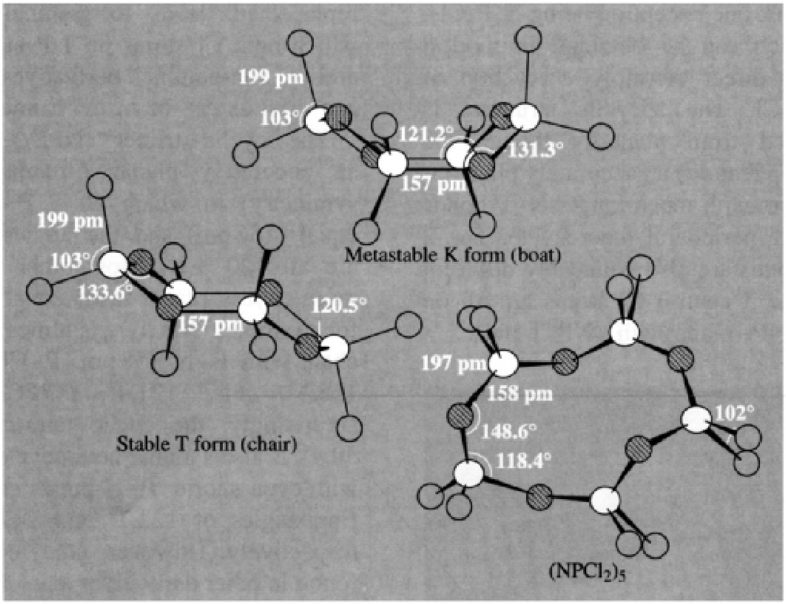


Figure 12.24 Molecular structure and dimensions of the two forms of $(NPCl_2)_4$ and of $(NPCl_2)_5$.

4-coordinate P. The experimental facts that have to be interpreted by any acceptable theory of bonding are:

(i) the rings and chains are very stable;

(ii) the skeletal interatomic distances are equal around the ring (or along the chain) unless there is differing substitution at the various P atoms;

(iii) the P–N distances are shorter than expected for a covalent single bond (~177 pm) and are usually in the range 158 ± 2 pm (though bonds as short as 147 pm occur in some compounds);

(iv) the N–P–N angles are usually in the range 120 ± 2° but the P–N–P angles in various compounds span the range from 120–148.6°;

(v) skeletal N atoms are weakly basic and can be protonated or form coordination complexes, especially when there are electron-releasing groups on P;

(vi) unlike many aromatic systems the phosphazene skeleton is hard to reduce electrochemically;

(vii) spectral effects associated with organic π-systems (such as the bathochromic ultraviolet shift that accompanies increased electron delocalization) are not found.

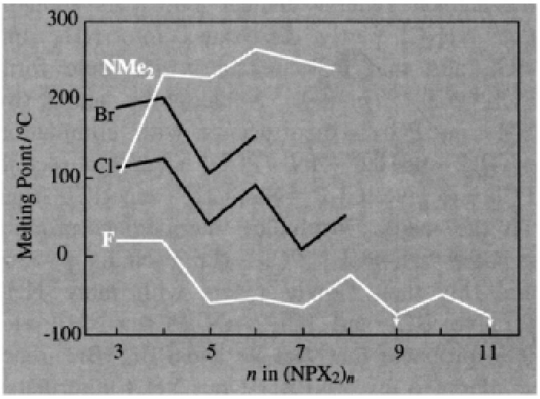
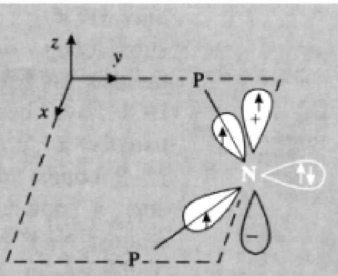
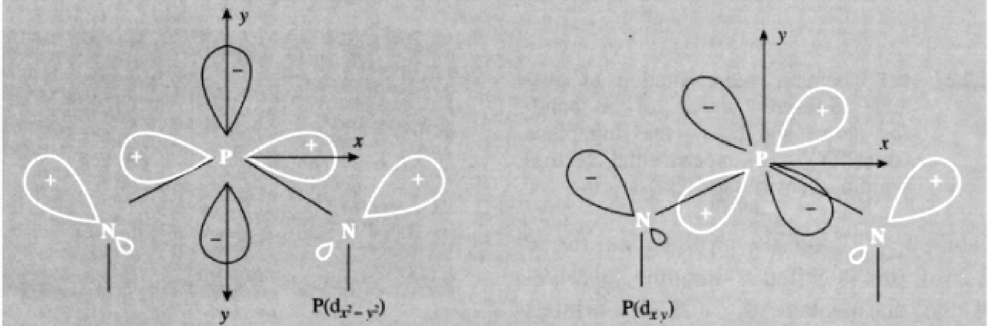


Figure 12.25 Melting points of various series of *cyclo*-polyphosphazenes $(NPX_2)_n$ showing the higher values for n even.

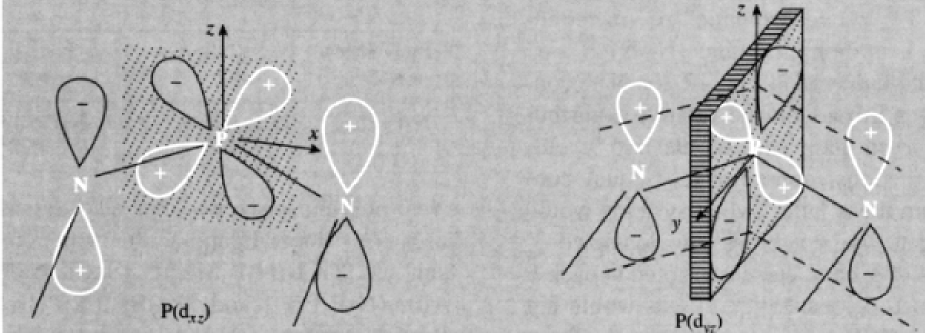
In short, the bonding in phosphazenes is not adequately represented by a sequence of alternating double and single bonds –N=P–N=P– yet it



(a) Hybridization at N, showing a lone-pair of electrons in sp^2 and three electrons for bonding in p_z and the other two sp^2 hybrids



(b) Possible π ' interactions in the xy plane (ring plane) between the N lone-pair electrons and vacant d orbitals on adjacent P atoms (shown looking down the z-axis on to the xy plane).



(c) Perspective representation of possible π bonding (heteromorphic $p_\pi - d_\pi$ interaction between Np_z and $P(d_{xz})$ orbitals and possible homomorphic $p_\pi - d_\pi$ interactions of Np_z through the $P(d_{yz})$ orbital).

Figure 12.26 A possible description of bonding in phosphazenes.

differs from aromatic $\sigma-\pi$ system in which there is extensive electron delocalization via $p\pi-p\pi$ bonding. The possibility of $p\pi-d\pi$ bonding in N–P systems has been considered by many authors since the mid-1950s but there is still no consensus, and for nearly every argument that can be mounted in favour of P(3d)-orbital contributions another can be raised against it. It seems generally agreed that 2 electrons on N occupy an sp^2 lone-pair in the plane of the ring (or the plane of the local PNP triangle) as in Fig. 12.26a. The situation at P is less clear mainly because of uncertainties concerning the d-orbital energies and the radial extent (size) of these orbitals in the *bonding situation* (as distinct from the free atom). In so far as symmetry is concerned, the sp^2 lone-pair on each N can be involved in coordinate bonding in the *xy* plane

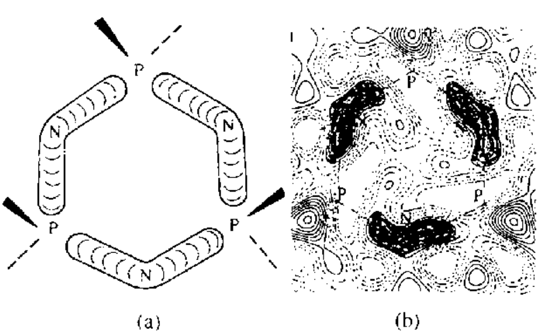
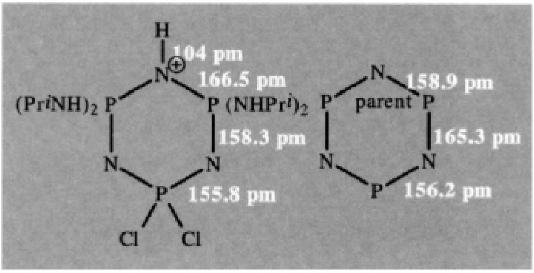


Figure 12.27 (a) Schematic representation of possible 3-centre islands of π bonding above and below the ring plane for $(NPX_2)_3$. (b) experimental electron bonding density (see text).

to "vacant" $d_{x^2-y^2}$ and d_{xy} orbitals on the P (Fig. 12.26b); this is called π'-bonding. Involvement of the out-of-plane d_{xz} and d_{yz} orbitals on the phosphorus with the singly occupied p_z orbital on N gives rise to the possibility of heteromorphic (N–P) "pseudoaromatic" $p_\pi-d_\pi$ bonding (with d_{xz}), or homomorphic (N–N) $p_\pi-p_\pi$ bonding (through d_{yz}) as in Fig. 12.26c. The controversy hinges in part on the relative contributions of the π' in-plane and of the two π out-of-plane interactions; approximately equal contributions from these latter two π systems would tend to separate the π orbitals into localized 3-centre islands of π character interrupted at each P atom, and broad delocalization effects would not then be expected. This is shown schematically in Fig. 12.27(a) and is consistent with the bonding electron density (b) as found by deformation density studies on the benzene clathrate of hexa(1-aziridinyl)cyclotriphosphazene, $2(\overline{CH_2CH_2N})_6$-$P_3N_3.C_6H_6$.[163] The possibility of exocyclic π bonding between $P(d_{z^2})$ and appropriate orbitals on the substituents X has also been envisaged.

Reactions. The N atom in *cyclo*-polyphosphazenes can act as a weak Brønsted base (proton acceptor) towards such strong acids as HF and $HClO_4$; compounds with alkyl or NR_2 substituents on P are more basic than the halides, as expected, and their adducts with HCl have been well characterized. There is usually a substantial lengthening of the two N–P bonds adjacent to the site of protonation and a noticeable contraction of the next-nearest N–P bonds. For example, the relevant distances in $[HN_3P_3Cl_2(NHPr^i)_4]Cl$ and the parent compound are:[164]



Typical basicities (pK'_a measured against $HClO_4$ in $PhNO_2$) for ring-*N* protonation are:

$N_3P_3(NHMe)_6$	$N_3P_3(NEt_2)_6$	$N_3P_3Et_6$
8.2	8.2	6.4
$N_3P_3Ph_6$	$N_3P_3(OEt)_6$	*trans*-$N_3P_3Cl_3(NMe_2)_3$
1.5	−0.2	−5.4

Cyclo-polyphosphazenes can also act as Lewis bases (*N* donor-ligands) to form complexes such as $[TiCl_4(N_3P_3Me_6)]$, $[SnCl_4(N_3P_3Me_6)]$, $[AlBr_3(N_3P_3Br_6)]$ and $[2AlBr_3.(N_3P_3Br_6)]$. Not all such adducts are necessarily ring-*N* donors and the 1:1 adduct of $(NPCl_2)_3$ with $AlCl_3$ is thought to be a chloride ion donor, $[N_3P_3Cl_5]^+$-$[AlCl_4]^-$. By contrast, the complex $[Pt^{II}Cl_2(\eta^2$-$N_4P_4Me_8)].MeCN$ features transannular bridging of 2 N atoms by the $PtCl_2$ moiety.[165] An intriguing example of a *cyclo*-polyphosphazene acting as a multidentate macrocyclic ligand occurs in the bright orange complex formed when $N_6P_6(NMe_2)_{12}$ reacts with equal amounts of $CuCl_2$ and CuCl. The crystal structure of

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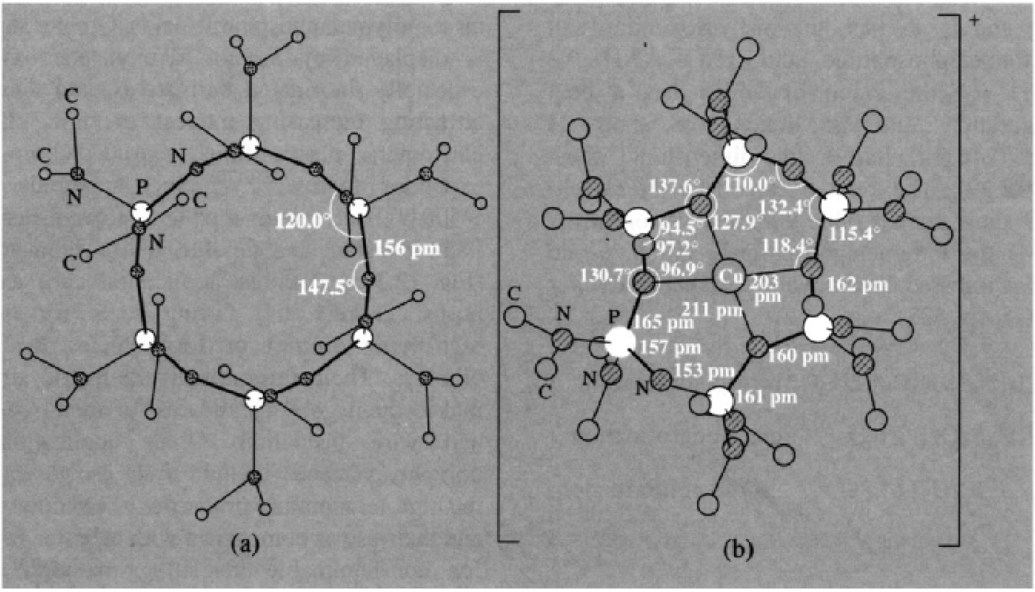
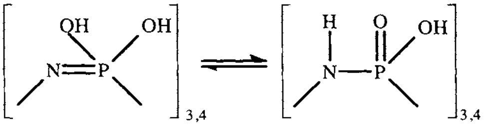


Figure 12.28 Structure of (a) the free ligand $N_6P_6(NMe_2)_{12}$, and (b) the η^4 complex cation $[CuCl\{N_6P_6(NMe_2)_{12}\}]^+$ showing changes in conformation and interatomic distances in the phosphazene macrocycle. The Cl is obscured beneath the Cu and can be regarded as occupying either the apical position of a square pyramid or, since ∠N(1)-Cu-N(1′) is large (160.9°), an equatorial position of a distorted trigonal bipyramid. Note that coordination tightens the ring, already somewhat crowded in the uncomplexed state, the mean angles at P being reduced from 120.0° to 107.5°, and the mean angles at N being reduced from 147.5° to 133.6°. The lengthening of the 8 P–N bonds contiguous to the 4 donor N atoms from 156 to 162 pm is significant, the other P–N distances (mean 156 pm) remaining similar to those in the free ligand.

the resulting $[N_6P_6(NMe_2)_{12}CuCl]^+[CuCl_2]^-$ has been determined (Fig. 12.28b) and detailed comparison with the conformation and interatomic distances in the parent heterocycle (Fig. 12.28a) gives important clues as to the relative importance of the various π and π' bonding interactions involving N (and P) atoms.(166) Incidentally, the compound also affords the first example of the linear 2-coordinate Cu^I complex $[CuCl_2]^-$. The related (and more extensive) organometallic chemistry of the phosphazenes has been reviewed.(167)

As P is isoelectronic with N, it has been found possible to prepare 8-membered diazahexaphosphocins such as $\overline{\text{NPPh}_2\mathbf{P}\text{PPh}_2\text{NPPh}_2\mathbf{P}\text{P}}\text{Ph}_2$, analogous to $(NPPh_2)_4$.(168) The two subrogated **P** atoms can chelate to $PdCl_2$ to form a square planar complex. (169)

Many of the cyclic and chain dichloro derivatives $(NPCl_2)_n$ can be hydrolysed to n-basic acids and the lower members form well-defined salts frequently in the tautomeric metaphosphimic-acid form, e.g.:



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