

**Figure 12.10** (a) Zig-zag  $P_4$  chain,  $M = \{Cr(CO)_5\}$ ; (b)  $\eta^5$ -*cyclo*- $P_5$ ,  $M$  various; (c)  $\eta^6$ -*cyclo*- $P_6$ ,  $M$  various (see text).

red crystalline compound  $[Li(dme)_3]^+{}_2[(SiMe_3)\{Cr(CO)_5\}_2P=P=P\{Cr(CO)_5\}_2(SiMe_3)]^{2-}$  which was obtained by reacting  $Li[P(SiMe_3)_2\{Cr(CO)_5\}]$  with  $BrCH_2CH_2Br$  in 1,2-dimethoxyethane (dme). The interatomic distances  $P-P$  221.9 pm and  $P=P$  202.5 pm reflect the bond orders indicated.

Because *cyclo*- $P_5$  and *cyclo*- $P_6$  can be considered as isoelectronic with  $C_5H_5$  and  $C_6H_6$  their appearance as ligands is not entirely unexpected, but the recent synthesis and characterization of such complexes was nevertheless a noteworthy achievement.<sup>(43)</sup> Typical examples are  $[(Mn(CO)_3(\eta^5-P_5))]^{(60)}$  (formed by the direct action of  $KP_5$  on  $[Mn(CO)_5Br]$  in dmf at  $155^\circ C$ ) and  $[Fe(\eta^5-C_5H_5)(\mu:\eta^5,\eta^5-P_5)Fe(\eta^5-C_5Me_4R)]^{(43)}$  (Fig. 12.10(b)) for *cyclo*- $P_5$ ; and  $[\{Mo(\eta^5-C_5Me_5)\}_2(\mu:\eta^5,\eta^5-P_6)]^{(43)}$  (Fig. 12.10(c)) for planar *cyclo*- $P_6$ . Several *cyclo*- $As_5$  and *-As\_6* analogues are also known. The complex  $[\{Ti(\eta^5-C_5Me_5)\}_2(\mu:\eta^3,\eta^3-P_6)]$  features a puckered  $P_6$  ring in the chair conformation, so that the overall cluster core has a distorted cubane geometry.<sup>(61)</sup>

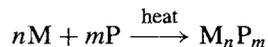
The most complex  $P_n$  ligand so far characterized is the astonishing  $\mu_5$  hexadentate  $P_{10}$  unit in  $[\{Cr(\eta^5-C_5H_5)(CO)_2\}_5P_{10}]$  (see ref. 62 for details).

## 12.3 Compounds

### 12.3.1 Phosphides<sup>(63-65)</sup>

Phosphorus forms stable binary compounds with almost every element in the periodic table and those with metals are called phosphides. Like borides (p. 145) they are known in a bewilderingly large number of stoichiometries, and typical formulae are  $M_4P$ ,  $M_3P$ ,  $M_{12}P_5$ ,  $M_7P_3$ ,  $M_2P$ ,  $M_7P_4$ ,  $M_5P_3$ ,  $M_3P_2$ ,  $M_4P_3$ ,  $M_5P_4$ ,  $M_6P_5$ ,  $MP$ ,  $M_3P_4$ ,  $M_2P_3$ ,  $MP_2$ ,  $M_3P_7$ ,  $M_2P_5$ ,  $MP_3$ ,  $M_3P_{11}$ ,  $M_3P_{14}$ ,  $MP_5$ ,  $M_3P_{16}$ ,  $M_4P_{26}$ ,  $MP_7$ ,  $M_2P_{16}$  and  $MP_{15}$ . Many metals (e.g. Ti, Ta, W, Rh) form as many as 5 or 6 phosphides and Ni has at least 8 ( $Ni_3P$ ,  $Ni_5P_2$ ,  $Ni_{12}P_5$ ,  $NiP_2$ ,  $Ni_5P_4$ ,  $NiP$ ,  $NiP_2$  and  $NiP_3$ ). Ternary and more complex metal phosphides are also known.

The most general preparative route to phosphides (Faraday's method) is to heat the metal with the appropriate amount of red P at high temperature in an inert atmosphere or an evacuated sealed tube:



An alternative route (Andrieux's method) is the electrolysis of fused salts such as molten

<sup>60</sup> M. BAUDLER and T. ETZBACH, *Angew. Chem. Int. Edn. Engl.* **30**, 580-2 (1991).

<sup>61</sup> O. J. SCHERER, H. SWAROWSKY, G. WOLMERSHÄUSER, W. KAIM and S. KOHLMANN, *Angew. Chem. Int. Edn. Engl.* **26**, 1153-5 (1987).

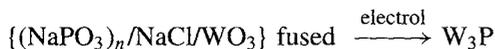
<sup>62</sup> L. Y. GOH, R. C. S. WONG and E. SINN, *Organometallics* **12**, 888-94 (1993).

<sup>63</sup> A. WILSON, *The metal phosphides*, Chap. 3 (pp. 289-363) in ref. 23, see also p. 256.

<sup>64</sup> A. D. F. TOY, in *Comprehensive Inorganic Chemistry*, Vol. 2, Pergamon Press, Oxford, 1973 (Section 20.2, Phosphides, pp. 406-14).

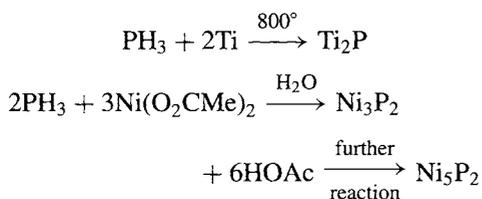
<sup>65</sup> D. E. C. CORBRIDGE, *Phosphorus* (3rd edn.), Elsevier, Amsterdam, 1985, Section 2.2 Metallic Phosphides, pp. 56-69. (See also 5th edn. 1995.)

alkali-metal phosphates to which appropriate metal oxides or halides have been added:

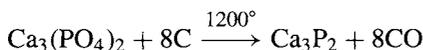


Variation in current, voltage and electrolyte composition frequently results in the formation of phosphides of different stoichiometries. Less-general routes (which are nevertheless extremely valuable in specific instances) include:

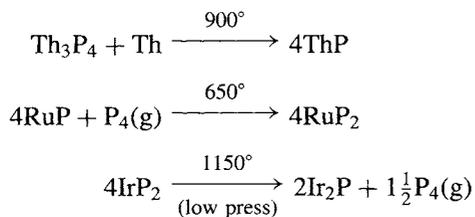
- (a) Reaction of  $\text{PH}_3$  with a metal, metal halide or sulfide, e.g.:



- (b) Reduction of a phosphate such as apatite with C at high temperature, e.g.:



- (c) Reaction of a metal phosphide with further metal or phosphorus to give a product of different stoichiometry, e.g.:



Phosphides resemble in many ways the metal borides (p. 145), carbides (p. 297), and nitrides (p. 417), and there are the same difficulties in classification and description of bonding. Perhaps the least-contentious procedure is to classify according to stoichiometry, i.e. (a) metal-rich phosphides ( $M/P > 1$ ), (b) monophosphides ( $M/P = 1$ ), and (c) phosphorus-rich phosphides ( $M/P < 1$ ):

(a) *Metal-rich phosphides* are usually hard, brittle, refractory materials with metallic lustre, high thermal and electrical conductivity, great

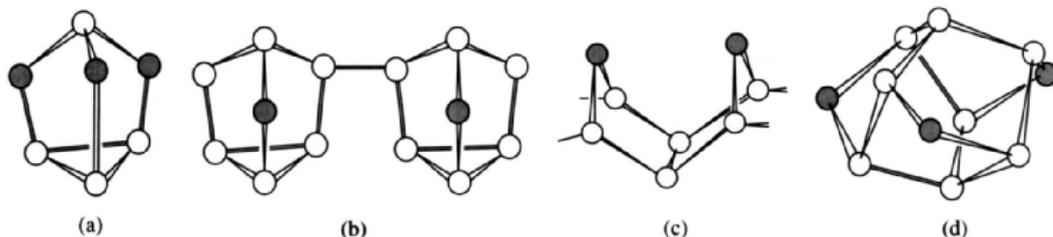
thermal stability and general chemical inertness. Phosphorus is often in trigonal prismatic coordination being surrounded by 6 M, or by 7, 8 or 9 M (see Fig. 6.7 on p. 148 and Fig. 12.6). The antifluorite structure of many  $\text{M}_2\text{P}$  also features eightfold (cubic) coordination of P by M. The details of the particular structure adopted in each case are influenced predominantly by size effects.

(b) *Monophosphides* adopt a variety of structures which appear to be influenced by both size and electronic effects. Thus the Group 3 phosphides MP adopt the zinc-blende structure (p. 1210) with tetrahedral coordination of P, whereas SnP has the NaCl-type structure (p. 242) with octahedral coordination of P, VP has the hexagonal NiAs-type structure (p. 556) with trigonal prismatic coordination of isolated P atoms by V, and MoP has the hexagonal WC-type structure (p. 299) in which both Mo and P have a trigonal prismatic coordination by atoms of the other kind. More complicated arrangements are also encountered, e.g..<sup>(65)</sup>

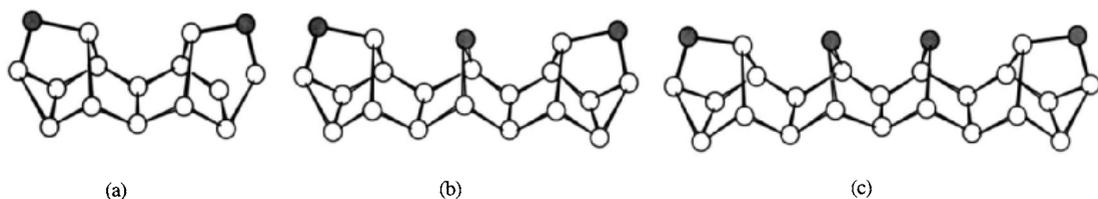
TiP, ZrP, HfP: half the P trigonal prismatic and half octahedral;

MP (M = Cr, Mn, Fe, Co, Ru, W): distorted trigonal prismatic coordination of P by M plus two rather short contacts to P atoms in adjacent trigonal prisms, thus building up a continuous chain of P atoms; NiP is a distortion of this in which the P atoms are grouped in pairs rather than in chains (or isolated as in VP).

(c) *Phosphorus-rich phosphides* are typified by lower mps and much lower thermal stabilities when compared with monophosphides or metallic phosphides. They are often semiconductors rather than metallic conductors and feature increasing catenation of the P atoms (cf. boron rich borides, p. 148).  $\text{P}_2$  units occur in  $\text{FeP}_2$ ,  $\text{RuP}_2$  and  $\text{OsP}_2$  (marcasite-type, p. 680) and in  $\text{PtP}_2$  (pyrites type, p. 680) with P–P 217 pm. Planar  $\text{P}_4$  rings (square or rectangular) occur in several  $\text{MP}_3$  (M = Co, Ni, Rh, Pd, Ir) with P–P typically 223 pm in the square ring of  $\text{RhP}_3$ . Structures are also known in which the P atoms form chains ( $\text{PdP}_2$ ,  $\text{NiP}_2$ ,  $\text{CdP}_2$ ,  $\text{BaP}_3$ ),



**Figure 12.11** Schematic representation of the structures of polycyclic polyphosphide anions (open circles P, shaded circles P<sup>-</sup>) (a) P<sub>7</sub><sup>3-</sup>, (b) {P<sub>7</sub><sup>-</sup>}<sub>x</sub>, (c) ≡P<sub>8</sub><sup>2-</sup>≡<sub>x</sub>, (d) P<sub>11</sub><sup>3-</sup>.



**Figure 12.12** Schematic representation of the structures of (a) P<sub>16</sub><sup>2-</sup>, (b) P<sub>21</sub><sup>3-</sup>, (c) P<sub>26</sub><sup>4-</sup>, (open circles P, shaded circles P<sup>-</sup>)

double chains (ZnPbP<sub>14</sub>, CdPbP<sub>14</sub>, HgPbP<sub>14</sub>), or layers (CuP<sub>2</sub>, AgP<sub>2</sub>, CdP<sub>4</sub>); in the last 3 phosphides the layers are made up by a regular fusion of puckered 10-membered rings of P atoms with the metal atoms in the interstices. The double-chained structure of MPbP<sub>14</sub> is closely related to that of violet phosphorus (p. 482).

In addition, phosphides of the electropositive elements in Groups 1, 2 and the lanthanoids form phosphides with some degree of ionic bonding. The compounds Na<sub>3</sub>P<sub>11</sub> and Sr<sub>3</sub>P<sub>14</sub> have already been mentioned (p. 484) and other somewhat ionic phosphides are M<sub>3</sub>P (M = Li, Na), M<sub>3</sub>P<sub>2</sub> (M = Be, Mg, Zn, Cd), MP (M = La, Ce) and Th<sub>3</sub>P<sub>4</sub>. However, it would be misleading to consider these as fully ionized compounds of P<sup>3-</sup> and there is extensive metallic or covalent interaction in the solids. Such compounds are characterized by their ready hydrolysis by water or dilute acid to give PH<sub>3</sub>.

Recent extensive structural studies by X-ray crystallography and by <sup>31</sup>P nmr spectroscopy have revealed an astonishing variety of *conjuncto*-polyphosphides with quasi-ionic

cluster structures.<sup>(66,67)</sup> Thus, the yellow compound Li<sub>3</sub>P<sub>7</sub> (which has been known since 1912) and its Na–Cs analogues have been found to contain the P<sub>7</sub><sup>3-</sup> cluster shown schematically in Fig. 12.11(a). The cluster can be regarded as being related to the P<sub>4</sub> tetrahedron (p. 479) by the notional insertion of three 2-connected P<sup>-</sup> atoms (cf. the structure of P<sub>4</sub>S<sub>3</sub>, p. 507, with which it is precisely isoelectronic). Substitution of P by As leads to a series of closely related anions [P<sub>7-x</sub>As<sub>x</sub>]<sup>3-</sup> x = 1–5, (?6),<sup>(68)</sup> and As<sub>7</sub><sup>3-</sup> is also known for Na, Rb, Cs). Catenation of the P<sub>7</sub><sup>3-</sup> unit, as shown in Fig. 12.11(b), leads to the stoichiometry M<sup>+</sup>P<sub>7</sub><sup>-</sup>. The repeating unit =P<sub>8</sub>=, which is clearly related to a segment in the structure of Hittorf's allotrope (p. 482), is shown in Fig. 12.11(c). A more complex

<sup>66</sup> H. G. VON SCHNERING, in A. H. COWLEY (ed.) *Rings, Clusters and Polymers of the Main Group Elements*, ACS Symposium Series No. 232, Washington D. C. 1983, pp. 69–80.

<sup>67</sup> M. BAUDLER, *Angew. Chem. Int. Edn. Engl.* **21**, 492–512 (1982); **26**, 419–41 (1987).

<sup>68</sup> W. HÖNLE and H. G. VON SCHNERING, *Angew. Chem. Int. Edn. Engl.* **25**, 352–3 (1986).

cluster occurs in the yellow/orange compounds  $M_3^+P_{11}^{3-}$  (Fig. 12.11d):  $P_{11}^{3-}$  can be thought of as comprising two axial  $PP_3$  tetrahedra joined by a central belt of three 2-connected  $P^-$  atoms, so that the sequence of cluster planes contains 1,3,(3),3,1 P atoms, respectively.

Even more complex *conjuncto*-polyphosphide anions can be constructed, such as those of stoichiometry  $P_{16}^{2-}$ ,  $P_{21}^{3-}$  and  $P_{26}^{4-}$ , Fig. 12.12(a)(b)(c).<sup>(66,67)</sup> These bear an obvious structural relationship to  $=P_8=$  (Fig. 12.11c) and to Hittorf's phosphorus (Fig. 12.4) and can be viewed as ladders of P atoms with alternate P–P and  $P(P^-)P$  rungs, terminated at each end by a ring-closing  $P(P^-)$  unit. The P–P distances and PPP angles in these various species are much as expected. These cluster anions, and those mentioned in the preceding paragraphs, can be partially or completely protonated (see next subsection) and they also occur in neutral organopolyphosphanes (p. 495).

A completely different structural motif has very recently been found in the red-brown phosphide  $Ca_5P_8$ , formed by direct fusion of Ca metal and red P in the correct atom ratio in a corundum crucible at  $1000^\circ\text{C}$ .<sup>(69)</sup> The structure comprises  $Ca^{2+}$  cations and  $P_8^{10-}$  anions, the latter adopting a staggered ethane conformation. (Note that  $P^+$  is isolobal with C and  $P^{2-}$  with H so that  $C_2H_6 = [(P^+)_2(P^{2-})_6] = P_8^{10-}$ .) The internal P–P distance is 230.1 pm and the terminal P–P distances 214.9–216.9 pm, while the internal PPP angles are  $104.2$ – $106.4^\circ$  and the outer angles are  $103.4$ – $103.7^\circ$ .

Few industrial uses have so far been found for phosphides. "Ferrophosphorus" is produced on a large scale as a byproduct of  $P_4$  manufacture, and its uses have been noted (p. 480). Phosphorus is also much used as an alloying element in iron and steel, and for improving the workability of Cu. Group 3 monophosphides are valuable semiconductors (p. 255) and  $Ca_3P_2$  is an important ingredient in some navy sea-flares since its reaction with water releases spontaneously flammable

phosphines. By contrast the phosphides of Nb, Ta and W are valued for their chemical inertness, particularly their resistance to oxidation at very high temperatures, though they are susceptible to attack by oxidizing acids or peroxides.

### 12.3.2 Phosphine and related compounds

The most stable hydride of P is phosphine (phosphane),  $PH_3$ . It is the first of a homologous open-chain series  $P_nH_{n+2}$  ( $n = 1$ – $9$ ) the members of which rapidly diminish in thermal stability, though  $P_2H_4$  and  $P_3H_5$  have been isolated pure. There are ten other (unstable) homologous series:  $P_nH_n$  ( $n = 3$ – $10$ ),  $P_nH_{n-2}$  ( $n = 4$ – $12$ ), and  $P_nH_{n-4}$  ( $n = 5$ – $13$ ) and so on up to  $P_nH_{n-18}$  ( $n = 19$ – $22$ )<sup>(67)</sup>; in all of these there is a tendency to form cyclic and condensed polyphosphanes at the expense of open-chain structures. Some 85 phosphanes have so far been identified and structurally characterized by nmr spectroscopy and other techniques, although few have been obtained pure because of problems involving thermal instability, ready disproportionation, light-sensitivity and great chemical reactivity.<sup>(67,70,71)</sup> Phosphorane,  $PH_5$ , has not been prepared or even detected, despite numerous attempts, although  $HPF_4$ ,  $H_2PF_3$  and  $H_3PF_2$  have recently been well characterized.<sup>(72,73)</sup>

$PH_3$  is an extremely poisonous, highly reactive, colourless gas which has a faint garlic odour at concentrations above about 2 ppm by volume. It is intermediate in thermal stability between  $NH_3$  (p. 421) and  $AsH_3$  (p. 557). Several convenient routes are available for its preparation:

1. Hydrolysis of a metal phosphide such as  $AlP$  or  $Ca_3P_2$ ; the method is useful even

<sup>69</sup> M. BAUDLER and K. GLINKA, *Chem. Rev.* **93**, 1623–67 (1993).

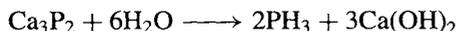
<sup>71</sup> M. BAUDLER and K. GLINKA, *Chem. Rev.* **94**, 1273–97 (1994). See also *Z. anorg. allg. Chem.* **621**, 1133–9 (1995).

<sup>72</sup> A. J. DOWNS, G. S. MCGRADY, E. A. BARNFIELD and D. W. H. RANKIN, *J. Chem. Soc., Dalton Trans.*, 545–50 (1989).

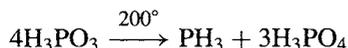
<sup>73</sup> A. BECHERS, *Z. anorg. allg. Chem.* **619**, 1869–79 (1993).

<sup>69</sup> C. HADENFELDT and F. BARTELS, *Z. anorg. allg. Chem.* **620**, 1247–52 (1994).

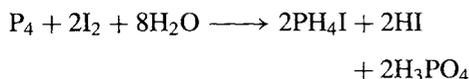
up to the 10-mole scale and can be made almost quantitative



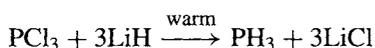
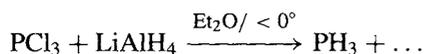
2. Pyrolysis of phosphorous acid at 205–210°; under these conditions the yield of PH<sub>3</sub> is 97% though at higher temperatures the reaction can be more complex (p. 512)



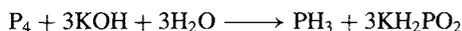
3. Alkaline hydrolysis of PH<sub>4</sub>I (for very pure phosphine):



4. Reduction of PCl<sub>3</sub> with LiAlH<sub>4</sub> or LiH:



5. Alkaline hydrolysis of white P<sub>4</sub> (industrial process):



Phosphine has a pyramidal structure, as expected, with P–H 142 pm and the H–P–H angle 93.6° (see p. 557). Other physical properties are mp –133.5°, bp –87.7°, dipole moment 0.58 D, heat of formation  $\Delta H_f^\circ$  –9.6 kJ mol<sup>–1</sup> (uncertain) and mean P–H bond energy 320 kJ mol<sup>–1</sup>. The free energy change (at 25°C) for the reaction  $\frac{1}{4}\text{P}_4(\alpha\text{-white}) + \frac{3}{2}\text{H}_2(\text{g}) = \text{PH}_3(\text{g})$  is –13.1 kJ mol<sup>–1</sup>, implying a tendency for the elements to combine, though there is negligible reaction unless H<sub>2</sub> is energized photolytically or by a high-current arc. The inversion frequency of PH<sub>3</sub> is about 4000 times less than for NH<sub>3</sub> (p. 423); this reflects the substantially higher energy barrier to inversion for PH<sub>3</sub> which is calculated to be ~155 kJ mol<sup>–1</sup> rather than 24.7 kJ mol<sup>–1</sup> for NH<sub>3</sub>.

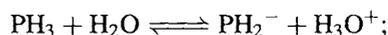
Phosphine is rather insoluble in water at atmospheric pressure but is more soluble in

organic liquids, and particularly so in CS<sub>2</sub> and CCl<sub>3</sub>CO<sub>2</sub>H. Some typical values are:

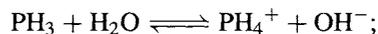
Solvent (T°C)	H <sub>2</sub> O (17°)	CH <sub>3</sub> CO <sub>2</sub> H (20°)	C <sub>6</sub> H <sub>6</sub> (22°)
Solubility/ml PH <sub>3</sub> (g) per 100 ml solvent	26	319	726
Solvent (T°C)	CS <sub>2</sub> (21°)	CCl <sub>3</sub> CO <sub>2</sub> H	
Solubility/ml PH <sub>3</sub> (g) per 100 ml solvent	1025	1590	

[Note: 1 ml PH<sub>3</sub>(g) ≈ 1.5 mg]

Aqueous solutions are neutral and there is little tendency for PH<sub>3</sub> to protonate or deprotonate:



$$K_A = 1.6 \times 10^{-29}$$

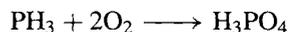


$$K_B = 4 \times 10^{-28}$$

In liquid ammonia, however, phosphine dissolves to give NH<sub>4</sub><sup>+</sup>PH<sub>2</sub><sup>–</sup> and with potassium gives KPH<sub>2</sub> in the same solvent. Again, phosphine reacts with liquid HCl to give the sparingly soluble PH<sub>4</sub><sup>+</sup>Cl<sup>–</sup> and this reacts further with BCl<sub>3</sub> to give PH<sub>4</sub>BCl<sub>4</sub>. The corresponding bromides and PH<sub>4</sub>I are also known.

More generally, phosphine readily acts as a ligand to numerous Lewis acids and typical coordination complexes are [BH<sub>3</sub>(PH<sub>3</sub>)], [BF<sub>3</sub>(PH<sub>3</sub>)], [AlCl<sub>3</sub>(PH<sub>3</sub>)], [Cr(CO)<sub>2</sub>(PH<sub>3</sub>)<sub>4</sub>], [Cr(CO)<sub>3</sub>–(PH<sub>3</sub>)<sub>3</sub>], [Co(CO)<sub>2</sub>(NO)(PH<sub>3</sub>)], [Ni(PF<sub>3</sub>)<sub>2</sub>(PH<sub>3</sub>)<sub>2</sub>] and [CuCl(PH<sub>3</sub>)]. Further details are in the Panel and other aspects of the chemistry of PH<sub>3</sub> have been extensively reviewed.<sup>(74)</sup>

Phosphine is also a strong reducing agent: many metal salts are reduced to the metal and PCl<sub>5</sub> yields PCl<sub>3</sub>. The pure gas ignites in air at about 150° but when contaminated with traces of P<sub>2</sub>H<sub>4</sub> it is spontaneously flammable:



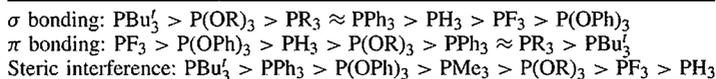
When heated with sulfur, PH<sub>3</sub> yields H<sub>2</sub>S and a mixture of phosphorus sulfides. Probably the most important reaction industrially is

<sup>74</sup> E. FLUCK, Chemistry of phosphine, *Topics in Current Chem.* **35**, 1–64 (1973). A review with 493 references.

### Phosphine and its Derivatives as Ligands<sup>(7,75-78)</sup>

A wide variety of 3-coordinate phosphorus(III) compounds are known and these have been extensively studied as ligands because of their significance in improving our understanding of the stability and reactivity of many coordination complexes. Among the most studied of these ligands are PH<sub>3</sub>, PF<sub>3</sub> (p. 495), PCl<sub>3</sub> (p. 496), PR<sub>3</sub> (R = alkyl), PPh<sub>3</sub> and P(OR)<sub>3</sub>, together with a large number of "mixed" ligands such as Me<sub>2</sub>NPF<sub>2</sub>, PMePh<sub>2</sub>, etc., and many multidentate (chelating) ligands such as Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, etc.

In many of their complexes PF<sub>3</sub> and PPh<sub>3</sub> (for example) resemble CO (p. 926) and this at one time encouraged the belief that their bonding capabilities were influenced not only by the factors (p. 198) which affect the stability of the  $\sigma$  P→M interaction which uses the lone-pair of electrons on P<sup>III</sup> and a vacant orbital on M, but also by the possibility of synergic  $\pi$  back-donation from a "nonbonding"  $d_{\pi}$  pair of electrons on the metal into a "vacant"  $3d_{\pi}$  orbital on P. It is, however, not clear to what extent, if any, the  $\sigma$  and  $\pi$  bonds reinforce each other, and more recent descriptions are based on an MO approach which uses all ( $\sigma$  and  $\pi$ ) orbitals of appropriate symmetry on both the phosphine and the metal-containing moiety. To the extent that  $\sigma$  and  $\pi$  bonding effects on the stability of metal-phosphorus bonds can be isolated from each other and from steric factors (see below) the accepted sequence of effects is as follows:

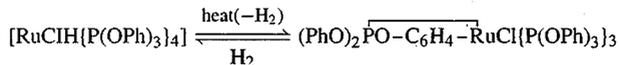


Steric factors are frequently dominant, particularly with bulky ligands, and their influence on the course of many reactions is crucial. One measure of the "size" of a ligand in so far as it affects bond formation is C. A. Tolman's cone angle (1970) which is the angle at the metal atom of the cone swept out by the van der Waals radii of the groups attached to P. This will, of course, be dependent on the actual interatomic distance between M and P. For the particular case of Ni, for which a standard value of 228 pm was adopted for Ni-P, the calculated values for the cone angle are:

Ligand	PH <sub>3</sub>	PF <sub>3</sub>	P(OMe) <sub>3</sub>	P(OEt) <sub>3</sub>	PMe <sub>3</sub>	P(OPh) <sub>3</sub>	PCl <sub>3</sub>
Cone angle	87°	104°	107°	109°	118°	121°	125°
Ligand	PEt <sub>3</sub>	PPh <sub>3</sub>	PPr <sub>3</sub> <sup>i</sup>	PBU <sub>3</sub> '	P( <i>o</i> -tol) <sub>3</sub>	P(mesityl) <sub>3</sub>	
Cone angle	132°	145°	160° <sup>3</sup>	182°	195°	212°	

Bulky tertiary phosphine ligands exert both steric and electronic influences when they form complexes (since an increase in bulkiness of a substituent on P increases the inter-bond angles and this in turn can be thought of as an increase in "p-character" of the lone-pair of electrons on P). For example, the sterically demanding di-*t*-butylphosphines, PBU<sub>2</sub>R (R = alkyl or aryl), promote spatially less-demanding features such as hydride formation, coordinative unsaturation at the metal centre, and even the stabilization of unusual oxidation states, such as Ir<sup>II</sup>. They also favour internal C- or O- metallation reactions for the same reasons. Indeed, the metallation of C-H and C-P bonds of coordinated tertiary phosphines can be considered as examples of intramolecular oxidative addition, and these have important mechanistic implications for homogeneous and heterogeneous catalysis.<sup>(79)</sup>

Other notable examples are the orthometallation (orthophenylation) reactions of many complexes of aryl phosphines (PAR<sub>3</sub>) and aryl phosphites P(OAr)<sub>3</sub> with platinum metals in particular, e.g.:



<sup>75</sup> Chapter 5 in ref. 2, Phosphorus(III) ligands in transition-metal complexes, pp. 177-207.

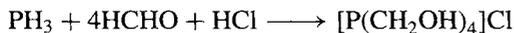
<sup>76</sup> C. A. MCAULIFFE and W. LEVASON, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Elsevier, Amsterdam, 1979, 546 pp. A review with over 2700 references. See also C. A. MCAULIFFE (ed.), *Transition-Metal Complexes of Phosphorus, Arsenic and Antimony Donor Ligands*, Macmillan, London, 1972.

<sup>77</sup> O. STELZER, *Topics in Phosphorus Chemistry* **9**, 1-229 (1977). An extensive review with over 1700 references arranged by element and by technique but with no assessment or generalizations.

<sup>78</sup> R. MASON and D. W. MEEK, *Angew. Chem. Int. Edn. Engl.* **17**, 183-94 (1978).

<sup>79</sup> G. PARSHALL, Homogeneous catalytic activation of C-H bonds, *Acc. Chem. Res.* **8**, 113-7 (1975).

its hydrophosphorylation of formaldehyde in aqueous hydrochloric acid solution:



The tetrakis(hydroxymethyl)phosphonium chloride so formed is the major ingredient with urea-formaldehyde or melamine-formaldehyde resins for the permanent flame-proofing of cotton cloth.

Of the many other hydrides of phosphorus, diphosphane (diphosphine),  $\text{P}_2\text{H}_4$ , is the most studied. It is best made<sup>(71)</sup> by treating CaP with cold oxygen-free water. Passage of  $\text{PH}_3$  through an electric discharge at 5–10 kV is an alternative method for small amounts.  $\text{P}_2\text{H}_4$  is a colourless, volatile liquid (mp  $-99^\circ$ ) which is thermally unstable even below room temperature and is decomposed slowly by water. Its vapour pressure at  $0^\circ\text{C}$  is 70.2 mmHg but partial decomposition precludes precise determination of the bp ( $63.5^\circ$  extrap);  $d \simeq 1.014 \text{ g cm}^{-3}$  at  $20^\circ\text{C}$ . Electron-diffraction measurements on the gas establish the *gauche*- $\text{C}_2$  configuration (p. 428) with P–P 222 pm, P–H 145 pm, and the angle H–P–H  $91.3^\circ$ , though vibration spectroscopy suggests a *trans*- $\text{C}_{2h}$  configuration in the solid phase. These results can be compared with those for the halides  $\text{P}_2\text{X}_4$  on p. 498.

The next member of the open-chain series  $\text{P}_n\text{H}_{n+2}$  is  $\text{P}_3\text{H}_5$ , i.e.  $\text{PH}_2\text{P}(\text{PH})_2$ , a colourless liquid that can be stored in the dark at  $-80^\circ$  for several days.<sup>(67,71)</sup> It can be made by disproportionation ( $2\text{P}_2\text{H}_4 \longrightarrow \text{P}_3\text{H}_5 + \text{PH}_3$ ) but it is difficult to purify because of its own fairly ready disproportionation and reactivity, e.g.  $2\text{P}_3\text{H}_5 \longrightarrow \text{P}_4\text{H}_6 + \text{P}_2\text{H}_4$ ; and  $\text{P}_3\text{H}_5 + \text{P}_2\text{H}_4 \longrightarrow \text{P}_4\text{H}_6 + \text{PH}_3$ . Tetraphosphane(6),  $\text{P}_4\text{H}_6$ , exists as an equilibrium mixture of the two structural isomers  $\text{H}_2\text{P}(\text{PH})_2\text{PH}_2$  (*n*) and  $\text{P}(\text{PH}_2)_3$  (*i*), and itself reacts with  $\text{P}_3\text{H}_5$  at  $-20^\circ$  according to the idealized stoichiometry  $\text{P}_4\text{H}_6 + \text{P}_3\text{H}_5 \longrightarrow 2\text{PH}_3 + \text{P}_5\text{H}_5$ , i.e. *cyclo*-(PH)<sub>5</sub>. All members of the series *cyclo*- $\text{P}_n\text{H}_n$  (*n* = 3–10) have been detected mass spectrometrically in the thermolysis products from  $\text{P}_2\text{H}_4$ .<sup>(70)</sup>

Polycyclic polyphosphanes are often best prepared by direct protonation of the corresponding polyphosphide anions (Figs. 12.11 and 12.12)

with HX, though other routes are also available. Thus, treatment of  $\text{P}_7^{3-}$  yields  $\text{P}_7\text{H}^{2-}$ ,  $\text{P}_7\text{H}_2^-$  and  $\text{P}_7\text{H}_3$  by successive protonation of the three 2-connected  $\text{P}^-$  sites. The alkyl derivatives are more stable than the parent polycyclic phosphanes and provide many examples of the elegant solution of complex conformational problems by the use of nmr spectroscopy.<sup>(67,70)</sup>

### 12.3.3 Phosphorus halides

Phosphorus forms three series of halides  $\text{P}_2\text{X}_4$ ,  $\text{PX}_3$  and  $\text{PX}_5$ . All 12 compounds may exist, although there is considerable doubt about  $\text{PI}_5$ .<sup>(80)</sup> Numerous mixed halides  $\text{PX}_2\text{Y}$  and  $\text{PX}_2\text{Y}_3$  are also known as well as various pseudohalides such as  $\text{P}(\text{CN})_3$ ,  $\text{P}(\text{CNO})_3$ ,  $\text{P}(\text{CNS})_3$  and their mixed halogeno-counterparts. The compounds form an extremely useful extended series with which to follow the effect of progressive substitution on various properties, and the pentahalides are particularly significant in spanning the “ionic-covalent” border, so that they exist in various structural forms depending on the nature of the halogen, the phase of aggregation, or the polarity of the solvent. Some subhalides such as  $\text{P}_4\text{X}_2$  and  $\text{P}_7\text{X}_3$ , and some curious polyhalides such as  $\text{PBr}_7$  and  $\text{PBr}_{11}$  have also been characterized. Physical properties of the binary halides are summarized in Table 12.3 (on the next page). Ternary (mixed) halides tend to have properties intermediate between those of the parent binary halides.

### Phosphorus trihalides

All 4 trihalides are volatile reactive compounds which feature pyramidal molecules. The fluoride is best made by the action of  $\text{CaF}_2$ ,  $\text{ZnF}_2$  or  $\text{AsF}_3$  on  $\text{PCl}_3$ , but the others are formed by direct halogenation of the element.  $\text{PF}_3$  is colourless, odourless and does not fume in air, but is very hazardous due to the formation of a complex with blood haemoglobin (cf.

<sup>80</sup> I. TORNIÉPORTH-OETTING and T. KLAPÖTKE, *J. Chem. Soc., Chem. Commun.*, 132–3 (1990).

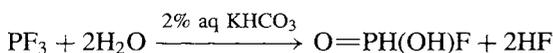
Table 12.3 Some physical properties of the binary phosphorus halides

Compound	Physical State at 25°C	MP/°C	BP/°C	P-X/pm	Angle X-P-X
PF <sub>3</sub>	Colourless gas	-151.5	-101.8	156	96.3°
PCl <sub>3</sub>	Colourless liquid	-93.6	76.1	204	100°
PBr <sub>3</sub>	Colourless liquid	-41.5	173.2	222	101°
PI <sub>3</sub>	Red hexagonal crystals	61.2	decomp > 200	243	102°
P <sub>2</sub> F <sub>4</sub>	Colourless gas	-86.5	-6.2	159 (P-P 228)	99.1° (F-P-P 95.4°)
P <sub>2</sub> Cl <sub>4</sub>	Colourless oily liquid	-28	~180 (d)	—	—
P <sub>2</sub> Br <sub>4</sub>	?	—	—	—	—
P <sub>2</sub> I <sub>4</sub>	Red triclinic needles	125.5	decomp	248 (P-P 221)	102.3° (I-P-P 94.0°)
PF <sub>5</sub>	Colourless gas	-93.7	-84.5	153 (eq) 158 (ax)	120° (eq-eq) 90° (eq-ax)
PCl <sub>5</sub>	Off-white tetragonal crystals	167	160 (subl)	—	See text
PBr <sub>5</sub>	Reddish-yellow rhombohedral crystals	<100 (d)	106 (d)	—	See text
PI <sub>5</sub> ?	Brown-black crystals	41	—	—	However, see ref. 80

CO, p. 1101). It is about as toxic as COCl<sub>2</sub>. The similarity of PF<sub>3</sub> and CO as ligands was first noted by J. Chatt<sup>(81)</sup> and many complexes with transition elements are now known,<sup>(82)</sup> e.g. [Ni(CO)<sub>n</sub>(PF<sub>3</sub>)<sub>4-n</sub>] (*n* = 0-4), [Pd(PF<sub>3</sub>)<sub>4</sub>], [Pt(PF<sub>3</sub>)<sub>4</sub>], [CoH(PF<sub>3</sub>)<sub>4</sub>], [Co<sub>2</sub>(μ-PF<sub>2</sub>)<sub>2</sub>(PF<sub>3</sub>)<sub>6</sub>], etc. Such complexes can be prepared by ligand replacement reactions, by fluorination of PCl<sub>3</sub> complexes, by direct reaction of PF<sub>3</sub> with metal salts or even by direct reaction of PF<sub>3</sub> with metals at elevated temperatures and pressures.

PF<sub>3</sub>, unlike the other trihalides of phosphorus, hydrolyses only slowly with water, the products being phosphorous acid and HF: PF<sub>3</sub> + 3H<sub>2</sub>O → H<sub>3</sub>PO<sub>3</sub> + 3HF.

The reaction is much more rapid in alkaline solutions, and in dilute aqueous KHCO<sub>3</sub> solutions the intermediate monofluorophosphorous acid is formed:



<sup>81</sup> J. CHATT, *Nature* **165**, 637-8 (1950); J. CHATT and A. A. WILLIAMS, *J. Chem. Soc.* 3061-7 (1951).

<sup>82</sup> T. KRUCK, *Angew. Chem. Int. Edn. Engl.* **6**, 53-67 (1967); J. F. NIXON, *Adv. Inorg. Chem. Radiochem.* **13**, 363-469 (1970); R. J. CLARKE and M. A. BUSCH, *Acc. Chem. Res.* **6**, 246-52 (1973).

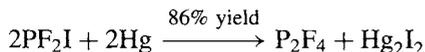
PCl<sub>3</sub> is the most important compound of the group and is made industrially on a large scale<sup>†</sup> by direct chlorination of phosphorus suspended in a precharge of PCl<sub>3</sub> — the reaction is carried out under reflux with continuous take-off of the PCl<sub>3</sub> formed. PCl<sub>3</sub> undergoes many substitution reactions, as shown in the diagram, and is the main source of organophosphorus compounds. Particularly notable are PR<sub>3</sub>, PR<sub>*n*</sub>Cl<sub>3-*n*</sub>, PR<sub>*n*</sub>(OR)<sub>3-*n*</sub>, (PhO)<sub>3</sub>PO, and (RO)<sub>3</sub>PS. Many of these compounds are made on the 1000-tonne scale pa, and the major uses are as oil additives, plasticizers, flame retardants, fuel additives and intermediates in the manufacture of insecticides.<sup>(83)</sup> PCl<sub>3</sub> is also readily oxidized to the important phosphorus(V) derivatives PCl<sub>5</sub>, POCl<sub>3</sub> and PSCl<sub>3</sub>. It is oxidized by As<sub>2</sub>O<sub>3</sub> to P<sub>2</sub>O<sub>5</sub> though this is not the commercial route to this compound (p. 505). It fumes in moist air and is more readily hydrolysed (and oxidized) by water than is PF<sub>3</sub>. With cold N<sub>2</sub>O<sub>4</sub> (-10°) it undergoes a curious oxidative coupling reaction to give Cl<sub>3</sub>P=N-POCl<sub>2</sub>,

<sup>†</sup> World production exceeds one third of a million tonnes pa; of this USA produces ~155 000 tonnes, Western Europe ~115 000 and Japan ~35 000 tonnes pa.

<sup>83</sup> D. H. CHADWICK and R. S. WATT, Chap. 19 in ref. 11, pp. 1221-79.



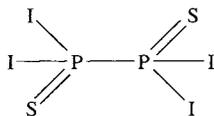
1966, using the very effective method of coupling two PF<sub>2</sub> groups at room temperature under reduced pressure:



The compound hydrolyses to F<sub>2</sub>POPf<sub>2</sub> which can also be prepared directly in good yield by the reaction of O<sub>2</sub> on P<sub>2</sub>F<sub>4</sub>.

P<sub>2</sub>Cl<sub>4</sub> can be made (in low yield) by passing an electric discharge through a mixture of PCl<sub>3</sub> and H<sub>2</sub> under reduced pressure or by microwave discharge through PCl<sub>3</sub> at 1–5 mmHg pressure. The compound decomposes slowly at room temperature to PCl<sub>3</sub> and an involatile solid, and can be hydrolysed in basic solution to give an equimolar mixture of P<sub>2</sub>H<sub>4</sub> and P<sub>2</sub>(OH)<sub>4</sub>.

Little is known of P<sub>2</sub>Br<sub>4</sub>, said to be produced by an obscure reaction in the system C<sub>2</sub>H<sub>4</sub>–PBr<sub>3</sub>–Al<sub>2</sub>Br<sub>6</sub>.<sup>(86)</sup> By contrast, P<sub>2</sub>I<sub>4</sub> is the most stable and also the most readily made of the 4 tetrahalides; it is formed by direct reaction of I<sub>2</sub> and red P at 180° or by I<sub>2</sub> and white P<sub>4</sub> in CS<sub>2</sub> solution, and can also be made by reducing PI<sub>3</sub> with red P, or PCl<sub>3</sub> with iodine. Its X-ray crystal structure shows that the molecules of P<sub>2</sub>I<sub>4</sub> adopt the *trans*-, centrosymmetric (C<sub>2h</sub>) form (see N<sub>2</sub>H<sub>4</sub>, p. 428, N<sub>2</sub>F<sub>4</sub>, p. 439). Reaction of P<sub>2</sub>I<sub>4</sub> with sulfur in CS<sub>2</sub> yields P<sub>2</sub>I<sub>4</sub>S<sub>2</sub>, which probably has the symmetrical structure



but most reactions of P<sub>2</sub>I<sub>4</sub> result in cleavage of the P–P bond, e.g. Br<sub>2</sub> gives PBrI<sub>2</sub> in 90% yield. Hydrolysis yields various phosphines and oxoacids of P, together with a small amount of hypophosphoric acid, (HO)<sub>2</sub>(O)PP(O)(OH)<sub>2</sub>.

Several ternary diphosphorus tetrahalides, P<sub>2</sub>X<sub>n</sub>Y<sub>4–n</sub>, (X, Y = Cl, Br, I) have recently

been detected in CS<sub>2</sub> solutions by <sup>31</sup>P nmr spectroscopy.<sup>(87)</sup> It has also been found that reactions CS<sub>2</sub> solution between P<sub>4</sub> and half a mole-equivalent of Br<sub>2</sub> yielded not only P<sub>2</sub>Br<sub>4</sub> but also small amounts of the new “butterfly” molecules *exo,exo*-P<sub>4</sub>Br<sub>2</sub> and *exo,endo*-P<sub>4</sub>Br<sub>2</sub>. The structure of these can be viewed as being formed by the scission of one P–P bond in the P<sub>4</sub> tetrahedron by Br<sub>2</sub> (cf. the structure of B<sub>4</sub>H<sub>10</sub>, p. 154) which is also a 22 valence-electron species). The molecules P<sub>4</sub>BrCl and P<sub>4</sub>Cl<sub>2</sub> were also identified, following chlorination of the bromide solution using Me<sub>3</sub>SnCl. Other products of the initial reactions included P<sub>7</sub>Br<sub>3</sub> and P<sub>7</sub>I<sub>3</sub> which are structurally related to P<sub>7</sub>H<sub>3</sub> (p. 495). None of these novel subhalides has been isolated pure.<sup>(87)</sup>

### Phosphorus pentahalides

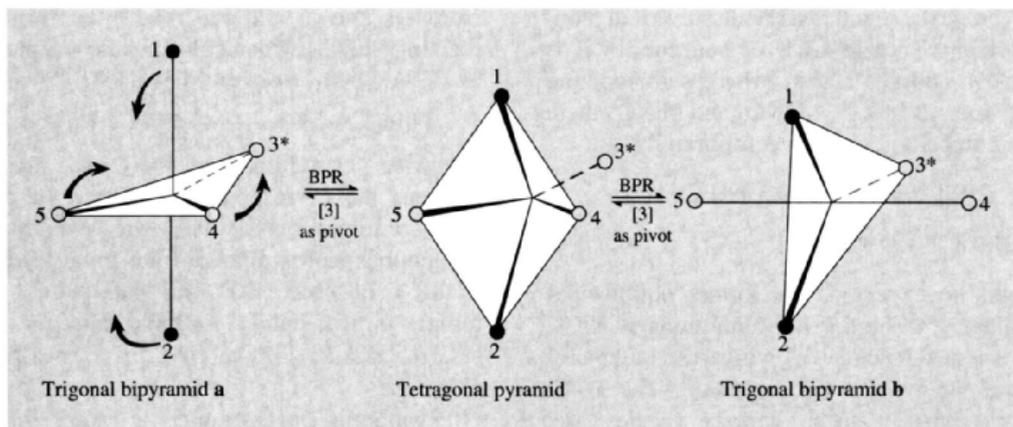
Considerable theoretical and stereochemical interest attaches to these compounds because of the variety of structures they adopt; PCl<sub>5</sub> is also an important chemical intermediate. Thus, PF<sub>5</sub> is molecular and stereochemically non-rigid (see below), PCl<sub>5</sub> is molecular in the gas phase, ionic in the crystalline phase, [PCl<sub>4</sub>]<sup>+</sup>[PCl<sub>6</sub>]<sup>–</sup>, and either molecular or ionically dissociated in solution, depending on the nature of the solvent. PBr<sub>5</sub> is also ionic in the solid state but exists as [PBr<sub>4</sub>]<sup>+</sup>[Br]<sup>–</sup> rather than [PBr<sub>4</sub>]<sup>+</sup>[PBr<sub>6</sub>]<sup>–</sup>. The pentaiodide does not exist<sup>(80)</sup> (except perhaps as PI<sub>3</sub>.I<sub>2</sub>, but certainly not as PI<sub>4</sub><sup>+</sup>I<sup>–</sup> as originally claimed<sup>(88)</sup>).

PF<sub>5</sub> is a thermally stable, chemically reactive gas which can be made either by fluorinating PCl<sub>5</sub> with AsF<sub>3</sub> (or CaF<sub>2</sub>), or by thermal decomposition of NaPF<sub>6</sub>, Ba(PF<sub>6</sub>)<sub>2</sub> or the corresponding diazonium salts. Single-crystal X-ray analysis (at –164°C) indicates a trigonal bipyramidal structure with P–F<sub>ax</sub> (158.0 pm) being

<sup>86</sup> R. I. PYRKIN, YA. A. LEVIN and E. I. GOLDFARB, *J. Gen. Chem. USSR* **43**, 1690–6 (1973). See also A. HINKE, W. KUCHEN and J. KUTTER, *Angew. Chem. Int. Edn. Engl.* **20**, 1060 (1981).

<sup>87</sup> B. W. TATTERSHALL and N. L. KENDALL, *Polyhedron* **13**, 1517–21 (1994).

<sup>88</sup> N. G. FESHCHENKO V. G. KOSTINA and A. V. KIRSANOV, *J. Gen. Chem. USSR* **48**, 195–6 (1978).



**Figure 12.13** Interchange of axial and equatorial positions by Berry pseudorotation (BPR).

significantly longer than  $P-F_{eq}$  (152.2 pm).<sup>(89)</sup> This confirms the deductions from a gas phase electron-diffraction study ( $D_{3h}$ :  $P-F_{ax}$  158 pm,  $P-F_{eq}$  153 pm). However, the  $^{19}\text{F}$  nmr spectrum, as recorded down to  $-100^\circ\text{C}$ , shows only a single fluorine resonance peak (split into a doublet by  $^{31}\text{P}$ - $^{19}\text{F}$  coupling) implying that on this longer time scale (milliseconds, as distinct from “instantaneous” for electron diffraction) all 5 F atoms are equivalent. This can be explained if the axial and equatorial F atoms interchange their positions more rapidly than this, a process termed “pseudorotation” by R. S. Berry (1960); indeed,  $\text{PF}_5$  was the first compound to show this effect.<sup>(90)</sup> The proposed mechanism is illustrated in Fig. 12.13 and is discussed more fully in ref. 91; the barrier to notation has been calculated as  $16 \pm 2 \text{ kJ mol}^{-1}$ .<sup>(92)</sup>

The mixed chlorofluorides  $\text{PCl}_4\text{F}$  (mp  $-59^\circ$ , bp  $+67^\circ$ ) and  $\text{PCl}_3\text{F}_2$  (mp  $-63^\circ$ ) are also trigonal bipyramidal with axial F atoms; likewise  $\text{PCl}_2\text{F}_3$  (mp  $-125^\circ$ , bp  $+7.1^\circ$ ) has 2 axial and 1 equatorial F atoms and  $\text{PClF}_4$  (mp  $-132^\circ$ ,

bp  $-43.4^\circ$ ) has both axial positions occupied by F atoms.<sup>(93)</sup> These compounds are obtained by addition of halogen to the appropriate phosphorus(III) chlorofluoride, but if  $\text{PCl}_5$  is fluorinated in a polar solvent, ionic isomers are formed, e.g.  $[\text{PCl}_4]^+[\text{PCl}_4\text{F}_2]^-$  (colourless crystals, subl  $175^\circ$ ) and  $[\text{PCl}_4]^+[\text{PF}_6]^-$  (white crystals, subl  $135^\circ$  with decomposition). The crystalline hemifluoride  $[\text{PCl}_4]^+[\text{PCl}_5\text{F}]^-$  has also been identified. The analogous parallel series of covalent and ionic bromofluorides is less well characterized but  $\text{PBr}_2\text{F}_3$  is known both as an unstable molecular liquid (decomp  $15^\circ$ ) and as a white crystalline powder  $[\text{PBr}_4]^+[\text{PF}_6]^-$  (subl  $135^\circ$  decomp). It can be noted that  $\text{PF}_3(\text{NH}_2)_2$  is a trigonal bipyramidal molecule with  $C_{2v}$  symmetry (i.e. equatorial  $\text{NH}_2$  groups),<sup>(94)</sup> whereas the most stable form of tetra-arylfuorophosphoranes is ionic,  $[\text{PR}_4]^+\text{F}^-$ , although molecular monomers  $\text{R}_4\text{PF}$  and an ionic dimer  $[\text{PR}_4]^+[\text{PR}_4\text{F}_2]^-$  also exist.<sup>(95)</sup>

$\text{PCl}_5$  is even closer to the ionic-covalent borderline than is  $\text{PF}_5$ , the ionic solid  $[\text{PCl}_4]^+[\text{PCl}_6]^-$  melting (or subliming) to give a covalent molecular

<sup>89</sup> D. MOOTZ and M. WIEBCKE, *Z. anorg. allg. Chem.* **545**, 39–42 (1987).

<sup>90</sup> R. S. BERRY, *J. Chem. Phys.* **32**, 933–8 (1960).

<sup>91</sup> R. LUCKENBACH, *Dynamic Stereochemistry of Pentacoordinate Phosphorus and Related Elements*, G. THIEME, Stuttgart, 1973, 259 pp.

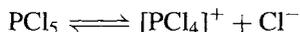
<sup>92</sup> C. J. MARSDEN, *J. Chem. Soc., Chem. Commun.*, 401–2 (1984).

<sup>93</sup> C. MACHO, R. MINKWITZ, J. ROHMAN, B. STEGER, W. WÖLFEL and H. OBERHAMMER, *Inorg. Chem.* **25**, 2828–35 (1986), and references cited therein.

<sup>94</sup> C. J. MARSDEN, K. HEDBERG, J. M. SHREEVE and K. D. GUPTA, *Inorg. Chem.* **23**, 3659–62 (1984).

<sup>95</sup> S. J. BROWN, J. H. CLARK and D. J. MACQUARRIE, *J. Chem. Soc., Dalton Trans.*, 277–80 (1988).

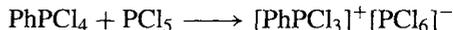
liquid (or gas). Again, when dissolved in non-polar solvents such as  $\text{CCl}_4$  or benzene,  $\text{PCl}_5$  is monomeric and molecular, whereas in ionizing solvents such as  $\text{MeCN}$ ,  $\text{MeNO}_2$  and  $\text{PhNO}_2$  there are two competing ionizing equilibria.<sup>(96)</sup>



As might be expected, the former equilibrium predominates at higher concentrations of  $\text{PCl}_5$  (above about  $0.03 \text{ mol l}^{-1}$ ) whilst the latter predominates below this concentration. The P-Cl distances (pm) in these various species are:  $\text{PCl}_5$  214 (axial), 202 (equatorial);  $[\text{PCl}_4]^+$  197;  $[\text{PCl}_6]^-$  208 pm. Ionic isomerism is also known and, in addition to  $[\text{PCl}_4]^+[\text{PCl}_6]^-$ , another (metastable) crystalline phase of constitution  $[\text{PCl}_4]_2^+[\text{PCl}_6]_2^-\text{Cl}^-$  can be formed either by application of high pressure or by crystallizing  $\text{PCl}_5$  from solutions of dichloromethane containing  $\text{Br}_2$  or  $\text{SCl}_2$ .<sup>(97)</sup> When gaseous  $\text{PCl}_5$  (in equilibrium with  $\text{PCl}_3 + \text{Cl}_2$ ) is quenched to 15 K the trigonal-bipyramidal molecular structure is retained; this forms an ordered molecular crystalline lattice on warming to  $\sim 130 \text{ K}$ , but further warming towards room temperature results in chloride-ion transfer to give  $[\text{PCl}_4]^+[\text{PCl}_6]^-$ .<sup>(98)</sup> The first alkali metal salt of  $[\text{PCl}_6]^-$ ,  $\text{CsPCl}_6$ , has only recently been made.<sup>(99)</sup>

The delicate balance between ionic and covalent forms is influenced not only by the state of aggregation (solid, liquid, gas) or the nature of the solvent, but also by the effect of substituents. Thus  $\text{PhPCl}_4$  is molecular with Ph equatorial whereas the corresponding methyl derivative is ionic,  $[\text{MePCl}_3]^+\text{Cl}^-$ . Despite this the  $[\text{PhPCl}_3]^+$

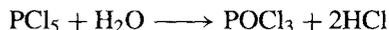
cation is known and can readily be formed by reacting  $\text{PhPCl}_4$  with a chlorine ion acceptor such as  $\text{BCl}_3$ ,  $\text{SbCl}_5$ , or even  $\text{PCl}_5$  itself:<sup>(100)</sup>



Likewise crystalline  $\text{Ph}_2\text{PCl}_3$  is molecular whereas the corresponding Me and Et derivatives are ionic  $[\text{R}_2\text{PCl}_2]^+\text{Cl}^-$ . However, all 3 tri-organophosphorus dihalides are ionic  $[\text{R}_3\text{PCl}]^+\text{Cl}^-$  (R = Ph, Me, Et). The pale-yellow, crystalline mixed halide  $\text{P}_2\text{BrCl}_9$  appears to be  $[\text{PCl}_4]_6^+[\text{PCl}_3\text{Br}]_2^+[\text{PCl}_6]_4^-[\text{Br}]_4^-$  (i.e.  $\text{P}_{12}\text{Br}_6\text{Cl}_{54}$ ).<sup>(101)</sup>

Phosphorus pentabromide is rather different. The crystalline solid is  $[\text{PBr}_4]^+\text{Br}^-$  but this appears to dissociate completely to  $\text{PBr}_3$  and  $\text{Br}_2$  in the vapour phase; rapid cooling of this vapour to 15 K results in the formation of a disordered lattice of  $\text{PBr}_3$  and  $\text{PBr}_7$  (i.e.  $[\text{PBr}_4]^+[\text{Br}_3]^-$ ) and this mixture reverts to  $[\text{PBr}_4]^+\text{Br}^-$  on being warmed to 180 K.<sup>(98)</sup> The corresponding trichloride,  $[\text{PBr}_4]^+[\text{Cl}_3]^-$  is also known.<sup>(102)</sup>  $[\text{PI}_4]^+$  has been identified only as its salt  $[\text{PI}_4]^+[\text{AsF}_6]^-$ .<sup>(80)</sup>

$\text{PCl}_5$  is made on an industrial scale by the reaction of  $\text{Cl}_2$  on  $\text{PCl}_3$  dissolved in an equal volume of  $\text{CCl}_4$ . World production probably exceeds 20 000 tonnes pa. On the laboratory scale  $\text{Cl}_2$  gas (or liquid) can be passed directly into  $\text{PCl}_3$ .  $\text{PCl}_5$  reacts violently with water to give  $\text{HCl}$  and  $\text{H}_3\text{PO}_4$  but in equimolar amounts the reaction can be moderated to give  $\text{POCl}_3$ :



$\text{PCl}_5$  chlorinates alcohols to alkyl halides and carboxylic acids to the corresponding  $\text{RCOCl}$ . When heated with  $\text{NH}_4\text{Cl}$  the phosphonitric chlorides are obtained (p. 536). These and other reactions are summarized in the diagram.<sup>(8)</sup>

<sup>96</sup> R. W. SUTER, H. C. KNACHEL, V. P. PETRO, J. H. HOWATSON and S. G. SHORE, *J. Am. Chem. Soc.* **95**, 1474-9 (1973).

<sup>97</sup> A. FINCH, P. N. GATES, H. D. B. JENKINS and K. P. THAKUR, *J. Chem. Soc., Chem. Commun.*, 579-80 (1980). See also H. D. B. JENKINS, L. SHARMAN, A. FINCH and P. N. GATES, *Polyhedron* **13**, 1481-2 (1994) and references cited therein.

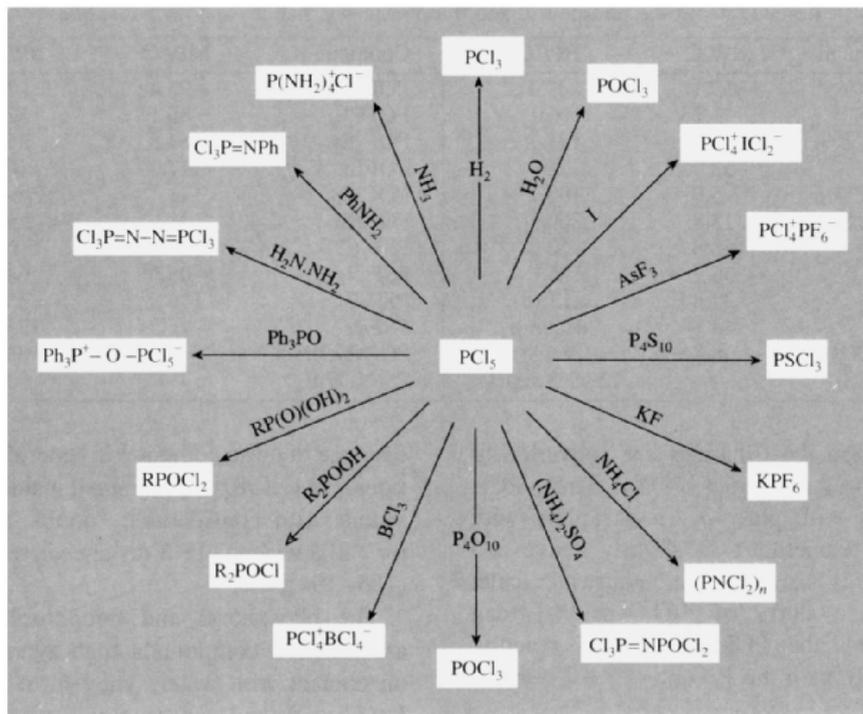
<sup>98</sup> A. FINCH, P. N. GATES and A. S. MUIR, *J. Chem. Soc., Chem. Commun.*, 812-4 (1981). See also H. D. B. JENKINS, K. P. THAKUR, A. FINCH and P. N. GATES, *Inorg. Chem.* **21**, 423-6 (1982).

<sup>99</sup> A. S. MUIR, *Polyhedron* **10**, 2217-9 (1991).

<sup>100</sup> K. B. DILLON, R. J. LYNCH, R. N. REEVE and T. C. WADDINGTON, *J. Chem. Soc., Dalton Trans.*, 1243-8 (1976). See also M. A. H. A. AL-JUBOORI, P. N. GATES and A. S. MUIR, *J. Chem. Soc., Chem. Commun.*, 1270-1 (1991).

<sup>101</sup> F. F. BENTLEY, A. FINCH, P. N. GATES, F. J. RYAN and K. B. DILLON, *J. Inorg. Nucl. Chem.* **36**, 457-9 (1974). See also *J. Chem. Soc., Dalton Trans.*, 1863-6 (1973).

<sup>102</sup> K. B. DILLON, M. P. NISBET and R. N. REEVE, *Polyhedron* **7**, 1725-6 (1988). See also H. D. B. JENKINS, *Polyhedron* **15**, 2831-4 (1996).



The chlorination of phosphonic and phosphinic acids and esters are of considerable importance.  $\text{PCl}_5$  can also act as a Lewis acid to give 6-coordinate P complexes, e.g.  $\text{pyPCl}_5$ , and  $\text{pyz-PCl}_5$ , where  $\text{py} = \text{C}_5\text{H}_5\text{N}$  (pyridine) and  $\text{pyz} = \text{cyclo-1,4-C}_4\text{H}_4\text{N}_2$  (pyrazine).<sup>(103)</sup>

### Pseudohalides of phosphorus(III)

Paralleling the various phosphorus trihalides are numerous pseudohalides and mixed pseudohalide-halides of which the various isocyanates and isothiocyanates are perhaps the best known. Most are volatile liquids, e.g.

Compound	$\text{P}(\text{NCO})_3$	$\text{PF}(\text{NCO})_2$	$\text{PF}_2(\text{NCO})$
MP/°C	-2	-55	~ -108
BP/°C	169.3	98.7	12.3

Compound	$\text{PCl}(\text{NCO})_2$	$\text{PCl}_2(\text{NCO})$	$\text{P}(\text{NCS})_3$
MP/°C	-50	-99	-4
BP/°C	134.6	104.5	~120/1 mmHg

Compound	$\text{PF}_2(\text{NCS})$	$\text{PCl}_2(\text{NCS})$
MP/°C	-95	-76
BP/°C	90.3	148(decomp)

The corresponding phosphoryl and thiophosphoryl pseudohalides are also known, i.e.  $\text{PO}(\text{NCO})_3$ ,  $\text{PS}(\text{NCO})_3$ , etc. Preparations are by standard procedures such as those on the diagram for  $\text{PCl}_3$  (p. 497). As indicated there,  $\text{P}(\text{CN})_3$  has also been made: it is a highly reactive white crystalline solid mp  $203^\circ$  which reacts violently with water to give mainly phosphorous acid and HCN.

### 12.3.4 Oxohalides and thiohalides of phosphorus

The propensity of phosphorus(III) compounds to oxidize to phosphorus(V) by formation of an additional  $\text{P}=\text{O}$  bond is well illustrated by the

<sup>103</sup> B. N. MEYER, J. N. ISHLEY, A. V. FRATINI and H. C. KNACHEL, *Inorg. Chem.* **19**, 2324-7 (1980) and references therein.