

**Figure 12.4** Structure of Hittorf's violet monoclinic phosphorus showing (a) end view of one pentagonal tube, (b) the side view of a single tube (dimensions in pm).

same as in  $P_4$ ) but the average P-P-P angle is  $101^\circ$  (instead of  $60^\circ$ ).

Black phosphorus, the thermodynamically most stable form of the element, has been prepared in three crystalline forms and one amorphous form. It is even more highly polymeric than the red form and has a correspondingly higher density (orthorhombic 2.69, rhombohedral 3.56, cubic  $3.88 \text{ g cm}^{-3}$ ). Black phosphorus (orthorhombic) was originally made by heating white  $P_4$  to  $200^\circ$  under a pressure of 12 000 atm (P. W. Bridgman, 1916). Higher pressures convert it successively to the rhombohedral and cubic forms (Fig. 12.3). Orthorhombic black P (mp  $\sim 610^\circ$ ) has a layer structure which is based on a puckered hexagonal net of 3-coordinate P atoms with 2 interatomic angles of  $102^\circ$  and 1 of  $96.5^\circ$  (P-P 223 pm). The relation of this form to the rhombohedral and cubic forms is shown in Fig. 12.5. Comparison with the rhombohedral forms of As, Sb and Bi is also instructive in showing the increasing tendency towards octahedral coordination and metallic properties (p. 551). Black P is semiconducting but its electrical properties are probably significantly affected by impurities introduced during its preparation.

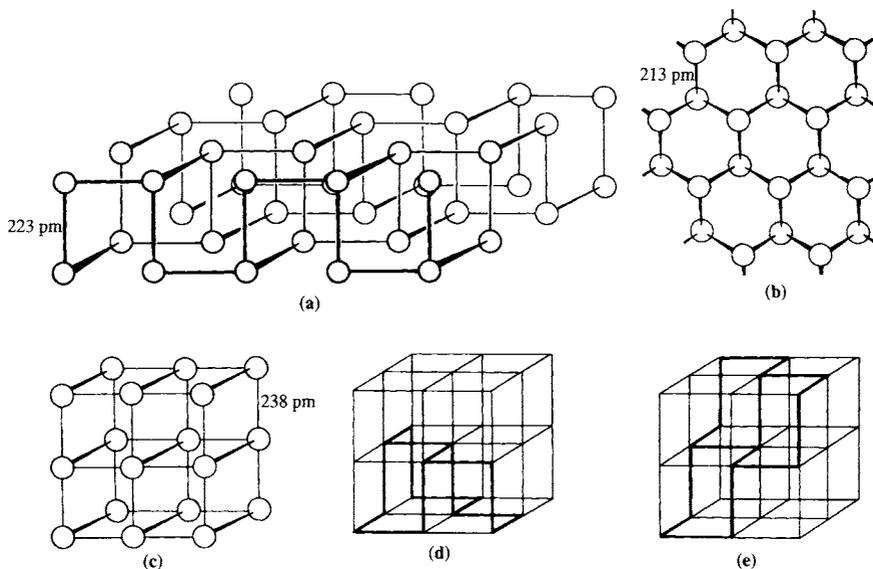
### 12.2.4 Atomic and physical properties<sup>(26)</sup>

Phosphorus has only one stable isotope,  $^{31}_{15}\text{P}$ , and accordingly (p. 17) its atomic weight is known with extreme accuracy, 30.973 762(4). Sixteen radioactive isotopes are known, of which  $^{32}\text{P}$  is by far the most important; it is made on the multikilogram scale by the neutron irradiation of  $^{32}\text{S}(n,p)$  or  $^{31}\text{P}(n,\gamma)$  in a nuclear reactor, and is a pure  $\beta$ -emitter of half life 14.26 days,  $E_{\text{max}}$  1.709 MeV,  $E_{\text{mean}}$  0.69 MeV. It finds extensive use in tracer and mechanistic studies. The stable isotope  $^{31}\text{P}$  has a nuclear spin quantum number of  $\frac{1}{2}$  and this is much used in nmr spectroscopy.<sup>(27)</sup> Chemical shifts and coupling constants can both be used diagnostically to determine structural information.

In the ground state, P has the electronic configuration  $[\text{Ne}]3s^2 3p_x^1 3p_y^1 3p_z^1$  with 3 unpaired

<sup>26</sup> Mellor's *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 8, Suppl. 3, *Phosphorus*, Longman, London, 1971, 1467 pp.

<sup>27</sup> D. G. GORENSTEIN (ed.) *Phosphorus-31 NMR; Principles and Applications* Academic Press, London, 1984, 604 pp. J. G. VERKADE and L. D. QUIN (eds.), *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH Publishers, Weinheim, 1987, 717 pp.



**Figure 12.5** The structures of black phosphorus: (a) portion of one layer of orthorhombic P (idealized), (b) rhombohedral form, portion of one hexagonal layer, (c) cubic form, 4 unit cells, (d) distortion of (a) to the cubic form, and (e) distortion of (b) to the cubic form.

electrons; this, together with the availability of low-lying vacant 3d orbitals, accounts for the predominant oxidation states III and V in phosphorus chemistry. Ionization energies, electronegativity, and atomic radii are compared with those of N, As, Sb and Bi on p. 550. White phosphorus ( $\alpha$ -P<sub>4</sub>) has mp 44.1° (or 44.25° when ultrapure), bp 280.5° and a vapour pressure of 0.122 mmHg at 40°C. It is an insulator with an electrical resistivity of  $\sim 10^{11}$  ohm cm at 11°C, a dielectric constant of 4.1 (at 20°) and a refractive index  $n_D$  (29.2°) 1.8244. The heat of combustion of P<sub>4</sub> to P<sub>4</sub>O<sub>10</sub> is  $-2971 \text{ kJ mol}^{-1}$  and the heat of transition to amorphous red phosphorus is  $-29 \text{ kJ (mol P}_4\text{)}^{-1}$ .

### 12.2.5 Chemical reactivity and stereochemistry

The spontaneous chemiluminescent reaction of white phosphorus with moist air was the first property of the element to be observed and was the origin of its name (p. 473); its spontaneous ignition temperature in air is  $\sim 35^\circ$ . We have already seen (p. 481) that the reactivity

of phosphorus depends markedly upon which allotrope is being studied and that increasing catenation of the polymeric red and black forms notably diminishes both reactivity and solubility. The preference of phosphorus for these forms rather than for the gaseous form P<sub>2</sub>, which is its most obvious distinction from nitrogen, can be rationalized in terms of the relative strengths of the triple and single bonds for the 2 elements. Reliable values are hard to obtain but generally accepted values are as follows:

$E(\text{N}\equiv\text{N})/\text{kJ}$		$E(\text{P}\equiv\text{P})/\text{kJ}$	
per mol of N	946	per mol of P	490
$E(>\text{N}-\text{N}<)/\text{kJ}$	159	$E(>\text{P}-\text{P}<)/\text{kJ}$	
per mol of N	(or 296)	per mol of P	200
Ratio	5.95	Ratio	2.45
	(or 3.20)		

It is clear that, for nitrogen, the triple bond is preferred since it has more than 3 times the energy of a single bond, whereas for phosphorus the triple-bond energy is less than 3 times the single-bond energy and so allotropes having 3 single bonds per P atom are more stable than that with a triple bond.

Table 12.2 Stereochemistry of phosphorus

CN	Geometry	Examples
0	—	P(g) — in equilibrium with P <sub>2</sub> (g) above 2200°C
1	—	P <sub>2</sub> (g) — in equilibrium with P <sub>4</sub> (g) above 800°C; HC≡P; FC≡P; MeC≡P (p. 544)
2	Bent <sup>(28)</sup>	HP=CH <sub>2</sub> , <sup>(29)</sup> [P(CN) <sub>2</sub> ] <sup>-</sup> , <sup>(30)</sup> [(C <sub>6</sub> H <sub>4</sub> S(NR)C) <sub>2</sub> P] <sup>+X<sup>-</sup></sup> (p. 544), <i>cyclo</i> -C <sub>5</sub> H <sub>5</sub> P, 2,4,6-Ph <sub>3</sub> C <sub>5</sub> H <sub>2</sub> P; Me <sub>3</sub> P=PCF <sub>3</sub> ; P <sub>7</sub> <sup>3-</sup> anion <sup>(31)</sup> (isoelectronic with P <sub>4</sub> S <sub>3</sub> ) in Sr <sub>3</sub> P <sub>14</sub> ; P <sub>11</sub> <sup>3-</sup> anion in Na <sub>3</sub> P <sub>11</sub> ; diazaphospholes <sup>(32)</sup>
3	Planar	[PhP{Mn(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> }] <sub>2</sub> <sup>(33)</sup> , [(fluorenyl)=P{=C(SiMe <sub>3</sub> ) <sub>2</sub> }] <sup>-(33a)</sup>
4	Pyramidal Tetrahedral	P <sub>4</sub> , PH <sub>3</sub> , PX <sub>3</sub> , P <sub>4</sub> O <sub>6</sub> , [PhP{Co(CO) <sub>4</sub> }] <sub>2</sub> <sup>(34)</sup> PH <sub>4</sub> <sup>+</sup> , Cl <sub>3</sub> PO, P <sub>4</sub> O <sub>10</sub> , PO <sub>4</sub> <sup>3-</sup> , polyphosphates, MP (zinc-blende type, M = B, Al, Ga, In), [Co <sub>3</sub> (CO) <sub>9</sub> (μ <sub>3</sub> -PPh)] <sub>2</sub> <sup>(35)</sup> , [(P <sub>4</sub> )Ni{(Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N}] <sub>2</sub> <sup>(36)</sup> many complexes of PR <sub>3</sub> etc., with metal centres
5	Local C <sub>2v</sub> Trigonal bipyramidal	PBr <sub>4</sub> <sup>-</sup> , [PBr <sub>2</sub> (CN) <sub>2</sub> ] <sup>-</sup> . <sup>(37)</sup> [μ(η <sup>3</sup> -P <sub>3</sub> ){Ni(triphos)} <sub>2</sub> ] <sup>2+</sup> <sup>(38)</sup> PF <sub>5</sub> , PPh <sub>5</sub>
6	Square pyramidal Octahedral Trigonal prismatic	[Co <sub>4</sub> (CO) <sub>8</sub> (μ-CO) <sub>2</sub> (μ <sub>4</sub> -PPh) <sub>2</sub> ], [Os <sub>5</sub> (CO) <sub>15</sub> (μ <sub>4</sub> -POMe)] <sup>(39)</sup> PF <sub>6</sub> <sup>-</sup> , PCl <sub>6</sub> <sup>-</sup> , MP (NaCl-type, M = La, Sm, Th, U etc.) Rh <sub>4</sub> P <sub>3</sub> , Hf <sub>3</sub> P <sub>2</sub> (also contains seven- and eight-fold coordination of P by M), [(μ <sub>6</sub> -P){Os(CO) <sub>3</sub> }] <sub>6</sub> <sup>-(40)</sup>
7	Irregular (4 + 2) Capped trigonal prismatic	[Co <sub>6</sub> (CO) <sub>14</sub> (μ-CO) <sub>2</sub> P] <sup>-</sup> Ta <sub>2</sub> P, Hf <sub>2</sub> P (contains P in seven-, eight-, and nine-fold coordination by M)
8	Cubic Bicapped trigonal prismatic	M <sub>2</sub> P (antifluorite type (p. 118), M = Ir, Rh) Hf <sub>2</sub> P
9	Tricapped trigonal prismatic Monocapped square antiprismatic	M <sub>3</sub> P (M = Ti, V, Cr, Mn, Fe, Ni, Zr, Nb, Ta) M <sub>2</sub> P (PbCl <sub>2</sub> -type, M = Fe, Co, Ru) [Rh <sub>9</sub> (CO) <sub>21</sub> P] <sub>2</sub> <sup>-(41)</sup>

<sup>28</sup>E. FLUCK, *Topics in Phosphorus Chemistry* **10**, 193–284 (1980).

<sup>29</sup>H. W. KROTO, J. F. NIXON, K. OHNO and N. P. C. SIMMONS, *J. Chem. Soc., Chem. Commun.*, 709 (1980).

<sup>30</sup>W. S. SHELDRIK, J. KRONER, F. ZWASCHKA and A. SCHMIDPETER, *Angew. Chem. Int. Edn. Engl.* **18**, 934–5 (1979).

<sup>31</sup>W. DAHLMANN and H. G. VON SCHNERING, *Naturwissenschaften* **59**, 420 (1972). W. WICHELHAUS and H. G. VON SCHNERING, *ibid.* **60**, 104 (1973).

<sup>32</sup>J. H. WEINMAIER, A. SCHMIDPETER, *et al.*, *Angew. Chem. Int. Edn. Engl.* **18**, 412 (1979); *Chem. Ber.* **113**, 2278–90 (1980); *J. Organometallic Chem.* **185**, 53–68 (1980).

<sup>33</sup>G. HUTTNER, H.-D. MÜLLER, A. FRANK, and H. LORENZ, *Angew. Chem. Int. Edn. Engl.* **14**, 705–6 (1975).

<sup>33a</sup>R. APPEL, E. GAITZSCH and F. KNOCH, *Angew. Chem. Int. Edn. Engl.* **24**, 589–90 (1985).

<sup>34</sup>J. C. BURT and G. SCHMID, *J. Chem. Soc., Dalton Trans.*, 1385–7 (1978).

<sup>35</sup>L. MARKÓ and B. MARKÓ, *Inorg. Chim. Acta* **14**, L39 (1975).

<sup>36</sup>P. DAPPORIO, S. MIDOLLINI and L. SACCONI, *Angew. Chem. Int. Edn. Engl.* **18**, 469 (1979).

<sup>37</sup>W. S. SHELDRIK, A. SCHMIDPETER, F. ZWASCHKA, K. B. DILLON, A. W. G. PLAIT and T. C. WADDINGTON, *J. Chem. Soc., Dalton Trans.*, 413–8 (1981) see also *Angew. Chem. Int. Edn. Engl.* **18**, 935–6 (1979).

<sup>38</sup>M. DI VAIRA, S. MIDOLLINI and L. SACCONI, *J. Am. Chem. Soc.* **101**, 1757–63 (1979). For analogous complexes in which μ-(η<sup>3</sup>-P<sub>3</sub>) bridges RhCo, RhNi, IrCo, and RhRh, see C. BIANCHINI, M. DI VAIRA, A. MELI and L. SACCONI, *Angew. Chem. Int. Edn. Engl.* **19**, 405–6 (1980).

<sup>39</sup>J. M. FERNANDEZ, B. F. G. JOHNSON, J. LEWIS and P. R. RAITHY, *J. Chem. Soc., Chem. Commun.*, 1015–6 (1978).

<sup>40</sup>S. B. COLBRAN, C. M. HAY, B. F. G. JOHNSON, F. J. LAHOZ, J. LEWIS and P. R. RAITHY, *J. Chem. Soc., Chem. Commun.*, 1766–8 (1986).

<sup>41</sup>J. L. VIDAL, W. E. WALKER, R. L. PRUETT and R. C. SCHOENING, [Rh<sub>9</sub>P(CO)<sub>21</sub>]<sub>2</sub><sup>2-</sup>. *Inorg. Chem.* **18**, 129–36 (1979).

Phosphorus forms binary compounds with all elements except Sb, Bi and the noble gases. It reacts spontaneously with O<sub>2</sub> and the halogens at room temperature, the mixtures rapidly reaching incandescence. Sulfur and the alkali metals also react vigorously with phosphorus on warming, and the element combines directly with all metals (except Bi, Hg, Pb) frequently with incandescence (e.g. Fe, Ni, Cu, Pt). White phosphorus (but not red) also reacts readily with heated aqueous solutions to give a variety of products (pp. 493 and 513ff), and with many other aqueous and nonaqueous reagents.

The stereochemistry and bonding of P are very varied as will become apparent in later sections: the element is known in at least 14 coordination geometries with CN up to 9, though the most frequently met have CN 3, 4, 5 and 6. Some typical coordination geometries are summarized in Table 12.2 and illustrated in Fig. 12.6. Many of these compounds will be more fully discussed in later sections.

The great propensity of P atoms to catenate into chains, rings and clusters, P<sub>n</sub>, has already been noted during the discussion on allotropy (pp. 479–83). These groupings and other similar ones also feature in the structures of metal phosphides (p. 489), polyphosphanes (p. 492) and organopolyphosphanes (p. 542). Moreover, neutral or charged groupings, P<sub>n</sub>, (*n* = 2–6, 10) can also serve as ligands<sup>(42–44)</sup>, as can isolated P atoms in anions such as [(μ<sub>6</sub>-P){Os(CO)<sub>3</sub>]<sub>6</sub>]<sup>-(40)</sup> and other structures shown at the foot of Fig. 12.6. Two decades ago virtually nothing was known about this aspect of phosphorus chemistry, but it is now a burgeoning field, and the substantial progress which has been made in recent years now permits a general overview to be given.

<sup>42</sup> M. DI VAIRA and P. STOPPIONI, *Polyhedron* **6**, 351–82 (1987). (Review)

<sup>43</sup> O. J. SCHERER, *Angew. Chem. Int. Edn. Engl.* **24**, 924–43 (1985); **29** 1104–22 (1990). (Reviews)

<sup>44</sup> O. J. SCHERER (and 9 others), in R. STEUDEL (ed.), *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, 1992, pp. 193–208.

The P<sub>2</sub> group is isoelectronic with ethyne (p. 932) and with N<sub>2</sub> (pp. 414–6) and As<sub>2</sub>. It has emerged as a versatile ligand with several well characterized coordination modes as shown schematically in Fig 12.7. The first compound containing the P<sub>2</sub> ligand, [(Co(CO)<sub>3</sub>]<sub>2</sub>(μ,η<sup>2</sup>-P<sub>2</sub>)], was isolated as a red oil in 1973 and was clearly similar to the already known alkyne and As<sub>2</sub> complexes [{Co(CO)<sub>3</sub>]<sub>2</sub>{μ,η<sup>2</sup>-(CR)<sub>2</sub>}] and [{Co(CO)<sub>3</sub>]<sub>2</sub>(μ,η<sup>2</sup>-As<sub>2</sub>)]. It was formed by reaction of Na[Co(CO)<sub>4</sub>] with PCl<sub>3</sub> or PBr<sub>3</sub> in thf. The tetrahedrane-like core (Fig. 12.7a) was confirmed by X-ray analysis on the related PPh<sub>3</sub> derivative [Co<sub>2</sub>(CO)<sub>5</sub>(PPh<sub>3</sub>)(μ,η<sup>2</sup>-P<sub>2</sub>)].<sup>(45)</sup> Direct action of P<sub>4</sub> with appropriate carbonyl, cyclopentadienyl or alkoxide derivatives of Cr, Mo, W, etc. has yielded a wide range of such compounds of P<sub>2</sub> acting as a 4e-donor, in all of which the two ML<sub>n</sub> vertices can be considered as 15e-acceptors (i.e. d<sup>10</sup> + 5e, “isoelectronic” with P in Group 15) e.g., {Cr(Cp)(CO)<sub>2</sub>},<sup>(46)</sup> {Mo(Cp)(CO)<sub>2</sub>}, {W(py)(OPr<sup>t</sup>)<sub>2</sub>(μ-OPr<sup>t</sup>)},<sup>(47)</sup> etc., where Cp is (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) or one of its derivatives. With 14e or 16e metal-vertex acceptors the core adopts the more open “butterfly” configuration (Fig 12.7b) without direct M–M bonding, e.g. [{Ni(Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PEt<sub>2</sub>)<sub>2</sub>(μ,η<sup>2</sup>-P<sub>2</sub>)}]<sup>(48)</sup> and its {Ni(PEt<sub>3</sub>)<sub>2</sub>} and [Pt(PEt<sub>3</sub>)<sub>2</sub>] analogues. Further electron-pair donation from one or both of the P atoms can also occur to give compounds such as [Cr<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>4</sub>(μ,η<sup>2</sup>-P<sub>2</sub>)]{M(CO)<sub>5</sub>]<sub>1 or 2</sub> (M = Cr, Mo, W) (see Figs. 12.7 c, d).<sup>(49)</sup> In these, the P<sub>2</sub> group acts as a 6e or 8e donor, and bridges 3 or 4 M atoms respectively. See below — p. 488 — for examples cf. bis-P<sub>2</sub>, i.e. pseudo-P<sub>4</sub> complexes.)

<sup>45</sup> C. F. CAMPANA, A. VIZI-OROSZ, G. PÄLYI, L. MARKÒ and L. F. DAHL, *Inorg. Chem.* **18**, 3054–9 (1979).

<sup>46</sup> L. Y. GOH, C. K. CHU, R. C. S. WONG and T. W. HAMBLEY, *J. Chem. Soc., Chem. Commun.*, 1951–6 (1979).

<sup>47</sup> M. H. CHISHOLM, K. FOLTING, J. C. HUFFMAN and J. J. KOH, *Polyhedron* **4**, 893–5 (1985).

<sup>48</sup> H. SCHÄFFER, D. BINDER and D. FENSKE, *Angew. Chem. Int. Edn. Engl.* **24**, 522–4 (1985).

<sup>49</sup> L. Y. GOH, R. C. S. WONG and T. C. W. MAK, *J. Organometallic Chem.* **364**, 363–71 (1989) and **373**, 71–6 (1989).

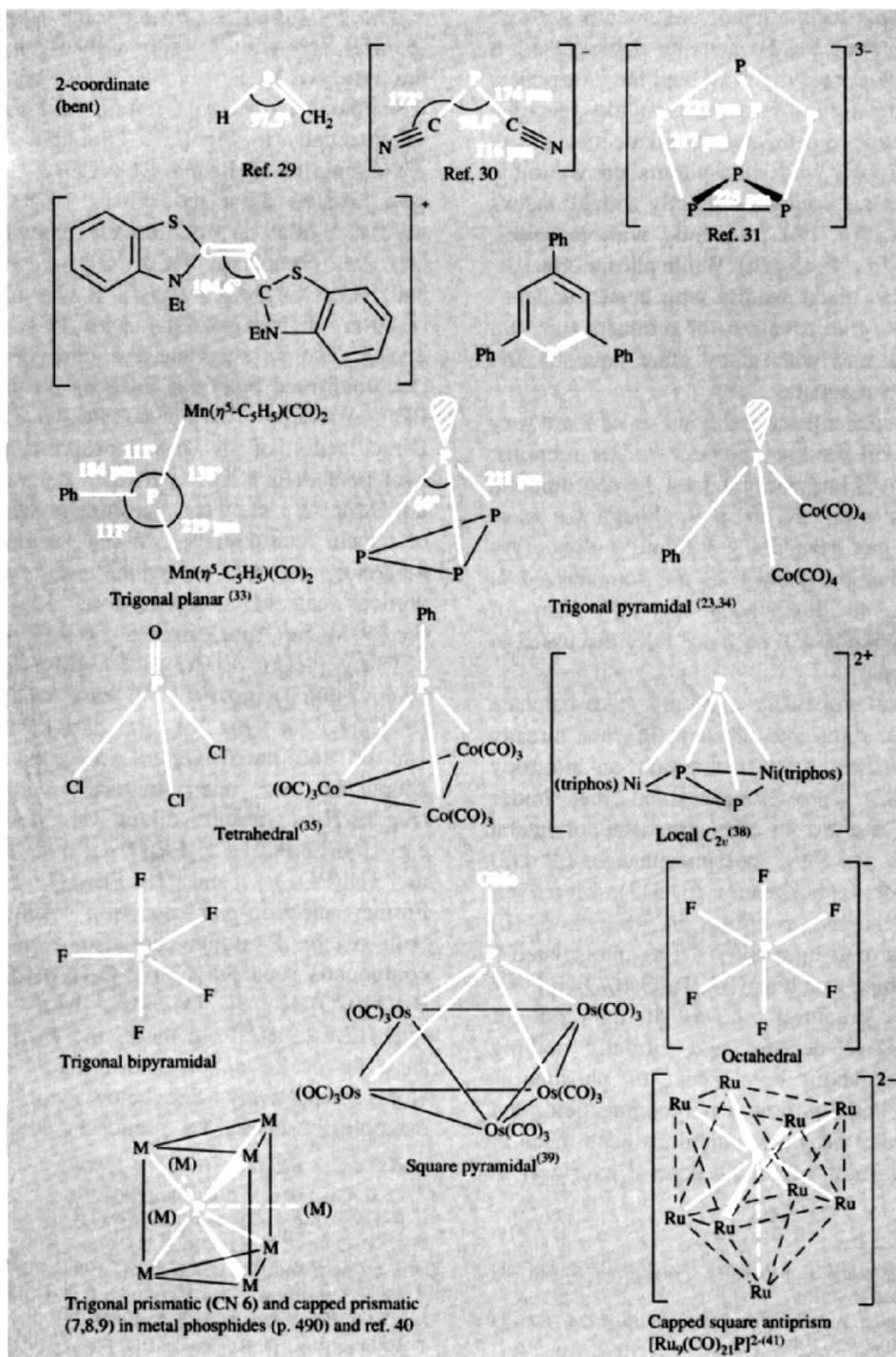
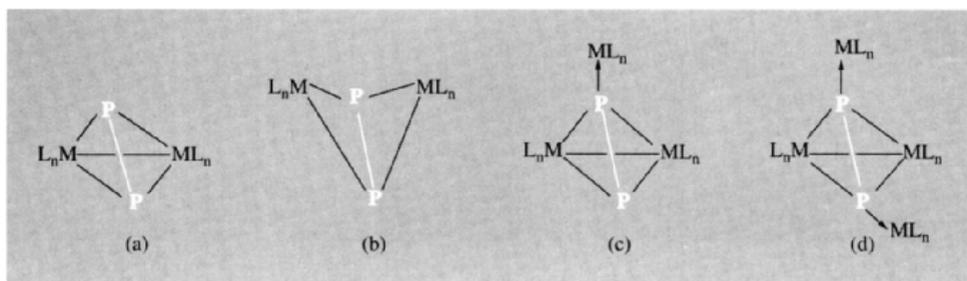
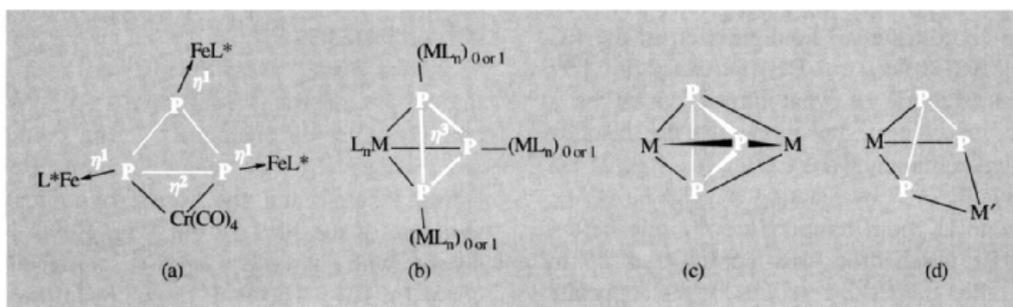


Figure 12.6 Schematic representation of some of the coordination geometries of phosphorus.



**Figure 12.7** (a)  $(\mu, \eta^2\text{-P}_2)$  4e-donor to 15e  $\text{ML}_n$  vertices. (b)  $(\mu, \eta^2\text{-P}_2)$  4e-donor to 14e or 16e  $\text{ML}_n$ . (c) Triply bridging  $(\mu_3, \eta^2\text{-P}_2)$ , a formal 6e-donor. (d) Quadruply bridging  $(\mu_4, \eta^2\text{-P}_2)$  8e-donor.



**Figure 12.8** (a) *Cyclo-P*<sub>3</sub> as an  $\eta^1$  and  $\eta^2$  donor (see text). (b) *Cyclo-P*<sub>3</sub> as an  $\eta^3$  donor; addition of  $\eta^1$  donation to 1, 2 or 3 further metal centres is possible. (c) Bis- $\eta^3$  ligation of *cyclo-P*<sub>3</sub> to coordinated metal centres  $\text{M}(\text{L}_n)$ . (d) More open  $\eta^2, \eta^3$  coordination of  $\text{P}_3$  to different metal centres, e.g.  $\text{M} = \{\text{Ni}(\text{triphos})\}^+$ ,  $\text{M}' = \{\text{Pt}(\text{PPh}_3)_2\}$  (see text).

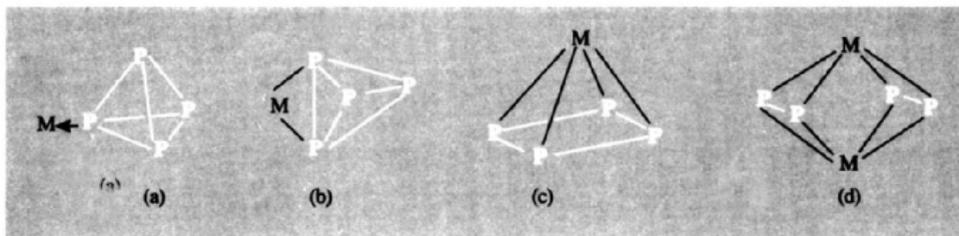
The *cyclo-P*<sub>3</sub> ligand can act in either the  $\eta^1, \eta^2$  or  $\eta^3$  mode as shown schematically in Fig. 12.8(a)–(c).<sup>(42,50)</sup> Each of the three P atoms in 8(b) can also have a further pendant  $\text{ML}_n$  group attached thereby making the *cyclo-P*<sub>3</sub> ligand  $\mu_2, \mu_3$  or  $\mu_4$ . In addition, the more open structure 8(d) is known in the binuclear cation  $\{(\text{triphos})\text{Ni}\{\text{P}_3\text{Pt}(\text{PPh}_3)_2\}\}^+$ , where triphos is 1,1,1-tris(diphenylphosphinomethyl)ethane,  $\{\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3\}$ .<sup>(42)</sup> The  $\eta^1$  and  $\eta^2$  modes in Fig. 12.8(a) have only recently been established (in  $\{(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe}(\text{P})_3\text{-Cr}(\text{CO})_4\}$ )<sup>(50)</sup> but the  $\eta^3$  mode in Fig. 12.8(b) has been known since 1976 when it was found that one of the main products of the reaction between  $\text{P}_4$  and  $[\text{Co}_2(\text{CO})_8]$  was the reactive

pale-yellow solid  $[\text{Co}(\text{CO})_3(\eta^3\text{-P}_3)]$ .<sup>(51)</sup> Numerous other examples featuring Co, Rh and Ir, and the isoelectronic cationic metal centres with Ni, Pd and Pt are now known. Metals in earlier groups require more electron donation from pendant ligands to achieve the 15-electron vertex configuration isolobal with the subrogated P atom in  $\text{P}_4$ , e.g.  $\{\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\}$ . The binuclear  $\eta^3, \eta^3$  mode of *cyclo-P*<sub>3</sub> (Fig. 12.8c) and its  $\text{As}_3$  homologues were extensively studied by L. Sacconi and others in the early 1980s.<sup>(38,42,43)</sup>

As a ligand,  $\text{P}_4$  can adopt various geometries,<sup>(42,43)</sup> including the  $\text{P}_4$  tetrahedron, planar *cyclo-P*<sub>4</sub> (both square and trapezoidal), and a planar zig-zag chain. In principle, the tetrahedral cluster  $\text{P}_4$  could ligate in  $\eta^1, \eta^2$  and  $\eta^3$  modes,

<sup>50</sup> L. WEBER, U. SONNENBERG, H.-G. STAMMLER and B. NEUMANN, *Z. anorg. allg. Chem.* **605**, 87–99 (1991).

<sup>51</sup> A. VIZI-OROSZ *J. Organomet. Chem.* **111**, 61–4 (1976).



**Figure 12.9** Schematic representation of various coordination modes: (a)  $\eta^1$ -P<sub>4</sub>; (b)  $\eta^2$ -P<sub>4</sub>; (c)  $\eta^4$ -cyclo-P<sub>4</sub>; (d)  $(\mu, \eta^2$ -P<sub>2</sub>)<sub>2</sub> (see text).

though only the first two have so far been established (Fig. 12.9 (a), (b)). [Note, however, the face-coordinated  $\eta^3$  configuration in the Bi<sub>4</sub> complex [(CO)<sub>4</sub>Fe( $\mu_4, \eta^3$ -Bi<sub>4</sub>){Fe(CO)<sub>3</sub>}<sub>3</sub>]<sup>2-</sup>.]<sup>(52)</sup> The first example of what turned out to be a complex involving the  $\eta^1$  mode was the unstable red-brown compound [(Fe(CO)<sub>4</sub>)<sub>3</sub>( $\mu_3$ -P<sub>4</sub>)] which was made in 1977 by reacting P<sub>4</sub> with Fe<sub>2</sub>(CO)<sub>9</sub> in benzene at room temperature.<sup>(53)</sup> One vertex of the P<sub>4</sub> tetrahedron was coordinated  $\eta^1$  to one of the {Fe(CO)<sub>4</sub>} groups while opposite edges of the P<sub>4</sub> cluster were bonded  $\eta^2$  to the other two {Fe(CO)<sub>4</sub>} groups. The first  $\eta^1$ -P<sub>4</sub> complex to be characterized by X-ray structural analysis was [( $\eta^3$ -np<sub>3</sub>)Ni( $\eta^1$ -P<sub>4</sub>)],<sup>(54)</sup> formed by direct reaction of white P<sub>4</sub> with the Ni<sup>0</sup> complex [Ni( $\eta^4$ -np<sub>3</sub>)] in thf at 0°C where np<sub>3</sub> is N(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>. Coordination results in a slight elongation of the tetrahedron with P<sub>basal</sub>-P<sub>apical</sub> 220 pm and P<sub>basal</sub>-P<sub>basal</sub> 209 pm (cf. 221 pm in  $\alpha$ -P<sub>4</sub>). The  $\eta^2$ -P<sub>4</sub> mode of coordination is featured in many complexes with Rh, Ir, etc., for example [RhCl( $\eta^2$ -P<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>],<sup>(55)</sup> formed by direct reaction of P<sub>4</sub> with [RhCl(PPh<sub>3</sub>)<sub>3</sub>] in CH<sub>2</sub>Cl<sub>2</sub> at -78°C. The coordinated edge is almost perpendicular to the {RhClL<sub>2</sub>} plane and is lengthened by

about 25 pm to 246.2 pm, whereas the other P-P distances are essentially unchanged from those in uncoordinated P<sub>4</sub>.<sup>(56)</sup>

Square planar *cyclo*-P<sub>4</sub> features as a ligand in [Nb( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>Bu<sub>2</sub><sup>-1,3</sup>)(CO)<sub>2</sub>( $\eta^4$ -P<sub>4</sub>)]<sup>(57)</sup> and the corresponding Ta analogue.<sup>(58)</sup> The compounds are formed by uv photolysis of P<sub>4</sub> with [M(cp\*)(CO)<sub>4</sub>] and the square-pyramidal *nido* structure of the MP<sub>4</sub> cluster (Fig. 12.9c) is consistent with its 14e (2n + 4) cluster-electron count (p. 161). The P-P distances in the coplanar P<sub>4</sub> ligand are in the range 214–218 pm for the Nb complex, with Nb-P<sub>4</sub>(centre) being 142 pm and the basal PPP angles being 92.6° and 88.4°. In the Ta complex, the P-P distances are 215–217 pm. A co-product of the photolysis reaction is the related bis-(P<sub>2</sub>) complex [Ta(C<sub>5</sub>H<sub>3</sub>Bu<sub>2</sub><sup>-1,3</sup>)(CO)( $\mu, \eta^2$ -P<sub>2</sub>)<sub>2</sub>], Fig. 12.9d, in which the P-P distance is 212 pm within each P<sub>2</sub> ligand and 357 pm between the coplanar P<sub>2</sub> ligands. Several similar binuclear bis-(P<sub>2</sub>) complexes are known, including Rh/Rh, and mixed metal species involving Nb/Ta and Ta/Co.<sup>(58)</sup>

A still more open configuration occurs in the zig-zag P<sub>4</sub> chain shown in Fig. 12.10(a).<sup>(59)</sup> This was found in the dianion of the deep

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