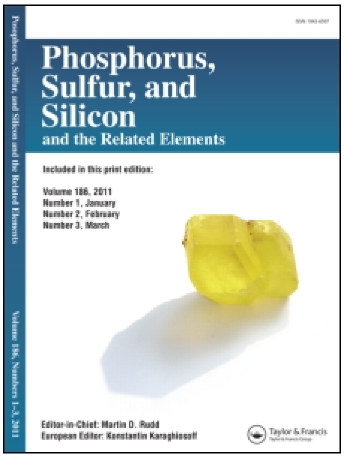

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HOW MANY KINDS OF PHOSPHORUS—PHOSPHORUS BONDS ARE POSSIBLE? REVIEW AND PERSPECTIVES

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HOW MANY KINDS OF PHOSPHORUS—PHOSPHORUS BONDS ARE POSSIBLE? REVIEW AND PERSPECTIVES

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Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday

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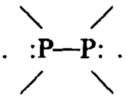
By coupling in pairs in all possible ways the eight hybridization types of a neutral phosphorus atom, 37 modes of formation of a phosphorus—phosphorus bond are obtained.

Some experimental results illustrate these modes and structural possibilities which offer the best hope of future success are predicted.

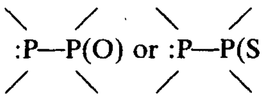
Two other possibilities were also envisaged. The one in which one phosphorus atom is neutral, the other being cationic comprises 39 different P—P$^+$ modes of hybridization. Coupling the eight neutral hybridization types of a phosphorus atom with the 13 possible anionic ones leads to 94 modes of formation of a P—P$^-$ bond.

Key words: P—P bonds, hybridization types, π chemistry perspectives.

In 1965, A. H. Cowley in his review "The Chemistry of the Phosphorus—Phosphorus Bond"[1] mentioned just three types of known P—P bonds (Scheme 1).

The most common of these is found in the diphosphanes **A** (previously called diphosphines). Since a phosphane is a tricoordinated phosphorus(III) derivative with a lone pair of electrons, the diphosphanes are obtained by introducing a single bond between the two phosphorus atoms i.e.  :P—P: .

The first diphosphane $Ph_2\ddot{P}—\ddot{P}Ph_2$ was prepared about a century ago.[2]

In principle, mono-oxidation of diphosphanes **A** by oxygen or sulfur for example leads to a new type of P—P bond (structure **B**), in which one of the phosphorus atoms remains tricoordinate, while the other becomes 4-coordinate pentavalent ($\sigma^4\lambda^5$);  :P—P(O) or :P—P(S). Dioxidation of **A** gives **C**, molecules in which

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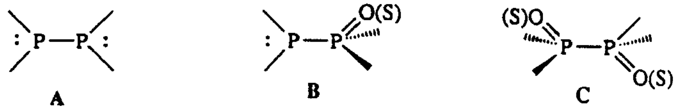
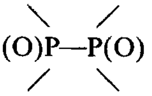
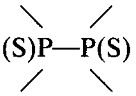
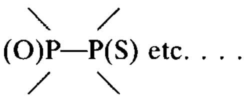
While we have selected at least fifteen publications from Professor Reinhard Schmutzler and coworkers describing novel results concerning the P—P bond of different categories, we suggest that there are a good many other kinds to explore in wishing our friend and colleague from Braunschweig even more success in the future.



SCHEME 1

both phosphorus atoms are $\sigma^4\lambda^5$, i.e.  $\mathrm{(O)P{-}P(O)}$ or  $\mathrm{(S)P{-}P(S)}$ or  $\mathrm{(O)P{-}P(S)}$ etc. . . .

It may be pointed out that in 1965, no bond with multiple character between two phosphorus atoms was known, at least from the chemist's viewpoint, since he or she is only satisfied when the compounds are isolable. The situation remained the same in 1978, the review of Lutsenko and Proskurnina[3] on organophosphorus compounds with a P—P bond reported only increasing amount of data for compounds of types **A**, **B** and **C**.

Since then, the panorama of phosphorus chemistry has changed completely. We wish to demonstrate in this review the extent and originality of recent discoveries, emphasising their completely unexpected character in some instances.

This also enables us to predict a number of possibilities yet to be discovered, from the present knowledge of chemical bonding.

It is necessary to define our approach more precisely. If one poses the question in the title to a chemist unfamiliar with phosphorus chemistry, he or she will simply answer that three types of P—P bonds are possible: single P—P, double P═P or triple P≡P, and this is factually correct.

If account is taken, however, of the hybridization of the phosphorus atoms involved in the bond, much greater variety is clearly possible, which will indeed determine the chemical properties of the molecular structures involved.

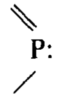
To quote just one example, while compounds of types **A** and **C** both have a single P—P bond, the disphosphanes **A** will possess specific properties, not present in **C**, in particular those resulting from the presence of the lone pair on the phosphorus atoms. This prompts us to consider initially the various possible hybridization modes of phosphorus.

By varying the coordination of the phosphorus atom (from 1 to 5) and considering the maximum number of electrons that this atom may utilise to form bonds (i.e. 5) neutral phosphorus-containing molecules must belong to one of the following nine classes, if radical species are excluded for the moment.

—$\ddot{\mathrm{P}}$: This is the phosphinidene moiety. At present, there is no proof that a molecule of the type R—$\ddot{\mathrm{P}}$: may exist in isolation at least in the chemical sense of "in a bottle."

≡P: The first unstable example of this type was H—C≡P: prepared by Gier in 1961.[4] Twenty years later, Becker and coworkers[5] described the first stable derivative belonging to this family, *t*-butyl-phosphaacetylene or phosphaalkyne Bu^t—C≡P:, which has given rise to an original and rich chemistry.[6]

By chance, the first interstellar molecule containing phosphorus, $:N{\equiv}P:$ belongs to this mode of hybridization.[7]



P: The discovery and development of the chemistry of dicoordinate trivalent ($\sigma^2\lambda^3$) derivatives has represented an unexpected and enthusiastic enterprise for the community of phosphorus chemists, very well described in a recent book.[8]

Perhaps 2,000 compounds of this type are now known, whereas not one existed in 1960. Progress is such that the iminophosphanes $-\ddot{P}{=}\ddot{N}-$, representing just one type of these species, have been described in a review containing 182 references.[9]

It should be stressed here that a rich harvest of new experimental results, obtained in the last ten years or so, has extended considerably the understanding of phosphorus chemistry.

This applies particularly to the possibility of bonding a phosphorus atom not only to main group fragments, but also those derived from transition metal complexes. The latter is possible in very different situations, where the phosphorus atom is the donor of 1, 2 or 3 electrons. We should also emphasise at this point, that a heterolytic, rather than a neutral approach[10] to the bonding is adopted throughout.

The following two compounds, the structures of which are known from X-Ray crystallography, illustrate two different possibilities for this type of hybridization: the phosphorus atom belonging to the type $-\ddot{P}{=}$ may donate

—one electron to a 17 electron (transition metal-ligand) group in
  $Cp(CO)_3M{-}P{=}C(SiMe_3)_2$ (M = W or Mo)[11] or,
—two electrons to a 16 electron (transition metal-ligand) group as in
  $Cp_2Mo{=}P{-}Ar$ (Ar = 2,4,6-$(Bu^t)_3C_6H_2$).[12]

More generally, the isolobal model which establishes a bridge between organic and transition metal chemistry[13] provides a useful tool in phosphorus chemistry to rationalise the extraordinary variety of recent years experimental results.

For organophosphorus chemists, one feels more comfortable about the structures of the complex inorganic fragments by relating them to known simpler organic analogs. The isolobal model teaches us how the first fragment quoted above, $Cp(CO)_3W$— being a d^5ML_6 moiety corresponds to a methyl group CH_3 and derived from a heptacoordinated structure of the metal. It will be represented by $[ML_6]_{17}$. Similarly Cp_2Mo is a d^4ML_6 fragment corresponding to a methylene group CH_2 (carbene) and noted $[ML_6]_{16}$. Abbreviations used here and in the following are: L: neutral two electron ligands; M: transition metal; Cp: cyclopentadienyl $\cong C_5H_5^-$, equivalent to three L noted L_3.

$\equiv P =$ This mode of hybridization contains a dicoordinate pentavalent ($\sigma^2\lambda^5$) phosphorus atom. Examples where the phosphorus is bound to main group elements are rare, the compound $HC{\equiv}P{=}S$ has been mentioned *en passant* by Appel and his coworkers.[14]

In coordination chemistry, the retention of the triple bond formalism is accepted here, when the phosphorus donates three electrons to a 15-electron (transition metal-ligand) moiety denoted as $[ML_n]_{15}$.

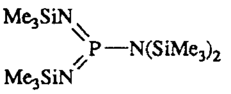
Under this convention, the compound $Cp(CO)_2Mo{\equiv}P{=}C(SiMe_3)_2$ described by Cowley *et al.*[15] belongs to this category. It contains a $[d^5ML_5]_{15}$ fragment, isolobal to the methyne CH group. In such a species, however, the representation of the bond between molybdenum and phosphorus differs considerably, depending on the authors from $Mo{\equiv}P$ to $Mo{\Leftarrow}P$ or even $\overset{-}{Mo}{=}\overset{+}{P}$.

$\diagdown$
—P: In this type of hybridization, the phosphorus utilises three electrons to form
$\diagup$
three covalent bonds ($\sigma^3\lambda^3$). These are the phosphanes (previously called phosphines) of which there are thousands of examples. Their use as ligands is very common in coordination chemistry.[16]

Horner is rightly acknowledged for the synthesis of the first chiral phosphane[17]: Me(Pr)(Ph)P.

Two other possibilities exist in the tricoordinate state:

$\diagdown\!\!\diagdown$
P— Tricoordinate ($\sigma^3\lambda^5$) compounds with only three substituents have been
$\diagup\!\!\diagup$
known since the middle 1970's. The environment of three nitrogen atoms has enabled the isolation and crystal structure determination[18] of the compound described below:



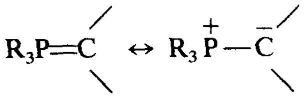
SCHEME 2

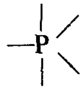
More than a hundred derivatives of this type have since been reported, their synthesis and properties are described in Germa and Navech review[19] and in the Regitz and Scherer book, more than 70 pages are devoted to this type of compound.[20]

$\diagdown$
$P{\equiv}$ Examples of this type are very scarce. In main group compounds, the
$\diagup$
X-Ray structure of $(^iPr_2N)_2P{\equiv}CSiMe_3$[21] is known, but the properties of this compound require canonical forms such as $\overset{+}{P}{=}\overset{-}{C}$ and $:P{-}\ddot{C}{-}$ not to be excluded.

In a recent article, quantum chemists have suggested that $F_2P{\equiv}N$: could be stable.[22]

$\diagdown$
$-P{=}$ Here phosphorus uses its five valence electrons to give the tetraco-ordi-
$\diagup$
nated pentavalent ($\sigma^4\lambda^5$) form. This mode of hybridization is fundamental in the chemistry of phosphorus. Tens of thousands of compounds belonging to this category have been described and it is noteworthy that phosphorus occurs in the living world essentially in the form of phosphoric mono- $(RO)P(O)(OH)_2$ and di-esters $(RO)_2P(O)(OH)$.[23]

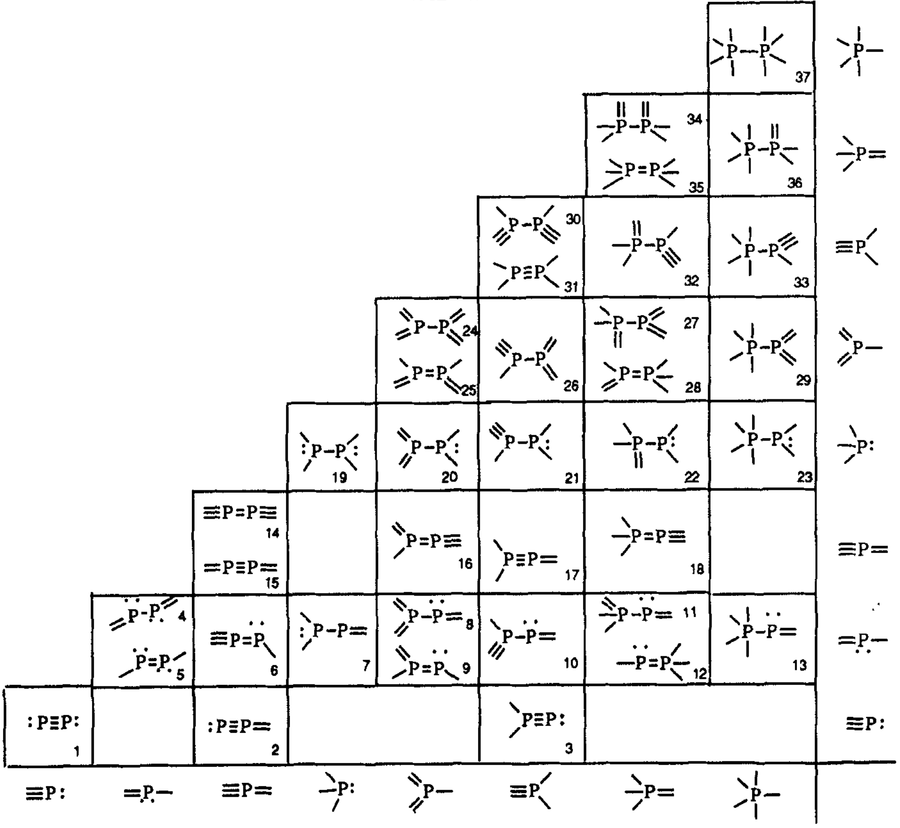
To this mode belong the phosphorus ylides  whose synthetic potential has been widely exploited, here we only quote the pioneering work by G. Wittig and collaborators.[24]

 Historically the first molecule of this family is undoubtedly PCl_5, prepared by Davy in 1810 from burning white phosphorus in "oxymuriatic gas" (chlorine).[25] PCl_5 exists partially in this form in the vapour state. Only in the 1950's has the chemistry of organophosphorus compounds containing one or several pentavalent phosphorus atoms been developed. We estimate from Specialist Periodical Reports that 4–5000 articles have appeared on this subject in the last 20 years.

This tabulation gives in total 9 hybridization types for a neutral phosphorus atom, from which it is reasonable to exclude the phosphinidene mode —P̈:, since a stable representative cannot be foreseen in the near future.

If the remaining 8 structures are coupled in pairs in all possible ways, every conceivable mode of formation of phosphorus—phosphorus bonds, based on a simple picture of chemical bonding (single, double or triple bond) may be derived. The 37 different possibilities are depicted in Table I.

TABLE I



It would be an interesting exercise to examine in detail all these possible types of P—P bonds individually, but that would become too extensive for this article. We therefore limit ourselves to presenting some general comments on Table I, in order to highlight experimental results which seem most suitable to illustrate the method, and to predict which structural possibilities offer the best hope of future success.

In Table I, it is noticeable that some boxes contain two different families of compounds. This is first evident in the case of dicoordinate trivalent phosphorus $-\ddot{P}=$.

In effect, two possibilities for phosphorus—phosphorus bonding may be envisaged here, with either a single or a double bond i.e.:

$$-\ddot{P}= \text{ leads to } \underset{(\text{mode } \mathbf{4})}{=\ddot{P}-\ddot{P}=} \quad \text{or} \quad \text{to } \underset{(\text{mode } \mathbf{5})}{-\ddot{P}=\ddot{P}-}$$

A second observation follows from our systematic approach: each time we write a triple bond between two phosphorus atoms $:P\equiv P:$, a "sister" structure with a lone pair localised on each phosphorus may implicitly be envisaged $:\ddot{P}-\ddot{P}:$ independently of the remaining substituents on phosphorus.

This remark has general application in chemistry; an acetylenic derivative $-C\equiv C-$ for example has a dicarbene structure $-\ddot{C}-\ddot{C}-$ among its canonical forms.

In phosphorus chemistry, the structures with localised lone pairs are frequently the stable forms.

Thus: $=\ddot{P}-\ddot{P}=$ (mode **4**); $=\ddot{P}-\underset{\diagdown}{\overset{\diagup}{P}}:$ (mode **7**); $:\underset{\diagup}{\overset{\diagdown}{P}}-\underset{\diagdown}{\overset{\diagup}{P}}:$ (mode **19**) are the stable forms of the isologs

$=P\equiv P=$ (mode **15**); $=P\equiv\underset{\diagdown}{\overset{\diagup}{P}}$ (mode **17**); $\underset{\diagup}{\overset{\diagdown}{P}}\equiv\underset{\diagdown}{\overset{\diagup}{P}}$ (mode **31**)

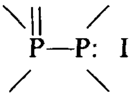
Without trying to be comprehensive, we now present some experimental results which show that the structures depicted in Table I are often effectively known.

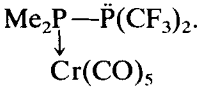
I—Diphosphanes (**19**) *and their mono* (**22**) *and di-oxidised* (**34**) *derivatives.*

In this section the three oldest known types of phosphorus—phosphorus bonds are grouped featured in Reference 1.

(**19**) $:\underset{\diagup}{\overset{\diagdown}{P}}-\underset{\diagdown}{\overset{\diagup}{P}}:$ From the anecdotal point of view, the simplest diphosphane $H_2\ddot{P}-\ddot{P}H_2$ has been proposed as the source of 'will-o'-the-'wisps.[26a] After one century of fruitless investigations, the demonstration of the existence of traces of this diphosphane in gases resulting from the anaerobic fermentation of feces is an original and interesting result.[26b] This result leads to a plausible explanation of 'will-o'-the-'wisps which may be due to methane combustion initiated by traces of spontaneously igniting $H_2\ddot{P}-\ddot{P}H_2$.

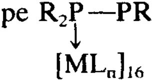
Since the publication of Cowley's review in 1965,[1] hundreds of diphosphanes and polyphosphanes, cyclic or otherwise, have been synthesised. The reviews of Baudler may be cited on the very aesthetic molecular structures that may be constructed in the area of cyclophosphanes[27a] also on the open chain polyphosphorus hydrides.[27b]

(22)  In this category the phosphorus atom can be donor of two electrons toward a 16-electron group in coordination chemistry, such as

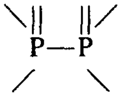


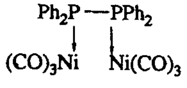
$Me_2\overset{\downarrow}{P}—\ddot{P}(CF_3)_2$, $Cr(CO)_5$.

According to the recent review of Caminade *et al.*[28] about 180 compounds of the type

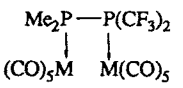


$R_2P—\ddot{P}R'_2 \downarrow [ML_n]_{16}$ are known.

(34)  Within transition metal chemistry, some 250 derivatives belonging to this hybridization mode are known. Just two examples are quoted here, **34a** where the X-Ray structure was published in 1967[29] and **34b** because it is one of the uncommon asymmetric derivatives.[30]



34a



M = Cr or Mo

34b

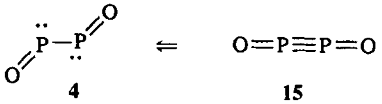
Table I mode **34**

II—Multiple bonds or localised lone pairs?

As indicated earlier, this simple approach to chemical bonding gives rise to molecules which are quite conceivable although their existence is highly improbable from thermodynamic considerations.

This is true for types **15**, **17** and **31** as mentioned above. We would like to return briefly to these cases in particular.

(15) $=P\equiv P=$ One of the privileges of quantum chemistry is to calculate the structural characteristics and properties of hypothetical molecules, and to suggest access routes to the experimentalist or warn him of unsurmountable fundamental difficulties. Thus, calculations have been performed on the dioxide $O=P\equiv P=O$.[31] Quantum chemistry and chemical instinct are in accordance here, in the sense that the stable structure is the trans planar form, **4**, rather than the one with a triple bond between the two phosphorus atoms **15**.



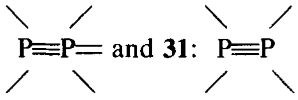
4 **15**

Table I mode **4** and **15** of diphosphorus dioxide

The calculated lengths of the P—P bonds in **4** and **15** are 2.282 and 1.754 Å, respectively.

It is possible that one day, a molecule will be better formulated as **15** rather than **4** in which case the groups bonded to phosphorus will almost certainly be sixteen-electron species from coordination chemistry.

The same remarks can be applied to mode **17**: $\mathrm{P{\equiv}P{=}}$ and **31**: $\mathrm{P{\equiv}P}$



III—In this paragraph are grouped bonding modes **6**, **10**, **14**, **16**, **18**, **21**, **26**, **30**, **32** *and* **33**.

These types of hybridization all possess two particular characteristics. Firstly, no examples have been found in the literature. Secondly, they all have in common a bond in which the phosphorus is formally a three-electron donor.

Nevertheless, known compounds should allow access to these derivatives by a reaction mentioned previously, a point which will be illustrated in mode **6**.

(**6**) $\mathrm{{\equiv}P{=}\ddot{P}{-}}$ A recent review[28] on the coordination chemistry of diphosphanes A and diphosphenes **5** ($\mathrm{R{-}\ddot{P}{=}\ddot{P}{-}R}$), did not indicate any molecule which could belong to this category.

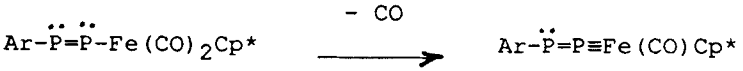
Since compounds of the structure $\mathrm{Ar{-}\ddot{P}{=}\ddot{P}{-}[ML_n]_{17}}$ exist however (for example the crystal structure of $\mathrm{Ar{-}\ddot{P}{=}\ddot{P}{-}Fe(CO)_2Cp^*}$, where Ar = $\mathrm{2,4,6\text{-}Bu^t_3C_6H_2}$ is known[32]), they can in principle be precursors of $\mathrm{Ar{-}\ddot{P}{=}P{\equiv}[ML_n]_{15}}$ belonging to mode **6** (Scheme 3).

IV—In this last section we describe in particular the 13 modes of P—P bonding for which examples have been reported in the literature, or envisaged as quite possible by the quantochemists since 1965, comprising types **1**, **2**, **3**, **4**, **5**, **7**, **9**, **11**, **12**, **13**, **23**, **36** *and* **37**.

(**1**) :P≡P: The diatomic phosphorus molecule is detected in the pyrolysis of white phosphorus P_4 above 800°C.[33] At atmospheric pressure, however, the molecule P_4 is dissociated into two P_2 fragments only at 1700°C. The length of the bond in P_2 is 1.895 Å, in accordance with its triple bond character. We will see that the double P=P and single P—P bonds are generally longer, respectively ≈2.0 Å and ≈2.2 Å (see Table IV).

In our classification, the molecule :P≡P: is clearly unique, in the sense that there is no possibility of substitution.

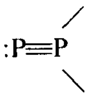
(**2**) :P≡P= Such molecules are easy to envisage if one imagines that the molecule P_2 may be mono-oxidised with O or S, giving :P≡P=O or :P≡P=S. Andrews and Whitnall[34] mentioned the first of these, P_2O from the oxidation of P_4 studied

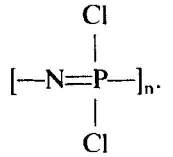


SCHEME 3

in an argon matrix. It should be noted that these authors write this molecule in a different limiting form, preferring $^{-}P{=}P^{+}{=}O$ to $:P{\equiv}P{=}O$.

An alternative approach which may now be envisaged involves the coordination chemistry of $:P{\equiv}P:$. Each time that the latter molecule is associated with a residue $[ML_n]_{16}$ the ensemble $:P{\equiv}P[ML_n]_{16}$ will belong to the hybridization mode under discussion.

(3)  In this family, a conceivable molecule would be $:P{\equiv}PCl_2$ analogous to dichlorophosphonitrile $:N{\equiv}PCl_2$ which does not exist "in a bottle," but can be considered as the potential precursor of a very important series of organophosphorus compound: the polyphosphazenes



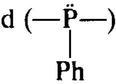
$$\left[—N{=}\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{P}}—\right]_n.$$

In the case of phosphorus, this precursor would lead to the formation of linear or cyclic polymers of the type $[—PCl_2{=}\ddot{P}—]_n$. This is a possibility for the future.

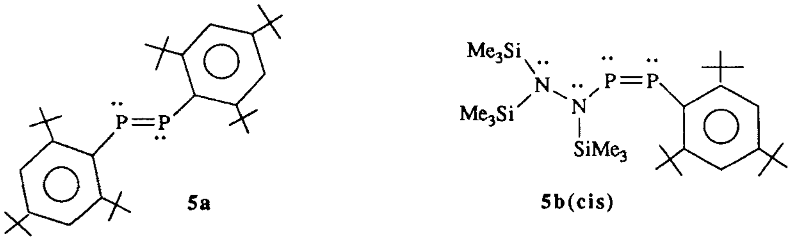
It may however be pointed out that ab initio calculations have been performed for the molecule $:P{\equiv}PH_2$,[35] and $P{\equiv}PF_2$.[36] For the latter a detailed analysis of the nature of the P—P bond in $:P{\equiv}PF_2$ has also been carried out by the same method.[36] The authors visualised the structure as corresponding to a planar configuration with a triple P≡P bond and a formally pentavalent central phosphorus atom. Their results indicate that this hypervalence results primarily from the ionic character of the P—F bonds, and that the triple bond involves essentially the s and p orbitals of phosphorus.

(4) $=\ddot{P}—\ddot{P}=$ If CH_2 groups are used as divalent substituents in this molecular model, 2,3-diphosphabutadiene is obtained. This family has some representatives; a particularly good example was described by Romanenko *et al.*[37] 1,1,4,4-tetradimethylbis amino-2,3-diphosphabuta-1,3-diene: $(Me_2N)_2C{=}\ddot{P}—\ddot{P}{=}C(NMe_2)_2$.

(5) $—\ddot{P}{=}\ddot{P}—$ For anyone familiar with phosphorus chemistry, a double bond between two dicoordinated phosphorus atoms was long considered to be unrealistic. In the literature, theoretical justifications for the non-existence of such molecules have been presented. For these authors, the P—P distance being long, the gain in energy from formation of a π bond seemed too small to allow the isolation of a stable product.

At the turn of the century "phosphabenzene" C_6H_5P was formulated as a dimer "$Ph—\ddot{P}{=}\ddot{P}—Ph$."[38] Cryoscopic measurements have shown the cyclic character of the compound  $(—\underset{\underset{\displaystyle Ph}{|}}{\ddot{P}}—)_n$, with 4 phosphorus atoms[39a] and rings with 5 and 6 phosphorus were described later and the crystal structure of the hexamer (n = 6) determined by X-ray diffraction.[39b]

It was thus a great event for phosphorus chemists when Yoshifuji and co-workers presented at the Durham meeting in 1981, the X-Ray structure of the first diphosphene Ar—$\ddot{P}=\ddot{P}$—Ar (Ar = 2,4,6-$(Bu^t)_3C_6H_2$) **5a**.[40]



5a **5b(cis)**

Table I mode 5

Since then, not only have more than a hundred derivatives belonging to this family been described, but in the case of compound **5b** the cis and trans isomers have been isolated, and their X-ray structures determined.[41]

(7) $>\!:P-\ddot{P}=$ This mode of formation of a single P—P bond results from the association of a phosphane $-\overset{\diagdown}{\underset{\diagup}{P}}:$ with a dicoordinate derivative $-\ddot{P}=$. The X-ray structure of compound **7a** illustrates unambiguously the existence of this mode of P—P bonding.[42] It is noteworthy that the four atoms of the $\ddot{N}-\ddot{N}-\ddot{P}-\ddot{P}$ skeleton each retain a lone pair of electrons, so that the reactivity of such molecules should be very interesting.

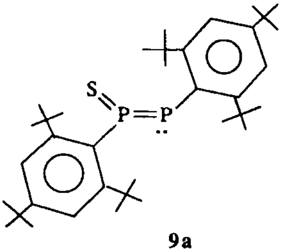
7a **7b**

Table I mode 7

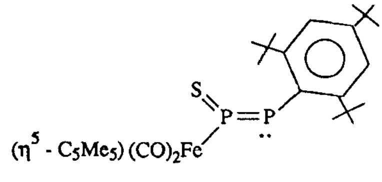
A further example $(^iPr_2N)_2\ddot{P}_A-\ddot{P}_B=\ddot{P}_CN^iPr_2$ **7b**, the structure of which is known,[43] shows the unusual feature that the coupling constant ${}^2J_{P(A)P(C)}$ 541 Hz is larger than the vicinal coupling constant ${}^1J_{P(B)P(C)}$: 534 Hz and ${}^1J_{P(A)P(B)} = 197$ Hz.

(**9**) $-\overset{\|}{P}=\ddot{P}-$ This mode is derived from diphosphene $-\ddot{P}=\ddot{P}-$; the oxidation of just one phosphorus atom leads to this type of hybridization. The divalent fragment to be introduced in this oxidation may be very variable, including not only $=C<$, $=N-$, $=O$, $=S$, $=Se$, but also a residue $[ML_n]_{16}$ from coordination chemistry.

In 1983, Yoshifuji *et al.* prepared the corresponding monosulfide from their diphosphene by reaction with active sulfur (S_8 in triethylamine), compound **9a**[44] and its X-ray structure has been determined. It presents a striking characteristic: the two ipso carbon atoms, the two phosphorus atoms and the sulfur are coplanar. Moreover there is no notable difference in the length of the P=P double bond between the diphosphene (2.034 Å) and its monosulfide (2.054 Å).



9a



9b

Table I mode **9**

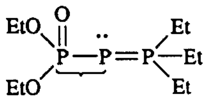
Another interesting result in this category comes from Weber *et al.*[45] Starting from a particular diphosphene in which a simple bond is formed with a residue $[ML_n]_{17}$, and thus a metalla-phosphene, they showed that sulfurization took place at the phosphorus bound to the metal. The X-ray structure of this compound **9b** has been published.[45a] From the same author we quote a thorough and detailed monograph dealing with $-\ddot{P}{=}\ddot{P}-$, $-\underset{\|}{P}{=}\ddot{P}-$ and $-\underset{\|}{P}{=}\underset{\|}{P}-$ i.e. modes **5**, **9**, and **25** in Table I.

(11) $\overset{\diagdown\!\!\diagdown}{\underset{/}{-P}}-\ddot{P}=$ This type of hybridization corresponds to a dicoordinate phosphorus atom $=\ddot{P}-$ to which a phosphoric residue $\overset{/}{\underset{\diagdown}{=P-}}$ is singly bonded. Examples of this genre exist in the literature. We have selected one (Scheme 4), described by Weber and Fluck[46] which is unusual in that, possessing three joined phosphorus atoms it displays two modes of P—P bonding. The part of the molecule bracketed corresponds to hybridization mode **11**, while the P=P double bond corresponds to mode **12**, described in the following section.

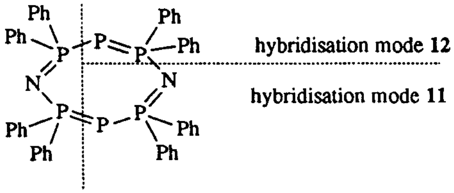
(12) $-\ddot{P}{=}\overset{/}{\underset{\diagdown}{P}}-$ One example of this type is illustrated above

Oxidative addition of a molecular species **A**–**B** at one of the two phosphorus atoms in a diphosphene leads formally to this mode of hybridization $-P{=}\overset{\overset{A}{/}}{\underset{\underset{B}{\diagdown}}{P}}-$.

The compounds have been called phosphoranylidene phosphanes. The cyclic molecule below (Scheme 5) described by Schmidpeter and Burget[47] possesses two types of fragments, again one corresponding to mode **12** and the other to mode **11**.



SCHEME 4



SCHEME 5

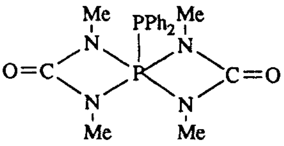
Examples of this type are rare and their formulae suggest several synthetic routes. The structure may arise as the result of coupling through the agency of lone pairs between a phosphinidene R—P̈: and a phosphane $\genfrac{}{}{0pt}{}{\diagdown}{\diagup}\!-P:$. In this sense it may possibly be obtained by reacting a phosphane with a cyclopolyphosphane $(-\overset{R}{\overset{|}{P}}-)_n$ which could be regarded as an incipient polyphosphinidene $:\underset{\cdot\cdot}{P}-R$.

Curiously this route was explored in 1961 by Burg and Mahler[48] who reacted $(-\overset{CF_3\diagdown}{\underset{\cdot\cdot}{P}}-)_n$ with $Me_3P:$, which led to the characterization of $CF_3-\ddot{P}=PMe_3$. Historically this compound contained a dicoordinate phosphorus atom, the first of its type, but at that time it raised more doubts than enthusiasm for its novelty.

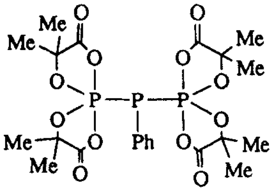
A more recent approach to the synthesis of a compound containing this type of hybridization is the intramolecular rearrangement by 1,3-migration of a trimethylsilyl group. Thus $(Me_3Si)(Ar)P-P(O)R_2$ rearranges to $Ar\ddot{P}=P(OSiMe_3)R_2$ (Ar = 2,4,6-$Me_3C_6H_2$; R = ^{t}Bu).[49]

(13) $\genfrac{}{}{0pt}{}{\diagdown|}{\diagup|}\!P-\ddot{P}=$ The reaction of phosphoranes synthesised in one of our laboratories[50] in the presence of triethylamine with dicoordinate phosphorus compounds containing a P—Cl bond such as $ArN=\ddot{P}-Cl$[51] (Ar = 2,4,6-$^tBu_3C_6H_2$) or $Cl-\ddot{P}=C(SiMe_3)_2$ leads to compounds of this type. Their low stability however, means that only solution data have been obtained so far.

(23) $\genfrac{}{}{0pt}{}{\diagdown|}{\diagup|}\!P-P\genfrac{}{}{0pt}{}{\diagup}{\diagdown}\!:$ In this type of molecule, a single bond joins a pentavalent phosphorus atom to a phosphane. Two examples have been selected, firstly **23a** since its X-ray structure is known.[52] The length of the P—P single bond (2.214 Å) is very similar to that observed in the majority of symmetrical or unsymmetrical diphosphorus compounds. The second **23b** prepared in one of our laboratories shows this type of bonding twice.[53]



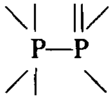
23a



23b

Table I box **23**

(36)



The synthesis and characterization of the first compound with this type of hybridization was described by R. Schmutzler *et al.*[54] in 1981. The authors, starting from a diphosphane, of hybridization mode **19** oxidised one phosphorus atom by tetrachloroorthobenzoquinone to give a λ^5P—λ^3P bonded compound of mode **23**. Oxidation of the second phosphorus atom by sulfur enabled them to obtain a compound belonging to mode **36**.

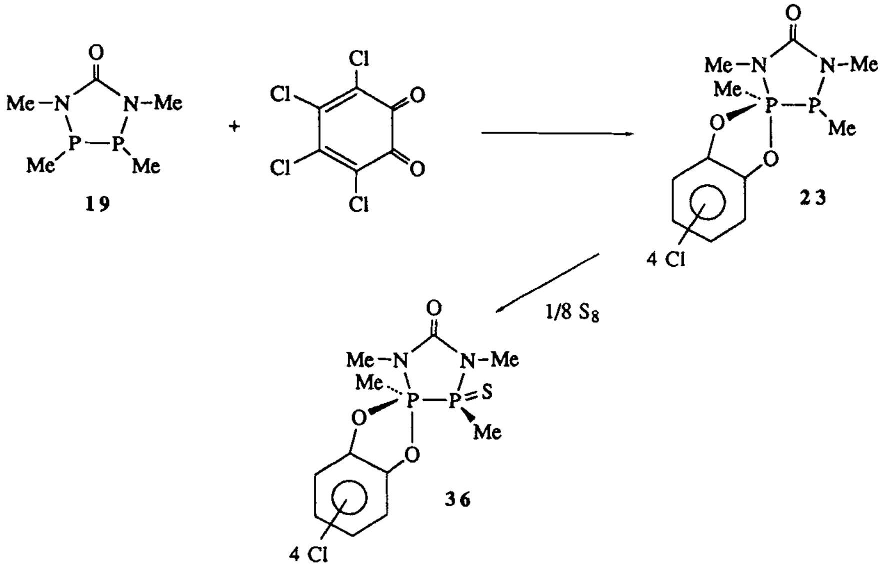
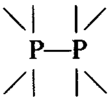


Table I modes **19**, **23**, **36**

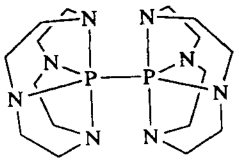
The X-Ray structure of this compound shows that the geometry around the penta-coordinate phosphorus atom is very strongly distorted, almost halfway between a trigonal bipyramid and a square pyramid. The P—P distance of 2.219 Å is slightly longer than in other compounds belonging to mode **23**: 2.195 Å[55] and to mode **22**: 2.193 Å.[56]

(37) 
$\mathrm{P{-}P}$

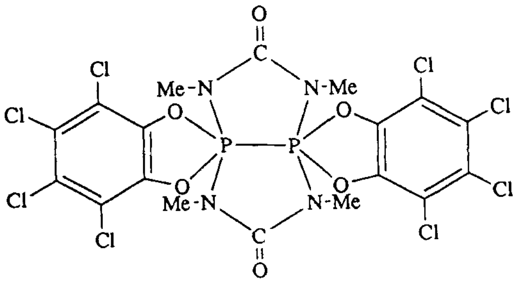
The $\lambda^5P\lambda^5P$ bond is reputed to be very labile. It may be stabilised however by including the two phosphorus atoms in a polycyclic structure. The first compound showing this mode of hybridization was thus obtained by Richman *et al.* (compound **37a**) with the two phosphorus atoms in a cyclam structure.[57] The length of the equatorial P—P bond in this compound is 2.264 Å.

The X-Ray structure of a compound of this type: **37b** has been reported by Roesky *et al.*[58] In this instance, the P—P bond is in an axial position and its length of 2.256 Å is similar to that in **37a**.

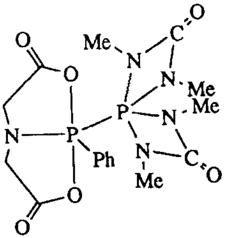
We have synthesised compound **37c** with a P—P bond of this type.[53] It is different from the others in the sense that it is asymmetric, and shows a P—P coupling constant of 750 Hz which is one of the largest values reported for a single P—P bond.



37a



37b



37c

Table I box **37**

It is thus apparent that about 40 modes of hybridization could be utilised to bond two phosphorus atoms. Indeed this approach does not exhaust all the conceivable possibilities and two directions of research come immediately to mind: to combine two phosphorus atoms, one of which is neutral, the second being either cationic (Table II) or anionic (Table III).

I) Table II. Species with a neutral phosphorus-cationic phosphorus bond

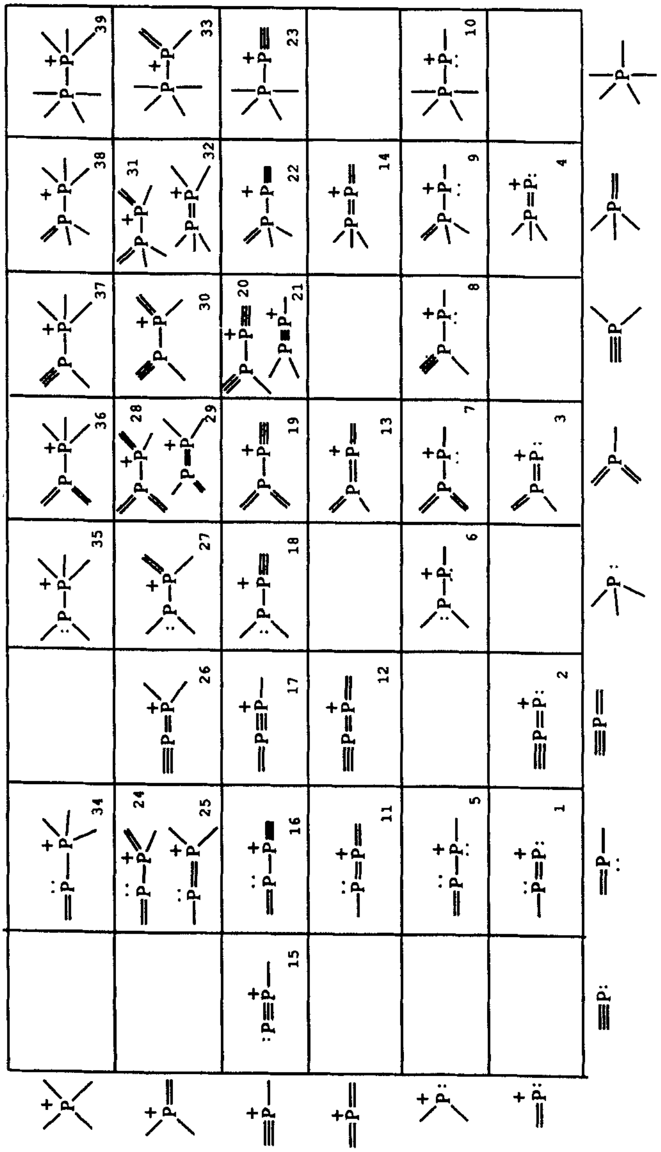
If a neutral molecule with two directly bound phosphorus atoms is considered, there are conceptually two ways of making one of them cationic:

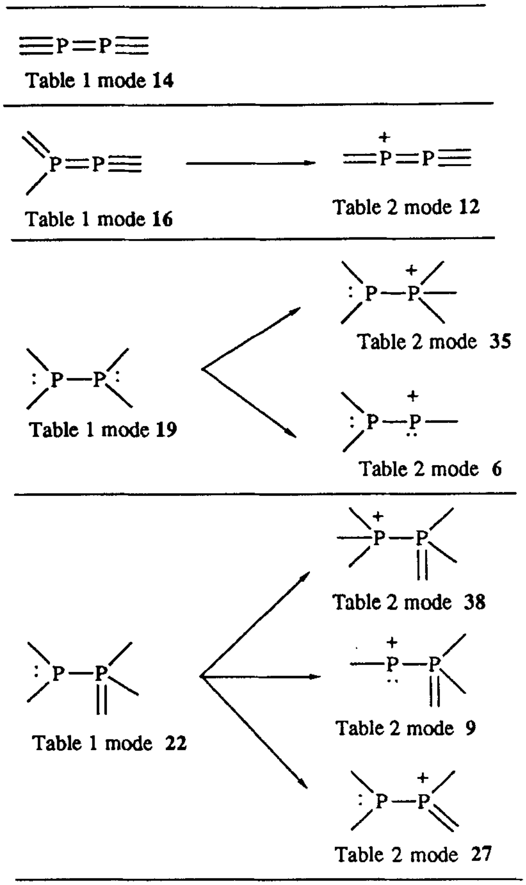
—promote heterolytic cleavage of one bond and remove the substituent in an anionic form (hydride, carbanion, halide etc. . . .)

—create an additional bond by utilizing a lone pair when it exists, i.e. protonation by H^+, alkylation by a carbocation etc. . . .

TABLE II

Species with a neutral phosphorus-cationic phosphorus bond





SCHEME 6

Scheme 6, thus shows that compounds of type **14** cannot lead to any cationic species, whereas **16** leads to only one type of cation, diphosphanes **19** to two types and compounds of type **22** to three different types.

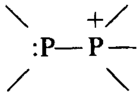
A systematic enumeration leads to 57 monocations but 18 of these are redundant, leaving 39 effective possibilities. The same result may be attained by an alternative route.

It is known that six cationic phosphorus types with a filled shell are conceivable, i.e.: $=P:^+$; $—\underset{..}{P}^+—$; $=P^+=$; $\equiv P^+—$; $\overset{/}{\underset{\backslash}{=P^+}}$ and $\overset{\backslash\ /}{\underset{/\ \backslash}{P^+}}$.

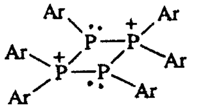
When crossed with the 8 neutral modes of hybridization, the latter lead also to 39 monocationic P—P bonded species.

Two examples are given here:

15(+) $:P\equiv\overset{+}{P}—$ The cation $^iPr_2N—P^+\equiv P:$ has been cited by Niecke and coworkers,[59] but only as the main peak in mass spectra of the diphosphirene $^iPr_2N—P—P{=}C—N^iPr(SiMe_3)$



35(+) $:P—P^{+}$— Phosphane—phosphonium: the X-ray structure of a tetra-phosphacyclobutane **35** containing alternate $P[2,6\text{-}(MeO)_2C_6H_3]$ and $P^{+}[2,6\text{-}(MeO)_2C_6H_3]_2$ has been described by Schmutzler *et al.*[60]



35a(+)

Ar = $2,6\text{-}(MeO)_2C_6H_3$

Table II mode **35**

Another example is the dication $[(C_6H_5)_3P^{+}—\ddot{P}H—P^{+}(C_6H_5)_3]\ [AlCl_4^{-}]_2$.[61]

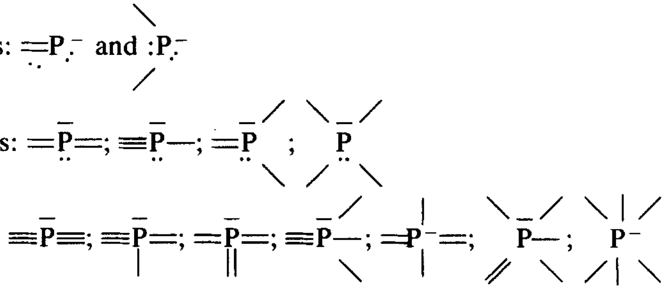
II) Table III: Species with a neutral-anionic P—P bond

How can the six electrons carried by an anionic phosphorus atom be arranged within the formal system of single, double and triple bonds? If anions with a filled shell only are considered, some ten possibilities are open to us.

The best-known anionic species are the phosphides R_2P^{-} and the hexahalogenophosphates $[PCl_6]^{-}$ and $[PF_6]^{-}$. The solid state structure of the $[PCl_6]^{-}$ ion has been determined by X-ray crystallography in $[PCl_4]^{+}$ $[PCl_6]^{-}$ [62] which is the structure of PCl_5 in solid state.

The metaphosphate ion $[PO_3]^{-}$ has given rise to numerous studies because it is thought to be an intermediate in the hydrolysis of phosphoric esters[23] while the X-ray structure of $[PS_3]^{-}$ is known.[63]

For the anions, if the number of electrons involved in their formulation is considered, we obtain:



—with two electrons: and ;

—with four electrons: ; ; ;

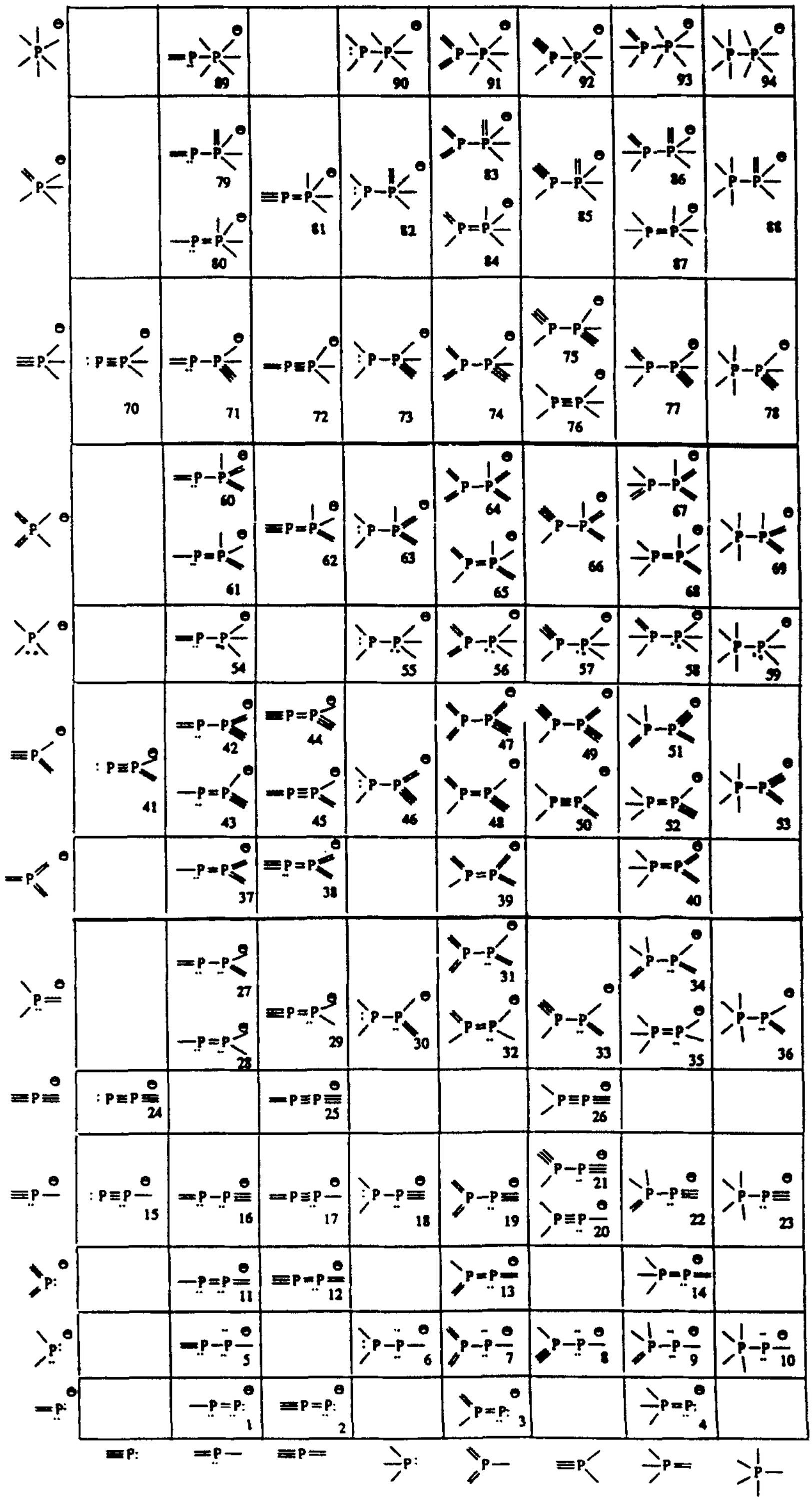
—with six electrons: ; ; ; ; ; ;

The ensemble clearly constitutes a suite of limiting structures, with other canonical forms possible in many cases. If these possibilities are crossed with the 8 neutral species, Table III can be derived, which comprises 94 possibilities.

Without trying to elaborate what is already known, what might become possible, or what remains forever unrealistic, it is interesting and intriguing to note that some recent and unexpected results pertain to families of compounds appearing in Table III.

TABLE III

Species with a neutral-anionic P—P bond. To increase the legibility, all the negative charges are detached and formally placed at the phosphorus atom right



Thus the anion ${}^{t}Bu_2\ddot{P}$—$\overset{-}{\underset{\cdot\cdot}{P}}$—$\ddot{P}{}^{t}Bu_2$ which contains the phosphane—phosphide bond twice (Table III hybridization mode **6**) is the precursor of the first phosphane—phosphinidene: ${}^{t}Bu_2\ddot{P}$—$\dot{\underset{\cdot}{P}}$. well characterised from its chemical properties.[64]

To quote just two other examples, a remarkable development concerns the chemistry of diphospha-anions of the type **34** (Table III) the "Phospha-Wittig" reaction[65a]:

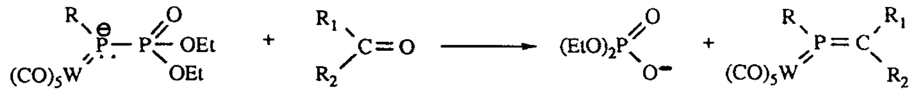


Table III mode **34**

Phospha-Wittig reaction

and the X-Ray structure[65b] of:

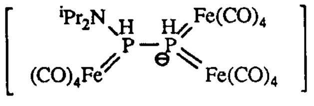


Table III mode **67**

Some other possibilities merit consideration

Our systematic approach leads to more than 150 different models, and moreover this does not cover all the known possibilities for the formation of a bond between two phosphorus atoms.

We have only considered entities with filled shells: 8 types of neutral, 6 cationic and 13 anionic types of hybridization.

Seventeen structures with radical character[66] have been disregarded. These could possibly be crossed with the 28 structures with filled shells, although this omission has been made deliberately.

In effect, there is experimental evidence for many organophosphorus radicals that the free electron is delocalised in such a way that it may not reasonably be taken as located on the phosphorus atom.

Some exceptions may be discovered in the future, but at present it is reasonable not to consider this possibility.[67]

In addition, several experimental results compel us to make a more serious criticism of the present approach. Without stating it explicitly, Tables I, II and III allow the construction of molecules or ions exclusively by formation of σ and π bonds. Thus molecular species which result from adduct formation between an electron-pair donor and an electron-pair acceptor have not been included. An interaction of this type results in a longer and weaker bond than a normal σ bond, because of the change in polarity of the atoms.

To take a specific example, trimethylphosphane Me_3P: can be a donor of two electrons, while a phosphorane is a Lewis acid capable of accepting a lone pair. The two molecules can effectively react together (Scheme 7) to give a phospho-

TABLE IV

Some selected P—P bond distances

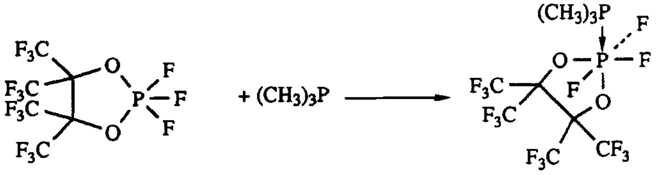
Compound		Distance (Å)	Bond character	Reference
Ph_2P-PPh_2 ↓ ↓ $(CO)_3Ni$ $Ni(CO)_3$		2.277(4)	**single**	29
37a		2.264(2)		57
37b		2.256(3)		58
35a(+)		2.231 2.232		60
Compound scheme 8		2.189 (av. in independent molecules)		69
ArP(S)=PAr	**9a**	2.054(2)	**double**	44
$Cp^*(CO)_2FeP(S)PAr$	**9b**	2.041(1)		45
ArP=PAr	**5a**	2.034(2)		40
$(Me_3Si)_2N-N(SiMe_3)P=PAr$	**5b**	2.027(3) cis 2.037(3) trans		41
:P ≡ P:		1.895	**triple**	33

rus→phosphorus bond. The first phosphorus atom is tetra-coordinate, with a dative bond, the second hexa-coordinated.

The X-ray structure of the compound is known, the length of the P—P bond being 2.234 Å.[68]

This kind of "globally neutral" molecule has not been considered in our tables.

Among the more esoteric possibilities that may be envisaged on the basis of nitrogen chemistry, structures containing two neighbouring cationic phosphorus atoms must not be excluded.



SCHEME 7

This occurs, for example, in the bond between two tetra-coordinate phosphorus atoms bridged by two molecules of urea[69] (Scheme 8), which does not feature in our treatment.

The X-ray structure of this compound exhibits a P—P distance (2.189 Å) not differing greatly from that observed in neutral diphosphorus species. In contrast, the increase of charge on the two phosphorus atoms induces a notable shortening of the endocyclic P—N to 1.637 Å, whereas in similar uncharged systems it is about 1.710 Å.

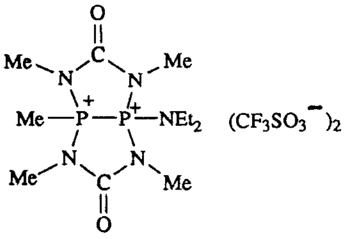
Another particular example in the literature[70] is shown in Scheme 9, although the structure as written must be considered as a limiting form.

A compound with an unexpected P—P bond has been described by Peacock and Geanangel,[71] and may be formulated as follows (Scheme 10), two sodium cations balancing the charge.

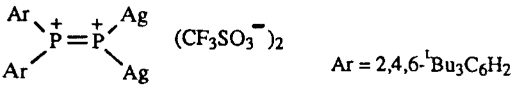
A further possibility not yet considered is an approach to one molecule or cation by two molecules of a donor. Thus the energetics of the species $[H_3P\rightarrow\underset{\cdot\cdot}{P}\leftarrow PH_3]^+$ has been calculated by W. W. Schoeller.[72] He concludes that the monocation $[Ph_3P—P—P(Ph)_3]^+$ quoted in Reference 61 is best formulated with a considerable negative charge (phosphide) on the central atom $\overset{\delta^+}{Ph_3P}—\overset{\delta^-}{P}—\overset{\delta^+}{PPh_3}$.

It should be emphasised, however that this is not a general difficulty and the phosphane—phosphenium adduct, for example, is included in our classification.

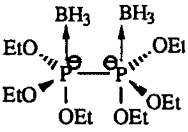
Many original discoveries may be expected for organophosphorus compounds containing the cyclopentadienyl group in their structure. In the case of a phosphorus atom, the ambivalence which must exist between a Cp group σ bonded to phosphorus compared with the corresponding delocalised system is now well known.



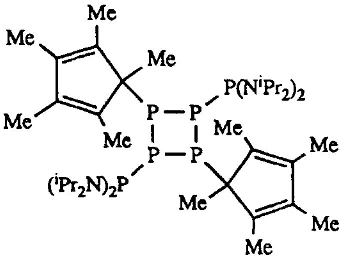
SCHEME 8



SCHEME 9



SCHEME 10



SCHEME 11

An example where the X-ray structure has been determined is shown in Scheme 11.[73]

It is highly probable that this field of research will be further extended via the recently discovered phospha-cyclopentadienyls.[74] In this connection, the recent singular results for Cp*—P=N—Si^iPr_3 may be mentioned, where the X-ray structure shows that this molecule may be considered as an adduct between Cp^{*-} and $[P{=}NSi^iPr_3]^+$.

In the near future when a Cp derivative is replaced in these derivatives by one of the numerous known phosphacyclopentadienyls[75] a new type of P—P bond, unknown at present, will be produced. If delocalization occurs in these systems as is often the case in cyclopentadienyl groups, a very new type of long P—P bond would result. Several different phospha-cyclopentadienyls are now known.[76,77]

CONCLUSIONS

By starting with an unsophisticated approach to the chemical bond, it has been possible to classify many of the experimental results obtained in the chemistry of phosphorus during the past 30 years. Within this period some 100,000 papers have centered on the chemistry of this element.

The most interesting conclusion is that despite this weight of material, there remains considerable scope for conjecture about future developments.

This is what we have tried to show in considering a somewhat restricted topic: how many different kinds of phosphorus—phosphorus bonds are possible? It is impossible to predict in the chemical panorama outlined above whether or not a new high-performance material may exist, or even whether an unknown chemical concept may arise.

REGRETS

Phosphorus Chemists tend to organize major meetings every two or three years, commencing with Heidelberg (1964) until the most recent in Toulouse in July 1992. The next meeting is scheduled to take place in Jerusalem in 1995.

Initially there were 150 participants, now there are close to 600. We regret that in this review, we have not been able to include the remarkable scientific contributions of many more of our colleagues.

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feignons d'organiser ce qui nous
dépasse.

We pretend to organize
something that is above us