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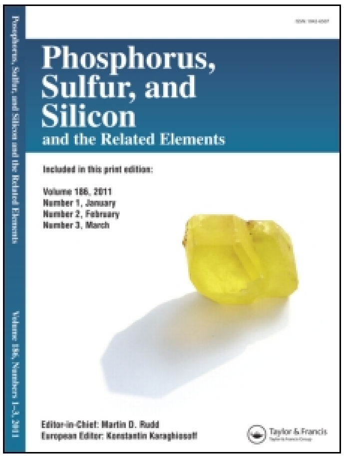

Phosphorus, Sulfur, and Silicon and the Related Elements

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Horizons in Phosphorus Chemistry

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PLENARY LECTURE

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HORIZONS IN PHOSPHORUS CHEMISTRY

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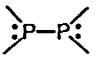
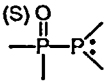
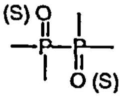
Abstract Where has phosphorus chemistry been and where is it going? To answer this question, we must explore current areas of activity, the concentration of research in these areas, and what appears to be trends and emerging areas that might suggest what the future may hold. For this purpose, we shall examine several sources of current research information. These comprise current literature, reviews and overviews, recent symposia and correlative articles. This should place us in a position to learn in which directions phosphorus chemistry may be headed in the 21st century. We must keep in mind that some of the best discoveries leading to new areas of importance result from so called "accidental" discoveries. However, a perceptive mind stimulated by research at the forefront of knowledge is best tuned to seize these opportunities. It is hoped that this discussion will provide insight into our own research and perhaps suggest new and untried approaches. One approach is to examine related chemistries to learn their similarities and differences. This often leads to new ways of looking at a research area which makes one think more broadly in the design of experiments that could lead to new horizons.

The first phosphorus meeting in this series took place in Heidelberg, Germany in 1964. An article in *Chem. Revs.* by Alan Cowley [1a] appeared in 1965 and described three known types of compounds containing phosphorus–phosphorus bonds, Chart 1. In 1978, a review by Lutsenko and Proskurnina [1b] reported only increasing numbers of examples of these same three kinds of compounds.

In the last 15 years, the situation has changed completely. Phosphorus chemistry has greatly expanded in the scope of chemical types that are now known and in the exploration of the subsequent chemistry. Since 1965, it is estimated that about 100,000 papers on phosphorus chemistry have appeared in the literature.

What I wish to present today is some of the phosphorus chemistry that has resulted during this time with a view to what might come about in the future. The material to be presented is not by any means comprehensive. Also it would be presumptuous of me to assign importance to one area over another. Thus, what is presented may be thought of as an excursion through the vast field of phosphorus chemistry with an object of awakening constructive thoughts that might prove valuable in furthering our own research areas. For this purpose, part of the presentation will be based on a description of possible phosphorus–phosphorus bonds, known and unknown, as summarized in an article by Lydia Lamandé,

CHART 1 Known P–P bonds in 1965.

			
Mode	**19**	**22**	**34**

Cowley, *Chem. Revs.* [1a].

By 1978, only the same three types were known.

Lutsenko & Proskurnina, *Usp. Khim.* [1b]

Present Number	hundreds	~ 180	~ 250

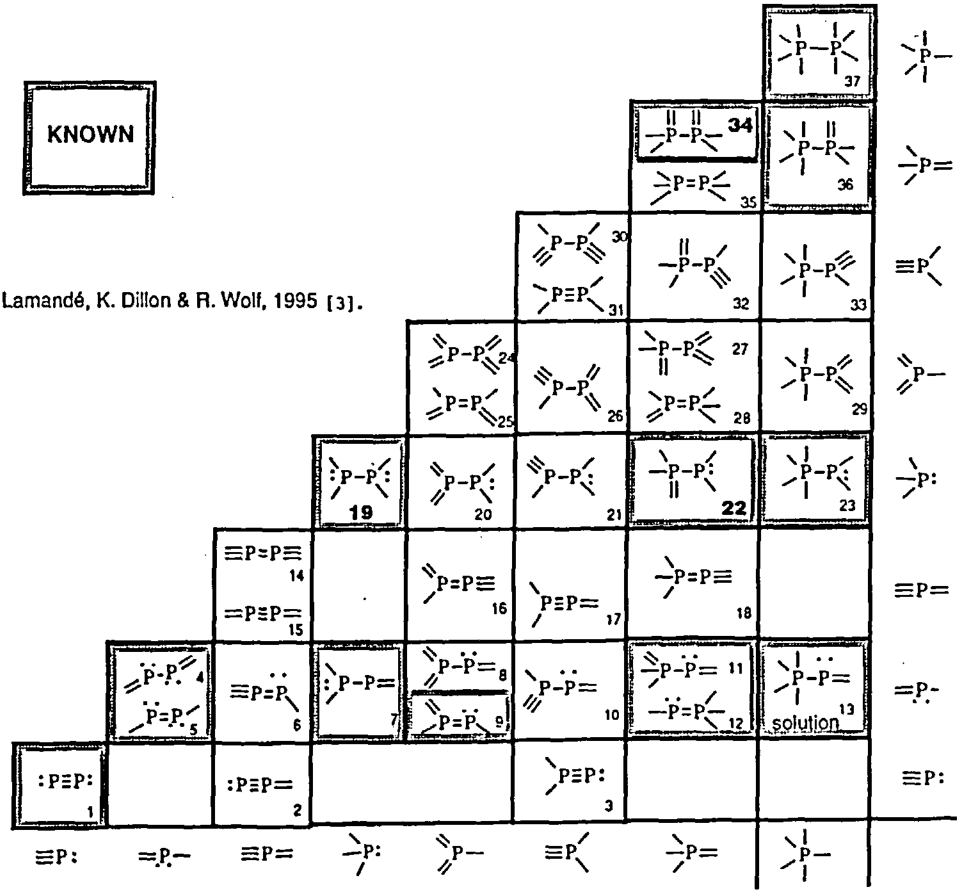
Keith Dillon, and Robert Wolf [3]. As far as ascertaining future directions in phosphorus chemistry, each one of us is in a slightly different position based on our own special expertise and area of concentration. Consequently, insight into the future will depend on this varying perspective and, in addition, on unforeseen events that frequently are encountered in the course of research.

If we assume the eight possible hybridization types shown in Table 1 for a neutral phosphorus atom, we are able to couple them in pairs to obtain 37 modes of formation of phosphorus–phosphorus bonds, Table 2 [3]. The boxes that are shaded indicate compositions that are known in the condensed phase, either in solid or solution form, other than diatomic phosphorus which is detected in the gas phase from the pyrolysis of white phosphorus above 800°C [4].

TABLE 1 Eight hybridization types of neutral phosphorus atoms utilizing coordination numbers 1 to 5.

$\equiv P:$	rare	$=\overset{\mid}{P}=$	~ 100
$=\overset{\mid}{P}:$	~ 2000 (*e.g.*, $-\ddot{P}=\ddot{N}-$)	$-\overset{\mid}{P}\equiv$	very rare
$\equiv P=$	rare	$-\overset{\mid}{\underset{\mid}{P}}=$	tens of thousands (ylides & phosphates)
$-\overset{\cdot\cdot}{\underset{\mid}{P}}-$	thousands	$>\overset{\mid}{\underset{\mid}{P}}-$	~ 6000

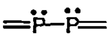
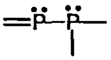
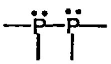
TABLE 2 Neutral phosphorus–phosphorus bonds.



L. Lamandé, K. Dillon & R. Wolf, 1995 [3].

One reason for the absence of certain modes of P–P bonding is that structures with localized electron pairs are frequently the more stable forms. Thus Modes **4**, **7**, and **19** in Table 2 having phosphorus-phosphorus single bonds represent stable forms in contrast to the respective Modes, **15**, **17**, and **31**, which are unknown isologs and have phosphorus–phosphorus triple bonds. These modes are compared in Table 3 [3].

TABLE 3 Structures with localized lone pairs are frequently the stable forms.

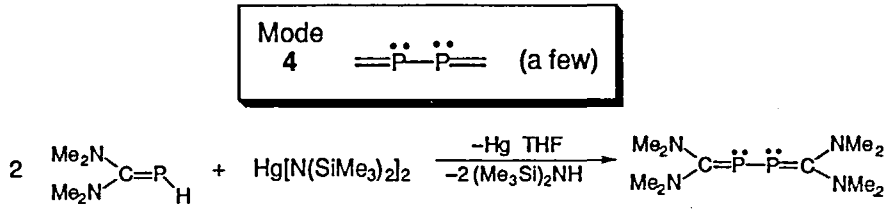
Stable form	Mode	Unknown Isolog	Mode
	(4)		(15)
	(7)		(17)
	(19)		(31)

Let us examine the method of synthesis used to obtain the first examples of some of stable modes of phosphorus-phosphorus bonds. With reference to Table 2, Schemes 1–7 illustrate the syntheses of compounds corresponding to Modes **4**, **5** and **9**, **7**, **11** and **12**, **23**, **36**, and **37**, respectively. In these schemes, an estimate of the number of known derivatives of each type is shown in parentheses.

In the synthesis of the =P̈–P̈= unit in Scheme 1, Romanenko and coworkers [5] caused the cleavage of P–H bonds in a condensation reaction where the liberated hydrogen atoms were taken up by the nitrogen atom of hexamethyldisilazide moieties.

Yoshifuji and coworkers [6] obtained the first isolated diphosphene with a localized P=P bond, Scheme 2, corresponding to Mode **5** by the reaction of magnesium metal with the sterically encumbered molecule, (2,4,6–tri–*t*–butylphenyl)phosphonous dichloride in THF solution. The diphosphene is stable in air. Its reaction with elemental sulfur in Et_3N at room temperature resulted in a Mode **9** formulation [7]. The X-ray structures of the diphosphene and its monosulfur derivative show little difference in the lengths of the P=P double bond.

SCHEME 1

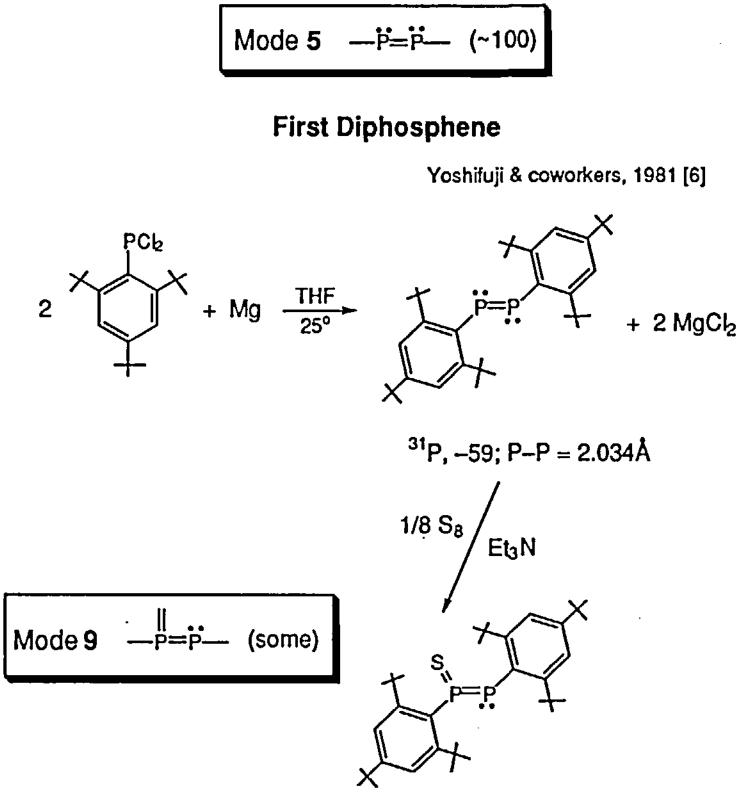


^{31}P, 33.9 [a]

Romanenko & coworkers, 1985 [5].

[a] All ^{31}P NMR chemical shifts here and to follow are in ppm.

SCHEME 2



First Diphosphene

Yoshifuji & coworkers, 1981 [6]

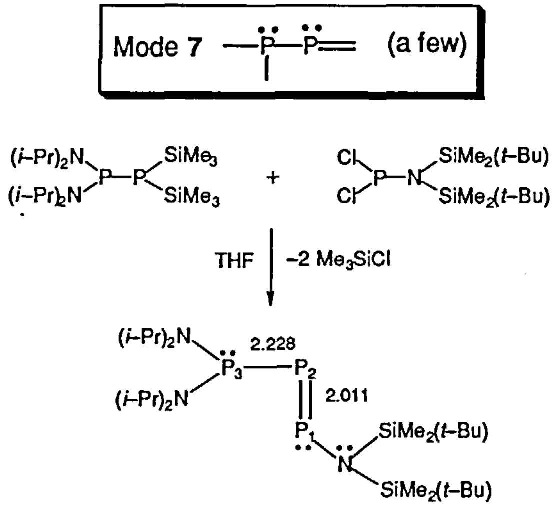
^{31}P, -59; P–P = 2.034Å

^{31}P, 255.8, 247.8; P–P = 2.054Å

Yoshifuji & coworkers, 1983 [7]

A few examples of diphosphenes corresponding to Mode 7 are known, one of which was prepared by Schoeller, Niecke, and coworkers [8] (Scheme 3) by treating a diphosphane in a condensation reaction with an aminophosphonous dichloride in THF. Each phosphorus and nitrogen atom apparently retains a lone pair of electrons which might allow an extensive reaction chemistry.

SCHEME 3



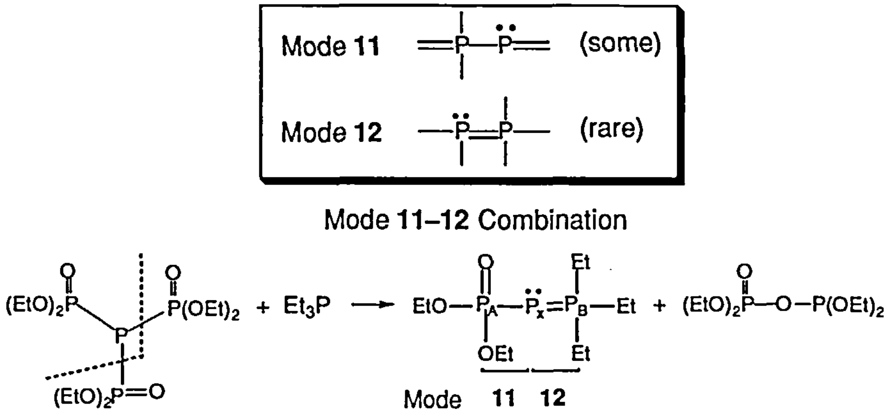
	P_3	P_2	P_1
^{31}P	67.9	442.9	577.6

Schoeller, Niecke & coworkers, 1989 [8].

In Scheme 4, a rare combination of Modes **11** and **12** was found by Weber and Fluck [9] by treating triethylphosphine with $[(Et_2O)_2PO]_3P$ which underwent an elimination reaction to yield the triethylphosphine–diethyloxyphosphoryl–phosphinidene product.

The previous schemes, 1–4, illustrated examples of modes containing low coordinate phosphorus. Modes **23**, **36**, and **37**, shown in Schemes 5–7, respectively, relate to bonding with five-coordinate phosphorus.

SCHEME 4

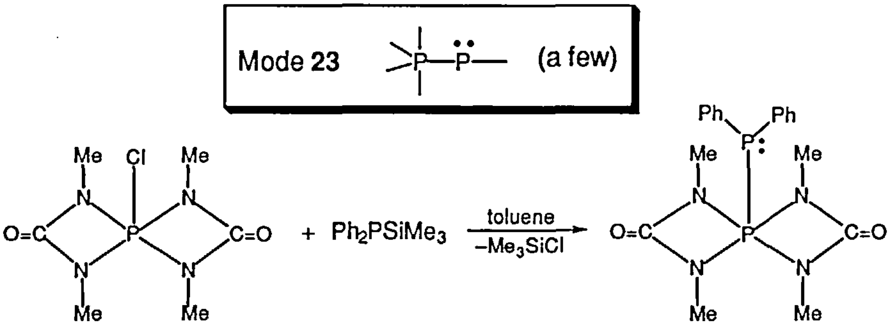


	P_A	P_x	P_B
^{31}P	−57.3	217.8	−44.2

Weber and Fluck, 1976 [9].

The first example of a Mode 23 compound was described by Schmutzler, Schomburg, and coworkers [10], Scheme 5. They reacted a chlorophosphorane with Ph_2PSiMe_3 in toluene solution. This caused a direct introduction of a Ph_2P group at a five–coordinate phosphorus center. The X-ray structure revealed a P–P bond length of 2.214Å, in the single bond range.

SCHEME 5

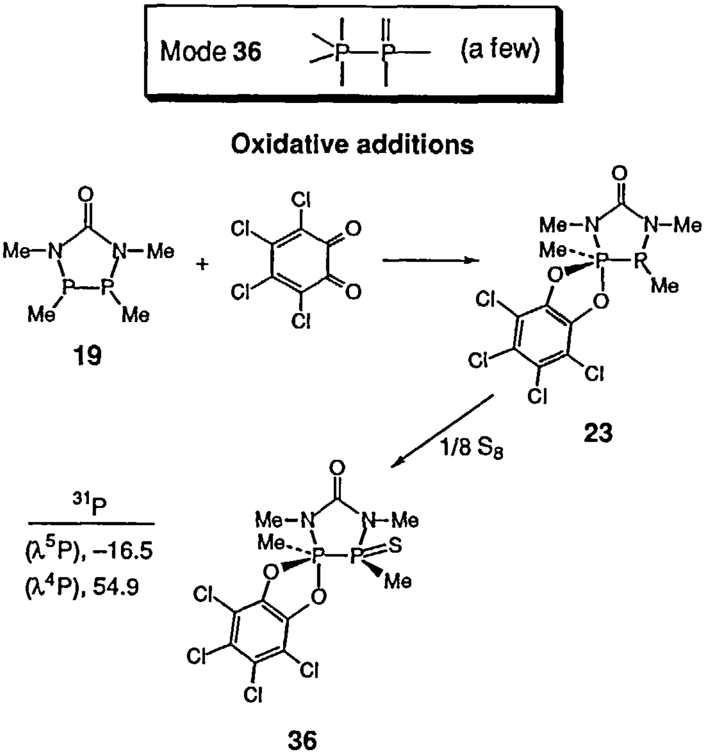


$^{31}P(\lambda^5P)$, −65.8; (λ^3P), −10.6   P–P = 2.214Å
(first example)

Schmutzler, Schomburg & coworkers, 1983 [10]

This same group [11] also reported the first synthesis of λ^5P–λ^4P diphosphorus compound, represented by Mode 36 in Scheme 6. This was accomplished by an oxidative addition of tetrachloro-*o*-benzoquinone to an N,N′-dimethylurea-bridged diphosphine (Mode 19) to obtain a λ^5P–λ^3P Mode 23 derivative. Treatment of the latter with elemental sulfur gave the new diphosphorus compound with the phosphorus bound methyl groups in a *trans* orientation as shown by an X-ray study. The geometry at the pentacoordinate phosphorus atom is displaced about 56% from a trigonal bipyramidal toward a square pyramid.

SCHEME 6



^{31}P

(λ^5P), –16.5
(λ^4P), 54.9

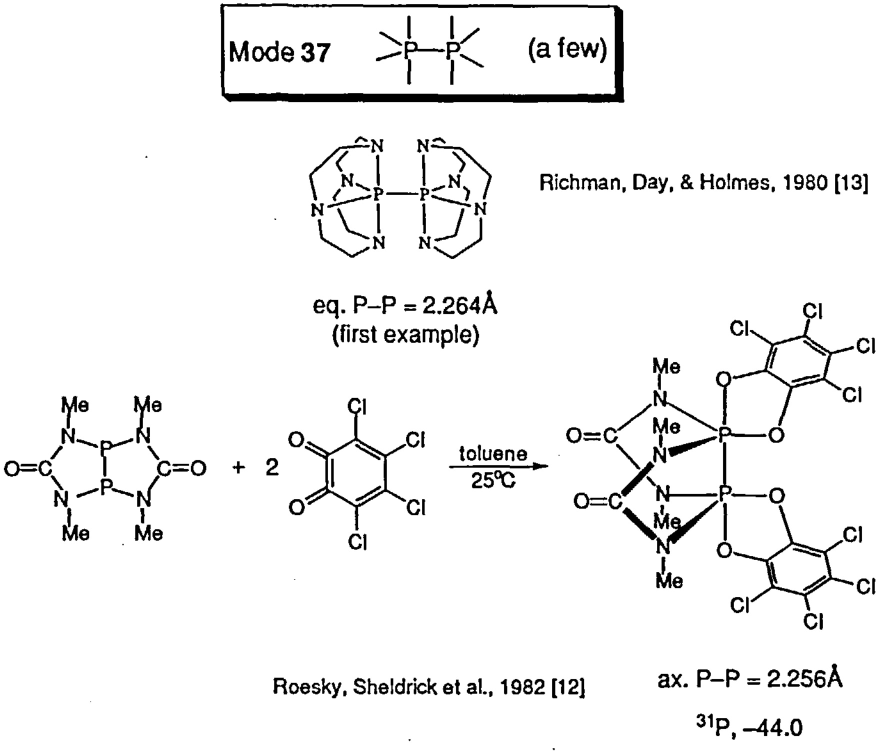
Modes 19, 23, 36

P–P = 2.216Å
(first example)
TBP →SP, 56%

Schomburg, Schmutzler & Weferling, 1981 [11].

Using this same type of oxidative addition with tetrachloro-*o*-benzoquinone as just described, Roesky, Amirzadeh-Asl, and Sheldrick [12] obtained a $\lambda^5P-\lambda^5P$ compound (Mode 37) depicted in Scheme 7. An X-ray study shows TBP geometries at each phosphorus atom where the P–P bond is in an axial position. This compares with the first example of a Mode 37 compound, the cyclam structure reported by Richman, Day, and Holmes [13] which has the P–P bond in an equatorial position.

SCHEME 7

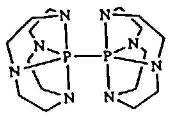
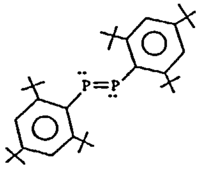
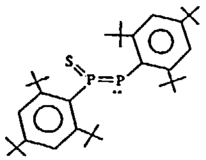


However, in this molecule the geometry is displaced one-third the way from a TBP toward a square pyramid. This may account partially for the equality in the two P–P bond lengths.

A listing of some P–P bond lengths varying in multiple bond character is given in Table 4 to compare with other examples discussed in this article.

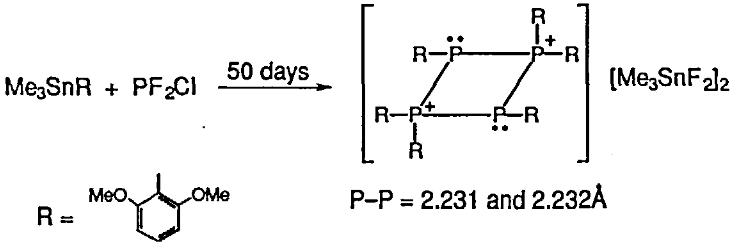
In addition to neutral compounds containing phosphorus–phosphorus bonds, it is instructive to consider both cationic and anionic derivatives. According to the procedure of Wolf and coworkers [3], they list 39 possibilities for cationic species comprised of phosphorus–phosphorus bonding and 94 kinds of anionic species. The number of known compounds that are cationic are few, whereas a considerable number of anionic derivatives

TABLE 4 P–P bond lengths

Mode	Examples	P–P, Å	
37		2.264(2)	Richman, Day & Holmes, 1980 [13]
5		2.034(2)	Yoshifuji et al., 1981 [6]
9		2.054(2)	Yoshifuji et al., 1983 [7]
1	$P_4 \xrightarrow{\Delta} :P\equiv P:$	1.895	Bock & Müller, 1984 [4]

have been reported [3]. Schemes 8 [14] and 9 [15] illustrate the synthesis of an example of each. There are also compounds containing adjacent cationic [16] or anionic [17] phosphorus centers. Synthesis of these are shown in Scheme 10.

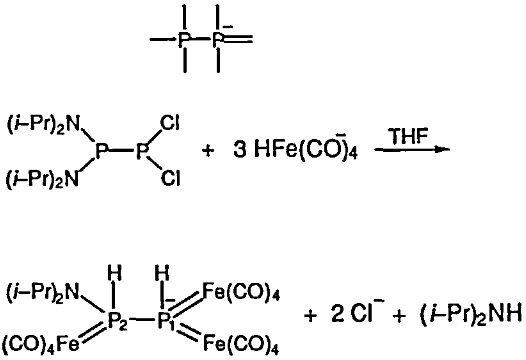
SCHEME 8 A cationic compound



P–P = 2.231 and 2.232Å

Huer, Ernst, Schmutzler, Schomburg, 1989 [14]

SCHEME 9 An anionic compound

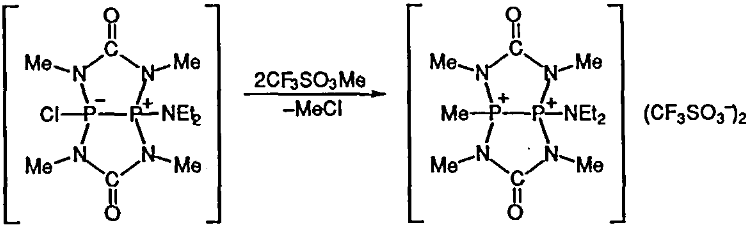


$^{31}P_1$, 77.8; $^{31}P_2$, 1.91 P–P = 2.283Å

Niecke, Majoral & coworkers, 1989 [15]

SCHEME 10 Other possibilities

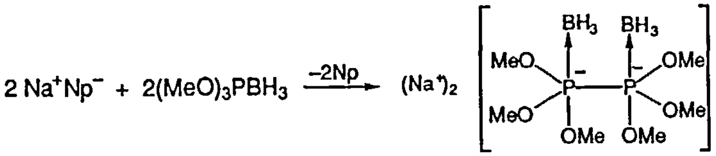
2 adjacent cationic phosphorus atoms



^{31}P, 42.7P–P = 2.189Å

Schomberg, Bettermann, Ernst, Schmutzler, 1985 [16]

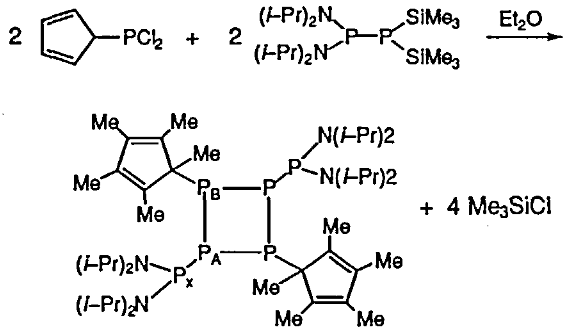
2 adjacent anionic phosphorus atoms



Peacock & Geanangel, 1976 [17]

The use of cyclopentadienyl introduces a range of other possibilities. The formation of a tetraphosphetane in Scheme 11 illustrates a member of this class [18].

SCHEME 11 Cp–P attachment



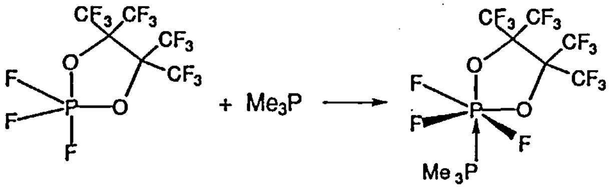
	A	B	X
^{31}P	−60.1	23.7	101.7

Ave. P–P (ring) = 2.234Å

Westermann & Nieger, 1991 [18]

There are a number of other types of compounds that contain phosphorus–phosphorus bonding. Among these are those that are radicals, those that are molecular adducts, formed as a result of Lewis acid–base interaction, *e.g.* that shown in Scheme 12 [19], and the

SCHEME 12 Hexacoordinated adduct via P–P bonding

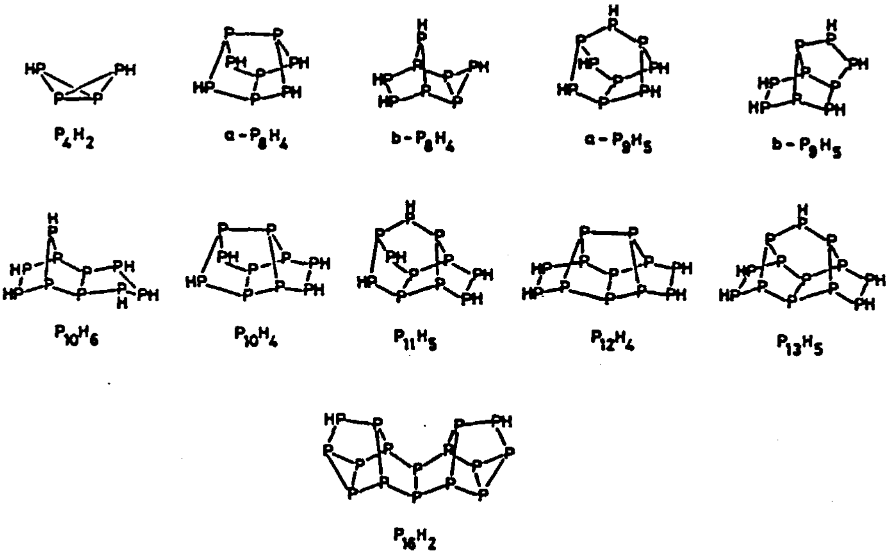


P–P = 2.234Å

Sheldrick & Röschenthaler, 1978 [19]

extensive array of polyphosphorus compounds both open chain [20] and cyclic [21] derivatives whose chemistry has been elucidated largely by Marianne Baudler and her coworkers. Structures of polycyclic phosphorus hydrides [21] in Scheme 13 indicate the range assigned to this class.

SCHEME 13 Structures of polycyclic phosphorus hydrides

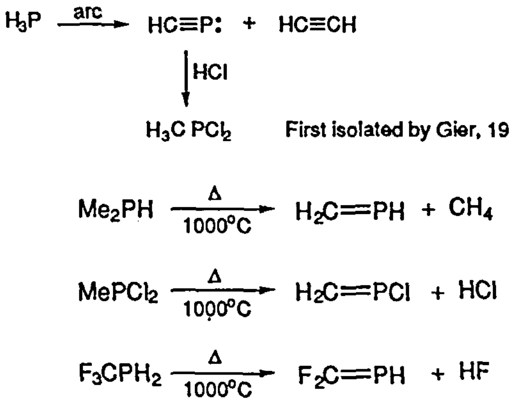


Baudler, 1987 [21]

We have reviewed samplings concerning the vast literature devoted to compounds containing phosphorus-phosphorus bonds that varied from monocoordinate to hexacoordinate in composition. Let us now examine some of the recent areas of phosphorus chemistry that involve connectivities to other atoms, usually C, N, O, S, F, Cl, Br, H, and metal atoms. Again the whole range of coordinate forms will be considered. In doing so, we may gain an appreciation of the growth that has occurred in phosphorus chemistry in recent times, and it is hoped that some projection into future work may be visualized. Much of the material in what is to follow is based on articles in a thematic issue of *Chemical Reviews* devoted to phosphorus chemistry that appeared in August, 1994.

The syntheses of several types of unstable P–C multiple bonds in Scheme 14 are all performed at high temperature from the thermal decomposition of phosphines [22, 23]. Microwave structures are included in Scheme 15 [24–26] along with ^{31}P chemical shifts [27, 28]. As an indication of instability, for example, HC≡P is a colorless gas which is spontaneously inflammable in air and polymerizes above –130°C [22]. Stabilization can be achieved with the use of a *t*-butyl group, Scheme 16.

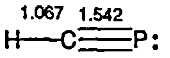
SCHEME 14 Unstable compounds with phosphorus carbon multiple bonds



First isolated by Gier, 1961 [22]

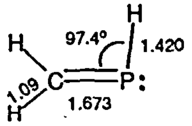
Kroto, Nixon and coworkers, 1976 [23]

SCHEME 15 Microwave structures



^{31}P, −32 [27]

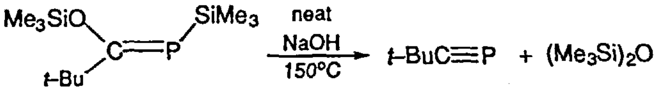
Tyler, 1964 [24]. Frost, Lee, McDowell, 1973 [25].



^{31}P, 231 [28]

Kroto, Nixon & Ohno, 1981 [26]

SCHEME 16 Stable phosphaalkynes

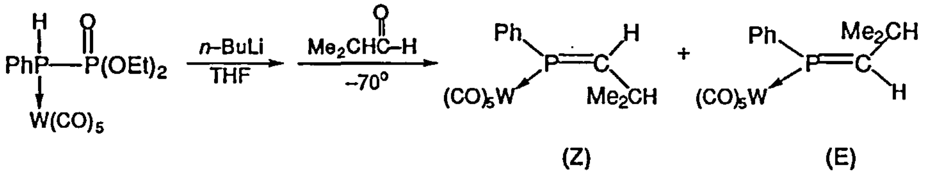


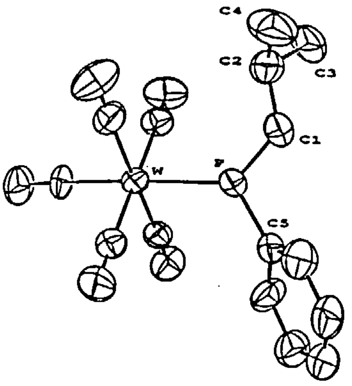
^{31}P, −69.2

Becker, Gresser, Uhl, 1981 [29]

This class of low-coordinate compounds has proven useful in synthesis in organophosphorus and organometallic chemistry. Schemes 17 and 18 illustrate these applications.

SCHEME 17 Phospha-Wittig reactions yielding phosphorus-carbon double bonds

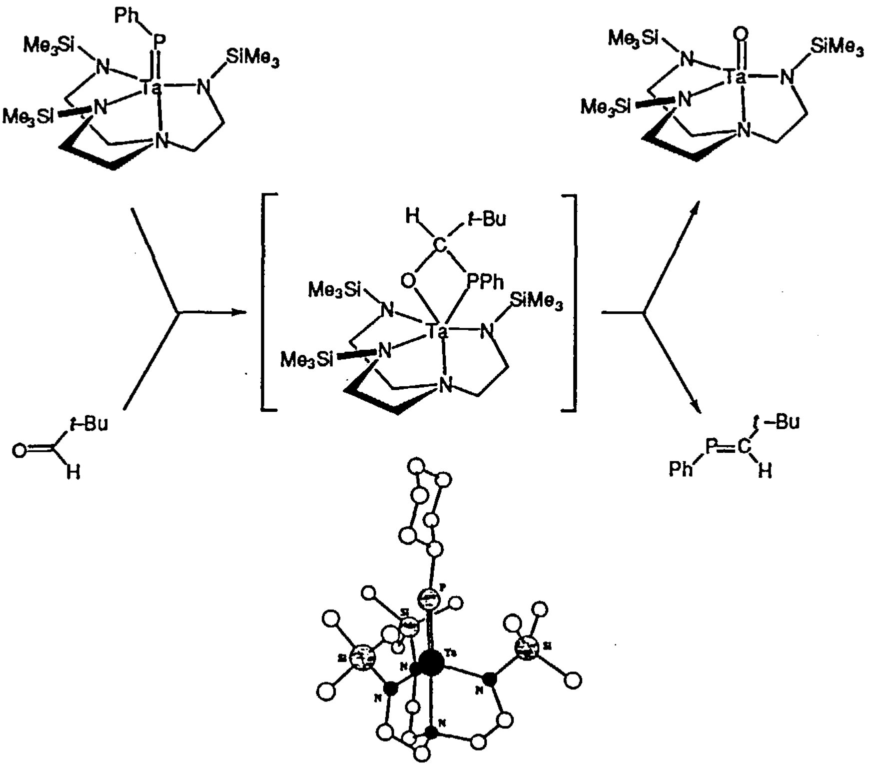




ORTEP of (Z)ISOMER

Mathey and coworkers, 1990 [30]

SCHEME 18 First stable phosphinidine tantalum complexes as phospha–Wittig reagents



Cummins, Schrock, Davis, 1993 [31]

Another related area dealing with unsaturation in phosphorus bonds concerns the class of phosphonium ylides, Table 5, where metalated and main group element attachments have proven useful as reagents in organic synthesis [32–39].

Discussions of the mode of bonding in phosphonium ylides center on a resonance hybrid between a dipolar form and a double bond form [40].

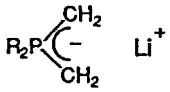
$$R_3\overset{+}{P}-\overset{-}{C}R_2 \longleftrightarrow R_3P{=}CR_2$$

On the basis of chemical reactivity, the dipolar form is considered more important [40–42]. This is in agreement with data from physical measurements indicating a build-up of charge at carbon [40, 43]. Theoretical treatments are in agreement with the results of physical measurements [40]. One model [40, 43–45] (Scheme 19) that has considerable support describes the phosphorus carbon bond comprising two electron pairs with the electron density strongly skewed toward carbon. The bond is viewed as a composite of a σ bond to

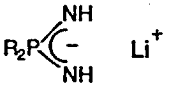
TABLE 5 A sampling of parent phosphonium ylides (from a review by Cristau, 1994)

$R_3P{=}CH_2$

Staudinger, 1919 [33]
Wittig, 1949 [34]



Wittig, 1949 [34]



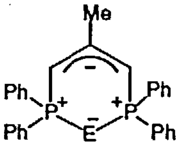
Scherer, 1969 [35]

$R_3P{=}N{-}Li$

Schmidbaur, 1967 [37]

$R_3P{=}N{-}PR_3^+\ X^-$

Appel, 1961 [36]

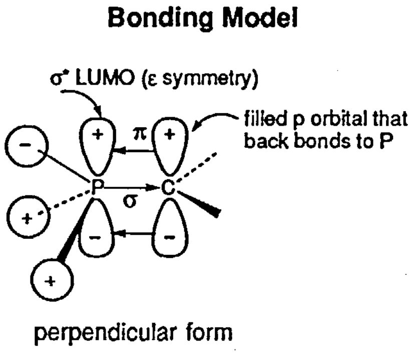


E = CH, N, BH_2, P, As

Schmidbaur & coworkers, 1991–1993 [38–39]

SCHEME 19 Bonding model for phosphonium ylides

$$R_3\overset{+}{P}{-}\overset{-}{C}R_2 \longleftrightarrow R_3P{=}CR_2$$

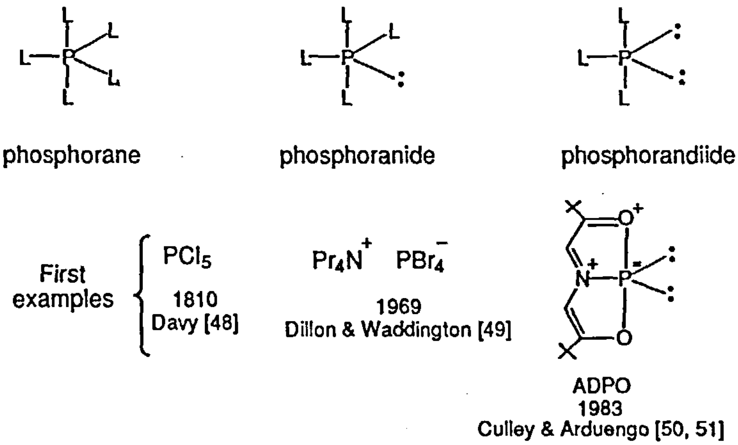


Review by Gilheany, 1994 [40]

carbon from the lone pair of electrons from phosphorus and a π back–bond from a filled p orbital on the anionic–like carbon to one of two possible acceptor orbitals on phosphorus which are antibonding in character with respect to the other ligands on phosphorus. Since the back bonding is to antibonding phosphorus orbitals in both perpendicular and parallel conformations of the phosphonium ylide, this would rationalize the low barrier to rotation about the phosphorus–carbon bond, in the range of 4–5 kJ/mol [45–47].

Next we will look at phosphoranides, phosphorandiides, and their metal complexes. Scheme 20 shows these formulations and their relationship to phosphoranes, the latter of

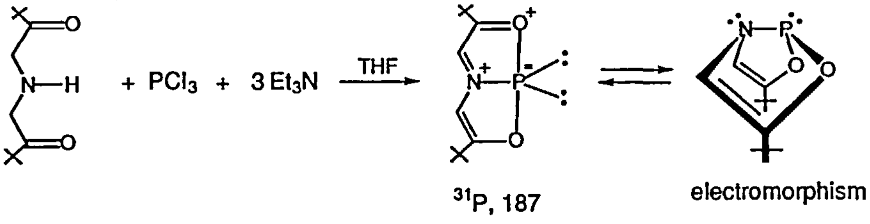
SCHEME 20



ADPO = 5 aza–2,8–dioxa–1–phosphabicyclo[3.3.0]octa–2,4,6–triene

which have been known for an extremely long time [48] compared to the phosphoranides [49] and diides [50, 51]. Phosphoranides play a role as models for reactive intermediates in nucleophilic substitution reactions at phosphorus(III) centers [52]. The formations of members of these two classes follow relatively simple syntheses, Schemes 21 [51] and 22 [49]. However, the availability of suitable starting ligands and ease of hydrolysis, *e.g.* ADPO rapidly hydrolyzes in moist CH_2Cl_2 in minutes at room temperature [53], no doubt enters into the late arrival of the phosphorandiides. In the case of phosphoranides, stability may be increased by forming cyclic organophosphoranides (Scheme 23 [55]) and by incorporating strongly electron withdrawing ligands such as CN, CF_3, or C_6F_5 [52]. As yet, no transition metal complexes have been formed with acyclic phosphoranides [52], although such possibilities exist.

SCHEME 21 Synthesis of the first phosphoranidiide



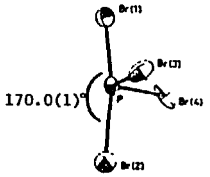
Culley & Arduengo, 1984 [51]

SCHEME 22 First phosphoranide
(Dillon and Waddington, 1969 [49])

$$n\text{-}Pr_4N^+Br^- + PBr_3 \xrightarrow{ClCH_2CH_2Cl} [n\text{-}Pr_4N]^+[PBr_4]^-$$

^{31}P, −229 ppm ^{31}P, −150 ppm

Fumes readily in air



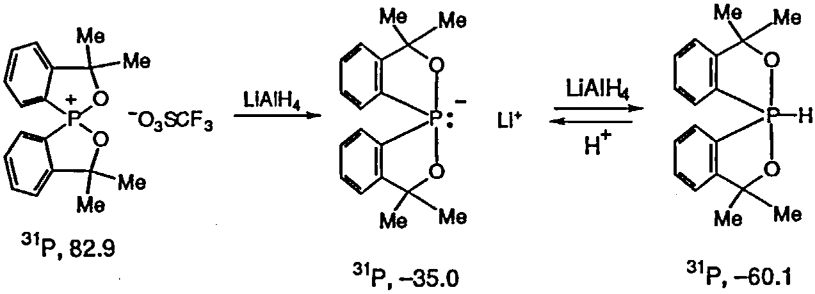
Sheldrick et al., 1981 [54]

ORTEP plot of PBr_4^- in $[Pr_4N]^+[PBr_4]^-$.

P–Br_{ax} = 2.527(4)Å, 2.620(4)Å

P–Br_{eq} = 2.221(3), 2.255(3)Å

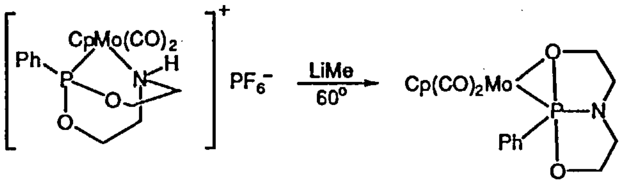
SCHEME 23 First cyclic organophosphoranide



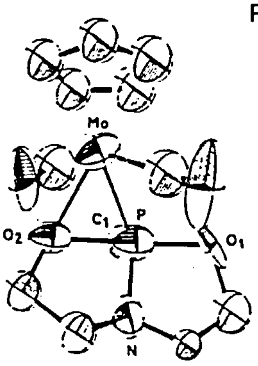
Granoth & Martin, 1978 [55]

The first phosphoranide metal complex was obtained by Riess and coworkers [56] and is shown in Scheme 24. With platinum, the formation of both (cyclen P)PtCl(PPh_3) [57] and

SCHEME 24 First phosphoranide metal derivative



$P–N_{eq}$ = 1.69Å ^{31}P, 23.8

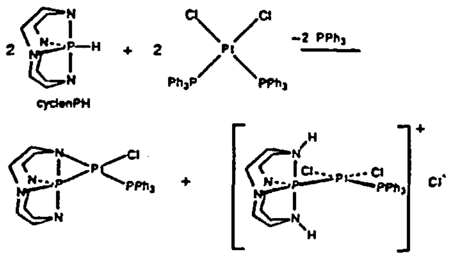


Molecular structure of the Mo complex; only the C–1 atom of the phenyl group bonded to phosphorus is included, for clarity.

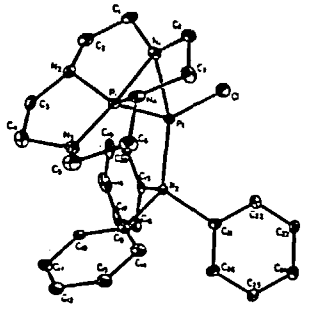
Riess & coworkers, 1981 [56]

[(*cis*-H_2 cyclen P)$PtCl_2(PPh_3)]^+Cl^-$ [58] occurred from the reaction of *cis*-$Cl_2Pt(PPh_3)_2$ with cyclen PH in THF, Scheme 25 [59].

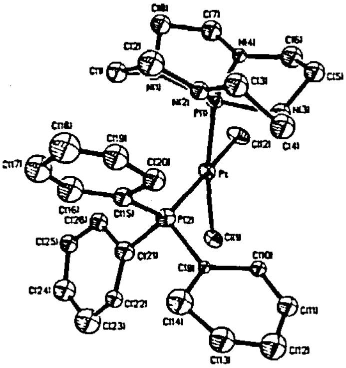
SCHEME 25 Phosphoranide metal complexes



^{31}P, -55 ^{31}P, -59



ORTEP view of (cyclen P)$PtCl(PPh_3)$ [57]

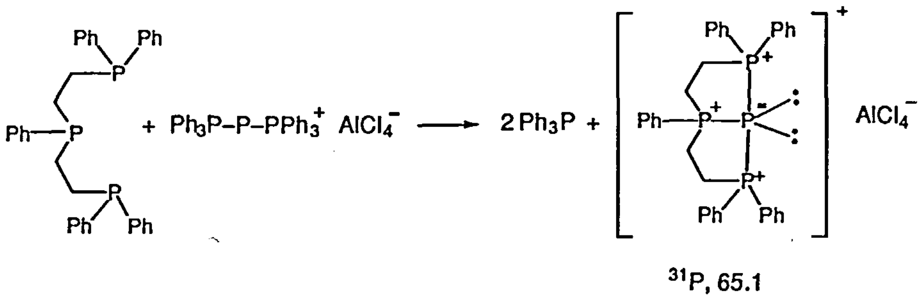


ORTEP drawing of the cation [(*cis*-H_2cyclen P)$PtCl_2PPh_3]^+Cl^-$ [58]

Lattman and coworkers, 1987 [57–59]

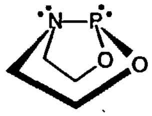
An all phosphorus phosphorandiide was synthesized by Schmidpeter and Lochschmidt [60] in 1985 (Scheme 26), shortly after the report of Culley and Arduengo on ADPO [50, 51].

SCHEME 26 All phosphorus phosphorandiide



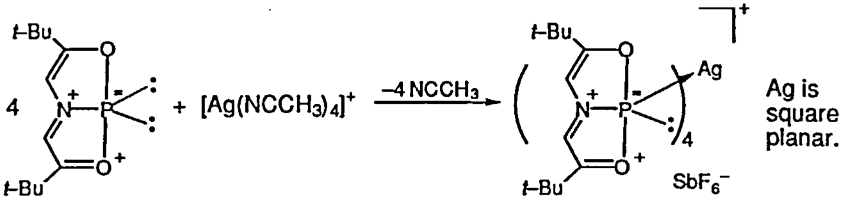
Schmidpeter & Lochschmidt, 1985 [60]

Due to the electromorphism associated with phosphorandiides like ADPO in Scheme 21, metal complexation can take place via the planar or folded geometries, both of which are considered potential ground state structures where the more classical folded arrangement is calculated to be about 14 kcal/mol above the planar form [61]. Wolf and coworkers [62–65] have found many related structures in the folded form for saturated bicyclic compounds.



For ADPO derivatives, only when the metal interaction with phosphorus is sufficiently weak as with Ag^+ is the planar form observed, Scheme 27 [66]. For most transition metals, the bond to phosphorus exceeds the 14 kcal/mole barrier and the folded geometry prevails. By contrast, antimony or arsenic in place of phosphorus in ADPO type compounds have higher barriers from the planar geometry to the less stable folded form such that the planar form on metal coordination is the preferred geometry [61], Scheme 27 [67].

SCHEME 27 Phosphorandiide metal complexes



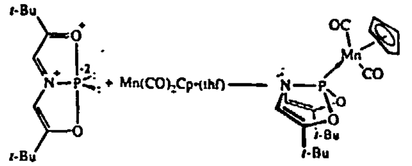
ADPO

^{31}P, 187

$[(ADPO)_4Ag]^+SbF_6^-$

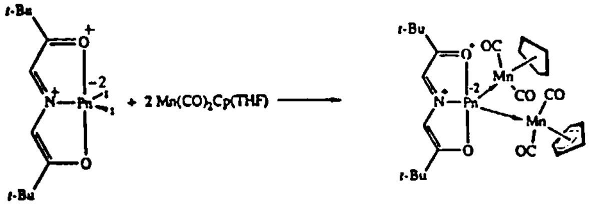
^{31}P, 166

Arduengo, Dias & Calabrese, 1991 [66]



ADPO·MnCp(CO)$_2$

^{31}P, 256



ADPnO

ADPnO·[MnCp(CO)$_2$]$_2$

Pn = Sb, As

Arduengo et al., 1991 [67]

We turn now to metal complexes of the phosphazenes and phosphazanes. A large variety of materials are possible due to the different electron donor abilities of phosphorus and nitrogen [68]. Nitrogen, which is a hard base, has the ability of stabilizing metals in their higher oxidation states. In contrast, phosphorus, which acts as a soft base, is more prone to stabilize metals in lower oxidation states. The first metal phosphorus-nitrogen compounds date back to those of Payne and coworkers in 1962 [69], Scheme 28.

SCHEME 28 Metal coordinated phosphazenes and phosphazanes

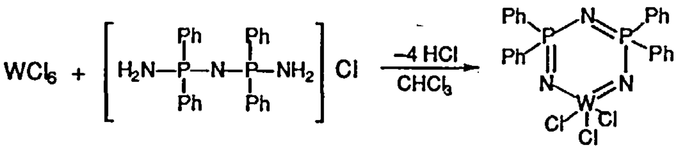
First Metal P–N Compounds

$Ph_2PNEt_2 \cdot HgI_2$

$[Ph_2PNEt_2CuI]_4$

Payne et al., 1962 [69]

First Cyclic Phosphazene with a Metal Atom in the Ring



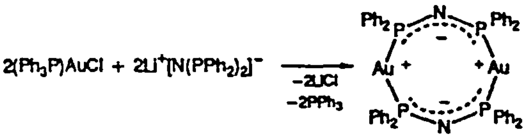
Roesky et al., 1986 [70]

The first cyclic phosphazene with a metal atom in the ring was synthesized more recently by Roesky et al. [70] in 1986, Scheme 28. Depending on the hardness of the metal, bonding to phosphorus or nitrogen is established to some degree. With softer metals like Au^+ [71] or R_2Ga^- [72], bonding takes place preferentially with the softer phosphorus atom, Scheme 29. With Me_2Al^- [72] and Ni^{2+} [73], bonding to both phosphorus and nitrogen occurs, Scheme 30, whereas with the use of Na^+, which is a hard acid, bonding with the harder nitrogen atom is found, Scheme 31 [74]. K^+ and Ca^{++} also bond to nitrogen atom similarly to Na^+ in terms of the local framework of the phosphazene [74]. This area has given rise to a great variety of cyclic main group and transition metal phosphazanes and phosphazenes, some of which have had applications as catalysts and precursors for new materials [68].

SCHEME 29 Metals bonded to phosphorus

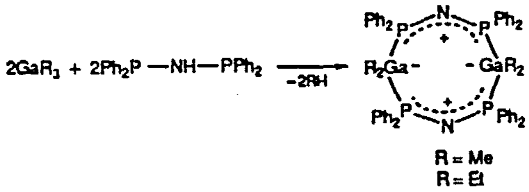
Soft P–Soft Metals

Negative charge over P–N–P skeleton



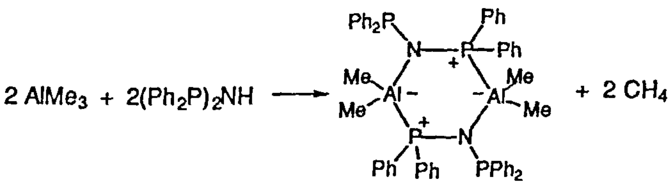
Uson et al., 1986 [71]

Positive charge over P–N–P skeleton

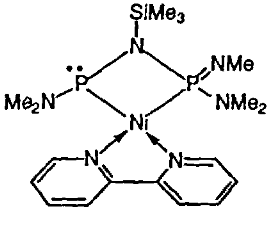


Schmidbaur & coworkers, 1983 [72]

SCHEME 30 Metals bonded to phosphorus and nitrogen



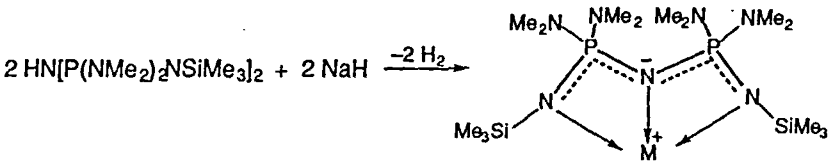
Schmidbaur et al., 1983 [72]



Scherer et al., 1985 [73]

SCHEME 31 Metals bonded to nitrogen

Hard N–Hard Metals



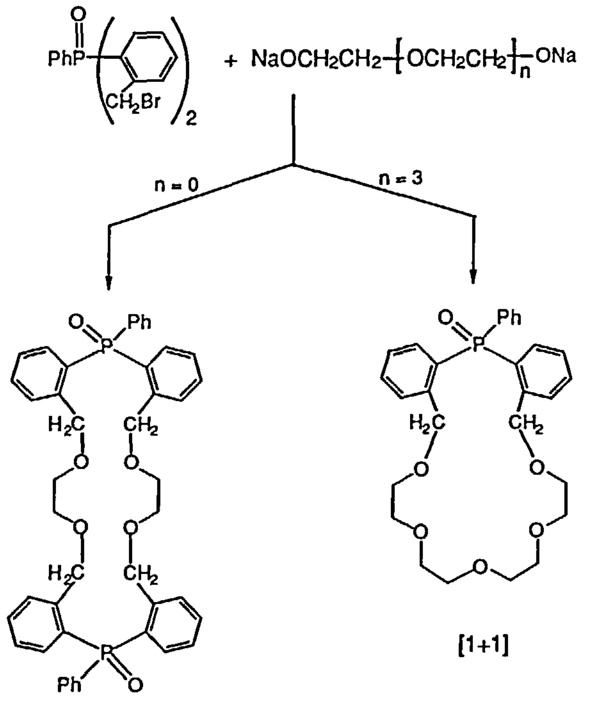
Roesky et al., 1993 [74]

$M^+ = Na^+, K^+, Ca^{2+}$

By incorporating phosphorus in macrocycle environments, advantage may be taken of its high complex fomring ability and its softness in stabilizing transition metals in low oxidation states [75]. Some of these phosphorus containing macrocycles have been found to transport transition metals through liquid membranes. Potential applications in homogeneous catalysis and phase-transfer catalysis are also visualized [75]. Members of this class are obtained by cyclocondensation reactions, the most common method. Several examples are depicted in Schemes 32 [76] and 33 [77–89].

SCHEME 32 Phosphorus macrocycles

Synthesis by cyclocondensation

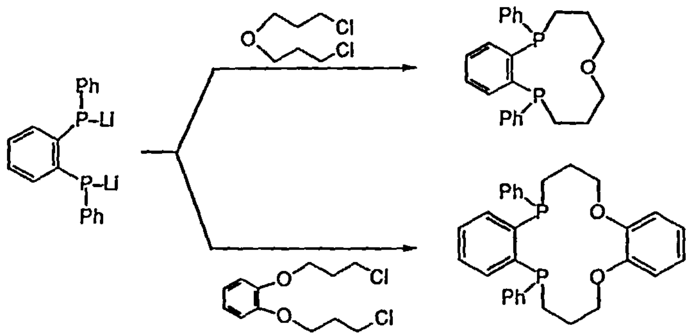


[2+2]

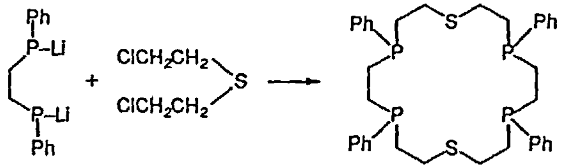
Kaplan, Weisman & Cram, 1979 [76]

This method was developed by Kyba and coworkers [75, 77–80] from 1977 to 1985, and further explored by Ciampolini and coworkers [75, 81–89] during 1980–1986. Other lesser used methods involve ring opening reactions and template reactions. Most of the ring opening reactions focus on cyclophosphazenes and tetraaminophosphorane derivatives [75].

SCHEME 33 Cyclocondensations were developed under high dilutions



Kyba & coworkers, 1980–1985 [77–80]

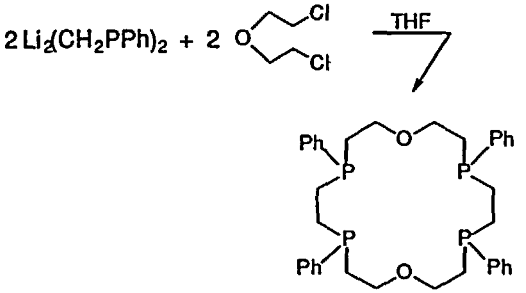


Ciampolini & coworkers, 1980–1986 [81–89]

Of the many metal complexes that are known [75], Scheme 34 shows the first crown ether phosphorus macrocycle encapsulating low spin cobalt(II) in both a square pyramid and an octahedron [90, 91].

An interesting reaction takes place between a polyoxy macrocycle and hexamethylphosphoric triamide. Instead of the expected pentacoordinate phosphorus product, hexacoordination is observed in the form of zwitterionic *p*–*t*-butylcalix[4]arene–P(H)NHMe$_2$ [92], Scheme 35. An X-ray structure of the lithium salt has been obtained [93].

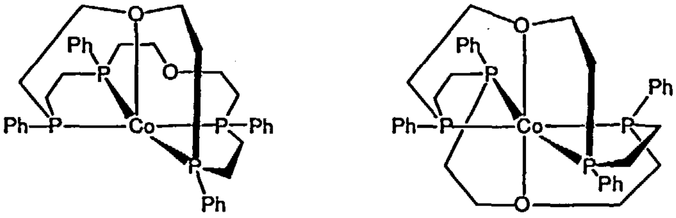
SCHEME 34 Macrocycle–Transition metal complexes



[18]ane P_4O_2
12% yield of the 5 isomers
(^{31}P, 21.7–23.6)

First Crown Ether Phosphorus Macrocycle

Low-Spin d^7 Co(II) Complexes



Square pyramid, Co–O = 2.26Å

Octahedron, Co–O = 2.35Å

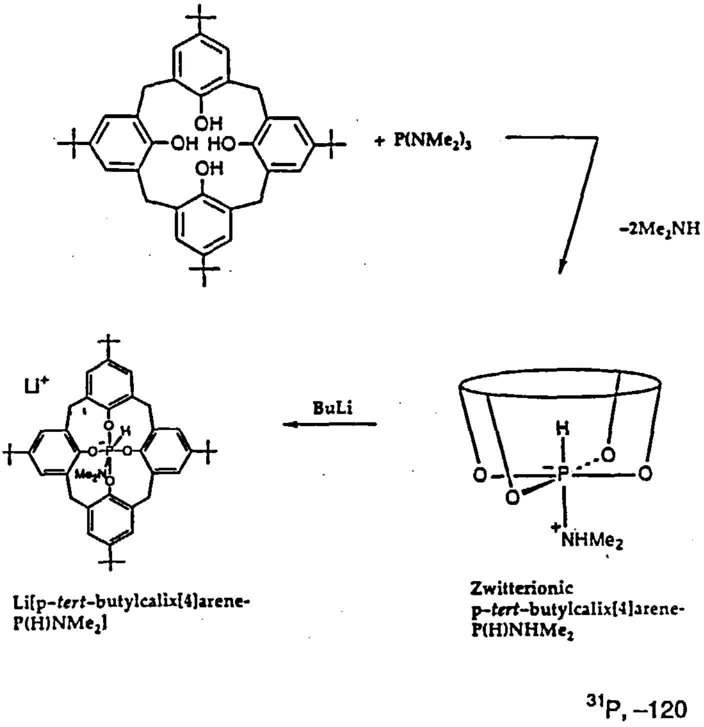
$[Co(\alpha\text{-}[18]aneP_4O_2]^{2+}[BPh_4]_2$

$[Co(\beta\text{-}[18]aneP_4O_2)]^{2+}[BPh_4]_2$

Ciampolini et al., 1980 [90], 1982 [91]

In our excursion through phosphorus chemistry, little mention had been made of compounds having a coordination number of six, although the number in this class is growing. Burgada and Setton have provided a recent summary of this topic [94]. We record here representative members formed by donor action for the most part and whose X-ray

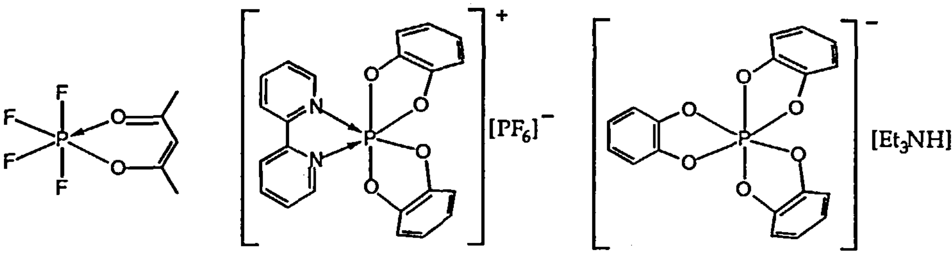
SCHEME 35 First Calixarene–Hypervalent main group atom structure



Lattman and coworkers, 1990 [92], 1991 [93]

structures have been determined, Schemes 36 [95–97], Table 6 [98–102], and Scheme 37 [103a]. Sulfur induced hexacoordination (Scheme 37) is the latest example where a range of structures have been formed [103] whose geometries lie progressively from a square pyramid toward an octahedron. Just as pentacoordinate phosphorus compounds [104a] have

SCHEME 36 Hexacoordination (X-ray)

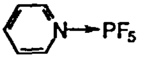
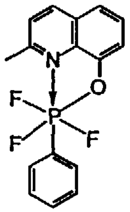
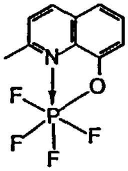
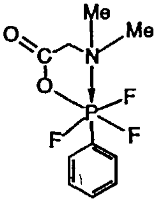


Sheldrick & Hewson, 1978 [95]

Sheldrick, Schmidpeter, von Criegern, 1978 [96]

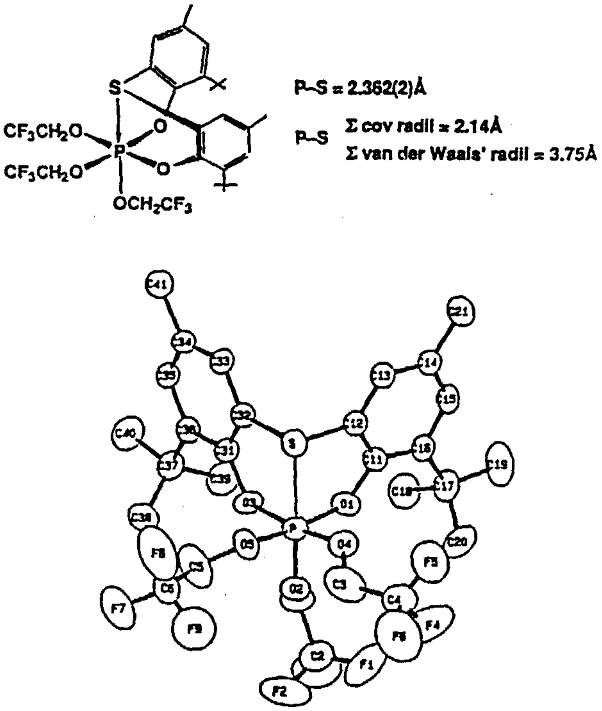
Allcock & Bissell, 1973 [97]

TABLE 6 Nitrogen induced hexacoordination

	P–N, Å		P–N, Å
	1.885(4)		1.980(3)
$H_3N \rightarrow PF_5$	1.842(2)		
	1.911(4)		2.013(4)
		P–N covalent	1.85

Schmutzler, Sheldrick, Schomburg & coworkers, 1974–1989 [98–102]

SCHEME 37 Sulfur induced hexacoordination

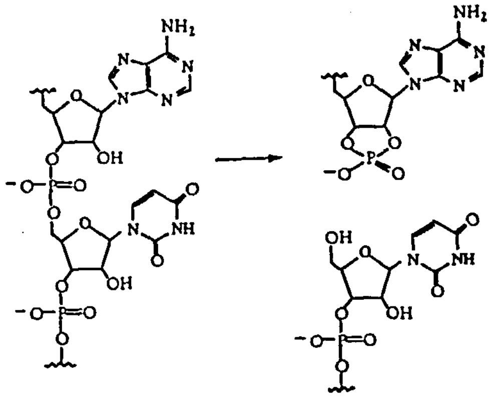


Holmes, Prakasha, & Day, 1993 [103a]

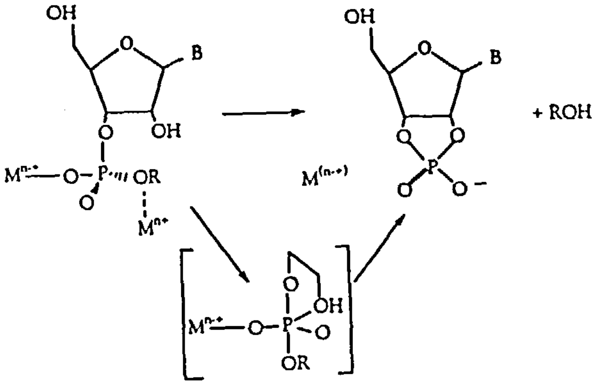
been found to provide useful models for nucleophilic displacement reactions at tetracoordinate centers [104b], hexacoordinate compounds should have applicability as models for nucleophilic displacements at pentacoordinate phosphorus centers.

In the area of enzyme action with phosphorus substrates; models are widely used to mimic catalytic features [104b]. An overview by Janet Morrow [105] discusses recent work on catalysts for substitution reactions of phosphorus(V) constituents of nucleic acids involving metal ion interactions. The metal ions assist by binding to the phosphate to increase its susceptibility to nucleophilic attack or by binding to the leaving group to assist its departure, Scheme 38 [105]. Hydrolytic cleavage of phosphate ester bonds by a number of important enzymes are known to use two metal ions [106–110]. In this connection, Tsubouchi and Bruice [111] reported a remarkable 10^{13} rate enhancement in the hydrolysis of a monoalkyl phosphonate ester assisted by two lanthanum cations. The two La^{3+} ions provide the first example of double metal cooperativity consisting of a proposed in-line intramolecular attack of metal-bound hydroxide in a TBP activated state and Lewis acid activation of the departing oxyanion leaving group, (Scheme 39), producing (8–hydroxy–2–quinolyl)methanol.

SCHEME 38 RNA cleavage by phosphate ester transesterification

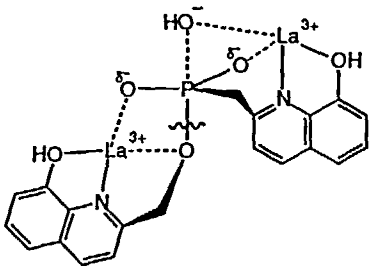


Metal Ion Catalyzed RNA Transesterification



Morrow, 1994 [105]

SCHEME 39 Phosphonate ester hydrolysis enhanced 10^{13} by lanthanide ions

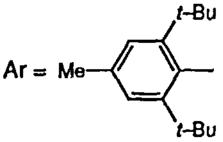


Proposed Intermediate

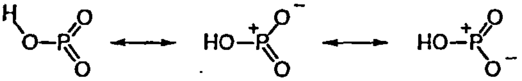
Tsubouchi & Bruice, 1994 [111]

Throughout this presentation, ^{31}P chemical shifts have been recorded and serve admirably to give an indication of the extent of coordination at phosphorus and structural changes encountered on going from the solid state to solution [112]. As discussed by Gorenstein [113], in connection with nucleic acid chemistry, ^{31}P NMR has come to be a powerful probe in providing valuable information on the phosphodiester backbone conformation present in nucleic acids and nucleic acid complexes in solution which at times may not be the same as that provided by X-ray diffraction in the solid state.

On the theoretical side, considerable progress in the interpretation of experimental ^{31}P chemical shifts has been made through computational methods. Quin and Chesnut [114a] and Chesnut and Rusiloski [114b] have summarized recent work in this area and provide an illustration on the extent of agreement achieved for isotropic shieldings at optimized geometries for some simple phosphorus compounds based on Ditchfield's gauge including the atomic orbital (GIA) coupled Hartree–Fock method [115], Table 7. The error is about 28 ppm over a range of 950 ppm. The agreement is deemed close enough to have predictive value. In this connection, the authors [114] cite evidence for a ^{31}P shift observed at 238 ppm which was assigned to the first phosphenite, ArO–P=O. The calculated shielding value



for a model compound (Ar = Ph) in a perpendicular *syn* form was 254 ppm which tends to confirm the structural assignment to the phosphenite. Also future experiments are encouraged to detect both the unknown metaphosphoric acid and the unknown phosphinidene oxide, H–P=O.



Values of 48.9 ppm for the fully planar form of the metaphosphoric acid and 649.3 ppm for the phosphinidene oxide have been calculated [114].

So can we say anything significant about the future of phosphorus chemistry. Each of you is in an unique position, with somewhat different perspectives, about new directions that phosphorus chemistry might take. It is difficult and no doubt hazardous to make such predictions. So much depends on unforeseen events, those rather rare but special occurrences that when properly recognized and followed up on may give rise to entirely

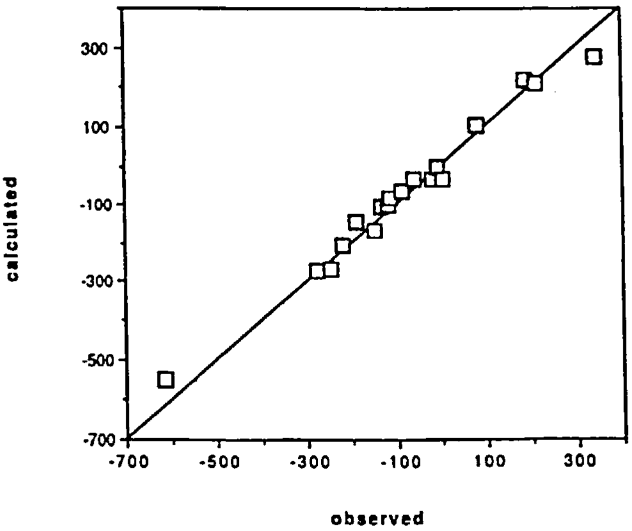
TABLE 7 ^{31}P chemical shifts

molecule	calc.[a]	obs.
P_4	−617.3	−551.4[b]
PH_2^-	−335.1	(−279.4)
H_3SiPH_2	−277.1	−274
PH_3	−249.2	−266.0[b]
H_2PPH_2	−222.1	−204
PF_6^-	−191.7	−143.7
CH_3PH_2	−149.7	−163.5
PH_4^+	−134.0	−105.3
$(CH_3)_2PH$	−115.7	−99
PF_5	−114.3	−80.2
$(CH_3)_3P$	−87.9	−63.3[b]
OPF_3	−58.1	−35.0[b]
HCP	−19.5	−32
PO_4^{-3}	−4.5	0.0[c]
C_6H_5CP	4.6	−32
PF_3	83.4	105.7
PCl_3	189.4	217.1[b]
C_5H_5P	211.7	211
rmse		28.3

[a] At optimized geometries.

[b] Gas phase result.

[c] 85% H_3PO_4.



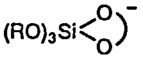
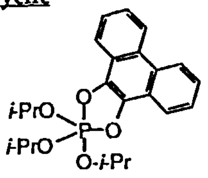
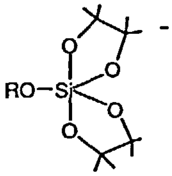
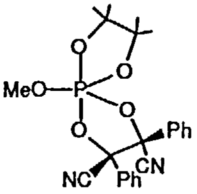
Quin and Chesnut, 1995 [114a]

new areas of chemistry. However, we can expect that the next quarter of a century should be at least as spectacular as the last in providing new discoveries leading to developments that at present cannot be anticipated. What I can say is that the chemistry of all the coordination types will enjoy continued exploration and advancement along with their synthetic and structural elucidation.

I feel there is a special need for the assistance afforded by theoretical methods of all types including computer graphics to better understand mechanistic features of reactants, intermediates, proposed transition states and products. Also in our planning, it would serve us well to look at related chemistries, perhaps not even in the same periodic family, that can give us additional perspective and insight not otherwise readily available and lend to a more rewarding and rapid advance of our research. Comparisons of this type that have proven useful in this way are found between isoelectronic phosphorus and silicon pentacoordinate molecules in our own research [104a, 116–118] (Table 8) and in structural analogies between SiO and PN species, as discussed by Schmidpeter and coworkers [119], Table 9. I appeal in particular to the younger members of the community to take a broad view of research and not spend your entire research career on too narrow a focus.

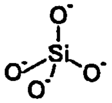
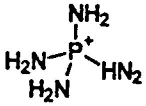
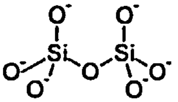
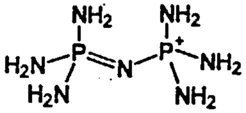
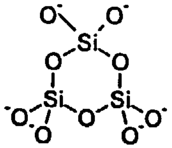
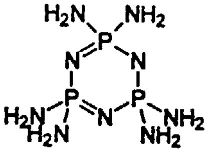
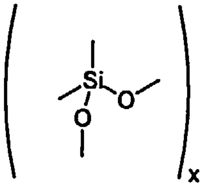
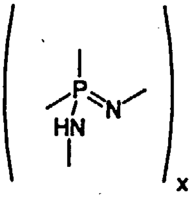
At the entrance of Bell Telephone Laboratories in Murray Hill, New Jersey, where I had been employed before joining university life once more, there is an inscription at the base of a statue of Alexander Graham Bell which may be particularly apropos to end my lecture: "Leave the beaten track occassionally and dive into the woods. You will be certain to find something you have never seen before." (Alexander Graham Bell)

TABLE 8 Comparative stability of pentaoxy silicates and pentaoxy phosphoranes [104a, 116–118]

	Acyclic		
$Si(OR)_5^-$	detected but not isolated	$P(OPh)_5$	X-ray
	Monocyclic		
	no known examples		X-ray (many other examples) with rings from 5 to 8 membered
	Bicyclic		
	A few examples studied by X-ray		X-ray (many others with rings from 5 to 8 membered

All Si are K^+,18-crown-6 salts.

TABLE 9 Isoelectronic SiO and PN species

SiO_4^{4-}			$H_8PN_4^+$
$Si_2O_7^{6-}$			$H_{12}P_2N_7^+$
$Si_3O_9^{6-}$			$H_{12}P_3N_9$
$(SiO_2)_x$			$(HPN_2)_x$

Schmidpeter, Horstmann & Schnick, 1995 [119]

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