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Neutral Six-Coordinate Phosphorus

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I. Introduction

Until recently there has been little general awareness that neutral compounds can be formed in which the phosphorus center is six-coordinate, although six-coordinate anions such as PF_6^- are common. This particular ion sees wide use as a stabilizing and relatively nonreactive counterion in a wide variety of complex salts. Our interest however focuses on the isolation and characterization of neutral molecular species in which the phosphorus appears in this highly coordinated state, presumably the maximum possible coordination for this element. We sought to evaluate this highly coordinated atomic environment in systems that did not also have added stabilizing contributions from electrostatic interactions between cation and anion in the solid state. As would be expected, most of these neutral six-coordinate compounds are derived from pentavalent phosphorus; however, a few such systems based on trivalent phosphorus have been identified. In contrast to the relatively limited activity in this area of phosphorus chemistry, much has been published about neutral compounds which contain five- and six-coordinate silicon centres.[1−3] Highly coordinated silicon and phosphorus centers are both formally "hypervalent" and so have been the subject of interest and debate with regard to the question of d-orbital involvement in the bonding. The status of this concept has been reviewed recently,[4] especially in the context of binding in phosphorus compounds.

In the quest for preparing and identifying neutral highly coordinated phosphorus centers, the difference in the chemical behavior of phosphorus and silicon appears to have a marked influence. In the higher coordination states, silicon appears to be less stable than phosphorus in that simple examples of particularly pentacoordinated phosphorus halide derivatives have long been known but the silicon analogues are not readily accessible. On the other hand, silicon appears, at first glance, to provide more ready access to the higher coordination environments. This difference is in part due to the propensity of the higher valence state of phosphorus, particularly when bound to oxygen, to readily eliminate substituents with ultimate formation of species of the same valence but in which the coordination of the phosphorus center has been reduced. The main examples are reactions in which $P=O$ bonds are formed. The chemical stability and resistance to polymerization of the $P=O$ functionality contrasts with the behaviour of silicon wherein the $Si=O$ bond is not readily accessible and the combinations with oxygen are generally polymeric. Phosphorus therefore can avoid the adoption of the higher coordination state whilst maintaining its electrovalence. In contrast to silicon, this results in a relative scarcity of neutral compounds which contain the six-coordinate phosphorus center. The chemical difference between phosphorus and silicon presents a synthetic challenge to explorers of each system. Nevertheless, neutral phosphorus compounds with a highly coordinatively saturated phosphorus center can be accessed in a number of different ways and a substantial body of literature has appeared on these systems in recent years in widely scattered sources. Contrasts of the reactivity behaviour of highly coordinated silicon and phosphorus in this context have been discussed very recently in some detail.[5]

There is also a growing realization that the highly coordinated phosphorus centers may play a more important role in reaction processes[5−7] involving organophosphorus chemistry than was previously recognized, although several early workers provided limited evidence that these high coordination states might be involved.[5] Of special interest to the subject of this review is the recognition that nucleophilic attack on pentacoordinate and pentavalent phosphorus could well involve a six-coordinate intermediate which would be similar to the stable species described herein.

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As the bulk of the chemistry surveyed herein derives from a foundation of pentavalent pentacoordinate phosphorus chemistry, it is also appropriate to note that this particular area has been extensively surveyed to 1980 in a comprehensive two-volume work by Holmes.[8] A large body of early work on the pentacoordinate phosphorus fluorine chemistry is described in a comprehensive review by Schmutzler.[9] Recent work on the chemistry of, in particular, the more highly coordinated organophosphorus derivatives, has been surveyed in a chapter by Burgada and Setton[10] in a multivolume treatise on organophosphorus chemistry.

Webster[11] has reviewed the literature to 1965 on the addition compounds of group V pentahalides. That review covered both adduct and ionized species of phosphorus(V) pentahalides. In 1987, Cherkasov and Polezhaeva[12] and more recently Markovskii et al.[13,14] have reviewed some aspects of their work on hexacoordinate phosphorus(V) chemistry. These reports will provide an additional guide to some aspects of the work described in the present review. The stereochemical and fluxional NMR behavior of five- and six-coordinate phosphorus compounds has also been reviewed providing more detailed analyses of the NMR properties of these and related compounds.[15] In this latter review the characteristic high-field ^{31}P NMR shift frequently used to identify these highly coordinated phosphorus centers is illustrated.

The objective of this review is to provide a comprehensive up-to-date survey of the chemistry of *neutral* six-coordinate phosphorus compounds. For the sake of brevity, we have omitted all separated ionic species. A representative selection of six-coordinated anionic species of phosphorus can be found in two review articles which list their NMR properties.[15,16] We have also omitted from our survey solid, metal-rich phosphide systems, some of which contain highly coordinated phosphorus centers.[17] In some cases six-coordinate phosphorus compounds have been written exclusively as zwitterionic species in which the hexacoordinate phosphorus(V) center is described as the anionic component of the molecule. Such compounds have been included in our survey as long as the overall molecular formula is that of a neutral molecule since in most cases it is easy to draw resonance forms which feature the neutral hexacoordinate phosphorus center. The present emphasis will be on the preparation of these compounds, their chemical reactivity and the physical techniques used to understand their structural and electronic nature. The first section deals with simple Lewis acid−base adducts. This is followed by sections describing chelating ligands grouped according to ring size and finally, in the latter sections, compounds formed utilizing multiple multidentate ligands. The literature surveys represented in this review have been completed to the end of 1995, and we have also searched the Cambridge crystal structure database for structural entries recorded to Feb 1996.

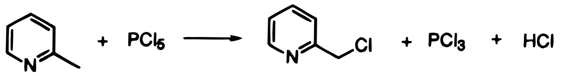
II. Hexacoordinate Phosphorus (V)

A. Lewis Acid−Base Adducts

The simplest route to a neutral six-coordinate phosphorus center is to use the Lewis acidity of the halogenophosphorus(V) compounds in combination with simple Lewis base donors. In most cases the donors are nitrogen or oxygen bases although several sulfur and a few phosphorus(III) donors have been used. A 1:1 pyridine adduct of pentachlorophosphorus(V) (**1**), PCl_5·py (**2**), was first proposed by both Holmes[18] and Gutmann[19] in 1954. Subsequently, Beattie and co-workers[20,21] isolated and analyzed (**2**) using vibrational spectroscopy. The 1:1 adduct ratio was determined by measuring the vapor pressure as a function of the amount of pyridine added in an evacuated system with solid **1**. The 1:1 ratio was then confirmed by a titration where the end point was indicated by the lack of further precipitation on addition of pyridine to a solution of **1** in CS_2.[20] The infrared and Raman spectra were recorded for **2** and also for $PCl_5{\cdot}C_5D_5N$ in the solid state.[21] A reasonable fit between calculated and experimental frequencies was demonstrated, and tentative assignments of some vibrational modes were made. Holmes and Gallagher[22] determined the heats of reaction of various adducts in nitrobenzene using calorimetry. The large heats of reaction ($\Delta H = 24.5-26.5$ kcal mol^{-1}) of these adducts coupled with cryoscopic and conductivity experiments, confirm that these species are essentially 1:1 molecular adducts which are undissociated in nitrobenzene. Introduction of fluorine substituents increases the electronegativity of the central phosphorus atom, which in turn increases its Lewis acidity. This is reflected in increased values for the heats of reaction ($\Delta H = 30-37$ kcal mol^{-1}) of these pentahalides with pyridine. Ultraviolet absorption spectra of various Lewis acid–base adducts were measured, and the results also support a molecular structure for **2**.[23] In contrast, Paul and co-workers reported univalent–univalent ionic solution behavior (22–25 cm^2 Ω^{-1} mol^{-1}) from conductivity measurements in nitrobenzene for the 1:1 products of **1** or PBr_5 with pyridine, β- and γ-picolines, quinoline, isoquinoline, and piperidine.[24] The corresponding infrared data also supported ion pairs of the type $[PX_4Base]X$, where X = Cl or Br and Base = nitrogen bases as above, *N*-methylacetamide, dimethylacetamide, and dimethylformamide[24,25] and suggested that the heavier halogens and/or bulkier donors do not support the six-coordinate center.

The reactivity of **2** with ammonium chloride has been reported by Lehr and Schwarz[26] in 1968 and by Zhivukhin and co-workers[27] in 1970. The reactivity of the species was expected to parallel the Lewis acidity of the phosphorus species, $[PCl_6]^- < \mathbf{2} < \mathbf{1} < [PCl_4]^+$. The former authors observed decreased reactivity of **2** with ammonium chloride in accord with a molecular structure, while the latter authors reported an increase in reactivity in accord with the ionic $[PCl_4{\cdot}py]Cl$ formulation. The discrepancies may be due to hydrolytic sensitivity.

Holmes and Gallagher[28] prepared and characterized $PCl_3F_2{\cdot}py$ and $PCl_4F{\cdot}py$ and these Lewis acid–base adducts were confirmed by ^{19}F NMR investigations. The spectra showed similar spin–spin coupling constants ($^1J_{PF}$) for both the phosphorane and the corresponding adduct, but the ^{19}F chemical shifts of these adducts were shifted upfield relative to the phosphorane as expected due to electron-pair donation from the nitrogen to the phosphorus atom, and thus the shifts provided evidence for compound formation. The ^{31}P NMR spectra of **2** have been reported separately by Wieker and co-workers,[29] Latscha,[30] and Dillon and co-workers.[31] Selected ^{31}P NMR data for the Lewis acid–base adducts, which form neutral six-coordinate phosphorus centers, are given in Table 1. The ^{31}P NMR chemical shift values reported by Wieker and co-workers[29] [−296 (solid) and −310 ppm (acetonitrile)] were subsequently attributed by Dillon and co-workers[31] to the hexachlorophosphate anion formed by partial hydrolysis. Latscha, Dillon, and co-workers reported ^{31}P NMR chemical shift values of −234[30] and −228 ppm,[31] respectively, for **2** measured in liquid pyridine. In addition, Dillon and co-workers analyzed the 1:1 adducts of **1** with a range of substituted pyridines and concluded that, in general, (i) the ^{31}P NMR chemical shift were almost independent of the basicity of the pyridine and (ii) the stability of the adduct is dominated by steric effects, which are more important than the electronic effects of the substituents. The former conclusion may be deduced directly from observation of the chemical shift values given in Table 1. The latter conclusion was demonstrated by the behavior of 2-halogenopyridine derivatives which were found to be sterically hindered resulting in an exchange process between the adduct and **1** and that the 2-bromopyridine derivative is relatively more extensively dissociated than the less basic 2-chloro and the 2-fluoro adducts. Methylpyridines were found to react to form either a 1:1 adduct or the chlorinated methyl product (eq 1). Again, the more sterically hindered 2-methylpyridine derivative showed rapid decomposition, while the 3-methylpyridine derivative decomposed more slowly.

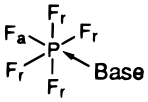


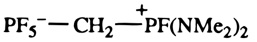
(1)

Ishley and Knachel[32] attempted to elucidate the addition compound of **1** with pyrazine, but they were unable to correlate their conflicting results to the nature of the product: analytical data supported a 1:1 stoichiometry, the cryoscopic molecular weight was within 2% of half the expected value of 288 based on the formula $PCl_5(C_4H_4N_2)$, conductance measurements suggested an ionic species, while variable-temperature NMR spectroscopy showed equivalent proton chemical shifts down to −100 °C. They speculated on the possibility of a metal-sandwich type structure utilizing the π system of pyrazine and the empty $d_{x^2-y^2}$ orbital of the phosphorus atom, but supporting evidence was inconclusive.

The Friedel–Crafts catalytic activity of various stannic and phosphoric fluorides (again due to their Lewis acidity) prompted Woolf[33] in 1956 to investigate the complex formation characteristic of these species. This led to the isolation of phosphorus pentafluoride adducts of various bases including pyridine and acetonitrile. Formulation as 1:1 adducts was based on weight increase measurements. A few years later, Muetterties and co-workers[34] demonstrated the octahedral nature of the phosphorus atom in $PF_5{\cdot}$base adducts by ^{19}F NMR spectroscopy in acetonitrile solution. The spectra showed the expected 1:4 intensity ratio of resonances corresponding to one axial (i.e., *trans* to the donor atom) and four radial (i.e., *cis* to the donor atom) fluorine atoms. The fine structure of the doublet of quintets for the axial and the doublet of doublets for the radial fluorine atoms were indicative of a geometry with C_{4v} symmetry. However, subsequent conductivity data and hydrolysis studies by Kolditz and Rehak[35] sug-

Table 1. NMR Data for Six Coordinate Phosphorus Lewis Acid−Base Adduct Centers[a]



compound	δ_P (ppm)	$^1J_{PF}$ (Hz)	ref
$PCl_5\cdot py$ (**2**)	−234 −228		30 31
$PCl_3F_2\cdot py$		983	28
$PCl_4F\cdot py$		1049	28
$PF_5\cdot CH_3CN$ (**3**)	−146	787 770	29 36
$PF_5\cdot py$ (**4**)		759(a), 788(r)	39
$PF_5\cdot N(CH_3)_3$		733(a), 838(r)	39
$PF_5\cdot 3\text{-}Me\text{-}py$		757(a), 791(r)	39
$PF_5\cdot 3,5\text{-}Me\text{-}py$		754(a), 789(r)	39
$PF_5\cdot MeNH_2$		759(a), 780(r)	41
$PF_5\cdot EtNH_2$		758(a), 785(r)	41
$PF_5\cdot Bu^tNH_2$		758(a), 802(r)	41
$PF_5\cdot NMe_2H$		752(a), 808(r)	42
$PF_5\cdot(\beta\text{-picoline})$	−145.5	761(a), 803(r)	84
$PF_5\cdot$(quinoline)	−141.1	751(a), 811(r)	84
$PF_5\cdot NH_3$ (**6**)	−146.5	753(a), 761(r)	43
$PF_5\cdot PMe_3$	−120[b]	784(a), 900(r)[b]	47
$PF_5\cdot N\text{-}SiMe_3$(pyrazole)	−143.4	758, 752	37
$PF_5\cdot N\text{-}SiMe_3$(5,6-dimethylbenzimidazole)	−141.6	750, 762	37
$PF_5\cdot PHMe_2$	−149[c]	783(a), 873(r)[c]	47
$PCl_5\cdot OPPh_3$	−297		51
$PCl_5\cdot OP(n\text{-}C_4H_9)_3$	−296		51
 $PF_5^{-}-CH_2-\overset{+}{P}F(NMe_2)_2$	−141	734(a), 809(r)	52
 $PF_5^{-}-NMe-\overset{+}{P}FNMeC(O)NMeC(O)NMe$	−145	734(a), 766(r)	53
$PCl_5\cdot 3\text{-}Me\text{-}py$	−228.0		31
$PCl_5\cdot py$	−228.0		31
$PCl_5\cdot 3\text{-}I\text{-}py$	−229.7		31
$PCl_5\cdot 3\text{-}F\text{-}py$	−229.3		31
$PCl_5\cdot 3\text{-}Br\text{-}py$	−228.3		31
$PCl_5\cdot 3\text{-}Cl\text{-}py$	−228.6		31
$PCl_5\cdot 4\text{-}CN\text{-}py$	−227.5		31
$PCl_5\cdot 3\text{-}CN\text{-}py$	−228.1		31
$PCl_5\cdot pyz$	−224.9		31
$PCl_5\cdot 3,5\text{-}Cl_2\text{-}py$	−222.7		31
$PCl_5\cdot 2\text{-}CN\text{-}py$	−170.8		31
$PCl_5\cdot 2\text{-}F\text{-}py$	−184.7		31

[a] *a* = axial (*trans* to the base donor), r = radial fluorine atoms. [b] $^1J_{PP}$ = (+)715, 720 Hz, $\delta_P{}^{III}$ = +24 ppm, sign of the coupling constant was determined for this compound.[47] [c] $^1J_{PP}$ = 714, 723 Hz, $\delta_P{}^{III}$ = +11 ppm.[47]

gested that $PF_5\cdot N{\equiv}CCH_3$ (**3**) undergoes significant autoionization (eq 2), which was in sharp contrast

$$\underset{(3)}{2PF_5\cdot NCCH_3} \rightleftharpoons [PF_4(NCCH_3)_2][PF_6] \quad (2)$$

to the observations of Muetterties and co-workers described above. In response, Tebbe and Muetterties[36] confirmed their earlier results using NMR techniques and found no significant autoionization of **3** in acetonitrile solution at concentrations through the range 3−12 M. They further ascribed the conductivity data observed by Kolditz and Rehak possibly being due to partial hydrolysis. In agreement, Wieker et al.[29] later reported the ^{31}P NMR spectra of an ca. 18% solution of PF_5 in acetonitrile as conclusive proof that the equilibrium (eq 2) lies far to the left. The observation of a sextet at −146 ppm confirmed a $PF_5\cdot N{\equiv}CCH_3$ species (**3**) as opposed to a PF_6^- anion. In later years the value of ^{31}P NMR data for the characterization of the coordination at phosphorus have become seminal.[15] The data for $PX_5\cdot$Base adducts[15−37] are assembled in Table 1.

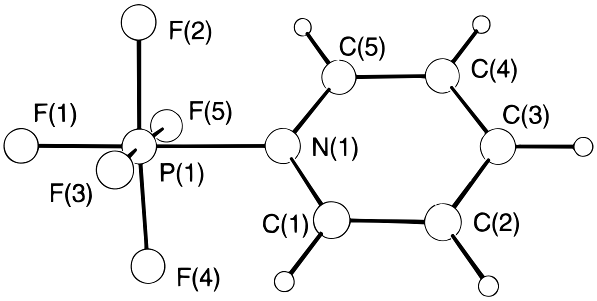


Figure 1. X-ray crystal structure of **4**[38] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.

In 1974, Sheldrick[38] reported the crystal structure of $PF_5\cdot py$ (**4**) (Figure 1) giving the first structural characterization of this type of molecule based on phosphorus(V). The molecule possesses octahedral geometry with the plane of the pyridine ring staggered at angles of 40.8° and 49.2° relative to the perpendicular F−P−F axes. Distortion from the most sterically favorable 45° was attributed to the great number of H···F interactions. The N−P coordinate bond [1.898 (4) Å] polarizes the electron density and hence reduces the length of the *trans* (axial)P−F bond [1.594(3) Å]. The mean value of the coplanar radial (*cis*) P−F bonds in this species was 1.607(1) Å. Many structures have now been analyzed for these six coordinate species and parametric details of selected bond lengths for the six-coordinate phosphorus center are given in Table 2.

The ^{19}F NMR spectra of $PF_5 \cdot B$ adducts, where B = trimethylamine, 3-methylpyridine, or 3,5-dimethylpyridine were analyzed, and the experimental data were correlated with computer simulations of the system.[39] It was concluded that these compounds could be interpreted as first-order AB_4X spin systems.

Formation of phosphorus pentafluoride monoalkylamine[40,41] and dialkylamine adducts[42] have been reported as have the adducts with other nitrogen heterocycles.[37] The reactions of alkylamines with phosphorus pentafluoride (**5**) frequently leads to the formation of more than one product, but the 1:1 adducts can often be separated from other products by sublimation. The adducts of **5** with aniline, 2,6-dimethylaniline, and *n*-propylamine were isolated as intermediates in an investigation of the reaction between **5** with various primary amines, some of which could not be isolated, presumably because the adducts were too sterically hindered for stability. The establishment of the adducts was based on infrared spectral data and the stoichiometry of the reaction system.[40] Methylamine reacts to form a 1:2 adduct, $PF_5 \cdot 2MeNH_2$, but upon dissolution, the fine structure in the NMR spectra indicated that the product contained only octahedral phosphorus atoms analogous to the ethylamine and *tert*-butylamine adducts.[41] Side or further reaction may occur when an excess of amine is used, thus forming the corresponding bis(alkylamino)trifluorophosphoranes (eq 3). Alternatively, the 1:1 adducts may also thermally decompose (eq 4). Dialkylamine adducts thermally decompose

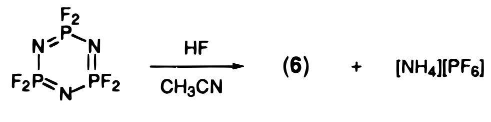
$$PF_5 + \textit{excess}\ RNH_2 \longrightarrow PF_5 \cdot \textit{n}RNH_2 \longrightarrow (RNH)_2PF_3 \quad (3)$$

$$2PF_5 \cdot RNH_2 \longrightarrow PF_4(RNH) + [RNH_3][PF_6] \quad (4)$$

via a similar scheme to form PF_4NR_2 and $[NR_2H_2][PF_6]$, salts where R = Me, Et, and *n*-Pr.[42]

The adduct $PF_5 \cdot NH_3$ (**6**) was synthesized by two methods in 8 and 41% yields, respectively (eqs 5 and 6)[43] although it might well be expected that this

$$PF_5 + NH_3 \longrightarrow \textbf{(6)} \quad (5)$$



(6)

reaction would readily lead to the formation of highly condensed species by means of HF elimination especially promoted by the presence of the strong base.

The simple ammonia adduct **6** was characterized by means of infrared spectroscopy, multinuclear NMR spectroscopy, and X-ray crystallography (Figure 2). Spin−spin coupling constant data reported included values for $^{14}N-H$ ($^{1}J_{^{14}NH}$ = 51.2 Hz), $^{14}N-P-F(\textit{cis})$ ($^{2}J_{^{14}NF}$ = 11.8 Hz) and $^{14}N-P$ ($^{1}J_{^{14}NP}$ = 31.5 Hz) interactions. The N−P coordinate bond [1.842 (2) Å] is slightly shorter than the corresponding bond in **4** and the P−F bond distance *trans* to the nitrogen shows a much reduced shortening *vs* the radial P−F bonds (which range from 1.589(1) to 1.600(1) Å (average 1.595 Å)) than is the case in **4**. The P−N bond length in **4** approaches the sum of univalent covalent radii for these elements (1.80 Å).[44]

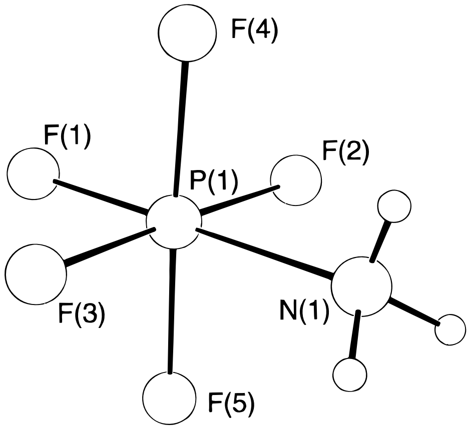


Figure 2. X-ray crystal structure of **6**[43] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.

Formation of Lewis acid−base adducts using organofluorophosphoranes was attempted by Muetterties and Mahler.[45] They concluded that the organic substituent (whether alkyl or aryl) causes sufficient reduction in acceptor strength of the Lewis acid that the complexes dissociate in solution.

Formation of a phosphorus(III)−phosphorus(V) dative bond was achieved by the addition of PF_5 to phosphines, $:PR_3$, where R_3 = Me_3, Me_2H, MeH_2, $Me_2(NMe_2)$, $Me(NMe_2)_2$, $(NMe_2)_3$, or n-Pr_3. On the basis of infrared and NMR spectroscopic evidence, Brown and co-workers[46] formulated these phosphorus pentafluoride−aminophosphine adducts based on exclusive coordination via a P−P dative bond, even though in these cases, the nitrogen atom may also serve as a potential donor site. These 1:1 adducts were found to be thermally unstable and, in particular, the stability decreased in the order $PF_5 \cdot PMe_3 > PF_5 \cdot PHMe_2 > PF_5 \cdot PH_2Me$.[47] Detailed NMR analysis of the P−P spin−spin coupling constants in such adducts was discussed by Schultz and Rudolph,[47] and clearly the large value of the directly bound P−P coupling constants supported the formulation as phosphine−P(V) adducts. The high-field shifts also supported the six-coordinated structure. No structural characterization of these simple adducts has yet been reported however this bond ($P^{III}-P^{V}$) has been characterized structurally in one related system (vide infra).

The addition reaction of dimethyl ether with PF_5 has been studied by means of pressure-composition isotherms at −78.5, −22.8, and 0 °C.[48] The profiles of the isotherms indicate a 1:1 addition product corresponding to $PF_5 \cdot OMe_2$. It was concluded that the experimentally determined heat of dissociation (25.4 kcal mol^{-1}) does not give a direct measure of

Table 2. Selected Bond Distances between P and Bound and Coordinating Donor Atoms in Some Neutral Six-Coordinate Phosphorus Compounds

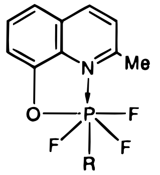
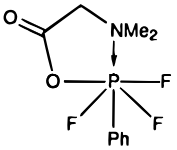
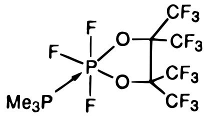
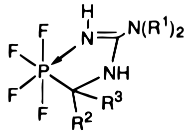
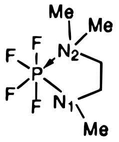
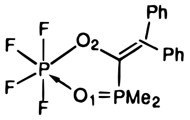
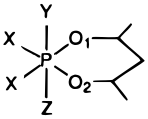
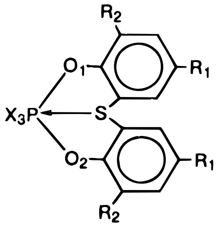
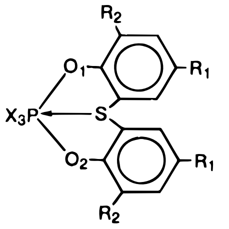
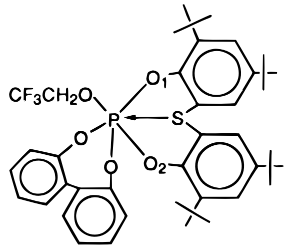
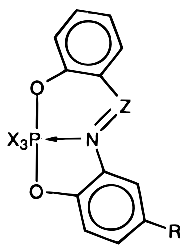
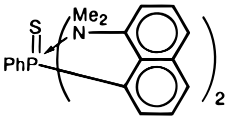
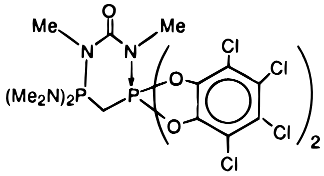
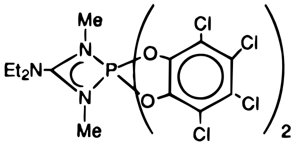
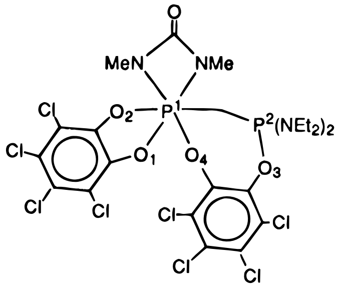
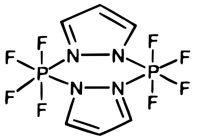
compound		bond	distance (Å)	ref
$PF_5 \cdot Py$	**4**	P←N	1.898(4)	38
$PF_5 \cdot NH_3$	**6**	P←N	1.842(2)	43
PF_5^-—NMe—$\overset{+}{P}$FNMeC(O)NMeC(O)NMe	**7**	P←N	1.826(5)	53
$Cl_4P[(NMe)_2CCl]$	**8**	P←N$_1$	1.91(4)	57
		P←N$_2$	1.85(6)	
$Cl_2(CF_3)_2P[(NR)_2CCl]$ R = cyclohexyl	**12c**	P←N$_1$	1.843(3)	65
		P←N$_2$	1.837(4)	
$CH_3(CF_3)_3P[O_2CN(CH_3)_2]$	**23a**	P−O$_1$	1.808(5)	76
		P−O$_2$	1.901(5)	
$F(CF_3)_3P[O_2CN(CH_3)_2]$	**23d**	P−O$_1$	1.832(3)	80
		P−O$_2$	1.778(3)	
$Cl_4P(NC_5H_4)NMe$	**24b**	P−N$_1$	1.845(4)	81
		P−N$_2$	1.763(4)	
	**25b** (R = F)	P−N	1.911(4)	82
		P−O	1.678(3)	
	25f (R = Ph)	P−N	1.980(3)	83
		P−O	1.689(3)	
	**27b**	P−N	1.013(4)	84
		P−O	1.706	
	**29**	P−O$_1$	1.673(8)	86
		P−O$_2$	1.697(7)	
		P−P	2.234(5)	
		P−F(*trans* to O)	1.577(7)	
		P−F (axial)	1.593(5)[a]	
	**30** ($R^1 = Et, R^2 = R^3 = Me$)	P−N	1.765(3)	88
		P−C	1.872(4)	
	31 ($R^1 = {}^iPr, R^2 = Me, R^3 = {}^iBu$)	P−N	1.772(3)	89
		P−C	1.898(4)	
	32 ($R^1 = {}^iPr, R^2 = Me, R^3 = Et$)	P−N	1.765(1)	90
		P−C	1.896(2)	
	**33**	P−F(axial)	1.633(1)	91
		P−F(rad, *trans* to N)	1.605	
		P−F(rad, *trans* to C)	1.630	
		P−N$_1$	1.717(1)	
		P−N$_2$	1.957(2)	
	**35**	P^V−O$_1$	1.732(2)	93
		P^V−O$_2$	1.685(2)	
		P(Me)−O$_1$	1.555(2)	
		P^V−F(axial)	1.59(1)(avg)	
		P^V−F(*trans* to O$_1$)	1.577(2)	
		P^V−F(*trans* to O$_2$)	1.593(2)	
	**39** (X = Y = Z = F)	P−O$_1$	1.720(4)	99
		P−O$_2$	1.717(4)	
	40b (X = F, Y = Z = CF$_3$)	P−O$_1$	1.745(5)	100
		P−O$_2$	1.741(5)	
	40c (X = Y = CF$_3$ Z = F)	P−O$_1$	1.746(1)	100
		P−O$_2$	1.752(1)	
	**42a** ($R_1 = R^2 = {}^tBu$, X = OPh)	P−S	2.640(2)	103
		P−O$_1$	1.676(3)	
		P−O$_2$	1.689(3)	
		P−OPh (avg)	1.64(2)	
	42c ($R_1 = Me, R^2 = {}^tBu$, X = OPh)	P−S	2.744(2)	103
		P−O$_1$	1.681(3)	
		P−O$_2$	1.673(2)	
		P−OPh (avg)	1.63(2)	
	42d ($R_1 = Me, R^2 = {}^tBu$, X = OPh)	P−S	2.363(2)	104
		P−O$_1$	1.698(5)	
		P−O$_2$	1.694(4)	
		P−OPh (avg)	1.64(3)	

Table 2 (Continued)

compound		bond	distance (Å)	ref
	**42e** ($R_1 = R^2$ = Me, X = OPh)	P−S	2.880(1)	103
		P−O$_1$	1.656(2)	
		P−O$_2$	1.680(1)	
		P−OPh (avg)	1.63(3)	
	42b ($R_1 = R^2 = {}^t$Bu, X = OCH_2CF_3 = ORf)	P−S	2.504(3)	101
		P−O$_1$	1.681(5)	
		P−O$_2$	1.684(6)	
		P−OR$_f$ (avg)	1.65(2)	
	42g ($R_1 = R_2 = {}^t$Bu, X = Cl)	P−S	2.3307(8)	108
		P−O$_1$	1.666(2)	
		P−O$_2$	1.662(2)	
		P−Cl(*trans* S)	2.0635(9)	
		P−Cl(*cis* S,avg)	2.147(2)	
	**61a** ($R_f = CH_2CF_3$)	P−S	2.373(5)	102
		P−O$_1$	1.699(8)	
		P−O$_2$	1.711(8)	
		P−OAr (avg)	1.65(2)	
		P−OR$_f$	1.655(8)	
	**43c** (X = Cl, Z = CH, R = ^{t}Bu)	P−N	1.867(9) (avg)[b]	108
		P−O$_1$	1.650(3)	
		P−O$_2$	1.669(3)	
		P−Cl (*trans* N)	2.085(5) (avg)[b]	
		P−Cl (*cis* N)	2.15(6) (avg)[b]	
	44a (X = F, Z = N, R = H)	P−N	1.88(1), 1.95(1)[c]	108
		P−O$_1$	1.653(3)	
		P−O$_2$	1.656(2)	
		P−F(*trans* N)	1.558(2)	
		P−F(*cis*,avg)	1.592(2)	
	**70**	P−S	1.957	126
		P−N (avg)	3.01	
		P−C (avg)	1.87	
	**73**	P−N	1.804(2)	127
		P−O (avg)	1.74	
	**75**	P−N[d]	1.788(3)[d]	128
		P−O (avg)	1.71	
	**77**	P^1−N(avg)	1.75	128
		P^1−O$_1$	1.728(5)	
		P^1−O$_2$	1.797(4)	
		P^1−O$_4$	1.729(5)	
	**81**	P−N(avg)	1.837(5)	37
		P−F(radial)(avg)	1.58(1)	
		P−F(axial)(avg)	1.58(2)	

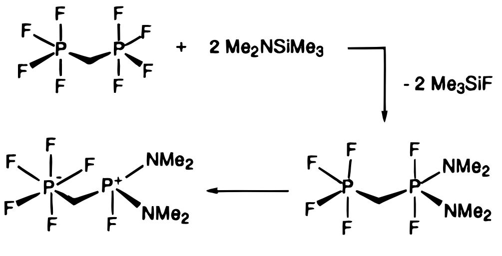
[a] Crystallographically equivalent atoms. [b] Three independent molecules in unit cell. [c] Nitrogen positions disordered. [d] Crystallographically equivalent nitrogens.

the O−P bond strength since no account was taken of the crystal lattice energy of the solid addition compound. Other ethereal adducts including diethyl, di-*n*-propyl, diisopropyl, di-*n*-butyl, dimethylthio, diethylthio, and dimethylseleno ether have also been reported.[49,50] Equimolar adduct compositions were established by quantitative syntheses and tensimetric titrations. Some of the adducts could only be isolated at low temperatures. Heats of dissociation were measured and an order of stability was established:

$$PF_5{\cdot}OMe_2 \sim PF_5{\cdot}SMe_2 > PF_5{\cdot}SeMe_2$$

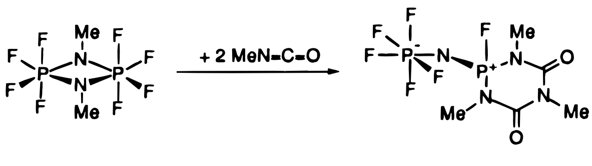
Reactions of PCl_5 with triphenylphosphine oxide and tri-*n*-butylphosphine oxide produced compounds identified as Cl_5POPPh_3 and $Cl_5POP(n\text{-}Bu)_3$, respectively.[51] Although the ^{31}P NMR chemical shifts were reported, it must be noted that no $^2J_{PP}$ coupling was observed, and that the chemical shift values (ca. −296 ppm) for the six-coordinate species is similar to that reported for the PCl_6^- anion.

Cowley and Lee[52] reported the reaction between $F_4PCH_2PF_4$ and Me_2NSiMe_3 with the expectation of producing $Me_2NPF_3CH_2PF_3NMe_2$. However, the reaction yielded the zwitterionic compound $F_5P^-{-}CH_2{-}{}^+PF(NMe_2)_2$. This zwitterion, characterized by multinuclear and variable-temperature NMR spectroscopy, may be formed as a result of an intramolecular fluoride ion transfer from an intermediate $F_4PCH_2PF_2(NMe_2)_2$ species (eq 7), but it is by no means clear why the substitution of F by NR_2 favors one of two phosphorus atoms. No $^2J_{PCP}$ coupling was observed, but this value could be expected to be small in compounds bridged by CH_2.



(7)

Recently, Schmutzler and co-workers[53] reported a related zwitterionic hexacoordinate phosphorus compound (**7**) formed by the reaction of $(MeNPF_3)_2$ with two equivalents of MeN=C=O (eq 8).



(8)

This compound contains two differently coordinated (λ^4, λ^6) phosphorus centers and was formulated as the zwitterion shown in Figure 4. In this case a substantial $^2J_{PNP}$ coupling constant was observed which verifies the diphosphorus composition. The X-ray structural analysis of **7** (Figure 3) showed two independent molecules in the crystal corresponding to distinct *cis* and *trans* isomers. [The dihedral angles of F(1)−P(1)−N(4)−P(2) and F(1′)−P(1′)−N(4′)−P(2′) are 174.8 and 5.8°, respectively]. The short P(1)−N(4) bond distance [1.584 (5) Å] compared with the longer P(2)−N(4) bond distance [1.826 (5) Å] would suggest considerable P(1)−N(4) double bond character represented by the neutral resonance structure of the molecule (Figure 4).[44]

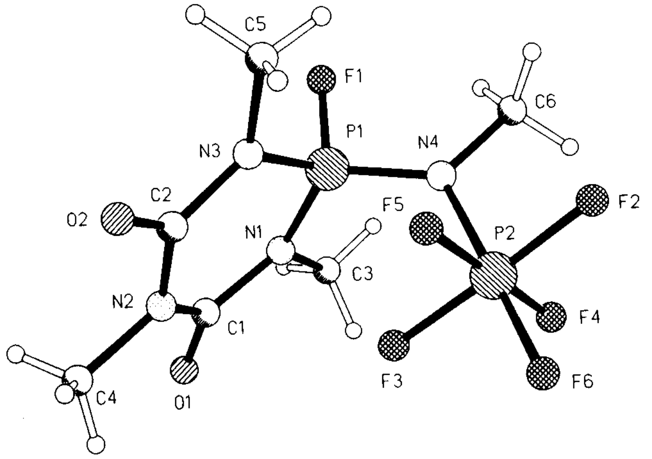
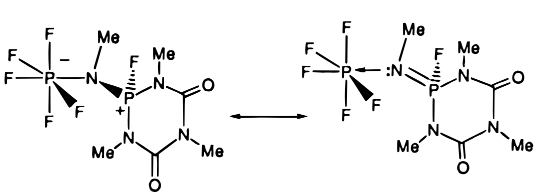


Figure 3. X-ray crystal structure of **7**.[53] Reproduced with permission of the original authors and the journal.



(7)

Figure 4. Zwitterionic and neutral resonance forms of **7**.

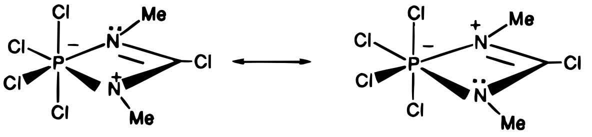
B. Monocyclic Derivatives (One Bidentate Chelate)

1. Chelates Forming Four-Membered Rings

In 1968, Latscha and Hormuth[54] reported that the reaction between **1** and *N,N*-dimethylurea gave the six-coordinate phosphorus compound, $PCl_4[(NMe)_2CCl]$ (**8**), based on ^1H, ^{31}P NMR, and infrared spectroscopic evidence. Selected ^{31}P NMR data for related monocyclic derivatives are given in Table 3. The same product was obtained from reaction of $PCl_3[(NMe)_2C{=}O]$ (**9**) with $MeN{=}CCl_2$ via elimination of MeN=C=O (eq 9)[55] and from reaction of (**9**) and (**1**) via elimination of $O{=}PCl_3$ (eq 10).[56] Ziegler and Weiss[57] confirmed the approximate octahedral six-coordinate geometry around the phosphorus(V) center by X-ray crystallography (see Table 2). The four-membered chelate ring was described as planar with an averaged resonance structure derived from $P{-}N^+$ mesomeric forms (Figure 5). However, the diffraction

$$\textbf{(9)} + MeN{=}CCl_2 \longrightarrow \textbf{(8)} + MeN{=}C{=}O \qquad (9)$$

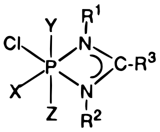
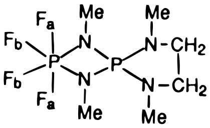
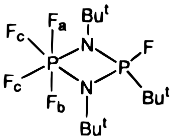
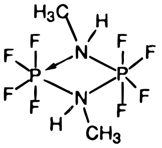
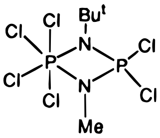
$$\textbf{(9)} + PCl_5 \longrightarrow \textbf{(8)} + O{=}PCl_3 \qquad (10)$$



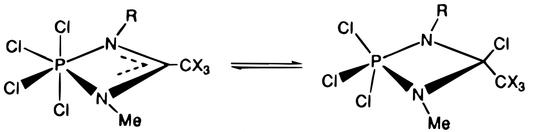
(8)

Figure 5. Mesomeric forms of **8**.

Table 3. NMR Data for Neutral Six-Coordinate Monocyclic Phosphorus Derivatives with Four-Membered Rings

compd		δ_P (ppm)[a]	$^{\phi}F$ ppm	$^nJ_{PF}$ (Hz)	ref
	**8** (X = Y= Z = Cl, $R^1 = R^2$ = Me, R^3 = Cl)	−202			54
	10a (X = Y= Z = Cl, R = Me, $R^3 = CCl_3$)	−193			58
	10b (X = Y= Z = Cl, R = Me, $R^3 = CF_3$)	−199			58
	10c (X = Y = Z = Cl, R = Et, $R^3 = CF_3$)	−197			58
	10a (X = Y= Z = Cl, R = ^{i}Pr, $R^3 = CF_3$)	−195			58
	11 (X = Y = Z = Cl, $R^1 = R^2$ = Me, R^3 = Ph)	−192			63
	12a (R^3 = Cl, $R^1 = R^2$ = cyhxyl, X = Y = Z = Cl)	−204.7			65
	12b (R^3 = Cl, $R^1 = R^2$ = cyhxyl, X = Z = Cl, Y = CF_3)	−181.7	−68.7	134.0 ($n = 2$)	65
	12c (R^3 = Cl, $R^1 = R^2$ = cyhxyl, X = Cl; Y = Z = CF_3)	−155.8	−66.8	170.5 ($n = 2$)	65
	12d (R^3 = Cl, $R^1 = R^2$ = cyhxyl, X = Y = Z = CF_3)	−154.9	−64.5[2], −58.7[1]	128.4(ax), 82.1(rad), ($n = 2$)	65
	12e (R^3 = Cl, $R^1 = R^2$ = ^{i}Pr, X = Y = Z = Cl)	−205.2		134.0 ($n = 2$)	
	12f (R^3 = Cl, $R^1 = R^2$ = ^{i}Pr, X = Z = Cl, Y = CF_3)	−181.8	−69.1	171.6 ($n = 2$)	65
	12g (R^3 = Cl, $R^1 = R^2$ = ^{i}Pr, X = Cl Y = Z = CF_3)	−155.7	−67.4	82.9(rad), 128.4(ax), ($n = 2$)	65
	12h (R^3 = Cl, $R^1 = R^2$ = ^{i}Pr, X = Y = Z = CF_3)	−155.3	−64.8[2], −59.0[1]		65
	12i (R^3 = Ph, $R^1 = R^2$ = ^{i}Pr, X = Y = Z = Cl)	−205.6			65
	**14**	−152		744(a), 789(b), ($n = 1$)	71
	**15**	−139		771(a), 843(b), 822(c), (n=1)	71
	**20**	−155			73
	**22**	−216			75

[a] Six-coordinate P center only.

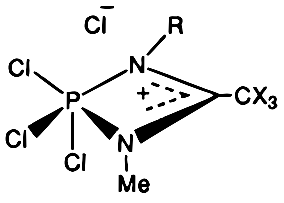


(10)

Figure 6. Halogen tautomers of **10** due to intramolecular chlorine atom migration.

intensities were obtained from film data and the final *R* value was not particularly good, so bond lengths derived from this study are not reliable.

Kal'chenko and co-workers[13,58,59] analyzed the isomerization of similar six-coordinate compounds, $PCl_4[(NR)_2CCX_3]$ (**10**), in which intramolecular chlorine atom migration occurs to give the five-coordinate phosphorus(V) derivatives, $PCl_3[(NR)_2CCX_3(Cl)]$, where X = Cl or F, R pairs are Me and Me, Me and Et, Me and *i*-Pr, or Me and *t*-Bu (Figure 6). Dynamic multinuclear (^1H, ^{13}C, and ^{31}P) NMR studies were used to follow the shift in equilibrium between the two isomers. Also the tetrachloroamidinate systems, $PCl_4(NMe)_2CX$ (X = CCl_3)[60] and (X = Ph, CCl_3, and CF_3)[61] were investigated with ^{35}Cl NQR spectroscopy. The ^{31}P NMR parameters for the six-coordinate species identified in this study are given in Table 3. It was found that rearrangement to the five-coordinate phosphorus isomer was favored by a rise in temperature, a decrease in the polarity of the solvent, a rise in electronegativity of the trihalomethyl group ($CF_3 > CCl_3$), and an increase in the size of the alkyl substituent on the nitrogen atom (Me < *i*-Pr < Et < *t*-Bu). A discrepancy in the behavior of the *N*-isopropyl derivative was attributed to the competing electronic effects. In the solid state, however, NQR evidence suggested that rapid cooling of $Cl_4P(NMe)_2CCl_3$ led to the five-coordinate isomer which then reverted to the six-coordinate form (which according to other evidence seems to be the predominant isomer in the solid state) upon warming above 77 K.[60] A more general study showed the presence of both isomeric forms in the solid and that chlorotropism can occur in the solid state.[61] The IR data suggested that $PCl_4(NMe)_2CCCl_3$ is stable in the solid state without signs of chlorotropism but that the process occurs in solution, shifting to the predominance of the six-coordinate form as the polarity of the solvent increases.[62] A mechanism for the isomerism was proposed based on the migration of an axial chlorine atom to form a contact ion pair in the transition state and the phosphorus adopts first a square-pyramidal geometry which is then easily rearranged to the final trigonal-bipyramidal configuration (Figure 7).[13,14] Aspects of this amidine chemistry[13] and the more

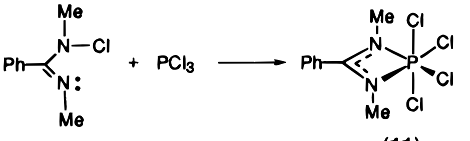


(10)

Figure 7. Proposed contact ion pair intermediate for axial chlorine atom migration mechanism in **10**.

general coordination isomerism behavior of phosphorus compounds[14] have been reviewed.

Kal'chenko and co-workers[63,64] also synthesized $PCl_4[(NMe)_2CPh]$ (**11**) by an oxidative addition reaction of *N*-chloro-*N*,*N*′-dimethylbenzamidine and phosphorus(III) trichloride (eq 11). Introduction of organic substituents on the phosphorus(V) atom in place of chlorine atoms was attempted using organochlorophosphines. In some cases also, especially when the required *N*-chloroamidine was inaccessible, the silylated amidine was used (eq 12). Intramolecular chlorine migration was again observed, and the equilibria between the five- and six-coordinate halogen tautomers were correlated with steric and electronic effects of the different organic substituents. NMR parameters for the six-coordinate species are also given in Table 3. In general in this system, it was found that organic substituents (Ph or CCl_3) directly attached to the phosphorus(V) center destablized the six-coordinate tautomer, probably as a consequence of the reduced negative charge delocalization on the phosphorus atom. A related species in which two of the X groups are replaced by an alkane diol are discussed in section C.2 (see eq 45).



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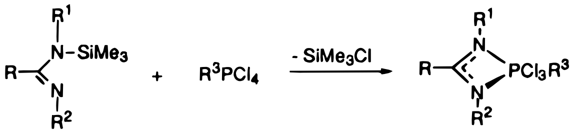
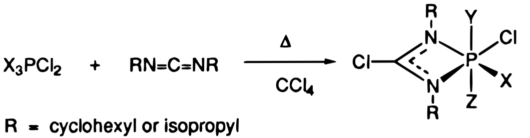


(12)

Cavell and co-workers[65,66] reported the synthesis of compounds of the type: $Cl_{4-n}(CF_3)_nP[(NR)_2CCl]$, where $n = 1-3$, R = cyclohexyl or isopropyl (Table 3) by means of an apparent carbodiimide insertion into a P–Cl bond of a five-coordinate phosphorane (eq 13).



R = cyclohexyl or isopropyl
X, Y, Z = Cl or CF_3

(12)

(13)

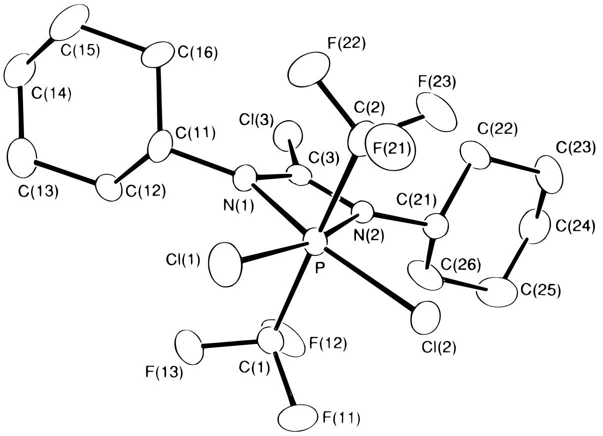


Figure 8. X-ray crystal structure of $Cl_2(CF_3)_2P[(NR)_2CCl]$ (**12c**),[65] where R = cyclohexyl. Reproduced with permission.

The compounds were analyzed by multinuclear (^1H, ^{19}F, and ^{31}P) NMR and infrared spectroscopy. In addition, the X-ray crystal structure of $Cl_2(CF_3)_2P[(NR)_2CCl]$ (**12c**),[65] where R = cyclohexyl, was determined (Figure 8). The compound displayed trans-axial trifluoromethyl groups as would be expected on the basis of the steric constraints. The phosphorus(V) atom is distorted considerably from the ideal octahedral arrangement with a N–P–N angle of 70.7° imposed by the formation of the strained four-membered ring. However, the phosphorus atom lies in the plane formed by the diimide ligand and the two halogens on P. The compounds were found to be generally unreactive except towards water and to nucleophilic substitution at the ring carbon atom (e.g., eqs 14 and 15, respectively). Only one or two

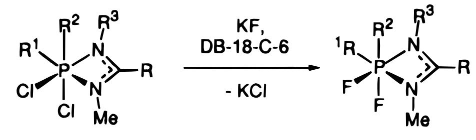
$$Cl_4P[(NR)_2CCl] + H_2O \longrightarrow Cl_2P{=}O[(NR)_2CCl] + 2\,HCl \qquad (14)$$

$$Cl_4P[(NR)_2CCl] + BuLi \longrightarrow Cl_4P[(NR)_2]CPh] + LiCl \qquad (15)$$

where R = isopropyl

of the chlorine atoms were substituted by fluorine atoms under vigorous conditions by metathesis reaction with AgF. Reaction with other fluorinating agents such as NaF gave PF_6^- species.

Kal'chenko and co-workers[67] reported the general conversion of **10** to the tetrafluoro analogues (**13a–e,i**), (Table 4) by fluorination with antimony trifluoride; however, the byproduct, antimony trichloride, was often difficult to separate. Alternatively potassium fluoride in the presence of dibenzo-18-crown-6 also achieved the transformation depicted in eq 16 after 2–3 h reflux in acetonitrile. A large variety of tetrafluorophosphorates (a term used by the Kiev group to describe this type of compound) was prepared, and their dynamic behavior studied. Unlike the tetrachloro analogues, these tetrafluorophosphorates showed no tautomerism due to intramolecular halogen migration, and thus the phosphorus center remains exclusively six-coordinate. When one of the fluorine atoms is replaced by a phenyl group, (**13f,j,k**), the phosphorus center becomes less electrophilic (acidic in the Lewis sense) and hexacoordination is destabilized. Thus, benzamidinium trifluorophenylphosphorate (**13f**) showed a typical



R = CCl_3, CF_3; R³ = Me, Et, *i*-Pr, *t*-Bu **(13)**

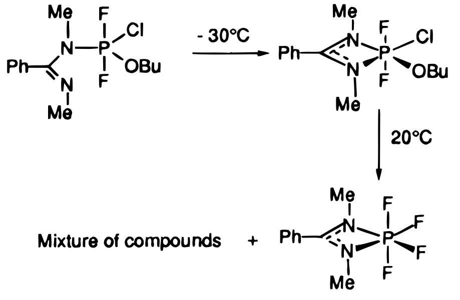
(16)

Table 4. NMR Parameters for *N,N′*-Dialkylamidinium Fluorophosphorates (13)

compd	R	Alk	R^1	R^2	δ_P, ppm	$^1J_{FP}$, Hz	ref
13a	CF_3	CH_3	F	F	−137.4	842, 850	67
13b	CF_3	C_2H_5	F	F	−146.8	850[a]	67
13c	CF_3	*i*-C_3H_7	F	F	−142.6	856[a]	67
13d	CF_3	*t*-C_4H_9	F	F	−147.5	858, 851, 889	67
13e	CCl_3	CH_3	F	F	−141.7	830, 852	67
13f	C_6H_5	CH_3	F	C_6H_5	−123.6	847, 894	67
13g	C_6H_5	CH_3	*o*-$C_6H_4O_2$		−116.3	801, 871	67
13h	CCl_3	CH_3	*o*-$C_6H_4O_2$		−120.9	808, 876	68
13i	C_6H_5	CH_3	F	F	−137.0	816.0, 836.0	68
13j	CF_3	CH_3	F	C_6H_5	−57.3[b,c]	883	67
13k	CCl_3	CH_3	F	C_6H_5	−58.0[b,c]	884	67

[a] Mean value of $^1J_{FP}$. [b] The spectrum was determined at 150 °C. [c] Value typical of five-coordinate phosphorus.

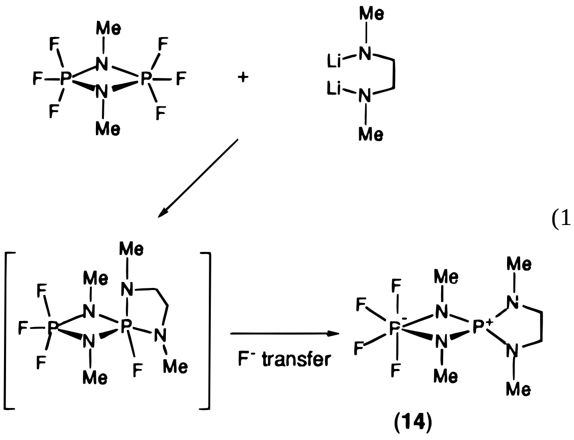
hexacoordinate ^{31}P NMR chemical shift (δ, −123.6 ppm), while the 2,2,2-trihaloacetamidino analogues (**13j**,**k**) showed ^{31}P NMR resonances in the range δ −57 to −58 ppm, typical of pentacoordination. The ^{31}P NMR parameters for the six-coordinate members of the system are given in Table 4. Dynamic ^1H and ^{31}P NMR spectroscopy was used to study the factors determining the configurational stability of this set of six-coordinate amidinium fluorophosphorates and to probe the mechanism of permutational isomerization. It was shown that the isomerism occurs by an irregular mechanism with the breaking of a P−N bond to form a five-coordinate intermediate.[68,69] The thermal stability of similar hexacoordinate phosphorus(V) compounds were also analyzed (eq 17).[70]



(17)

Disproportionation was observed after several days at 20 °C. The complex mixture of compounds produced was unidentified.

Formation of a P_2N_2 ring system can be considered as a phosphorus chelated to a −NPN− ligand. The overall neutrality of a six-coordinate phosphorus(V) atom was achieved by the formation of zwitterionic compounds (**14**, **15**; e.g., eqs 18 and 19)[71] derived from pentacoordinate phosphazenes by means of F^- transfer not unlike that suggested by Cowley and Lee[52] for the carbon-bridged zwitterionic compound $F_5PCH_2P(F)(NMe_2)_2$ (vide supra section II.A, and eq 7). The formulations for the proposed structures were based on a detailed multinuclear NMR study. Note also that, as for **7**, a $^2J_{PP}$ coupling constant was observed for both **14** and **15**, verifying the diphosphorus constitution of the compound.



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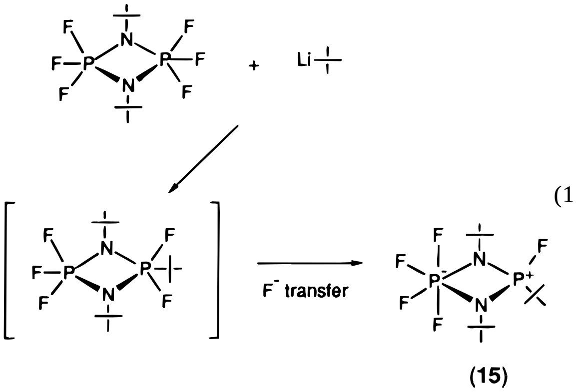


(19)

Utvary and co-workers have described the oligomerization,[72] the reactivity toward hydrogen fluoride,[73] and substituted hydrazine derivatives[74] of $(MeNPF_3)_2$ (**16**), all of which yield neutral six-coordinate phosphorus(V) compounds. Heating **16** at 130 °C in a bomb for several days gave a crystalline product, $(MeNPF_3)_4$ (**17**), which was isolated by solvent extraction.[72] The residue, $[(MeN)_4P_3F_6]^+[PF_6]^-$ (**18**), sublimed under high vacuum and eliminated PF_5 to leave $(MeN)_4P_3F_7$ (**19**). The reaction scheme (eq 20) shows the proposed mechanism for the thermal decomposition of **17** to **18** and a subsequent equilibrium with **19**. The structural assignments were based on multinuclear NMR and infrared spectroscopy, molecular weight determinations, mass spectrometry, and elemental analysis.

Reaction of **16** with dry hydrogen fluoride in chloroform yielded two products identified as $(MeNHPF_4)_2$ **20**, (Figure 9) and $[MeNH_3][PF_6]$. NMR and mass spectra are consistent with the proposed structure for **20**. The ionic species, $[MeNH_3][PF_6]$, was formed as a result of further hydrofluorination of **20**. Reaction of **16** with substituted hydrazines led to zwitterionic compounds in which the positive charge was described as being located on the more electron rich-nitrogen atom of the hydrazine substituent (eq 21).

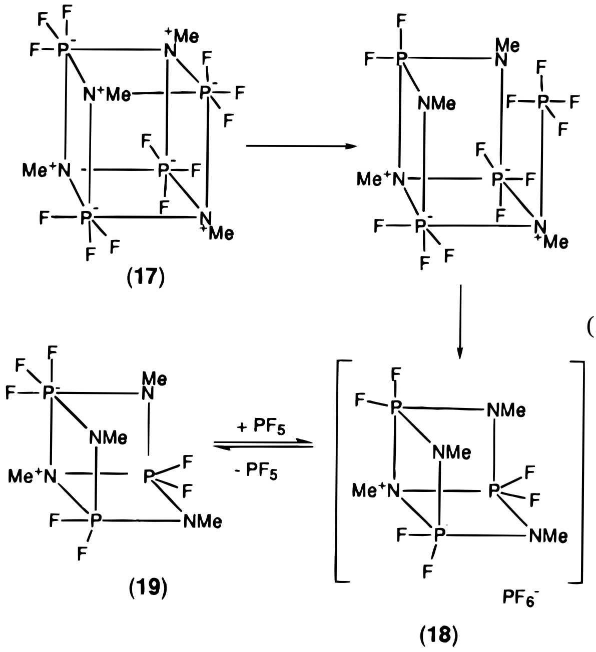
Similar chloro analogues of these P_2N_2 ring systems (**22**) have also been desribed,[75] but unlike the compounds described above by Schmutzler and co-

Table 5. NMR Spectral Parameters for Trifluoromethyl- and Fluoro(carbamato)phosphorus(V) Derivatives (23a−g)

compound	substituents on P	substituents on Carbamate	$\delta(^{31}P)^{a}$	$^{1}J_{PF}$ (Hz)	$\phi(CF_3)$	$\phi(F)$	$^{2}J_{PCF}$ (Hz)	ref
23a	$(CF_3)_3$, CH_3	O,O	−139		−64.6[2],[b] −63.7[1]		95.5[2], 70.9[1]	77
23b	$(CF_3)_3$, CH_3	O,S I[c]	−149		−61.6[2], −62.0[1]		95[2], 67[1]	77
		O, S II[c]	−158		−65.8[2], −65.8[1]		97[2], 74[1]	
23c	$(CF_3)_3$, CH_3	S,S	−186		−65.1[2], −62.5[1]		98[2], 67[1]	77
23d[d]	F_3, CF_3	O,O	−145.0[g]	654.0[2] (r)[b,d] 830.7[1] (a)	−69.7 (a)	−85.1[2] (r)[b,d] −58.9[1] (a)	145.0 (a)	80
23e[e]	F_3, CF_3	O,O	−133.9[g]	936.3[1] (r)[b,e] 921.5[2] (a)	−70.4 (r)	−84.0[1] (r)[b,e] −59.6[2] (a)	155.6 (r)	80
23f[f]	F_2, $(CF_3)_2$	O,O	−146.0[h]	1057.2 (r)	−70.0	−90.9 (r)	164.3 (a)	80
23g[f]	F, $(CF_3)_3$	O,O	−148.5[i]	997.4 (r)	−68.8[2](a) −69.1[1](r)	−103.7 (r)	141.5 (a) 97.5 (r)	80 80

[a] All values quoted relative to 85% H_3PO_4, some are converted from the reference used (P_4O_6) in the original work. Also all values herein are expressed as negative values indicating resonance to high field of the standard in contrast to the reverse convention used in earlier work. [b] Numbers in brackets indicate relative intensity; r = radial, a = axial (i.e., perpendicular to the plane of the bidentate ligand). [c] The spectra indicate that there are two compounds present which were attributed to two isomeric forms, one with S *trans* to CH_3 and the other with O *trans* to CH_3. The particular isomeric species **I** (33%) and **II** (66%) could not be correlated with a specific isomeric structure, so it is not known which is the more plentiful structure. [d] Isomer **B** in which one CF_3 and one F lie coplanar with the carbamate ligand; relative proportion 2. [e] Isomer **A** in which two F lie coplanar with the carbamate ligand, relative proportion 1. [f] Only one conformation observed. [g] 20 °C. [h] 32 °C. [i] 50 °C.

workers,[71] no *tert*-butyl groups are directly attached to the phosphorus atom (eq 22), rather the *tert*-butyl groups are on the 74 nitrogen.



(17)

(19)

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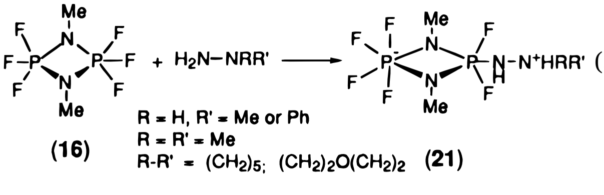
(20)



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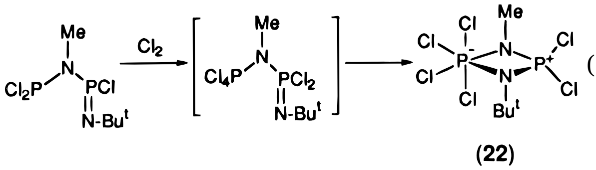

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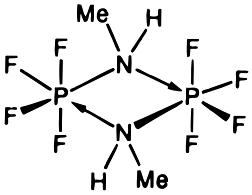


(20)

Figure 9. Proposed structure of **20**.

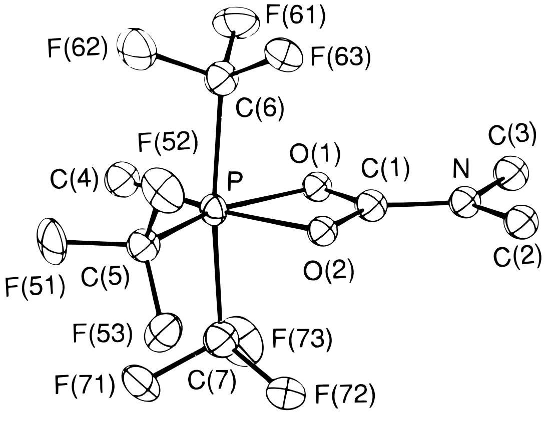


Figure 10. X-ray crystal structure of **23a**.[76,77] Reproduced with permission.

The aminophosphorane, $Me(CF_3)_3PNMe_2$, was reported by Cavell and co-workers[76,77] to undergo apparent insertion reactions with CO_2, COS, or CS_2 to form a six-coordinate chelated carbamato, monothiocarbamato, and dithiocarbamato complexes (Table 5) respectively, e.g., $Me(CF_3)_3P[O_2CNMe_2]$ (**23a**, Figure 10).[76,77]

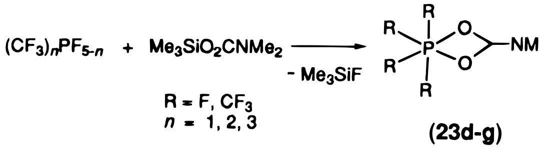
The molecular structure shows an octahedrally coordinated phosphorus(V) atom. The crystallographic parameters indicated little steric hindrance caused by adjacent CF_3 groups. ^{19}F and ^{31}P NMR spectra (parameters are given in Table 5) showed two isomers in the monothiocarbamato complex, $Me(CF_3)_3P[S(O)CNMe_2]$ (**23b**), corresponding to the geometrical isomers with *cis*- and *trans*-Me−P−S bonds. For the dithiocarbamato and the *cis*- and *trans*-monothiocarbamato analogues, the exchange process between axial and equatorial CF_3 groups was slow on the NMR timescale at +33 °C such that the two different ^{19}F resonances were observed. However, in

Table 6. NMR Parameters (Hz) for Compounds 24

X, Y	E	no.	$\sigma(^{31}P)^a$	$^1J_{PF(ax)}$	$^1J_{PF}(rad), ^1J'_{PF(rad)}$	ref
F_4	NMe	**24a**	−132.4	827	838, 862	81
Cl_4	NMe	**24b**	−195.7			81
$(CF_3)_3$, Cl	NMe	**24c**	−152.2			81
F_4	O	**24d**	−131.3	855 avg		81
Cl_4	O	**24e**	−184.5			81
F_4	S	**24f**	−136.4	968	747, 1002	81
F_4	N−Py	**24g**	-135.3^b	835	829, 864	81
Cl_4	N−Py	**24h**	−202.2			81

[a] Relative to 85% H_3PO_4. [b] Doublet of doublet of triplets.

23a the averaged resonances were only separated at −45 °C. Line shape analysis for **23a** gave the energy barrier of the CF_3 rearrangement process ($\Delta G^{\ddagger}_{98}$ = 13.5 ± 0.7 kcal) which was found to be independent of solvent and concentration.[78] Further studies indicated that the mechanism of formation involved formation of the carbamate in solution from amine and CX_2, and thus carbamate displaced the amino group to form the carbamato complex.[78] Using the independently synthesized (trimethylsilyl)carbamate gave a generally applicable route to analogous compounds with mixed trifluoromethyl and fluoro substituents, $F_{4-n}(CF_3)_nP[O_2CNMe_2]$ (**23d**−**g**), where n = 1−3, were prepared by reaction of the appropriate (trifluoromethyl)fluorophosphorane (eq 23).[79,80]

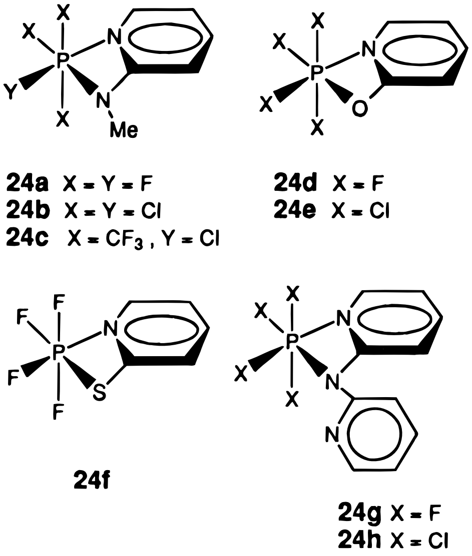


(23)

(23d-g)

All three of these CF_3 derivatives could form two or more possible geometrical isomers depending on the position of the trifluoromethyl and fluoro substituents. The compounds were readily identified by their ^{19}F and ^{31}P NMR spectra (data are given in Table 5) which displayed characteristic six-coordinate phosphorus(V) chemical shifts and first-order P−F spin−spin couplings. In general, there is a preference for axial CF_3 occupation where possible but solutions of $F_3(CF_3)P[O_2CNMe_2]$ (**23d**,**e**) showed both isomers corresponding to axial and equatorial CF_3 occupation with an axial:equatorial isomer ratio of ca. 2:1.[79,80]

Similar compounds forming asymmetric four membered chelate rings derived from ortho-substituted pyridines were reported (**24**, Figure 11).[66,81] The ^{31}P NMR parameters are given in Table 6. The compounds were synthesized, in general, by reaction of PF_5, PCl_5, or $(CF_3)_3PCl_2$ with the appropriate trimethylsilylated ligand with the elimination of trimethylsilyl halide. In a few instances elimination of HX from the parent alcohol, thiol, or amine can be employed, but this route is usually complicated by side reactions introduced by the liberated HX. The asymmetry of the ligands was reflected in the analysis of the *trans* influence of the compounds in the solid state by X-ray crystallography and in solution by NMR. The structure of {2-(methylamino)pyridinato}tetrachlorophosphorus (**24b**, Figure 12)[81] displays differing *trans* influences from the two nitrogen atoms; the shorter P−Cl(3) bond [2.077(2) Å] is *trans* to the heterocyclic ring donor nitrogen atom N(1), and the longer P−Cl(4) bond distance [2.103(2) Å] is *trans* to the σ-bound N(2) amine nitrogen atom. Another example is shown in the ^{31}P NMR of (2-mercaptopyridinato)tetrafluorophosphorus (**24f**, Figure 13),[81] where three different $^1J_{PF}$ couplings were identified corresponding to the two equivalent axial and two different equatorial fluorine atoms.



24a X = Y = F
24b X = Y = Cl
24c X = CF₃, Y = Cl
24d X = F
24e X = Cl
24f
24g X = F
24h X = Cl

Figure 11. Structures of heteroatom pyridine six-coordinate phosphorus(V) compounds (**24**).[81]

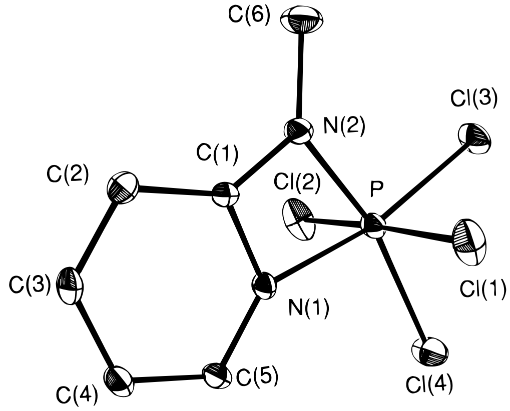


Figure 12. X-ray crystal structure of {2-(methylamino)pyridinato}tetrachlorophosphorus (**24b**).[81] Reproduced with permission.

2. Chelates Forming Five-Membered Rings

Schmutzler and co-workers[82] have utilized the oxinate ligand to provide a number of examples of neutral six-coordinate phosphorus(V) compounds formed with a monobasic five-membered ON chelate. The NMR parameters are given in Table 7. The reactions were carried out in sealed tubes under vacuum and in the absence of solvents (eq 24). The

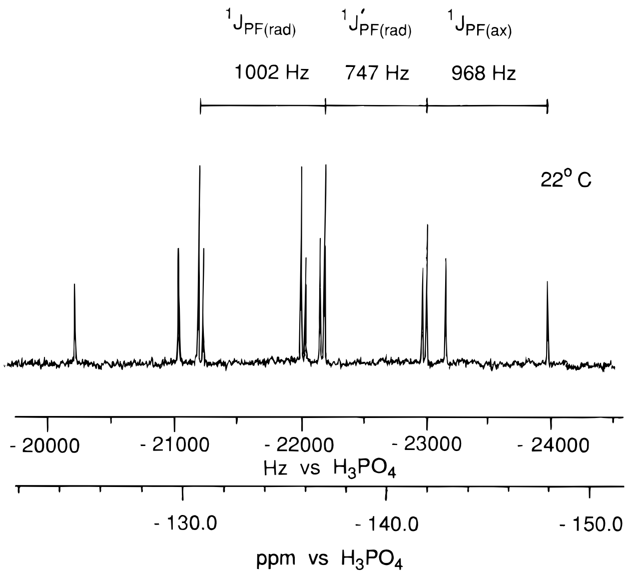
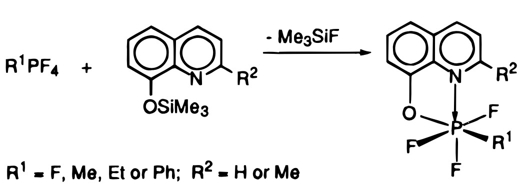


Figure 13. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (161.8 Mhz) spectrum of (2-mercaptopyridinato)tetrafluorophosphorus (**24f**)[81] in $CDCl_3$ solution at 22 °C. Reproduced with permission.



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(25)

X-ray crystal structure of (8-oxyquinaldinato)tetrafluorophosphorus (**25b**, Figure 14) shows that the coordination environment around the phosphorus atom is almost perfectly octahedral, with a N−P bond distance of 1.911 (4) Å, significantly longer than the σ-bond N−P distance (1.84−1.89 Å) in the base adducts of PF_5 discussed above.

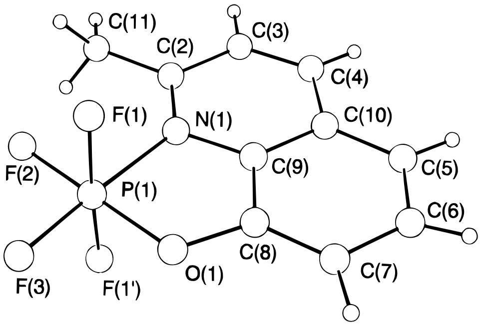


Figure 14. X-ray crystal structure of (8-oxyquinaldinato)-tetrafluorophosphorus, (**25b**),[82] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.

The stability of the intramolecular N→P donor bond was controlled by varying the electronegativity and hence the Lewis acidity of the phosphorus(V) center. This was achieved by replacing one or more of the fluorine atoms in PF_5 with methyl, ethyl, or phenyl substituents. When only one fluorine atom is replaced by Me, Et, or Ph the complexes, RF_3PL, where L = oxinato, are six-coordinate [^{31}P NMR δ, −105 to −146 ppm]. However, the reaction between dimethyltrifluorophosphorus and 8-(trimethylsiloxy)-quinoline produced a clean compound but with no evidence of a six-coordinate phosphorus(V) center [^{31}P NMR δ, −9.7 ppm]. In the six-coordinated cases, a radially coordinated R group was inferred from the multiplicity of the ^{31}P and ^{19}F NMR resonances but the exact stereochemistry (whether R is *cis* or *trans* to N) could not be identified. Consequently, Schmutzler and co-workers[83] determined the X-ray crystal structure of PhF_3PL (see Table 7 listing, **25f**, R = Ph, R^1 = Me), where HL is 8-hydroxyquinaldine (Figure 15). The N−P bond distance [1.980(3) Å] is significantly longer than that of the tetrafluoro- analogue (**25b,** Table 7, R = F, R^1 = Me), reflecting the weaker Lewis acidity of this phosphorus center. The radially coordinated phenyl substituent is positioned *trans* to the nitrogen atom and the preferred stereochemistry has been attributed to steric constraints.

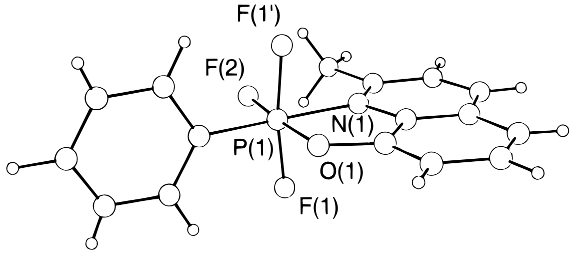
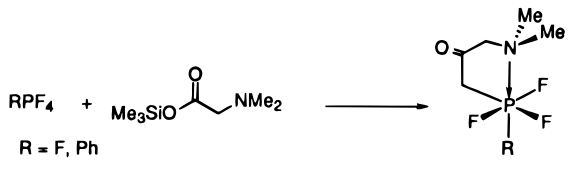


Figure 15. X-ray crystal structure of **25f**,[83] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.

Reactions of $(CH_2)_nPF_3$ (n = 4 or 5) with 8-(trimethylsiloxy)quinaldine afforded six- and five-coordinate phosphorus(V) compounds, respectively.[84] Although the presence of the $(CH_2)_nP$ ring would place these compounds formally in the bicyclic category, we are including them at this point because the flexible alkane ring system may be considered as analogues of a dialkyl moiety. The contrasts with the dimethyl system (vide supra) are notable. The complex $(CH_2)_4$-PF_2L (**26**), where L = oxinato, shows six coordination at phosphorus, whereas $(CH_2)_5PF_3$ does not form the six-coordinate species. The difference in behavior was attributed to a difference in the Lewis acidity of the phosphorus center in $(CH_2)_5PF_3$ compared to $(CH_2)_4PF_3$, the latter being a stronger acid as the result of ring strain. The stereochemistry of **26** was deduced on the basis of ^{31}P and ^{19}F NMR spectroscopy. A hexacoordinated phosphorus(V) environment for **26** was deduced from the ^{31}P NMR chemical shift difference between the product and starting material (δ, −68.3 and +29.8 ppm, respectively) but the $^{1}J_{PF}$ values did not show the expected difference between the two sites. Inequivalent ^{19}F NMR resonances [−17.8 and −55.2 ppm], however, suggested *cis* fluorine substitution. From previous crystallographic studies (see above) it was suggested that the R group would sit preferentially *trans* to the nitrogen atom and hence a geometry as shown in Figure 16 was suggested.

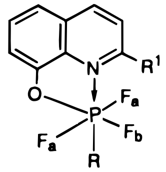
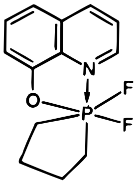
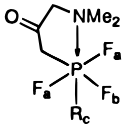
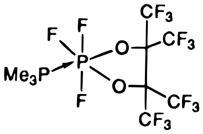
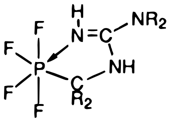
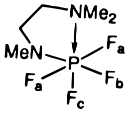
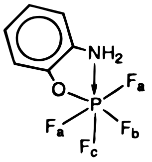
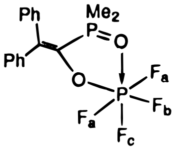
In the same paper,[84] the analogous chelation of *N,N*-dimethylglycine was also reported (eq 25). The



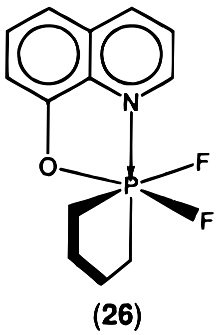
(25)

(27)

Table 7. Neutral Six-Coordinate NMR Data of Monocyclic Derivatives with Five-Membered Rings[a]

compound		substituent	δ_P (ppm)	$^1J_{PF}$ (Hz)[a]	ref
	**25**[b]	**a** R = F, R^1 = H **c** R = Ph **d** R = Et **e** R = Me	−118.7 −119.6 −105.0 −105.0	788, 756, 748 890, 890 920, 920 883, 883	82
	**26**		−68.3	825[c]	84
	**27a** **27b**	**a** R = F **b** R = Ph	−136.8 −119.6	851, 840, 751 935, 935	84
	**29**		−130[d]	898,726[d]	85
	**30−32**[e]	R = Me/Me,Et R′ = Et, Pr, ^{i}Pr	−130		88
	**33**		−121.9	843(a), 769(b), 756(c)	91
	**34**		−128.8	793(a), 755(b), 766(c)	92
	**35**		−129.9	775(a), 741(b)	93

[a] Only the ^{31}P shift data are reported in general. Identity of coupling constants does not imply identical ^{19}F environments, only that the axial and equatorial coupling constants are not numerically distinct. [b] No ^{31}P NMR data were given for the related compound **25b** (R = F, R^1 = CH_3 which was structurally characterized (Figure 14).[82] Similarly no NMR data have been given for **25f** which has also structurally characterized (Figure 15).[83] [c] Two fluorine environments −17.8 and −55.2 ppm. Broad lines are observed. [d] $^1J_{PP}$ = 710 Hz, $\delta_{P^{III}}$ = −34.5 ppm. [e] A number of derivatives are reported, all of which have the same chemical shift.



(26)

Figure 16. Proposed structure of **26**.

crystal structure of PhF_3PL, where HL = *N*,*N*-dimethylglycine (**27b**) (Figure 17)[84] shows that the phenyl ring lies *trans* to the coordinated nitrogen atom analogous to **26**.

In a study of various fluorophosphoranes containing the perfluoropinacolyl ring system it was reported that perfluoropinacolyltrifluorophosphorane (**28**) acts as a strong Lewis acid with trimethylphosphine to form a Lewis acid−base adduct (**29**, eq 26), which possesses a neutral six-coordinate phosphorus(V) center with one five-membered chelate ring. The presence of the P−P bond was inferred from the ^{31}P NMR shift and a large $^1J_{PP}$ value, comparable to the values noted previously for the simple phosphine−PF_5 adducts.[47] The detailed stereochemistry of the six-coordinate molecule was assigned by analysis of the ^{19}F NMR data.[85] Subsequently, the X-ray crystal structure of **29**,[86] (Figure 18) confirmed the geometry clearly indicating that the phosphine lies in the plane of the perfluoropinacolyl ring. This structure also represents the first determination of a P→P coordinate bond distance to a hexacoordinate phosphorus

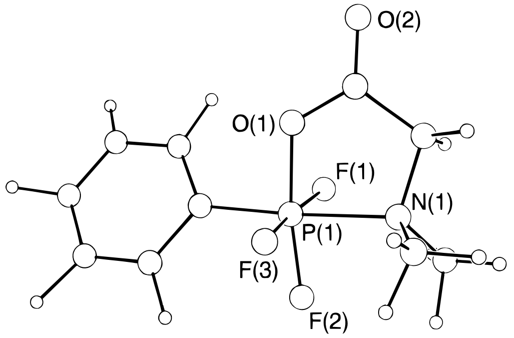


Figure 17. X-ray crystal structure of 2-(*N*,*N*-dimethylamino)acetoxyphenyltrifluorophosphorus (**27b**),[84] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.

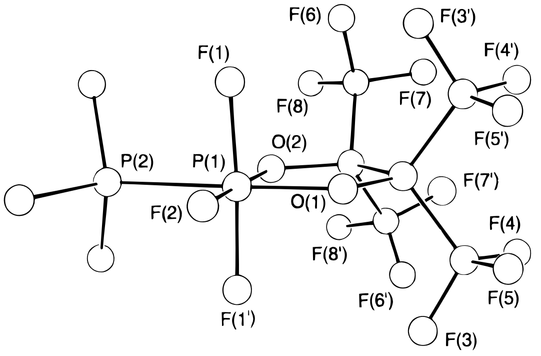


Figure 18. X-ray crystal structure of **29**,[86] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.

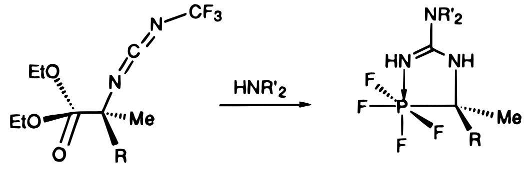
atom. The short P→P bond [2.234(5) Å] is only 0.01–0.03 Å longer than the range typically observed for P–P σ bonds between the lower valence and coordination states of phosphorus. This is significant in (i) extending the principle of essential constancy of the P–P bond distance to include coordinate dative bonds and (ii) underlines the remarkable Lewis acid strength of the P(V) center in the parent perfluoropinacolyltrifluorophosphorane (**28**) in which the phosphorus carries three fluorine and two oxygen atom substituents. The P–P bond distance in **29** is not much longer than the sum of the covalent radii for two phosphorus centers (2.20 Å).[44]

$$PF_3 + 2\,(CF_3)_2CO \longrightarrow \underset{\mathbf{(28)}}{PF_3L} \xrightarrow{PMe_3} \underset{\mathbf{(29)}}{PF_3L \cdot PMe_3} \qquad (26)$$

$$H_2L = (CF_3)_2C(OH)C(OH)(CF_3)_2$$

An unusual reaction was reported by Martynov and co-workers[87–90] in which hexacoordinate tetrafluorophosphorus(V) compounds were formed by the reaction of *O*,*O*-diethyl-1-(4,4,4-trifluoro-1,3-diazabutadien-1,2-yl)alkylphosphonates with dialkylamines (**30**–**32**, eq 27).

The reactions were carried out in diethyl ether in a sealed vessel at 50–60 °C for 10 h, and yields were between 33 and 47% after recrystallization. The structures **30**,[88] **31**,[89] and **32** (Figure 19)[90] were determined by X-ray crystallography and supported by multinuclear NMR experiments. In all cases, the geometry about the phosphorus atom is octahedral with P–F bond distances ranging from 1.599(2) to 1.640(2) Å, the P–N bond distances lie between 1.765 (1) and 1.772 (3) Å, and the P–C bond distances are 1.872(4)–1.898(4) Å. Overall, the N→P bond distances are comparable to the usual σ-bond N–P bond distances and intermolecular N–H···F–P interactions cause some minor deviations in the crystal lattice. The only significant difference between the three structures is that the envelope conformation in the five-membered rings are folded with the tip of the flap at the phosphorus atom in **30** and **31** and at the carbon atom (adjacent to the phosphorus atom) in **32**.



(27)

(30) R = Me, R' = Et
(31) R= *i*-Bu, R' = i-Pr
(32) R = Et, R' = *n*-Pr

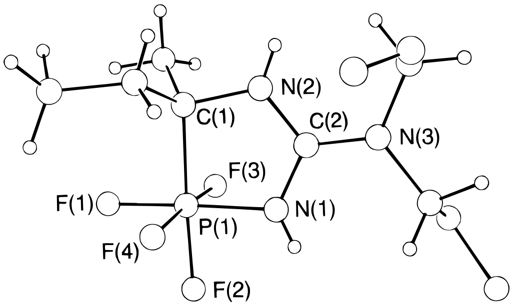
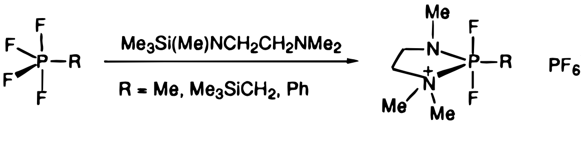


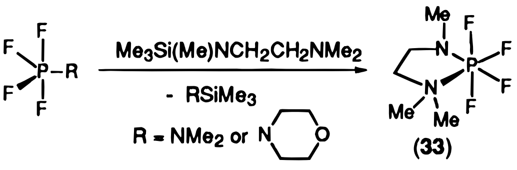
Figure 19. X-ray crystal structure of **32**,[90] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.

Schmutzler has reported the unusual formation of a hexacoordinate tetrafluorophosphorane containing a trimethylethylenediamine chelate.[91] In analogous reactions of $Me_3Si(Me)NCH_2CH_2NMe_2$ with RPF_4 (where R = Me, Me_3SiCH_2, Ph) there is a PF bond cleavage to afford a compound containing a five-coordinate phosphorus center (e.g., eq 28). However,



(28)

when the R group is a dimethylamino or morpholino group one obtains a neutral product containing a six-coordinate phosphorus center (eq 29). There was no

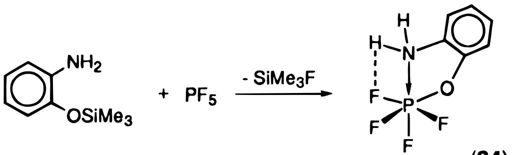


(33)

(29)

evidence for P–F bond cleavage, instead the aminotrimethylsilane was eliminated. Compound **33** shows fluxional behavior at room temperature in both the ^{19}F and ^{31}P NMR spectra. The five-membered ring compound formed adopts an envelope conformation based on the crystal structure determination with a relatively long (1.965 Å) dative P−N bond although the length is comparable to the simple adducts characterized above.[91]

Stoichiometric amounts of **5** and 2-(trimethylsilyloxy)aniline led quantitatively to the expected six-coordinate phosphorus(V) compound **34** (eq 30).[92] The

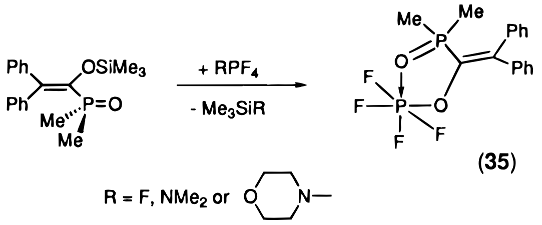


(30)

(34)

^{19}F NMR spectrum of **34** at room temperature showed nonequivalence for the two axial fluorine atoms, indicating that the molecule has no plane of symmetry. This was attributed to intramolecular hydrogen bonding between a hydrogen atom on the NH_2 group and an adjacent axial fluorine atom. When the Lewis acidity of the phosphorus center is reduced by using either $MePF_4$ or $PhPF_4$ only the five-coordinate species, $MePL_2$ or $PhPL_2$, respectively, were isolated, where H_2L = 2-aminophenol.

Reactions of RPF_4 (where R = F, dimethylamino, or morpholino) with [2,2-diphenyl-1-(trimethylsiloxy)-ethenyl]dimethylphosphane oxide yielded compounds with an unusual P=O→P bond **35** (eq 31).[93] The



(31)

(35)

X-ray crystal structure of **35** (Figure 20) show clearly the interaction of the octahedral PF_4 center with the P=O group. Significant delocalization may be inferred from the small difference between the P−O and formal P → O bond distances [1.685(2) and 1.732(2) Å, respectively].

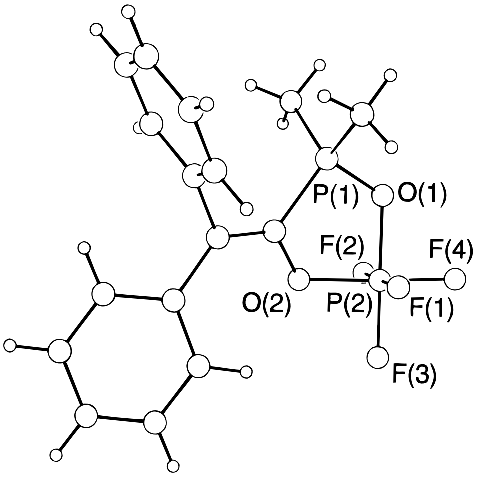
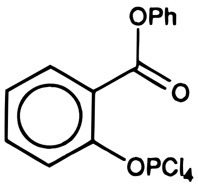


Figure 20. X-ray crystal structure of **35**,[93] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.

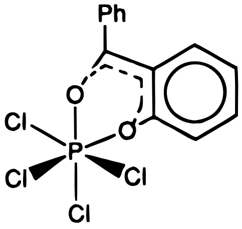
3. Chelates Forming Six-Membered Rings

The reaction of phenyl salicylate with PCl_5 was reported as far back as in 1898.[94] The structure proposed for the product (**36**) at that time was based on elimination of one hydrogen chloride molecule to produce a phosphorane with retention of a carbonyl group in the ligand (Figure 21). In 1961, Pinkus and co-workers[95] reinvestigated the system using conductivity, dipole moment measurements, molecular weight determinations, and infrared and UV spectroscopies to eliminate structure **36** and suggested instead that the phenyl salicylate and 2-hydroxybenzophenone ligands may coordinate in a bidentate fashion (e.g., as **37**). Lone-pair donation from the carbonyl group would complete the six-membered ring and electron delocalization would stabilize the structure (Figure 22) which would be another example of a neutral six-coordinate P(V) compound.



(36)

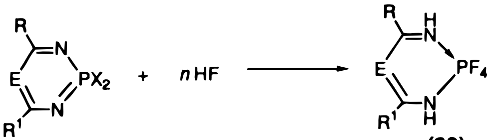
Figure 21. First proposed structure of product **36** obtained by the reaction between phenyl salicylate and **1**.



(37)

Figure 22. Proposed structure of (2-oxybenzophenonato)-tetrachlorophosphorus(V) (**37**).

Two short papers[96,97] have described the synthesis of novel six-coordinate phosphorus compounds by addition of hydrogen fluoride to difluoro or dichloro derivatives of diaza- and triazaphosphorins (eq 32).



(32)

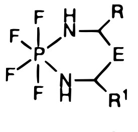
(38)

(38a)	X = F;	E = N;	R = R' = CF_3;	n = 2
(38b)	X = Cl;	E = CCl;	R = R' = Cl;	n = 4
(38c)	X = Cl;	E = CH;	R = R' = Cl;	n = 4
(38d)	X = Cl;	E = N;	R = R' = CF_3;	n = 4
(38e)	X = Cl;	E = N;	R = R' = CCl_3;	n = 4
(38f)	X = Cl;	E = N;	R = CCl_3; R' = Ph;	n = 4

In all cases, the compounds **38a**−**f** were characterized by multinuclear NMR spectroscopy. Phosphorus NMR parameters are given in Table 6. The six-coordinate phosphorus species was confirmed by the high-field chemical shift values observed (^{31}P NMR δ, −156.4 to −162.7 ppm). The multiplicity of the phosphorus resonance observed is often a quintet corresponding to equivalence of the fluorine atoms. However, upon removal of HF, the ^{31}P resonances of these compounds change to triplets of triplets as expected for two axial and two radial fluorine atoms.

In 1966, Brown and Bladon[98] reported the formation of (β-diketonato)tetrafluorophosphorus(V) com-

Table 8. NMR Data of Monocyclic Derivatives Forming Six-Membered Rings

compound		δ_P (ppm)	$^1J_{PF}$ (Hz)	ref
	**38a** (R = R^1 = CF$_3$, E = N)	−162.7	785(r),[a] 780(a)	96
	38b (R = R^1 = Cl, E = CCl)	−159.0	750	97
	38c (R = R^1 = Cl, E= CH)	−156.4	750	97
	38d (R = R^1 = CF$_3$, E = N)	−162.3	770	97
	38e (R = R^1 = CCl$_3$, E = N)	−159.6	770	97
	38f (R = CCl$_3$, R^1 = Ph, E = N)	−161.0	750	97
F_4P (acac)[b]	**39** (x = 0; 4F)	−148.2	824(a), 741(r)	98, 99
$F_{4-x}(CF_3)_xP(acac)$	**40a** (x = 1; 3F)	−151.7 (CF$_3$ radial) −151.0 (CF$_3$ axial)	884(r), 930(a) 897(r), 830(a)	100
	40b (x = 2; 2F)			100
	40c (x = 3; 1F)	−151.2 −158.4	987 891	100
$CH_3(CF_3)_3P(acac)$	**40d**	−147.8		100

[a] r = radial, a = axial (i.e., perpendicular to the plane of the bidentate ligand). [b] acac = acetylacetonate.

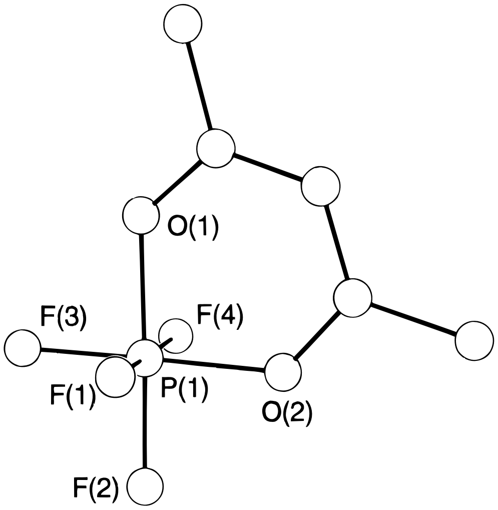


Figure 23. X-ray crystal structure of **39**,[99] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.

pounds (**39**) by addition of excess PF$_5$ to an ethereal solution of a β-diketone (acetylacetone, benzoylacetone or dibenzoylmethane) at −70 °C. Infrared, UV and multinuclear NMR spectroscopies were used to characterize the compounds (see Table 8). It was concluded that the compound was a neutral six-coordinate phosphorus(V) derivative with one chelated β-diketonate. The compound was shown to have a comparable physical nature to other main-group and metallic β-diketonates. Twelve years later, the X-ray crystal structure of (acetylacetonato)-tetrafluorophosphorus(V) (**39**) was reported (Figure 23)[99] which confirmed the earlier structural conclusions. Noteworthy features of the structure include an approximate plane of symmetry perpendicular to the six-membered ring. The chelate ring adopts a boat conformation with the phosphorus and central carbon atom displaced from the plane of the remaining four ring atoms. The P−O and P−F bond distances are 1.715(2)−1.723(2) and 1.568(2)−1.588(2) Å, respectively. The axial P−F bond distances are typically 0.005−0.01 Å larger than the corresponding radial P−F bond distances.

$$F_{5-x}(CF_3)_xP + H(acac) \xrightarrow[x\,=\,1\text{-}3]{} \underset{\textbf{(40a-c)}}{F_{4-x}(CF_3)_xP(acac)} + HF \qquad (33)$$

$$CH_3(CF_3)_3PCl + Na(acac) \longrightarrow \underset{\textbf{(40d)}}{CH_3(CF_3)_3P(acac)} + NaCl \qquad (34)$$

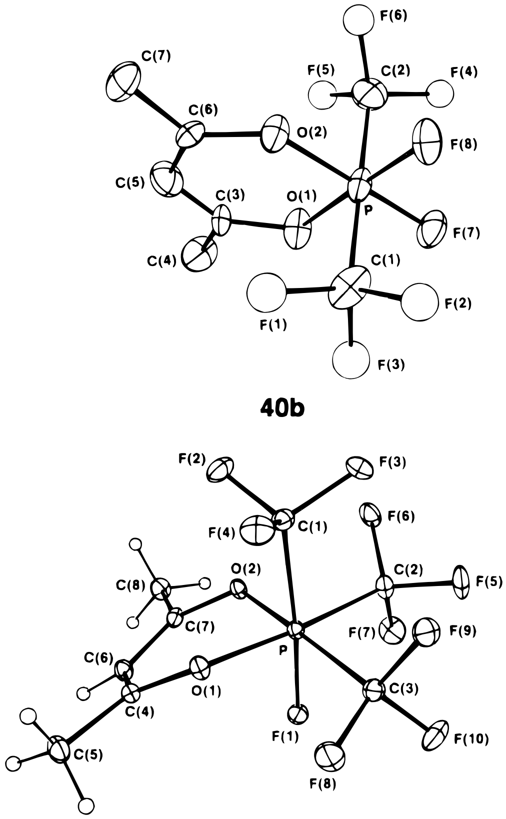
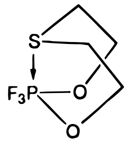
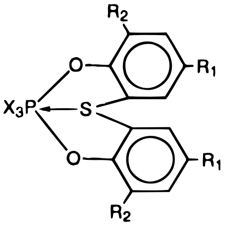
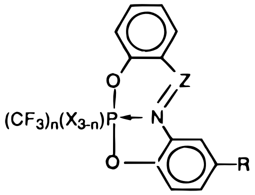


Figure 24. X-ray crystal structures of **40b** and **40c**.[100] Reproduced with permission.

The trifluoromethyl analogues (eqs 33 and 34), **40**, have been synthesized by Cavell and co-workers.[100] Although geometrical isomers could exist for all the compounds, only F$_3$(CF$_3$)P(acac) (**40a**) shows more than one specific structural isomer in the NMR spectra corresponding to axial or radial CF$_3$ position in the compound (axial : radial isomer distribution ca. 1:2). X-ray crystal structures of both F$_2$(CF$_3$)$_2$P(acac) (**40b**) and F(CF$_3$)$_3$P(acac) (**40c**) have been determined (Figure 24). The structures of **40b** and **40c** closely resemble that of **39a**. In **40c**, the acac ligand adopts a boat formation with the fold away from the larger CF$_3$ substituent. The CF$_3$ substituted analogues give somewhat longer P−O [1.745(5), 1.741(5) Å for **40b** and 1.746(1), 1.752(1) Å for **40c**] and P−F [1.615(4), 1.594(4) Å for **40b** and 1.612(1) Å for **40c**] bond distances, and this has been at-

Table 9. Bicyclic Rings: Six-Coordinate Phosphorus Centers with Tridentate Chelates

compound		δ_P (ppm)	$^1J_{PF}$ (Hz)	ref
	**41**	−142.3	727, 692	92
	**42a**[a] ($R_1 = {}^t$Bu, $R_2 = {}^t$Bu, X = OPh)	−82.6		103
	42c (R_1 = Me, $R_2 = {}^t$Bu, X = OPh)	−81.9		103
	42e (R_1 = Me, R_2 = Me, X = OPh)	−81.2		103
	42b ($R_1 = {}^t$Bu, $R_2 = {}^t$Bu, X = OCH_2CF_3)	−82.4[b]		101
	42d (R_1 = Me, $R_2 = {}^t$Bu, X = OCH_2CF_3)	−82.3		104
	42f ($R_1 = {}^t$Bu, R_2 = Me, X = OCH_2CF_3)	−77.3[c]		101
	42g ($R_1 = {}^t$Bu, $R_2 = {}^t$Bu, X = Cl)	−133.9		108
	**43a** (n = 0, X = F, Z = CH, R = ^{t}Bu)	−136.9		108
	43b (n = 0, X = F, Z = CH, R = NO_2)	−137.4	812(ax), 753(rad)[d]	108
	43c (n = 0, X = Cl, Z = CH, R = ^{t}Bu)	−136.4		108
	43d (n = 1, X = Cl, Z = CH, R = ^{t}Bu)	−140.6		108
	43e (n = 1, X = F, Z = CH, R = H)	−144.1	811(ax), 835(rad)	108
	44a (n = 0, X = F, Z = N, R = H)	−143.6	842(ax), 770(rad)	108
	44b (n = 1, X = F, Z = N, R = H)	−148.9 (trans to N)	894	108
		−146.0 (cis to N)	833(ax), 853(rad)	108

[a] See compounds **61** in Table 11. [b] Solid δ_P = −82.9. [c] Solid δ_P = −74.7. [d] rad = radial, ax = axial (i.e., perpendicular to the plane of the bidentate ligand).

tributed to the lower electronegativity of CF_3 compared with F and hence reduced Lewis acidity of the phosphorus atom.

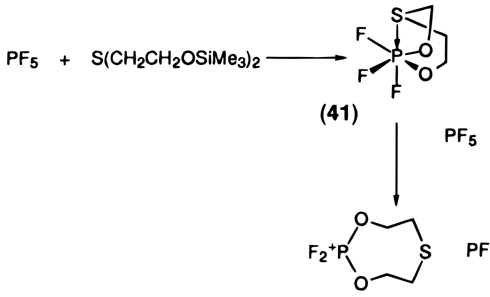
Isomerism of the series $F_{4-n}(CF_3)_nPL$, where L = acac[100] or carbamate[79,80] (see above) and n = 1−3, can be compared. Note that in the carbamate series there is a preference for axial CF_3 occupation with an additional complication in **23a** where the isomer ratio is 2:1 in favor of location of the CF_3 group in the axial position. In contrast, the acac analogues, show a reversed pattern in that **40a** shows an isomer ratio of 2:1 in favor of a radial CF_3 group and **40c** shows an axial F substituent. However, both $F_2(CF_3)_2PL$ analogues display *trans*-axial CF_3 coordination which is only consistent with steric arguments.

C. Bicyclic Derivatives

1. Tridentate Chelates.

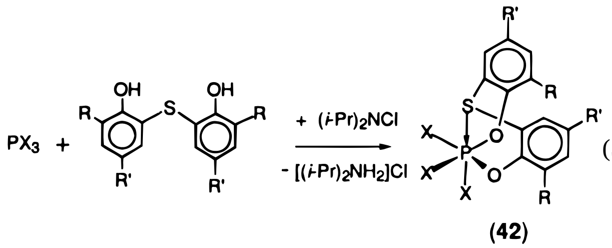
Until recently, there have been surprisingly few reports of compounds with a general formula of X_3PL, where X = monodentate and L = tridentate ligand. This may be attributed to the comparatively low Lewis acidity of a "X_3P" species even when X = F, thus reducing the ability of the phosphorus atoms to coordinate. It can therefore be anticipated that strong Lewis bases and/or other compensating prerequisites (e.g., strong chelate effect) would be required in L for stable X_3PL compounds to form.

No bicyclic neutral six-coordinate phosphorus compounds were observed in the reactions between PF_5 and $R(CH_2CH_2OSiMe_3)_2$, where R = O, NH, NMe, N-*tert*-Bu or NPh.[92] For R = S, the reaction proceeded smoothly to give the desired six coordinate product **41** (ca. 75%) with some ionization (eq 35). The six-coordinate phosphorus center was identified by the ^{31}P NMR spectrum, [δ −142.3 (dt) ppm], however, the doublet of triplets cannot unambiguously confirm the coordination geometry of the ligand (i.e., facial or meridional). Analogous reactions with $PhPF_4$ and $MePF_4$ resulted in ionic species only.



(35)

Holmes and co-workers[101−107] have recently described the synthesis, characterization, and related reactivity of various neutral phosphorus compounds of the type X_3PL (**42a**−**f**, see Table 9) where X = $-OCH_2CF_3$ or −OPh and H_2L = 2,2′-thiobis(4-methyl-6-*tert*-butylphenol), 2,2′-thiobis(4,6-di-*tert*-butylphenol), or 2,2′-thiobis(4,6-dimethylphenol) (eq 36). Yields



(36)

(42)

of 70−80% were reported for **42a**−**f**. For compounds **42a**−**e** the coordinate geometry around the phosphorus center is essentially a distorted octahedron with a S→P coordinate bond. Thus the ligand acts as a dibasic tridentate chelate and coordinates facially to the phosphorus(V) center (e.g., Figure 25). **42f** displays a trigonal-bipyramidal structure with essentially no P−S interaction and has been included for comparison purposes only. The ^{31}P NMR chemical shift of **42b** and **42f** are virtually unchanged in $CDCl_3$ solution compared with the solid-state resonances indicate retention of coordination geometry

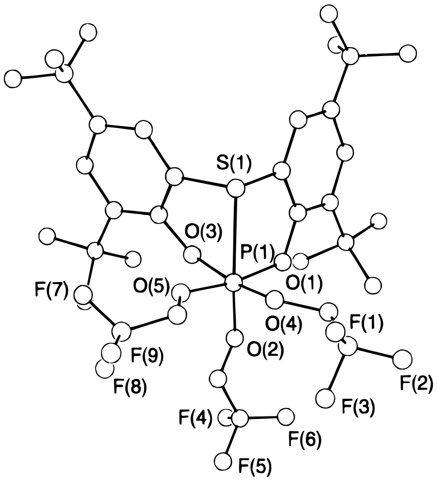


Figure 25. X-ray crystal structure of **42b**.[101] Reproduced with permission.

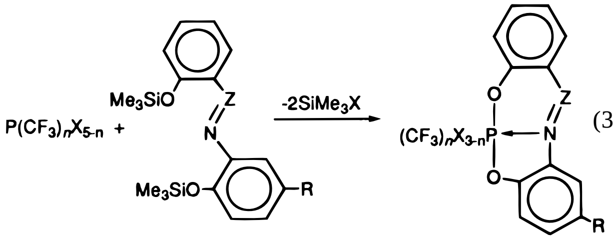
in solution. Note that the chemical shift range for the six-coordinate compounds (^{31}P NMR, δ −81.16 to −82.6 ppm) **42a**−**e** show only a small deviation from the five-coordinate analogue (^{31}P NMR, δ −77.30 ppm, **42f**). It was suggested that this may be due to the weak P−S interaction in the six-coordinate compounds which does not significantly influence the ^{31}P NMR chemical shift. A more detailed analysis and correlation of the ^{31}P NMR chemical shift values with cyclic oxyphosphoranes has recently been reviewed by Holmes and Prakasha.[106]

The decrease in P−S bond distance through the series **42e** to **42c** to **42a** parallels the increase in electron-pushing ability of the alkyl substituents on the aromatic rings (*t*-Bu > Me). The P−S bond is also affected by the Lewis acidity of the phosphorus center such that the more electronegative OCH_2CF_3 compared with OPh groups provide derivatives with shorter P−S bonds. However, all of the geometry effects observed in **42f** cannot be accounted for by these electronic considerations alone. The steric effects of R (ortho to O, eq 36) can be more readily appreciated when the chelate ring conformation is considered. The ring conformation in **42f** is chairlike with the phosphorus atom in an "anti" arrangement. The steric factors of R become significant when there is sufficient interaction with X. Thus, in the six-coordinate compounds the phosphorus atom adopt a "syn" arrangement to form a boatlike conformation and relieves steric crowding between R and X.

The ligand H_2L = 2,2′-thiobis(4,6-di-*tert*-butylphenol), one of the ligands used extensively by Holmes and co-workers, in the hands of Wong and Cavell[108] gave the facially chelated, six-coordinate, bicyclic trichlorophosphorus derivative of very similar structure to that illustrated in Figure 25. The P−S distance in **42g**[108] is the shortest yet recorded (2.331(1) Å Table 2) in this type of compound and slightly shorter than that observed in the OCH_2CF_3 derivative (**42b**) (Figure 25). These bond lengths, although shorter than the sum of the van der Waals radii of the elements are not as short as the sum of the covaalent radii of phosphorus and sulfur (2.12 Å corrected for electronegativity of the elements).[44] This further shortening of the P−S bond in **42g** relative to the related members of the series is presumably the result of the highly electronegative character of chlorine as this is the most electronegative substituent used in the work with this bicyclic sulfur-bridged ligand. This high electronegativity makes the phosphorus center very acidic and a good candidate for intramolecular Lewis acid−base interaction as described above.

Related compounds wherein the sulfur atom is replaced with a methylene group resulted only in five-coordinate derivatives as might be expected in view of the lack of a good donor center in the link.[101] Hydrolysis of compounds such as **42d** to phosphates have been studied and the reactivity of related compounds were also analyzed.[107] Related neutral hexacoordinated phosphorus compounds of this system, obtained when two X groups of **42b** were replaced by either a 2,2′-biphenoxy group or a saturated alkane diol giving **61** are described below in section D.

Recently, the coordination of tridentate Schiff bases and 2,2′-dihydroxyazobenzene to phosphorus(V) halides and (trifluoromethyl)phosphorus(V) halides to form neutral six-coordinate phosphorus(V) compounds (**43** and **44**) have been reported.[108,109] The compounds were synthesized from the bistrimethylsilylated form of the ligands and the appropriate phosphorane (eq 37).



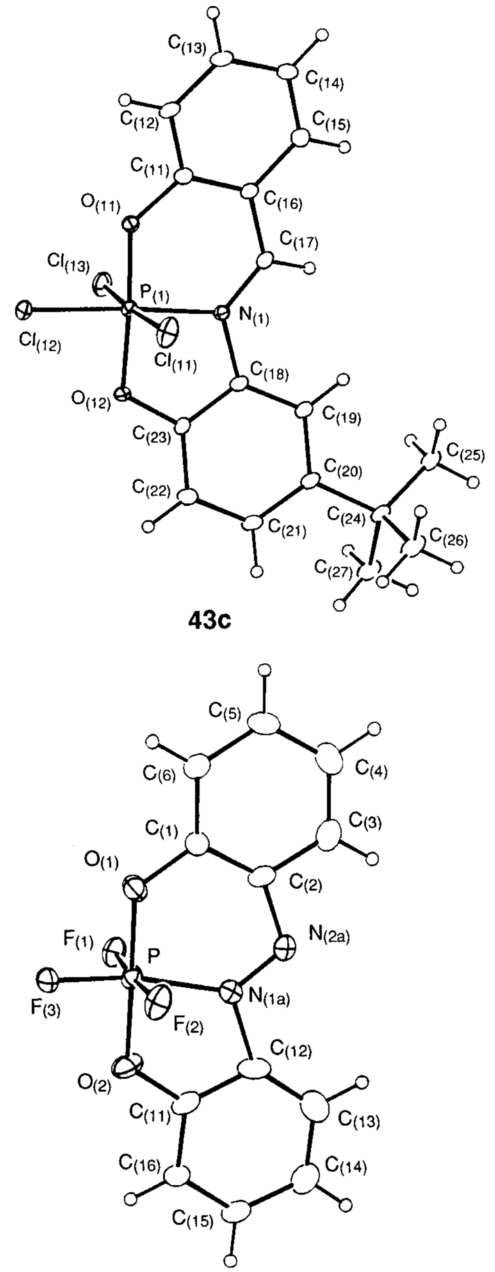
(37)

(43,44)

(43a)	*n* = 0,	X = F,	Z = CH,	R = *t*-Bu
(43b)	*n* = 0,	X = F,	Z = CH,	R = NO_2
(43c)	*n* = 0,	X = Cl,	Z = CH,	R = *t*-Bu
(43d)	*n* = 1,	X = Cl,	Z = CH,	R = *t*-Bu
(43e)	*n* = 1,	X = F,	Z = CH,	R = H
(43f)	*n* = 2,	X = Cl,	Z = CH,	R = H
(44a)	*n* = 0,	X = F,	Z = N	R = H
(44b)	*n* = 1,	X = F,	Z = N	R = H

The X-ray crystal structures of **43c** and **44a** have been determined (Figure 26). Both structures share common features, namely, the phosphorus center lies in an essentially octahedral environment, the ligands coordinate to the phosphorus atom with a meridional conformation formed from a bicyclic five- and six-membered chelate ring using an ONO donor set, and a shorter P−X bond *trans* to the nitrogen atom compared with the axial P−X bonds. This latter observation reflects the importance of the *trans* influence in the molecule due to the weaker dative P→N coordinate bond. The structure of **44a** possesses a disorder in the molecule corresponding to coordination from one or the other nitrogen atom in the ligand which reduces the reliability of the P−N coordinate bond length measurement in this case.

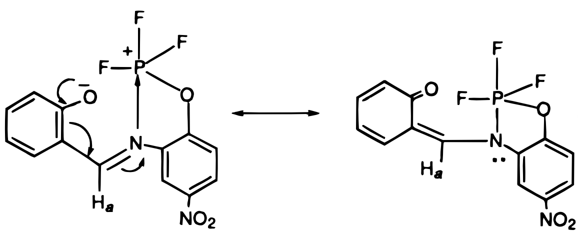
The compound **43b**, which has a highly electronegative NO_2 substituent in one of the aromatic rings produces an observable (by ^{1}H NMR spectroscopy) intermediate (which can be represented as two resonance forms) during the formation process (eq 38).



43c

44a

Figure 26. X-ray crystal structures of **43c** and **44a**.[108] Reproduced with permission

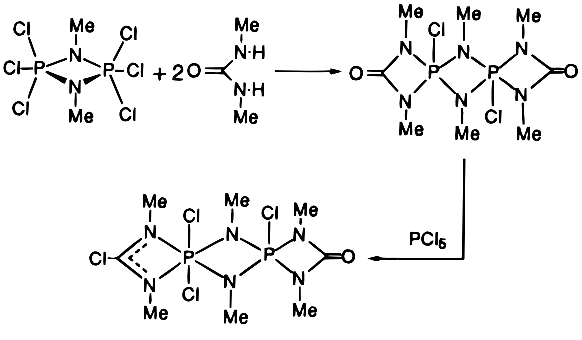


(38)

Geometrical isomers exist for the compounds derived from (trifluoromethyl)phosphoranes (i.e., for $n = 1$ or 2). With the exception of (**43d**), all the isomers may be unambiguously identified using multinuclear NMR spectroscopy. The homologous compounds **43e** and **44b** containing one CF_3 group show different isomeric distributions. In **43e**, NMR spectroscopy indicates exclusive *cis*-fluorine coordination. In **44b**, both *cis*- and *trans*-fluorine coordination were observed in the ratio ca. 1:1. The isomers do not exchange in solution, and separation was achieved by fractional recrystallization. To date, no single crystal diffraction data have been obtained for these examples.

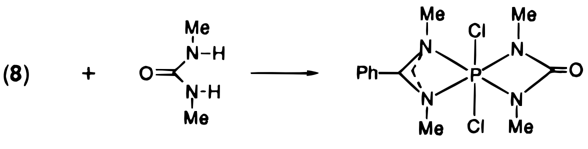
2. Two Bidentate Chelates

The reaction of $(MeNPCl_3)_2$ with 2 equiv of *N*,*N*′-dimethylurea produces a diphosphorus compound with three interconnected four-membered rings.[56] Subsequent chlorination regenerates $(MeNPCl_3)_2$ and a new diphosphorus compound (**45**) possessing one six- and one five-coordinate phosphorus center (eq 39). A similar reaction was observed using **8** and *N*,*N*′-dimethylurea (eq 40). The six-coordinate phosphorus centers were assigned based on ^{31}P NMR resonances (see Table 10) observed at −199 and −184 ppm for **45** and **46**, respectively.



(39)

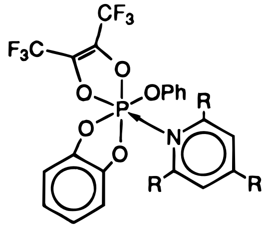
(45)



(40)

(46)

Ramirez and co-workers have suggested some neutral but mainly anionic six-coordinate phosphorus intermediates in base-catalyzed reactions of oxyphosphoranes with alcohols. Crystalline samples of related compounds **47** and **48** (Figure 27) were later reported, and earlier work was summarized.[110] The compounds were formed by addition of pyridine to the parent phosphorane at −20 °C in ether and were characterized by NMR and infrared spectroscopies and elemental analysis. Three possible geometrical isomers exist for these compounds (corresponding to the N atom *trans* to the phenoxy, catecholato, or hexafluorobiacetyl ligand), but no assignments were made in the absence of X-ray crystallographic data.



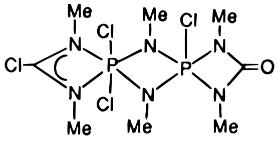
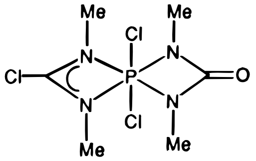
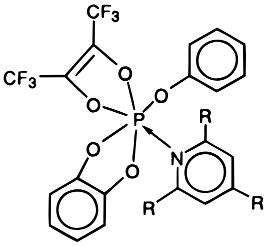
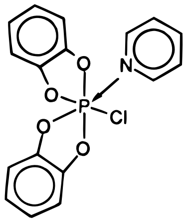
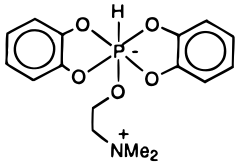
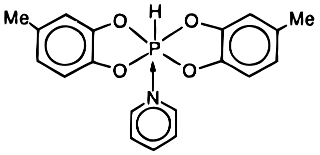
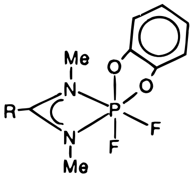
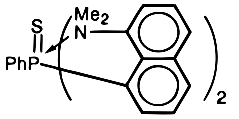
(47) R = H

(48) R = CH_3

Figure 27. Proposed structures of **47** and **48**.

In the equilibrium between **49** and **50** a six-coordinate phosphorus intermediate was proposed (eq

Table 10. Bicyclic Ring Systems: Six-Coordinate Phosphorus Centers with Two Bidentate Chelates

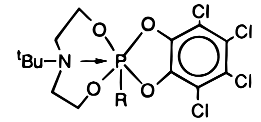
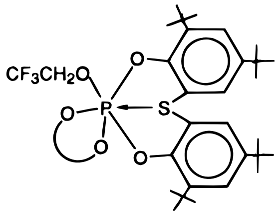
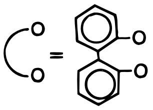
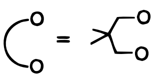
compound		δ_P (ppm)	ref
	**45**	−199	56
	**46**	−184	56
	**47** (R = H) **48** (R = CH_3)	−82.0 −56.1	110 110
	**51a**	−84.5	111
	**51b**	−97.1	112
	**51c**	−71	113, 114
	**54c** (R = Ph) **54b** (R = CCl_3)	−116.3 −120.9	67 67
	**70**	54(s)(major), 64.4^{c-e}	126

[a] $^1J_{PF}$ 801, 871 Hz. [b] $^1J_{PF}$ 808, 876 Hz. [c] The shifts are quoted as given by the authors however considering the value for **85**[137] (see Table 13) a negative value indicating high field might be more appropriate. [d] Two isomers observed in solution. [e] Solid; 1 signal, δ_P = 50.9 (see footnote c).

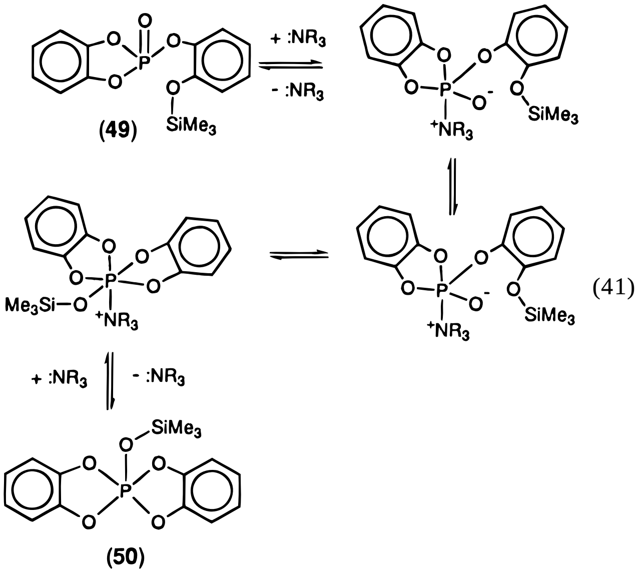
41).[111] Note the similarity between this six-coordinate intermediate and the above-mentioned isolated products **47** and **48**. The rate of equilibration varied with the nature of the tertiary base (represented as R_3N). At 28 °C in 0.55 M $CDCl_3$ solution and 10 mol % of base, the times required for **49** to equilibrate to a ca. 1:1 ratio of **49**:**50** were as follows: imidazole, 4 min; pyridine, 15 min; quinuclidine, 25 min; γ-collidine, 7.5 h; triethylamine, 8.5 h; and with no amine, this process took ca. 39 h. It was suggested that the observed silyl transfer from the aryl oxygen to phosphorane oxygen, (i.e., **49** to **50**), could reflect a significant and more general mechanism in silicon chemistry and further underline the significance of six-coordinate phosphorus species. The comparisons and contrasts of the reactivity of highly coordinated phosphorus and silicon centers and the implications for reaction mechanisms are discussed in more detail in the recent review article by Holmes.[5]

The reaction between bis(catecholato)chlorophosphorus(V) and pyridine was investigated by Schmidpeter and co-workers (eq 42).[112] The equilibrium studies were followed by ^{31}P NMR spectroscopy in $CHCl_3$, which also indicated a fast step for the first

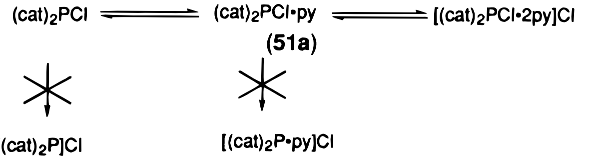
Table 11. Tricyclic, Six-Coordinate Phosphorus Centers with One Bi- and One Tridentate Ligand

compound		δ_P (ppm)	ref
	**57** (R = OH) **59** (R = Ph)	−95.9 −96.3	118 118
	**61a**[a] 	−69.3	102
	61b 	−82.0	107

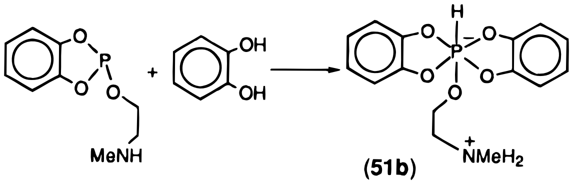
[a] See also compounds **42** in Table 9.



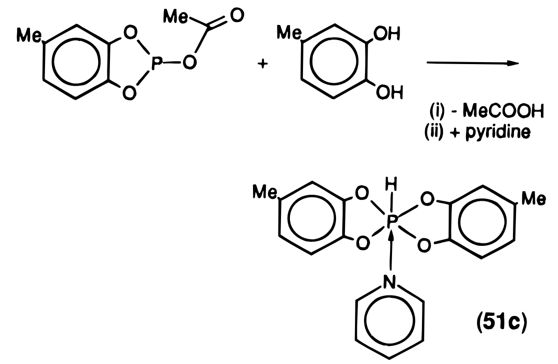
(41)



(42)



(43)



(44)

pyridine addition and a slower step for the second pyridine addition with chlorine dissociation. The neutral adducts were not isolated.

Formation of similar neutral six-coordinate bis(catecholato)hydridophosphorus(V) compounds (**51b**,**c**) has been discussed (e.g., eqs 43 and 44).[113−115] The ^{31}P NMR chemical shift values, variable-temperature NMR experiments, and correlation of concentrations of base with observed chemical shift difference with bis(catecholato)hydridophosphorus(V) (as in eq 44) were the criteria for hexacoordinate phosphorus structure assignment.

Kobayashi and Saegusa[116] have reported polymerizations of spiroacyloxyphosphoranes, and in many cases neutral or zwitterionic six-coordinate centers have been suggested (e.g., **52** and **53** in Figure 28). There was no experimental evidence for the intermediates themselves and formulations were based on empirical mechanistic rules.

Kal'chenko and co-workers have investigated the oxidative addition reactions of (catecholato)halophosphine with *N*-chloro-*N*,*N'*-dimethylbenzamidine or *N*-chloro-*N*,*N'*-dimethyltrichloroamidine (eq 45, cf. eq 11).[63,67] For R = CCl_3 and X = Cl (**54a**), intramolecular chlorine atom migration occurs to form a five-coordinate phosphorus(V) center (cf. **10**, Figure 6). For R = CCl_3 and X = F, half the product undergoes a similar intramolecular chlorine migration, but the remainder symmetrize to **54a** and **54b**. Again, **54a** undergoes further chlorine migration, but **54b** remains stable in solution (δ −120.9 ppm, $^1J_{PF}$ = 808, 876 Hz). The observation of two distinct $^1J_{PF}$ values

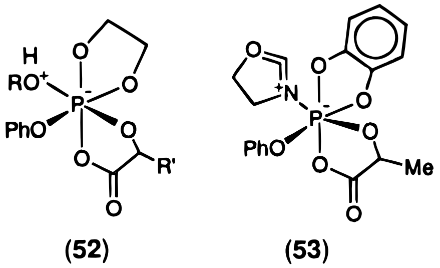
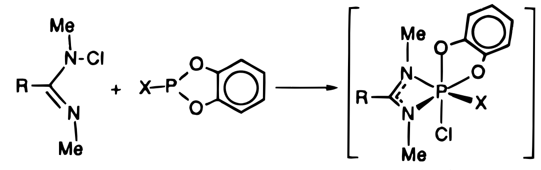
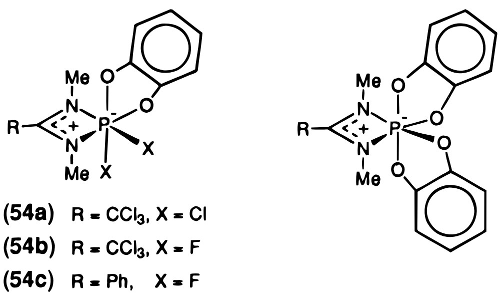


Figure 28. Proposed structures of **52** and **53**.



R = Ph or CCl_3; X = F or Cl

(45)



(54a) R = CCl_3, X = Cl
(54b) R = CCl_3, X = F
(54c) R = Ph, X = F
(54d) R = Ph, X = Cl
(55)

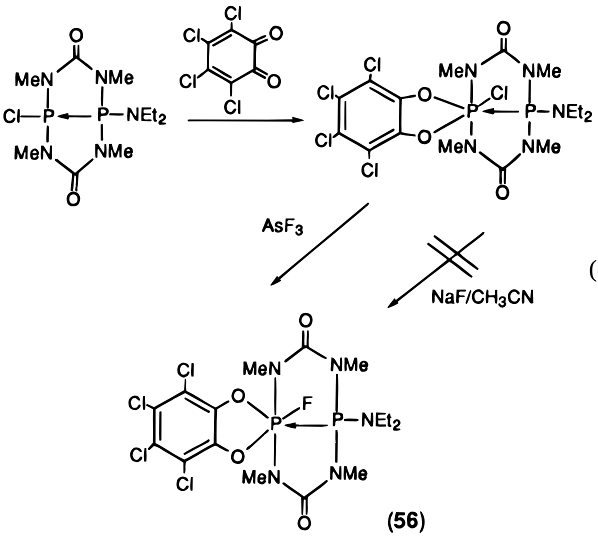
Figure 29. Proposed structures of **54a**–**d** and **55**.

led to a noncentrosymmetric *cis* assignment for the molecule. For R = Ph and X = F, symmetrization is complete and **54c** is stable (δ −116.3 ppm, $^{1}J_{PF}$ = 801, 871 Hz). The remaining **54d** intermediate, the same as for R = Ph and X = Cl, undergoes further symmetrization to form **11** and bis(catecholato) (*N*,*N*′-dimethylbenzamidinato)phosphorus(V) **55**, Figure 29). Variable-temperature ^{31}P NMR experiments on **54d** and **54c** have shown that the most probable courses of permutational isomerization occurs via a P−N bond-breaking mechanism.[68]

D. Tricyclic Derivatives

1. One Bi- and One Tridentate Chelate

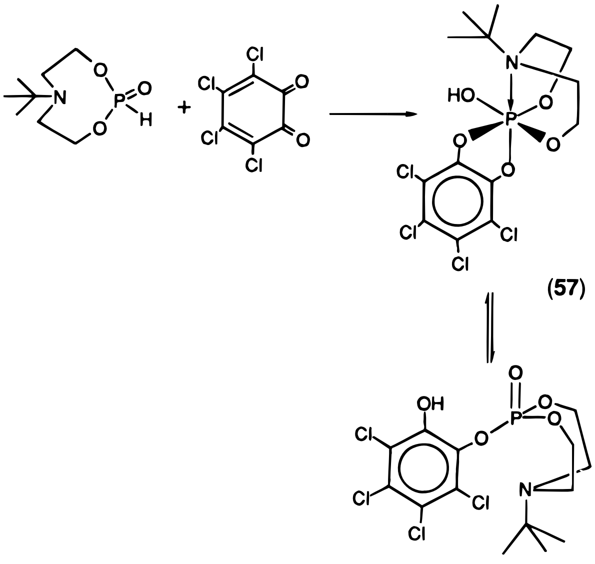
In a study of mixed-valence diphosphorus compounds, Schmutzler and co-workers[117] reported an oxidative addition reaction of an organophosphorus compound containing a phosphorus−phosphorus bond with tetrachloroorthobenzoquinone to form a diphosphorus species with one six-coordinate phosphorus(V) center. The other, trivalent phosphorus center, acts as a donor to the pentavalent phosphorus atom to form a six-coordinate phosphorus species (eq 46). The authors stated that the compounds had been characterized by ^{19}F and ^{31}P NMR spectroscopy, but no details were reported.



(46)

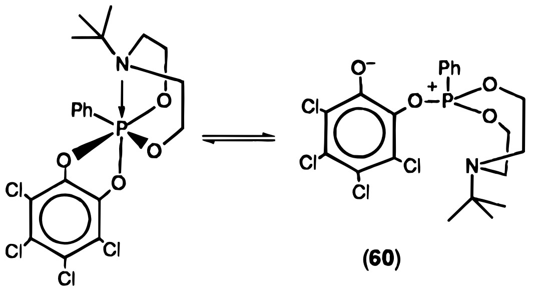
(56)

The oxidative addition reaction of a cyclic phosphonate with tetrachloroorthobenzoquinone produced an equilibrium mixture of a six-coordinate phosphorus compound with a P−OH bond (**57**) and the phosphate ester (**58**) in the ratio 2:3 (eq 47).[118] A similar product was obtained where the OH in **57** is replaced with a Ph group and an intensity ratio of 2:3 for **59** and **60** was observed (eq 48). The equilibrium mixtures were crystallized and characterized by elemental analysis and by ^{31}P NMR spectroscopy (Table 11) (**57**: δ −95.91; **58**: −2.34; **59**: −96.25; **60**: 14.54 ppm). No structural or stereochemical assignments were made; a N→P bond interaction was assumed to be present based on the high-field ^{31}P NMR chemical shift values and by analogy to other heterocyclic eight-membered rings of a similar type.



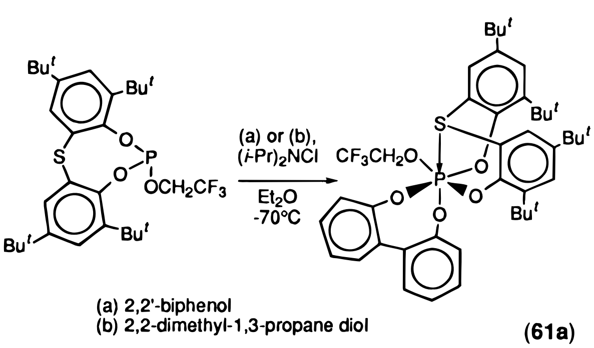
(57) (47)

(58)



(59) **(60)** (48)

In a series of neutral six-coordinate phosphorus(V) compounds described by Holmes and co-workers using the tridentate ligand, H_2L = 2,2′-thiobis(4-methyl-6-*tert*-butylphenol),[103,106,107] 2,2′-thiobis(4,6-di-*tert*-butylphenol)[101,102,104−107] or 2,2′-thiobis(4,6-dimethylphenol)[103,104,106,107] (see section C.1), the synthesis[102] and X-ray crystal structure of **61a** (Figure 30)[102] was also reported (eq 49).[102,107] The structure of the compound consists of a distorted octahe-



(a) 2,2′-biphenol
(b) 2,2-dimethyl-1,3-propane diol

(61a) (49)

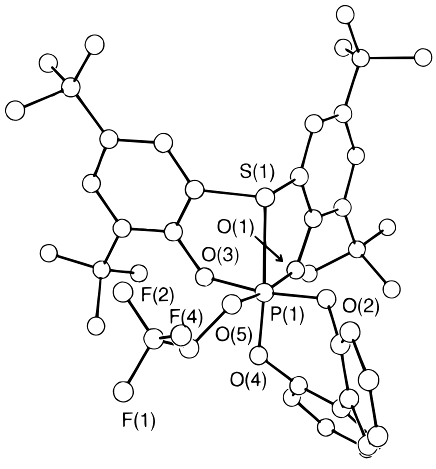


Figure 30. X-ray crystal structure of **61a**,[102] drawn from coordinates retrieved from the Cambridge database. Reproduced with permission.

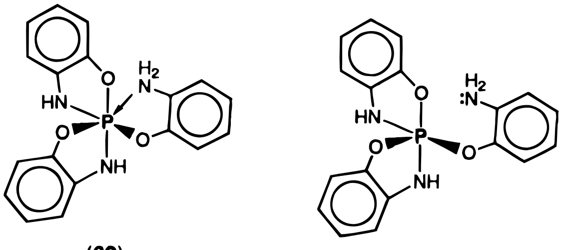
dral six-coordinate phosphorus center with a facially coordinated tridentate ligand and one of the oxygen atoms of the 2,2′-biphenolate ligand bound *trans* to the coordinated sulfur atom of. The P−S bond distance of 2.375(3) Å is comparable to analogous compounds previously reported by Holmes and coworkers (see Table 2).

2. Three Bidentate Chelates

From a coordination chemistry viewpoint, the simplest method for obtaining a neutral six-coordinate phosphorus(V) molecule from three bidentate ligands is by chelation using two dianionic ligands and one monoanionic ligand.

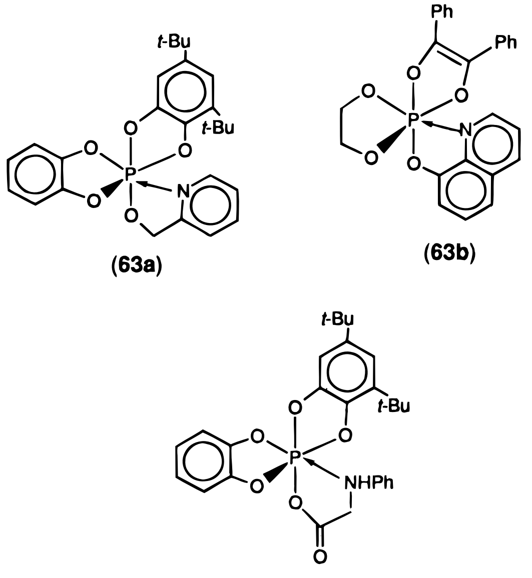
The reaction of hexachlorocyclotriphosphazine, $(NPCl_2)_3$, with 2-aminophenol, H_2L, in boiling xylene resulted in a species, $PL_2(HL)$ (**62**) (among other unidentified substituted cyclophosphazines).[119] Similar products were observed using $(NPF_2)_3$, $(NPBr_2)_3$, $(NPCl_2)_4$, or $(NPCl_2)_n$ (n = ca. 15 000). The HL ligand may be considered as an unidentate or a bidentate ligand which results in a five- or six-coordinate compound, respectively (Figure 31). Most of the NMR and infrared spectroscopic evidence in solution suggests a five-coordinate compound with a dangling $-NH_2$ moiety, however, the infrared spectrum in Nujol mull of **62** showed an absorbance attributed to a NH_2^+ moiety. The authors noted that this was only marginal evidence for the existence of the six-coordinate species in the solid state.

A series of neutral six-coordinate phosphorus(V) compounds with a PO_5N coordination sphere (e.g., **63**) have been described by Munoz and co-workers.[120] The compounds formed are of the general formula PL_2L', where H_2L and HL′ represent dianionic and monoanionic bidentate chelates respectively. For H_2L, the two ligands maybe the same or different and range from various substituted catechols to saturated and unsaturated 1,2-diols. For HL′, the σ-bond donor is usually an alcoholic or carboxylic moiety and the dative bond is via a nitrogen lone pair, thus ligands include 8-hydroxyquinoline, 8-hydroxyquinaldine, 2-pyridylcarbinol, and *N*-phenylglycine. In all cases, three five-membered chelate rings are formed with ^{31}P NMR resonances ranging from −77 to −94 ppm. Examples of the types of compounds formed are shown in Figure 32. The compounds were formed by oxidative addition reactions of PLL′ with benzil or other substituted orthobenzoquinones. Generally, the six-coordinate forms are the thermodynamically more stable species in solution at room temperature, but in a few cases, the five-coordinate form was also observed in solution.



(62)

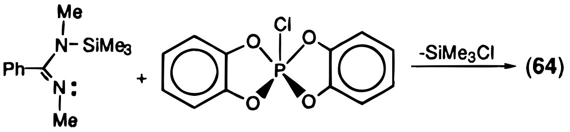
Figure 31. Compound **62** showing unidentate and bidentate behavior of its coordinating ligand.



(63a) **(63b)** **(63c)**

Figure 32. Examples of neutral six-coordinate phosphorus compounds **63a**−**c** described by Munoz *et al.*[120]

The ^{31}P NMR chemical shifts for bis(3-methoxycatecholato)(2-methyloxinato)phosphorus(V) (−78 ppm) and bis(3-methoxycatecholato)(2-methyloxypyridinato)phosphorus(V) (−87 ppm) were reported. On the basis of chemical shift values, six-coordinate phosphorus centers were proposed.[115] The formation of bis(catecholato)(*N*,*N*′-dimethylbenzamidinato)phosphorus(V) (**64**) by a symmetrization process described above (see section **C.2** and eqs 11 and 45). The same compound can be synthesized directly using *N*,*N*′-dimethyl-*N*-(trimethylsilyl)benzamidine and bis(catecholato)chlorophosphorus(V) (eq 50).[64] The permutational isomerization of **64** and related derivatives was investigated by dynamic multinuclear NMR spectroscopy.[121] It was concluded that permutational isomerization occurs according to a dissociative mechanism with the breaking of a P−O bond and forma-



(50)

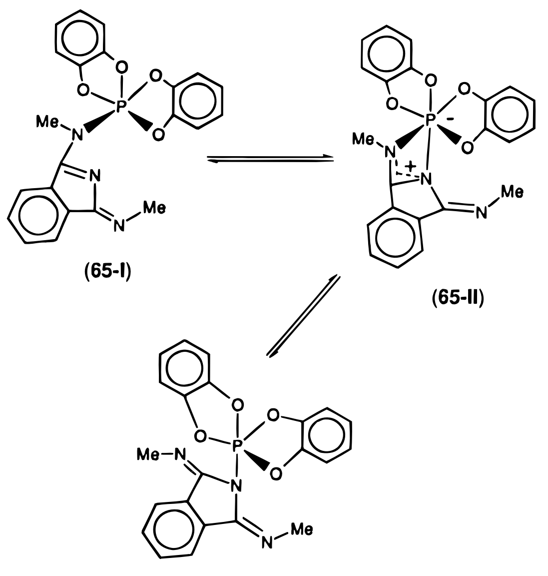
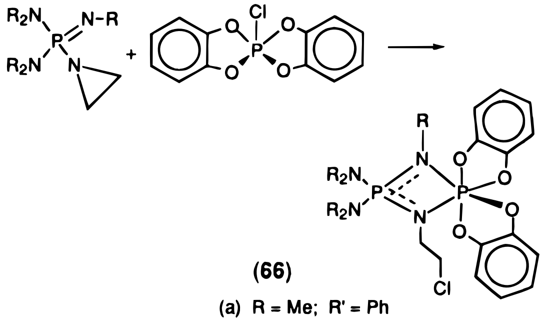


Figure 33. Equilibria between the various five- and six-coordinate forms of 3-{[bis(catecholato)phosphoranyl]methylamino}-1-(methylimino)-1*H*-isoindole (**65I–III**).[122]

tion of five-coordinate quadratic-pyramidal intermediates. The stereochemical result is inversion of the configuration about the phosphorus atom and axial–equatorial exchange of one of the five-membered chelate rings.

Reversible five- and six-coordinate isomerism of a phosphorus(V) species was demonstrated by 3-{[bis(catecholato)phosphoranyl]methylamino}-1-(methylimino)-1*H*-isoindole (Figure 33).[122] Dynamic ^{1}H and ^{31}P NMR studies indicate a fast reversible intramolecular isomerism between types **65-I** and **65-II**. The dissociation of **65-II** is probably limited by the formation of the energetically less favored type **65-III**.

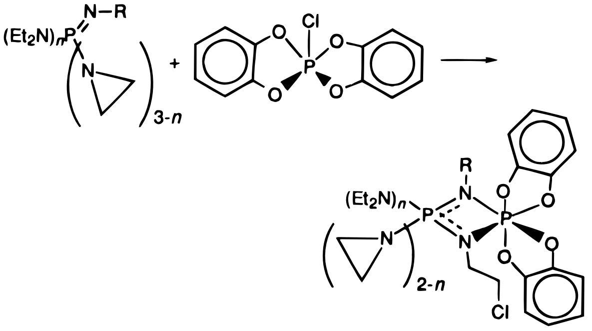
Formation of **66–68** proceeds through a migratory mechanism which is eased by the thermodynamic advantage of a diazadiphosphetidine transition state (eqs 51–53).[123,124]



(51)

(66)

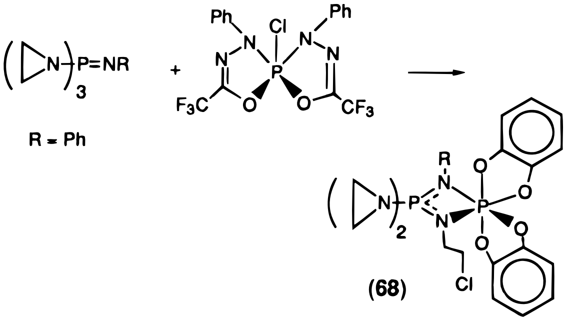
(a) R = Me; R' = Ph
(b) R = R' = Et
(c) R = R' = Pr



(52)

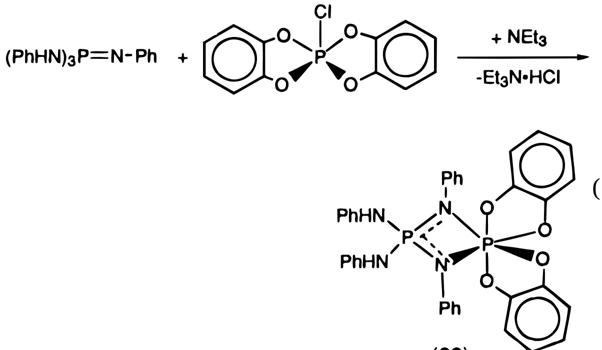
(67)

(a) R = Et; n = 1
(b) R = Ph; n = 0



(53)

(68)



(54)

(69)

Typical ^{31}P NMR chemical shifts for the six-coordinate phosphorus center lie between −113 and −116 ppm, $^2J_{PP}$ = 53–74 Hz. ^{1}H NMR spectra and elemental analyses were also reported for these compounds. It is notable that these compounds are reported to be water insoluble and also do not decompose when washed with water. A more direct synthesis of similar compounds were reported by the same authors (eq 54).[125] In contrast, these analogous compounds were easily hydrolyzed in water.

A six coordinate P(V) structure with a P=S component has been demonstrated by the crystal structure of the bis(8-(dimethylamino)-1-naphthyl)phenylphosphane sulfide (**70**, Figure 34). The compound shows a distorted six-coordinate environment about the phosphorus and the central structure is described as a bicapped tetrahedron. The structure resembles that of the similarly substituted P(III) complex (vide infra). The P–N bond lengths are relatively long (3.01 Å) but are shorter than the sum of van der Waals radii.[126]

Recently, Shevchenko and Schmutzler[127–130] have reported detailed studies of 1,3-diaza-4,6-diphosphorines (**71a**,**b**, Figure 35) with tetrachloroorthobenzoquinone. It has already been noted that the subtle change in steric behavior between **71a** and **71b** has produced significant differences in their chemical behavior.[130] An oxidative addition reaction of **71a** with 2 equiv of tetrachloroorthobenzoquinone is expected to produce two phosphorus(V) centers each oxidized by 1 equiv of tetrachloroorthobenzoquinone, but instead it was believed that this intermediate (**72**) rapidly rearranges to the more thermodynamically stable zwitterionic form (**73**, eq 55).[127]

The ^{31}P NMR spectrum of (**73**) displays two doublets at δ 55 and −115 ppm, $^2J_{PP}$ = 4.3 Hz, corresponding to the four- and six-coordinate centers,

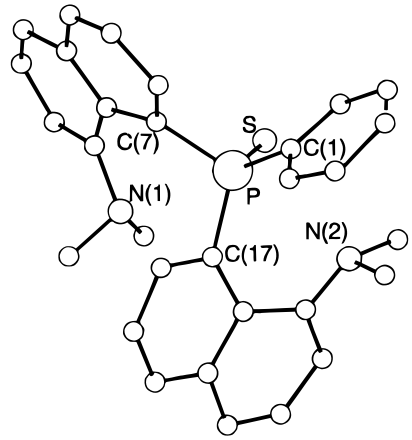
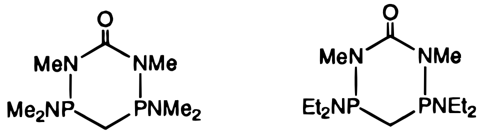
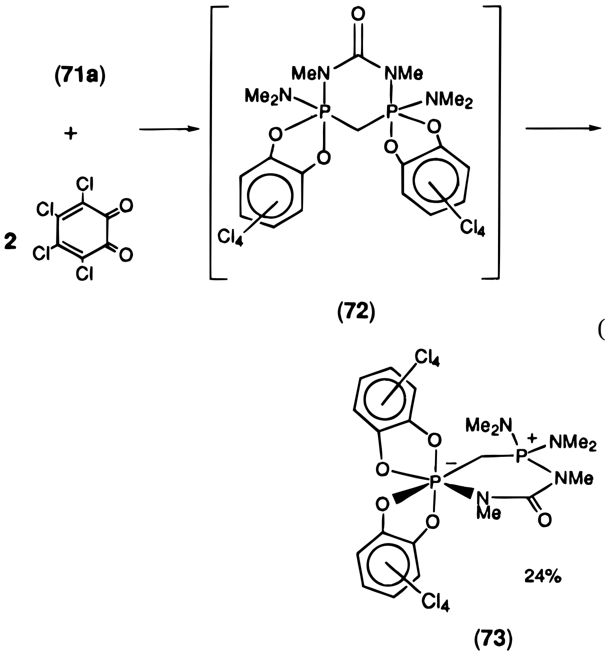


Figure 34. Structure of **70** drawn from information supplied by the authors.[126] Reproduced with permission.



(71a) **(71b)**

Figure 35. Proposed structures of the 1,3-diaza-4,6-diphosphorines, (**71a** and **71b**).



(55)

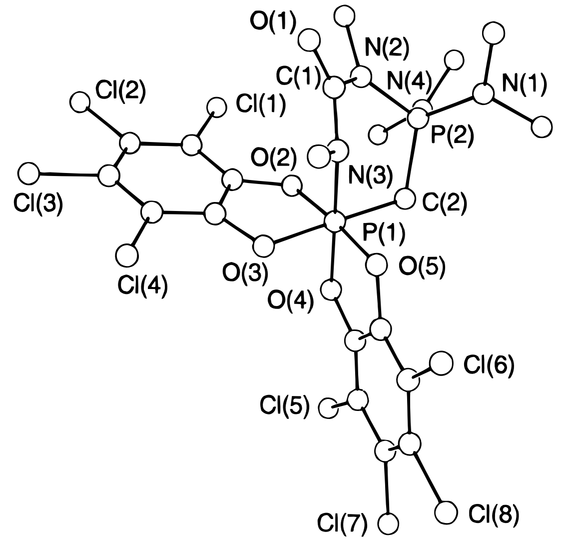
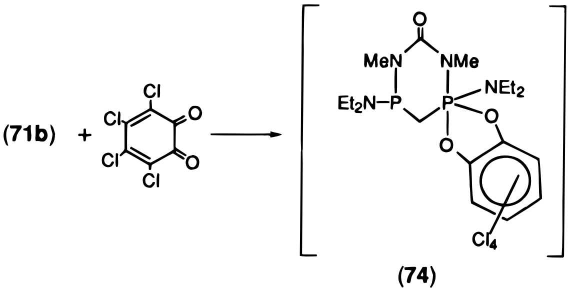


Figure 36. X-ray crystal structure of **73**,[127] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.



(56)

respectively. The X-ray crystal structure of **73** (Figure 36) shows the six-coordinate phosphorus(V) center possessing an octahedral arrangement with only minor deviations from the ideal 90° or 180° bond angles. The reactivity of **71** with tetrachloroorthobenzoquinone is more complicated, and different products are obtained depending on the sequence of addition of the second equivalent of tetrachloroorthobenzoquinone.[128] A monooxidized phosphorus(V) intermediate (**74**), obtained from the addition of 1 equiv of tetrachloroorthobenzoquinone, was identified by NMR spectroscopy (^{31}P δ 70.6 and −15.2 ppm, $^{2}J_{\mathrm{PP}} = 3.4$ Hz, eq 56).

Further addition of tetrachloroorthobenzoquinone produced a mixture of compounds including **75** (^{31}P δ −102.7 ppm) and **76** (Figure 37) whose structures were ultimately identified by X-ray crystallography.[128] Selected ^{31}P NMR data are given in Table 12. Compound **75** was obtained in 10% yield when the reaction was carried out in diethyl ether at −30 °C. The X-ray crystal structure of **75** (Figure 38)[128] shows the coordination at the phosphorus atom to be essentially an octahedron with the major deviation being imposed by the strained four-membered ring (N−P−N is 72.8°).

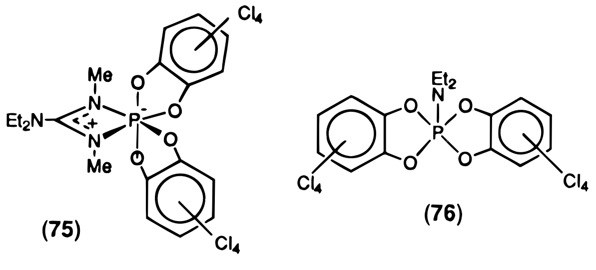


Figure 37. Proposed structures of **75** and **76**.

When the intermediate **74** was allowed to stand at 20 °C for 48 h before the addition of the second equivalent of tetrachloroorthobenzoquinone, a rearrangement occurs which facilitates a new reaction coordinate leading to the formation of **77** (9% yield, ^{31}P δ, 59.3 and −137.6 ppm, $^{2}J_{\mathrm{PP}} = 21.4$ Hz, eq 57).[128,129]

The X-ray crystal structure of **77** (Figure 39)[128] shows a distorted octahedral six-coordinate phosphorus center possessing three chelates of ring sizes four, five, and seven. The major distortions derive from the strained four-membered ring. Thermal decom-

Table 12. Tricyclic: Six-Coordinate Phosphorus Centers with Three Bidentate Chelates[a]

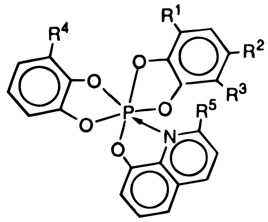
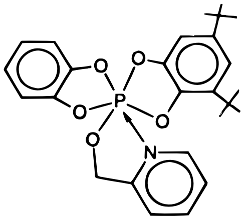
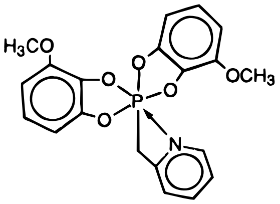
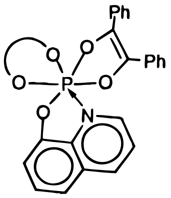
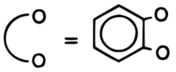
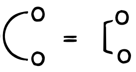
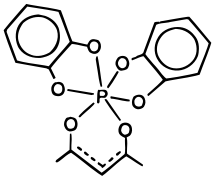
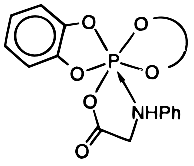
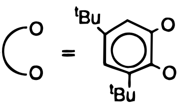
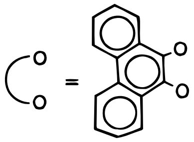
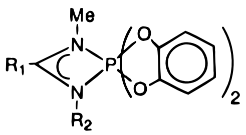
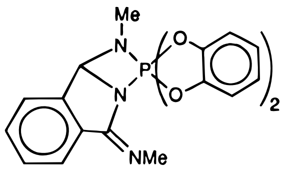
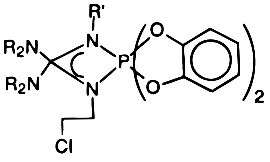
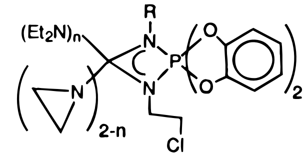
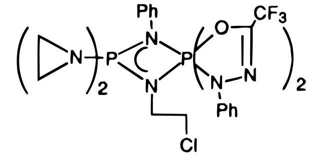
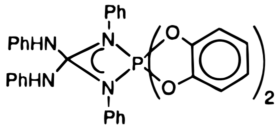
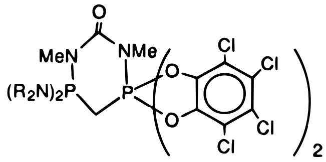
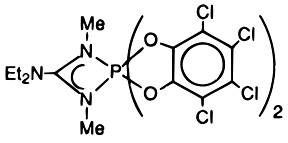
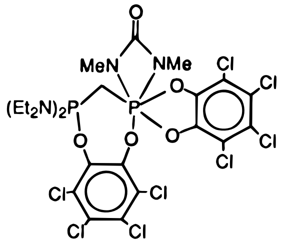
compound		δ_P (ppm)	ref
	$(R^1 = OCH_3, R_2 = R_3 = H, R_4 = OCH_3, R_5 = CH_3)$ $(R^1 = {}^tBu, R_2 = {}^tBu, R_3 = H, R_4 = H, R_5 = H)$ $(R^1 = {}^tBu, R_2 = H, R_3 = {}^tBu, R_4 = H, R_5 = CH_3)$	−78 −88 −77	120, 115 120 120
	**63a**	−86	120
		−87	115
		−94	120
	63b 	−85	120
		−104	120
	**63c** 	−90	120
		−89	120
	**55a** $(R_1 = Ph, R_2 = Me)$ **55b** $(R_1 = Ph, R_2 = {}^iPr)$ **55c** $(R_1 = CCl_3, R_2 = Me)$ **55d** $(R_1 = CF_3, R_2 = Me)$ **55e** $(R_1 = CF_3, R_2 = {}^iPr)$	−113.7 −96.4 −102.4 −97.9 −93.3	64 121 121 121 121
	**65**	−90 (±1)	122
	**66a** $(R = Me, R' = Ph)$ **66b** $(R = R' = Et)$ **66c** $(R = R' = Pr)$	−116.5 −114.3 −113.7	123 123 123

Table 12 (Continued)

compound	δ_P (ppm)	ref
 **67a** (R = Et, *n* = 1)	−115.4	124
67b (R = Ph, *n* = 0)	−112.0	124
 **68**	−111.3	124
 **69**	−115.1	125
 **73** (R = Me)	−115	127
80 (R = Et)	−115	130
 **75**	−102.7	128
 **77**	−137.6	128

[a] Some compounds are not numbered, as they are not discussed in the text and are close homologues of those which are numbered.

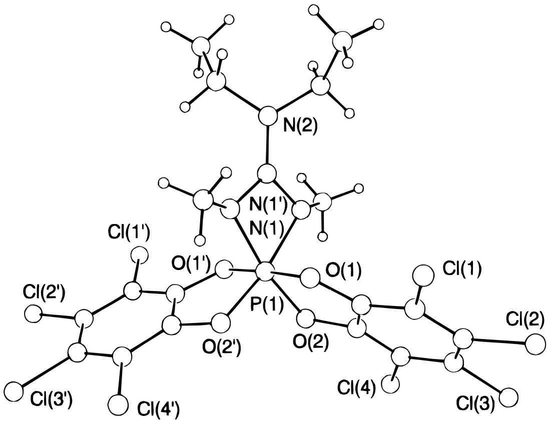
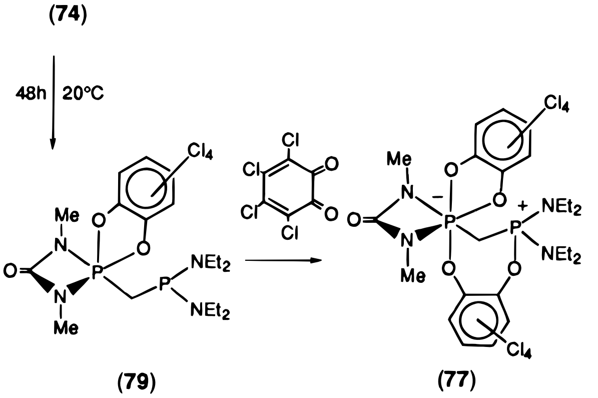


Figure 38. X-ray crystal structure of **75**,[128] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.

 (57)

position of **77** leads to formation of **75** and **76**. Although a different intermediate was initially proposed, confirmation for the formation of **79** was subsequently provided by its isolation and reaction products.[129,130] When **79** is reacted with CCl_4 at 80 °C, a mixture of compounds were formed including ylides **75** (1−2% yield) and **80** (6−8% yield). Note that compound **80**, which is a homologous to **73** (eq 55), could not be obtained in the same way.

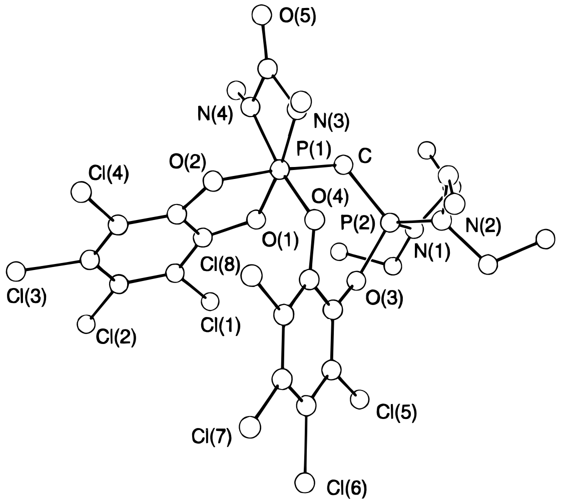
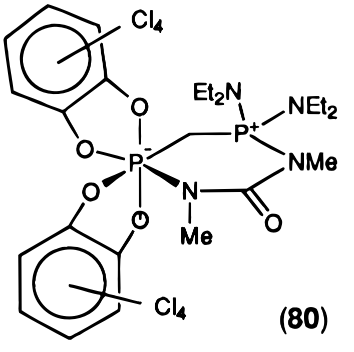


Figure 39. X-ray crystal structure of **77**,[128] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.



(80)

Figure 40. Proposed structure of **80**.

E. A Six-Coordinate Diphosphorus Heterocycle

An unusual six-membered heterocycle with two λ^6 phosphorus(V) centers was obtained from the reaction of PF_5 with silylated pyrazole[37] which gave **81**, The novel compound was structurally characterized (see Figure 41) and the six-coordinate environment at the two phosphorus centers revealed.

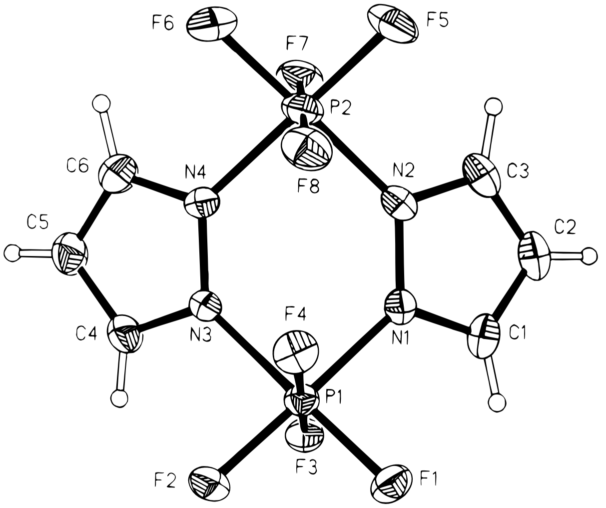
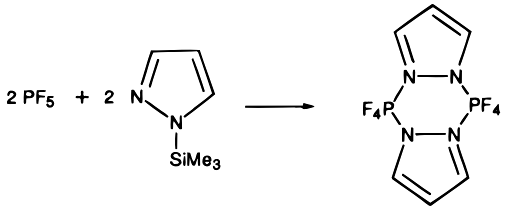


Figure 41. X-ray crystal structure of **81**.[37] Reproduced with permission of the original authors and the journal.

Related N-heterocycles (imidazole, benzimidazole) gave only the PF_5·base adducts (postulated as intermediates in reaction 58) which were discussed in section II.A. The NMR parameters of these adducts are included in the listing in Table 1. Thermolysis of the adducts did not give analogues of **81** but rather, the N$-$$PF_4$ phosphoranes were obtained.



(58)

(81)

F. Tetracyclic Substituents

The encapsulation of phosphorus in porphyrin centers typically yields a number of cationic species containing λ^6 P(V); however, the neutral compound **82** is of relevance to this review. Reaction of octaethylporphyrin dihydride with ethyl dichlorophosphine in the presence of pyridine followed by air oxidation gave the compound **82**, a purple solid, in moderate yield. The crystal structure (Figure 42)[131] revealed the six coordinate geometry at phosphorus with four P$-$N bonds (average 2.00 Å) and *trans* disposed ethyl (P$-$C 1.84(1) Å) and P=O substituents. The P=O bond is short (1.487(8) Å) with a length almost the same as that in Ph_3P=O. The P=O species is readily protonated to form a cationic λ^6 phosphorus(V) center with a P$-$OH functionality which is moderately acidic. This P$-$OH species is readily deprotonated with DBU to regain the P=O compound.[131]

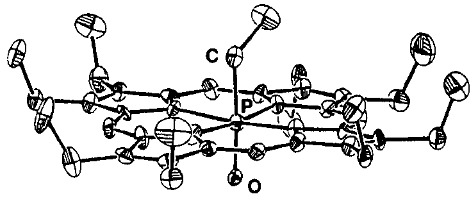


Figure 42. The structure of **82**. (Reprinted from ref 131. Copyright 1995 American Chemical Society.)

Calixirane derivatives of P(V) form a variety of species in which the phosphorus may be four, five, or six coordinate. Of relevance to this review is the compound **83**,[132−134] which contains an overall neutral molecule characterized as a zwitterionic species containing a six-coordinate P(V) center as indicated by the large ^{31}P NMR chemical shift (−120 ppm) value. The phosphorus is bound by four oxygens, a dimethylamine, and a directly bound hydrogen which is clearly indicated by the $^1J_{PH}$ value (733 Hz). The crystal structure of **83** (Figure 43) shows the six-coordinate geometry with a distorted octahedron surrounding the phosphorus. The phosphorus is displaced from the O_4 plane (by 0.141 Å) and the P$-$O bond lengths are within the normal single bond range.

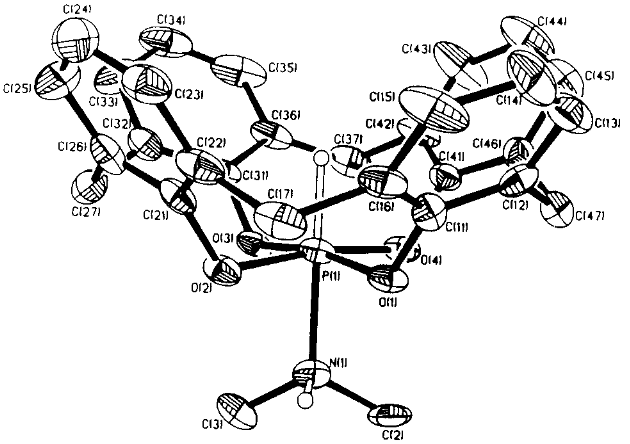


Figure 43. X-ray crystal structure of **83**.[132] Reproduced with permission.

III. Higher Coordination in Phosphorus(III) Derivatives

1. Pseudo-Six-Coordinate Phosphorus(III)

The bis(aminonaphthyl) derivatives of $PhPCl_2$ (**84**) show some evidence of increased coordination of the phosphorus center as revealed by crystal structure analysis (Figure 44).[126] In these cases the P−N coordination is relatively strong for this kind of interaction (P−N bond lengths are about 2.78 Å), significantly shorter than the sum of van der Waals radii, but the lengths are not by any means comparable to the P−N adducts discussed above. In addition the ^{31}P NMR shows a shift to higher field as expected for the increased coordination. The interaction appears, based on bond length arguments, to be stronger in this P(III) compound than in the pentavalent P=S derivative discussed above. This P(III) structure is also described as a distorted bicapped tetrahedron rather than an octahedron. The weaker interaction evinced in these compounds relative to the majority of six-coordinate species discussed in this review is a reflection of the fact that these P(III) centers are not as acidic as the P(V) centers.

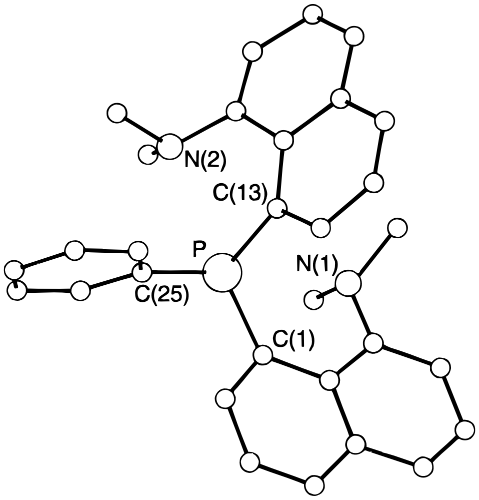


Figure 44. Structure of **84** drawn from information supplied by the authors (with permission).[126]

2. Pseudo-Seven-Coordinate Phosphorus(III)

These compounds are formed as the result of three monobasic bidentate ligands chelating to a phosphorus(III) center. The pseudo-seventh-coordination site is formed as a result of the stereochemically active lone pair of electrons on the phosphorus(III) center (Table 13).

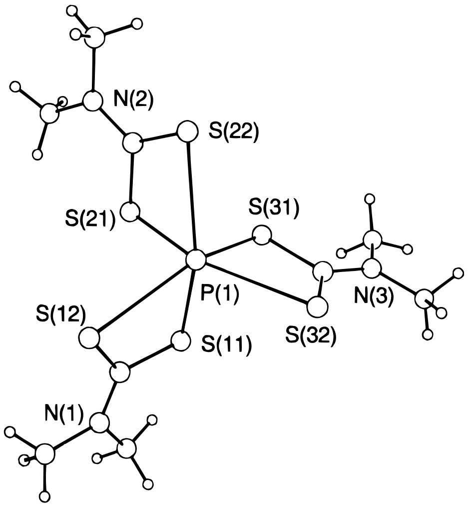
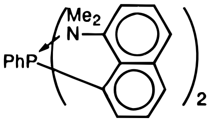
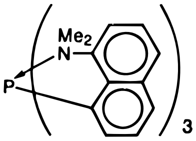
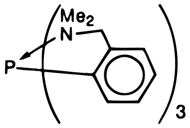


Figure 45. X-ray crystal structure of $P(S_2CNMe_2)_3$ (**85**),[137] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission.

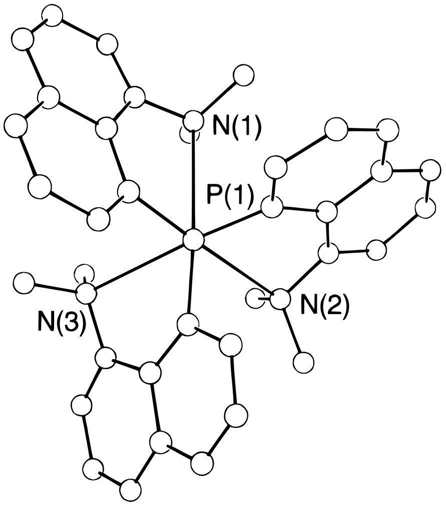
Reactions of aminophosphines with CS_2 were noted long ago,[135] and the system was extended by Nöth and others many years later.[136] The products were formulated as the "insertion" adducts of the aminophosphines with carbon dioxide, carbonyl sulfide, and carbon disulfide. The true nature of the structures as pseudo-seven coordinate derivatives of P(III) was revealed only by the X-ray crystal structural analysis of $P(S_2CNMe_2)_3$ (**85**) in 1980 by Paine and co-workers (Table 14).[137] The high-field ^{31}P NMR chemical shift value observed (−62.6 ppm) is consistent with a significant increase of coordination number relative to that of tricoordinate phosphines. The structure of **85** (Figure 45) can be described as a PS_6 polyhedron which has a geometry approximating a distorted trigonal antiprism or a distorted capped octahedron. In each of the three four-membered rings there is a short and a long P−S bond with an average bond distance of 2.178(9) and 2.966(31) Å, respectively. The short and long P−S bond distances can be attributed to covalent and dative/ionic interactions, respectively. If the geometry of the molecule is considered as a distorted octahedron, then each short P−S bond is *trans* to a long P−S bond or the short and long P−S bonds can be described as forming facial arrangements. It is to be expected that the analogous adducts will display similar features.

Two further examples of pseudo-seven-coordinate phosphorus(III) compounds have recently been described by Corriu and co-workers[138] through the X-ray structures of tris(8-dimethylamino-1-naphthyl)phosphane (**86**) and tris[2-(dimethylaminomethyl)-phenyl]phosphane (**87**, Figure 46). Both structures show dative $N\rightarrow P$ coordinate bonds *trans* to a C−P bond. The P−N bond distances (Table 14) are 2.805−2.853 and 2.999−3.071 Å for **86** and **87**, respectively, which are again shorter than the sum of the N and P van der Waals radii (3.4 Å) but much longer than a covalent N−P distance (1.80 Å). The stronger P−N interaction in **86** is attributed to the rigidity of the naphthyl rings which force the NMe_2 moiety to

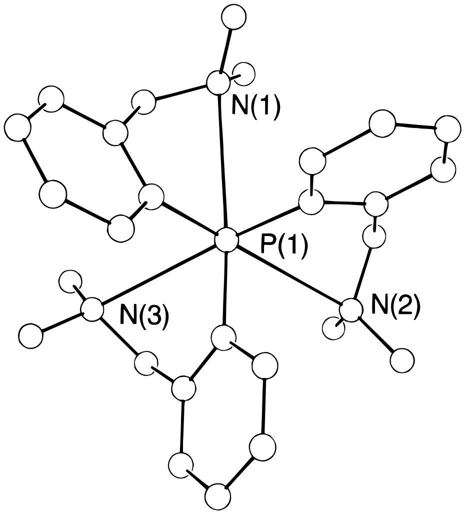
Table 13. Pseudo-Six- and Seven-Coordinate Phosphorus(III) Centers

compound		δ_P (ppm)	ref
	**84**	4.4[a]	126
$P[S_2CN(CH_3)_2]_3$	**85**	−62.6	137
	**86**	6.07	138
	**87**	−34	138

[a] Solid state δ (^{31}P) = −2.7 ppm.



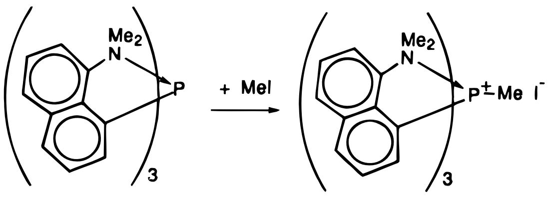
86



87

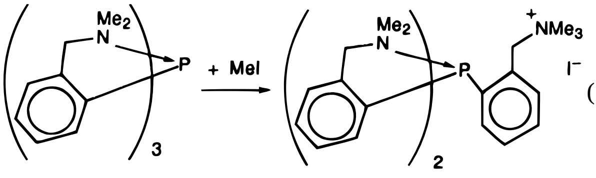
Figure 46. Structures of **86** and **87**[138] redrawn from coordinates retrieved from the Cambridge database. Reproduced with permission of the original authors and the journal.

interact with the phosphorus center. In **86**, the steric constraint is relieved and is reflected in its stability in solution and reactivity toward methyl iodide when compared with **86** (eqs 59 and 60). No pseudo-seven-coordinate derivatives of P(V) have been reported, and there are no examples of a phosphorus center carrying seven directly bound substituents.



(86)

(59)



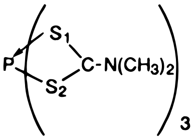
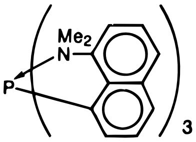
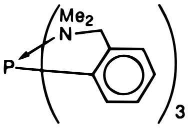
(87)

(60)

IV. Conclusions

It is clear that the six-coordinate environment about phosphorus is reasonably accessible in neutral compounds and that a large variety of stable molecular species may be constructed given an appropriate choice of substituents on the central atom. Highly electronegative substituents increase the Lewis acidity of the phosphorus center and so promote intramolecular acid−base adduct formation with a concomitant increase in the central atom coordination. Although a practical limit to the coordination and binding shell seems to be six bound entities attached to phosphorus, it is dangerous to suggest that the six-coordinate state will never be exceeded given the ingenuity of chemists and we will make no such assertion. The central charge on phosphorus appears to be readily able to support the attachment of at least six substituents to the central element. It is also clear that there appears to be no particular weakness in the bonding of the phosphorus center

Table 14. Selected Bond Lengths in Pseudo-Seven-Coordinate Compounds of Trivalent Phosphorus

compound		bond	bond lengths (Å)	ref
	**85**	P−S1 (avg) P−S_2 (avg)	2.966(31) 2.178(9)	137
	**86**	P−N	2.805−2.853	138
	**87**	P−N	2.999−3.071	138

[a] Crystallographic equivalent atoms. [b] Three independent molecules in unit cell. [c] Nitrogen positions disordered. [d] Crystallographically equivalent nitrogens.

itself to this large number of attached substituents and the notion of “hypervalency” (i.e., beyond the octet) with an implied consequence of weak or reactive bonding in such an environment is unprofitable. Reactivity is an important aspect of these systems that has not been systematically explored except in a few instances. Many pathways are possible which may involve either dissociative processes involving reduced coordination of the phosphorus or further association to access an even higher coordination state. With multidentate substituents however, the exchange of an *intra*molecular bonding interaction with a new bond to an attacking moiety may provide an attractive mechanistic pathway. Such processes may be difficult to identify unambiguously. Further exploration of the reactivity of the six-coordinate phosphorus environment would be profitable. The wealth of accessible coordination states demonstrated by phosphorus within its normal electrovalent states of 3 and 5 introduces virtually limitless possibilities for structural rearrangements. Several such examples have been illustrated in this review. Even the limited high-coordination system reviewed herein clearly offers further synthetic challenges and opportunities within the field of phosphorus chemistry. It is also to be expected that fruitful pursuit of the study of the reactivity of such highly coordinated molecular centers with a view to elucidating the fundamental reaction processes which operate within this framework of the higher coordination states of phosphorus will be undertaken. Such studies may also contribute to the understanding of the nature of those biochemically important reaction processes which traverse this domain.

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References

(1) Chuit, C.; Corriu, R. J. P.; Reyé, C.; Young, J. C. *Chem. Rev.* **1993**, *94*, 1371−1448.
(2) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17−31.
(3) Tandura, S. N.; Voronkov, M. G.; Alekseeva, N. V. *Top. Curr. Chem.* **1986**, *131*, 99−189.
(4) Gilheany, D. G. *Chem. Rev.* **1994**, *94*, 1339−1374.
(5) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927−950.
(6) Johnson, K. A.; Benkovic, S. J. In *The Enzymes*, 3rd ed.; Sigman, D. S., Boyer, P. D., Eds.; Academic Press: New York, 1990; Vol. XIX, p 177.
(7) Michalski, J.; Skowronska, A.; Bodalski, R. *Mechanisms of Reactions of Phosphorus Compounds.* In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L., Eds.; VCH: Deerfield Beach, FL, 1987; Chapter 8, pp 255−296.
(8) Holmes, R. R. *Pentacoordinated Phosphorus; ACS Monograph 175;* American Chemical Society: Washington, D. C., 1980; Vol I, Structure and Spectroscopy. *Pentacoordinated Phosphorus; ACS Monograph 176;* American Chemical Society: Washington, D.C., 1980; Vol. II, Reaction Mechanisms.
(9) Schmutzler, R. The Chemistry of the Phosphorus Fluorides. In *Advances in Fluorine Chemistry*; Stacey, M., Tatlow, J. C., Sharpe, A. G., Eds.; Butterworths: London, 1965; Vol. 5, pp 31−285.
(10) Burgada, R.; Setton, R. Phosphonium Salts, Ylides and Phosphoranes. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: London, 1994; Vol. 3, Chapter 3, pp 185−272.
(11) Webster, M. *Chem. Rev.* **1966**, *66*, 87−118.
(12) Cherasov, R. A.; Polezhaeva, N. A. *Russ. Chem. Rev. (Engl. Transl.)* **1987**, *56*, 163−181 (*Usp. Khim.* **1987**, *56*, 287−321).
(13) Markovskii, L.; Kalchenko, V.; Negrebetskii, V. *New J. Chem.* **1990**, *14*, 339-351.
(14) Markovskii, L. I.; Kalchenko, V. I.; Povolotsky, M. I. Reversible Coordination Isomerism of Organophosphorus Compounds. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structrual Analysis*; Quin, L., Verkade, J. G., Eds.; VCH: Deerfield Beach, FL, 1994; Vol. 2; Chapter 25, pp 333-343.
(15) Cavell, R. G. NMR Studies of the Stereochemistry and Fluxionality of Five- and Six-Coordinate Phosphorus Compounds. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L., Eds.; VCH: Deerfield Beach, FL, 1987; Vol. 1, Chapter 7, pp 231−254.
(16) Tebby, J. C. General Experimental techniques and Compilation of Chemical Shift Data. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L., Eds.; VCH: Deerfield Beach, FL, 1987; Vol. 1, Chapter 1, pp 1-60.
(17) Corbridge, D. E. C., *Phosphorus. An Outline of its Chemistry, Biochemistry and Technology*, 3rd ed.; Elsevier: Amsterdam, 1985; pp 56-65.
(18) Holmes, R. R. *Diss. Abs.* **1954**, *14*, 452.
(19) Gutmann, V. *Monatsh. Chem.* **1954**, *85*, 1077−1081.
(20) Beattie, I. R.; Webster, M. *J. Chem. Soc.* **1961**, 1730−1733.
(21) Beattie, I. R.; Gilson, T. R.; Ozin, G. A. *J. Chem. Soc. A* **1968**, 2772−2778.
(22) Holmes, R. R.; Gallagher, W. P.; Carter, J. R. P. *Inorg. Chem.* **1963**, *2*, 437−441.
(23) Hensen, K.; Sarholtz, W. *Theor. Chim. Acta* **1968**, *12*, 206−213.
(24) Paul, R. C.; Sehgal, M. L.; Chadha, S. L. *J. Ind. Chem. Soc.* **1970**, *47*, 1071−1075.

(25) Paul, R. C.; Chadha, S. L. *J. Ind. Chem. Soc.* **1968**, *6*, 754−755.

(26) Lehr, W.; Schwarz, M. *Z. Anorg. Allg. Chem.* **1968**, *363*, 43−50.

(27) Zhivukhin, S. M.; Kireev, V. V.; Popilin, V. P.; Kolesnikov, G. S. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1970**, *15*, 630−633.

(28) Holmes, R. R.; Gallagher, W. P. *Inorg. Chem.* **1963**, *2*, 433−437.

(29) Wieker, W.; Grimmer, A. R.; Kolditz, L. *Z. Chem.* **1967**, *7*, 434−435.

(30) Latscha, H. P. *Z. Naturforsch.* **1968**, *23b*, 139−144.

(31) Dillon, K. B.; Reeve, R. N.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1977**, 1410−1416.

(32) Ishley, J. N.; Knachel, H. C. *Inorg. Chem.* **1975**, *14*, 2558−2560.

(33) Woolf, A. A. *J. Inorg. Nucl. Chem.* **1956**, *3*, 285−288.

(34) Muetterties, E. L.; Bither, T. A.; Farlow, M. W.; Coffman, D. D. *J. Inorg. Nucl. Chem.* **1960**, *16*, 52−59.

(35) Kolditz, L.; Rehak, W. *Z. Anorg. Allg. Chem.* **1966**, *342*, 32−40.

(36) Tebbe, F. N.; Muetterties, E. L. *Inorg. Chem.* **1967**, *6*, 129−132.

(37) Well, M.; Jones, P. G.; Schmutzler, R. *J. Fluorine Chem.* **1991**, *53*, 261−275.

(38) Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1974**, 1402−1405.

(39) John, K.-P.; Schmutzler, R. *Z. Naturforsch.* **1974**, *29b*, 730−733.

(40) Harris, J. J.; Rudner, B. *J. Org. Chem.* **1968**, *33*, 1392−1400.

(41) Harman, J. S.; Sharp, D. W. A. *J. Chem. Soc. A* **1970**, 1138−1141.

(42) Brown, D. H.; Fraser, G. W.; Sharp, D. W. A. *J. Chem. Soc. (A)* **1966**, 171−174 (see also *Chem. Ind.* **1964**, 367).

(43) Storzer, W.; Schomburg, D.; Röschenthaler, G.-V.; Schmutzler, R. *Chem. Ber.* **1983**, *116*, 367−374.

(44) Pauling, L., *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(45) Muetterties, E. L.; Mahler, W. *Inorg. Chem.* **1965**, *4*, 119−121.

(46) Brown, D. H.; Crosbie, K. D.; Fraser, G. W.; Sharp, D. W. A. *J. Chem. Soc. A* **1969**, 551−554.

(47) Schultz, C. W.; Ruldolph, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 1898−1903.

(48) Gregor, I. K. *Aust. J. Chem.* **1965**, *18*, 1485−1489 (see also ref 50 for diisopropyl ether and: Gregor, I. K. *Aust. J. Chem.* **1966**, *19*, 1977−1982 for dimethyl sulfide, diethyl sulfide, and dimethyl selenide adduct studies).

(49) Gregor, I. K. *Chem. Ind.* **1965**, 385.

(50) Gregor, I. K. *Aust. J. Chem.* **1965**, *18*, 2035−2038.

(51) Binder, H.; Fluck, E. *Z. Anorg. Allg. Chem.* **1969**, *365*, 166−169.

(52) Cowley, A. H.; Lee, R. C.-Y. *Inorg. Chem.* **1979**, *18*, 60−63.

(53) Dunmur, R. E.; Thönnessen, H.; Müller, C.; Farkens, M.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Chem. Ber.* **1993**, *126*, 2653−2655.

(54) Latscha, H. P.; Hormuth, P. B. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 299. (*Angew. Chem.* **1968**, *80*, 281).

(55) Hormuth, P. B.; Latscha, H. P. *Z. Anorg. Allg. Chem.* **1969**, *369*, 59−63.

(56) Becke-Goehring, M.; Schwind, H. *Z. Anorg. Allg. Chem.* **1970**, *372*, 285−291.

(57) Ziegler, M. L.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 455−456. (*Angew. Chem.* **1969**, *81*, 424).

(58) Kal'chenko, V. I.; Negrebetskii, V. V.; Rudyi, R. B.; Markovskii, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1988**, *58*, 1079−1086. (*Zh. Obshch. Khim.* **1988**, *58*, 1216−1223].

(59) Kal'chenko, V. I.; Negrebetskii, V. V.; Rudyi, R. B.; Atmas', L. I.; Pavolotskii, M. I.; Markovskii, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1983**, *53*, 821−822 (*Zh. Obshch. Khim.* **1983**, *53*, 932−934).

(60) Romanenko, E. A. *Teor. Eksp. Khim.* **1989**, *25*, 237−240 (Russian) (*Chem. Abs.* **1990**, *112*, 7594m).

(61) Romanenko, E. A.; Kal'chenko, V. I.; Rudyi, R. B. *Teor. Eksp. Khim.* **1985**, *21*, 727−730 (Russian) (*Chem. Abs.* **1986**, *104*, 60842b).

(62) Sergienko, L. M.; Ratovskii, B. V.; Timokhin, B. V.; Dmitriev, V. K.; Kal'chenko, V. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1991**, *61*, 579−583 (*Zh. Obsch. Khim.* **1991**, *61*, 638−642).

(63) Kal'chenko, V. I.; Rudyi, R. B.; Negrebetskii, V. V.; Povolotskii, M. I.; Markovskii, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *54*, 1972-1981. (*Zh. Obshch. Khim.* **1984**, *54*, 2207−2217).

(64) Negrebetskii, V. V.; Bogel'fer, L. Y.; Sinitsa, A. D.; Krishtal', V. S.; Kal'chenko, V. I.; Markovskii, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1981**, *51*, 797−798. *(Zh. Obshch. Khim.* **1981**, *51*, 956−957).

(65) Kennepohl, D. K.; Santarsiero, B. D.; Cavell, R. G. *Inorg. Chem.* **1990**, *29*, 5081−5087.

(66) Kennepohl, D. K.; Cavell, R. G. *Phosphorus Sulfur Silicon* **1990**, *49/50*, 359−362.

(67) Kal'chenko, V. I.; Rudyi, R. B.; Negrebetskii, V. V.; Markovskii, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *54*, 2212−2219 (*Zh. Obshch. Khim.* **1984**, *54*, 2477−2485).

(68) Negrebetskii, V. V.; Kal'chenko, V. I.; Rudyi, R. B.; Markovskii, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1985**, *55*, 236−245 (*Zh. Obshch. Khim.* **1985**, *55*, 271−282).

(69) Negrebetskii, V. V.; Kal'chenko, V. I.; Rudyi, R. B.; Markovskii, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *54*, 61−65 (*Zh. Obshch. Khim.* **1984**, *54*, 71−75).

(70) Markovskii, L. N.; Sinitsa, A. D.; Kal'chenko, V. I.; Atamas', L. I.; Negrebetskii, V. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1982**, *52*, 389−390 (*Zh. Obshch. Khim.* **1982**, *52*, 445−446).

(71) Schlak, O.; Schmutzler, R.; Schiebel, H.-M.; Wazeer, M. I. M.; Harris, R. K. *J. Chem. Soc., Dalton Trans.* **1974**, 2153−2157.

(72) Utvary, K.; Czysch, W. *Monatsh. Chem.* **1972**, *103*, 1048−1054.

(73) Meindl, W.; Utvary, K. *Monatsh. Chem.* **1979**, *110*, 129−133.

(74) Galle, K.; Utvary, K. *Monatsh. Chem.* **1988**, *119*, 53−63.

(75) Filonenko, L. P.; Povolotskii, M. I.; Pinchuk, A. M. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *54*, 192−193 (*Zh. Obshch. Khim.* **1984,** *54*, 216−217).

(76) The, K. I.; Vande Griend, L.; Whitla, W. A.; Cavell, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 7379−7380.

(77) Cavell, R. G.; The, K. I.; Vande Griend, L. *Inorg. Chem.* **1981**, *20*, 3813−3818.

(78) Cavell, R. G.; Vande Griend, L. *Inorg. Chem.* **1983**, *22*, 2066−2070.

(79) Cavell, R. G.; Vande Griend, L. *Phosphorus Sulfur* **1983**, *18*, 89−92.

(80) Cavell, R. G.; Vande Griend, L. *Inorg. Chem.* **1986**, *25*, 4699−4704.

(81) Kennepohl, D. K.; Pinkerton, A. A.; Lee, Y. F.; Cavell, R. G. *Inorg. Chem.* **1990**, *29*, 5088−5096.

(82) John, K.-P.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1974**, 1841−1846.

(83) John, K.-P.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1974**, 2466−2468.

(84) Krebs, R.; Schmutzler, R.; Schomburg, D. *Polyhedron* **1989**, *8*, 731−738.

(85) Gibson, J. A.; Röschenthaler, G.-V.; Schmutzler, R. *J. Chem. Soc., Dalton Trans.* **1975**, 918−924.

(86) Sheldrick, W. S.; Gibson, J. A.; Röschenthaler, G.-V. *Z. Naturforsch.* **1978**, *33b*, 1102−1105.

(87) Martynov, I. V.; Aksinenko, A. Y.; Cheklov, A. N.; Pushin, A. N.; Sokolov, V. B. *Bull. Acad. Sci. USSR (Engl. Transl.)* **1987**, *36*, 1559. (*Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 1680).

(88) Martynov, I. V.; Cheklov, A. N.; Aksinenko, A. Y.; Sokolov, V. B.; Pushin, A. N. *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)* **1987**, *297*, 530−533. (*Dokl. Akad. Nauk SSSR* **1987**, *297*, 1132−1136).

(89) Cheklov, A. N.; Martynov, I. V.; Aksinenko, A. Y.; Sokolov, V. B. *Bull. Acad. Sci. USSR (Engl. Transl.)* **1988**, *37*, 815−817 (*Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, *37*, 936−937).

(90) Cheklov, A. N.; Martynov, I. V.; Aksinenko, A. Y.; Sokolov, V. B. *Sov. J. Coord. Chem. (Engl. Transl.)* **1989**, *15*, 683−688 (*Koord. Khim.* **1989**, *15*, 1192−1198).

(91) Kaukorat, T.; Jones, P. G.; Schmutzler, R. *Heteroat. Chem.* **1991**, *2*, 81−86.

(92) Robert, D.; Gawad, H. A.; Riess, J. G. *Bull. Soc. Chim. France* **1987**, 511−516.

(93) Well, M.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Chem. Ber.* **1993**, *126*, 1765-1768.

(94) Michaelis, A.; Kerkhof, W. *Chem. Ber.* **1898**, *31*, 2172−2179.

(95) Pinkus, A. G.; Ma, S. Y.; Custard, J., H. C. *J. Am. Chem. Soc.* **1961**, *83*, 3917-3918.

(96) Schöning, G.; Glemser, O. *Z. Naturforsch.* **1977**, *32b*, 117−118.

(97) Kornuta, P. P.; Kolotilo, N. V.; Markovskii, L. N. *J. Org. Chem. USSR (Engl. Transl.)* **1983**, *19*, 1573−1574. (*Zh. Organsch. Khim.* **1983**, *19*, 1772−1773).

(98) Brown, N. M. D.; Bladon, P. *J. Chem. Soc., Chem. Commun.* **1966**, 304.

(99) Sheldrick, W. S.; Hewson, M. J. C. *Z. Naturforsch.* **1978**, *33b*, 834−837.

(100) Burford, N.; Kennepohl, D.; Cowie, M.; Ball, R. G.; Cavell, R. G. *Inorg. Chem.* **1987**, *26*, 650−657.

(101) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1913−1920.

(102) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 3391−3397.

(103) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 2690-2695.

(104) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Inorg. Chem.* **1993**, *32*, 4360−4367.

(105) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Phosphorus Sulfur Silicon* **1993**, *75*, 249−252.

(106) Holmes, R. R.; Prakasha, T. K. *Phosphorus Sulfur Silicon* **1993**, *80*, 1−22.

(107) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1994**, *33*, 93−98.

(108) Wong, C. Y.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **1996**, *35*, 325−334.

(109) Cavell, R. G.; Wong, C. Y. *J. Fluorine Chem.* **1995**, *71*, 187−188.

(110) Ramirez, F.; Prasad, V. A. V.; Marecek, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 7269-7275.

(111) Ramirez, F.; Nowakowski, M.; Marecek, J. F. *J. Am. Chem. Soc.* **1976**, *98*, 4330-4332.

(112) Schmidpeter, A.; Criegern, T. V.; Blanck, K. *Z. Naturforsch.* **1976**, *31b*, 1058-1063.

(113) Burgada, R.; Bernard, D.; Laurenço, C. *Compt. Rend.* **1973**, *276c*, 297−299.

(114) Munoz, A.; Koenig, M.; Gence, G.; Wolf, R. *Compt. Rend.* **1974**, *278c*, 1353-1355.

(115) Munoz, A.; Gence, G.; Koenig, M.; Wolf, R. *Compt. Rend.* **1975**, *280c*, 395–397.

(116) Kobayashi, S.; Saegusa, T. *Pure Appl. Chem.* **1981**, *53*, 1663–1677.

(117) Bettermann, G.; Buhl, H.; Schmutzler, R.; Schomburg, D.; Wermuth, U. *Phosphorus Sulphur* **1983**, *18*, 77–80.

(118) Osman, F. H.; Gawad, M. M. A.; Abbasi, M. M. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1189–1192.

(119) Allcock, H. R.; Kugel, R. L. *J. Chem. Soc., Chem. Commun.* **1968**, 1606–1607.

(120) Cong, C. B.; Gence, G.; Garrigues, B.; Koenig, M.; Munoz, A. *Tetrahedron* **1979**, *35*, 1825–1839.

(121) Negrebetskii, V. V.; Kal'chenko, V. I.; Rudyi, R. B.; Markovskii, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1985**, *55*, 1761–1771 (*Zh. Obshch. Khim.* **1985**, *55*, 1982–1994).

(122) Negrebetskii, V. V.; Kal'chenko, V. I.; Balitskaya, O. V.; Kornilov, M. Y.; Markovskii, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *54*, 1982-1986 (*Zh. Obshch. Khim.* **1984**, *54*, 2217–2222).

(123) Zal'tsman, I. S.; Bespal'ko, G. K.; Pinchuk, A. M.; Marchenko, A. P. *J. Gen. Chem. USSR (Engl. Transl.)* **1989**, *59*, 1698–1699 (*Zh. Obshch. Khim.* **1989**, *59*, 1901–1902).

(124) Zal'tsman, I. S.; Bespal'ko, G. K.; Marchenko, A. P.; Pinchuk, A. M.; Sinitsa, A. D.; Tupchienko, S. K. *J. Gen. Chem. USSR (Engl. Transl.)* **1990**, *60*, 1942-1943. (*Zh. Obshch. Khim.* **1990**, *60*, 2175–2176).

(125) Rutkovskii, E. K.; Zal'tsman, I. S.; Feshchenko, N. G.; Pinchuk, A. M. *J. Gen. Chem. USSR (Engl. Transl.)* **1990**, *60*, 1491–1492 (*Zh. Obshch. Khim.* **1990**, *60*, 1670–1671).

(126) Chauhan, M.; Chuit, C.; Corriu, R. J. P.; Reyé, C.; Declercq, J.-P.; Dubourg, A. *J. Organomet. Chem.*, in press.

(127) Shevchenko, I. V.; Jones, P. G.; Fischer, A.; Schmutzler, R. *Heteroat. Chem.* **1992**, *3*, 177–180.

(128) Shevchenko, I. V.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Chem. Ber.* **1992**, *125*, 1325–1332.

(129) Shevchenko, I. V.; Schmutzler, R. *Heteroat. Chem.* **1993**, *4*, 307–312.

(130) Shevchenko, I. V.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Polyhedron* **1993**, *12*, 435–444.

(131) Yamamoto, Y.; Nadano, R.; Itagaki, M.; Akiba, K. *J. Am. Chem. Soc.* **1995**, *117*, 8287–8288.

(132) Khasnis, D. V.; Burton, J. M.; McNeil, J. D.; Santini, C. J.; Zhang, H.; Lattman, M. *Inorg. Chem.* **1994**, 2657–2662.

(133) Khasnis, D. V.; Burton, J. M.; Lattman, M.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1991**, 562–563.

(134) Khasnis, D. V.; Lattman, M.; Gutsche, C. D. *J. Am. Chem. Soc.* **1990**, *112*, 9422-9423.

(135) Michaelis, A. *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 1037–1047.

(136) Vetter, H. J.; Nöth, H. *Chem. Ber.* **1963**, *96*, 1308–1315.

(137) Light, R. W.; Hutchins, L. D.; Paine, R. T.; Campana, C. F. *Inorg. Chem.* **1980**, *19*, 3597–3604.

(138) Chuit, C.; Corriu, R. J. P.; Monforte, P.; Reyé, C.; Declercq, J.-P.; Dubourg, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1430–1432 (*Angew. Chem.* **1993**, *105*, 1529).

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