

Phosphoranides

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I. Introduction

Phosphoranides are hypervalent anionic phosphorus(III) species, having more than four electron pairs in the phosphorus valence shell; they may also be usefully regarded as the conjugate bases of phosphoranes containing P-H bonds. The ions considered in the present review possess single bonds between phosphorus and its substituents, and usually have the structure



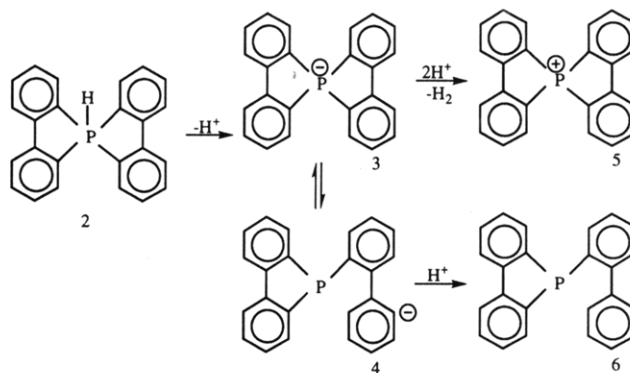
with the lone pair of electrons equatorial in a ψ -tbp arrangement, as expected from VSEPR considerations. This gives the phosphorus a 10-P-4 arrangement in the *N*-X-L nomenclature (*N* electrons around central atom X attached to L ligands), proposed by Martin and co-workers.¹ There have been no reports as yet of doubly-charged 12-P-5 ions of the type PX_5^{2-} , although theoretical studies of the PF_5^{2-} ion have been carried out; this is expected to display a distorted square pyramidal structure.²⁻⁵ (Similar ions, together with SbX_6^{3-} species, are well-established for antimony(III).) Other types of phosphoranides involving double bonding to phosphorus include the phosphorinyl lithium salts prepared by Märkl and Martin⁶ and the iminophosphoranide anions proposed as reactive intermediates by Cowley and Kemp,⁷ but these are not discussed further in the present review.

Phosphoranides are of considerable importance as models for the reactive intermediates (or the transition states) in nucleophilic substitution reactions at phosphorus(III) centers, and their participation in both inorganic⁸ and organic⁹⁻¹³ reactions had been postulated, even before their existence was demonstrated. Thus Muettterties and co-workers reported that CsF (or KF) absorbed PF_3 in a vacuum system at 130 °C, the products being red phosphorus and the metal hexafluorophosphate(V), and suggested that reaction might proceed through an $M PF_4$ intermediate.⁸ NaF did not react with PF_3 under these conditions. Wittig and Maercker considered the phosphoranide $[PPh_3-(C_6H_4Me)]^-Li^+$ (1) as a likely intermediate in the reaction between Ph_3P and LiC_6H_4Me to yield small amounts of $PPh_2(C_6H_4Me)$, but elicited no direct



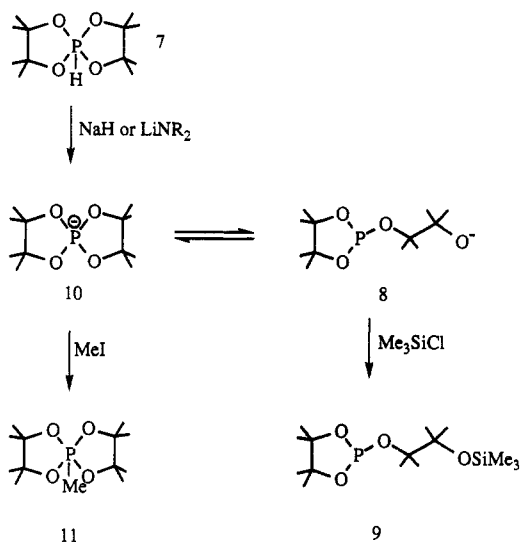
Keith Dillon was born near Leicester, England, in 1942. He was awarded his M.A. and D.Phil. degrees by the University of Oxford in 1966, for research on copper(II) complexes under the supervision of Dr. F. J. C. Rossotti. After post-doctoral posts at the Universities of Warwick and Oxford, he was appointed in 1970 to a lectureship in inorganic chemistry at the University of Durham, and was promoted to a senior lectureship in 1987. He has also spent a sabbatical period at the Université Paul Sabatier, Toulouse, France. Research interests include the coordination chemistry of main group elements, particularly phosphorus, tin, and boron, and the application of NMR and NQR spectroscopic techniques to inorganic systems.

evidence for it.⁹ Hellwinkel observed that a certain amount of the phosphonium salt 5 formed, as well as the phosphine 6, when the phosphorane 2 was treated with organometallic bases, followed by acidic workup.¹⁰



He rationalized the results by proposing an equilibrium between the phosphoranide 3 and the carbanion 4 in the intermediate stage. Savignac et al.¹² found that metalation occurred when spiroposphorane 7 was treated with NaH or $LiNR_2$, as shown by the disappearance of its ^{31}P NMR signal and the detection of a new resonance at 140 ppm, assigned to the open phosphine form 8. Subsequent reaction with Me_3SiCl caused O-silylation to yield 9 and did not affect this resonance, but with MeI as the alkylating agent phosphorane 11 was produced, supporting the participation of phosphoranide 10 as an intermediate in

equilibrium with 8, even if present only in low concentration. Kinetic studies by Kyba on nucleophilic



substitution reactions at P(III) centers, using chiral phosphines, however, showed that complete inversion of configuration at phosphorus occurred, indicating the absence of any pseudorotation in a possible phosphorane intermediate.^{14,15} He concluded that the reactions were essentially classical S_N2 processes, with no formation of an intermediate.¹⁵

The first phosphorane to be isolated was the PBr_4^- ion (as its Pr_4N^+ salt) by Dillon and Waddington in 1969, and its ^{31}P NMR spectrum was recorded,¹⁶ although the crystal structure was not determined until much later.¹⁷ Clear evidence for a cyclic organophosphorane anion was obtained from ^{31}P NMR spectroscopy by Granth and Martin in 1978.¹⁸ In the only previous review of phosphoranides, published in 1987, Riess¹⁹ divided the topic into halogeno and pseudohalogeno species such as PBr_4^- and $\text{PBr}_2(\text{CN})_2^-$,²⁰ cyclic organic phosphoranides, like the one described by Granth and Martin,¹⁸ and phosphoranides as ligands (to transition metals). More recent work has included the synthesis and characterization of several noncyclic phosphoranides with organo substituents present, which are more closely related to the pseudohalogeno derivatives.²¹⁻²⁷ This review has therefore been subdivided in a different way, with synthesis, structure, and reactivity of all types of noncoordinated phosphoranides being jointly considered, followed by metal derivatives.

Whenever the chemical shift of a three-coordinate phosphorus(III) precursor has been measured, a marked displacement to lower frequency, or higher field, occurs on formation of the phosphorane, as pointed out by Riess.¹⁹ Hence NMR spectroscopy constitutes a particularly valuable technique in many instances for indicating whether or not a phosphorane has been produced.

It is also relevant to mention three theoretical studies on phosphoranides of the PX_4^- type.²⁸⁻³⁰ The ion PH_4^- was deduced to have a C_{2v} structure, with P-H_{ax} and P-H_{eq} distances of 1.71(6) and 1.40(9) Å respectively, an $\text{H}_{\text{eq}}-\text{P}_{\text{eq}}-\text{H}_{\text{eq}}$ angle of 102.8°, and an $\text{H}_{\text{ax}}-\text{P}-\text{H}_{\text{ax}}$ angle (on the side away from the lone pair) of 166°. The corresponding $\text{Cl}_{\text{eq}}-\text{P}-\text{Cl}_{\text{eq}}$ and $\text{Cl}_{\text{ax}}-\text{P}-\text{Cl}_{\text{ax}}$ angles in

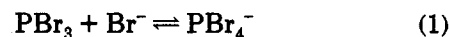
PCl_4^- were calculated as 99.8 and 185°, i.e. with the axial chlorines bent away from 180° and toward the lone pair.²⁸ Interestingly, this study was published two years after the structure of $\text{Et}_4\text{N}^+\text{PCl}_4^-$ had been determined by X-ray diffraction,³¹ unbeknown to these authors, and the $\text{Cl}_{\text{ax}}-\text{P}-\text{Cl}_{\text{ax}}$ angle is indeed greater than 180°. (The structure of this compound is described in section III.) The PF_4^- ion has also been calculated to have a C_{2v} structure, with bond angles of 99.8 and 167.8°. The most recent calculations on PH_4^- have shown that the structure based on VSEPR predictions is 1.453 eV more stable than its double-Rydberg (tetrahedral) isomer and has a larger ionization energy.³⁰

II. Synthesis

The most important preparative methods for phosphoranides comprise (A) addition of an anion to a phosphorus(III) precursor, (B) deprotonation by a suitable base of a phosphorane with a P-H bond, and (C) oxidation of an anionic phosphorus(I) species (a phosphide) by a halogen or interhalogen. There are also some specialized procedures which have been used in one or two instances. These various methods are discussed sequentially. Synthesis of transition metal complexes of phosphoranides, which usually involves a specific organometallic precursor, is considered in section V.

A. Addition

The first phosphorane to be isolated, as mentioned above, was PBr_4^- (as its Pr_4N^+ salt), from the reaction of PBr_3 with Pr_4NBr .¹⁶ A new ^{31}P resonance at 150 ± 2 ppm was observed, considerably less intense (ca. 0.5%) than the PBr_3 signal at 229 ppm, indicating that equilibrium (1) lies very much to the left, but the



phosphorane precipitated on cooling. Satisfactory elemental analyses were obtained, and the vibrational spectra supported a C_{2v} structure. Interestingly, X-ray crystallography has shown that it possesses a weak dimeric structure in the solid state,¹⁷ whereas $\text{Et}_4\text{N}^+\text{PBr}_4^-$ is monomeric,³² similar to $\text{Et}_4\text{N}^+\text{PCl}_4^-$,³¹ with one very long P-halogen axial bond. These are discussed in more detail in section III, and constitute the only examples so far where the structures of two phosphoranides with the same anion but different cations have been determined.

The ion pairs Cs^+PF_4^- and $\text{Cs}^+\text{PClF}_3^-$ have been isolated in argon matrices, after reaction of PF_3 with the appropriate cesium halide.³³ IR spectra again supported C_{2v} structures for these ions, with the chlorine occupying an axial position in PClF_3^- . Reaction of CsCl with PF_2Cl under similar conditions led to a complex IR spectrum, where it was not possible to assign specific bands to the PCl_2F_2^- ion. No products were detected from the action of CsF or CsCl on PCl_3 .

Addition of either 18-crown-6-sodium²⁰ or tetraalkylammonium¹⁷ chlorides, bromides or iodides to $\text{P}(\text{CN})_3$ resulted in a marked shift of the ^{31}P resonance to lower frequency, in a series of mobile equilibria. The chemical shift varied linearly with amount of halide until an equivalent quantity had been added and then remained

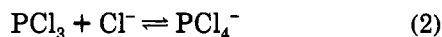
Table 1. $\delta^{31}\text{P}$ (ppm) for $[\text{P}(\text{CN})_3\text{X}]^-$

cation	solvent	X = Cl	X = Br	X = I	ref(s)
[18]-crown-6 Na^+	THF	-176.0	-182.4	-164.3	17, 20
	solid state		-177	-168	20
R_4N^+ ^a	CH_2Cl_2	-191.8	-179.4	-163.0	17, 31
	solid state	-192 ^b	-179 ^a	-162 ^c	17, 35
			-182 ^c		35
$\text{Ph}_3\text{P}=\text{CH}-\text{PPh}_3^+$	MeCN	-192.7	-176.5		31

^a For X = Cl, R = Et; for X = Br or I, R = Buⁿ. ^b Sample unstable—other peaks present (ref 35). ^c R = Prⁿ.

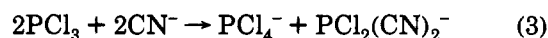
essentially constant, indicating complete formation of the phosphoranides.^{17,20} In each case the compounds could be isolated as solids; their structures are described in section III. The NMR results, including more recent ones³¹ for the cation $[\text{Ph}_3\text{P}=\text{CHPPh}_3]^+$, are listed in Table 1 and compare with a shift of ca. -137 ppm for $\text{P}(\text{CN})_3$ itself.³⁴ The close agreement between solution and solid-state values strongly supports the contention that the symmetrical dimer structure described for [18-crown-6 $\text{Na}(\text{THF})_2]^+[\text{P}(\text{CN})_3\text{X}]^-$ (X = Br or I) in section III is preserved in solution.

A single ^{31}P resonance was observed at a lower frequency than the normal PCl_3 position when Et_4NCl was added to PCl_3 in MeCN as solvent, presumably due to a mobile equilibrium between PCl_3 and PCl_4^- (eq 2).³¹ The lowest frequency (or limiting) shift

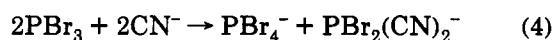


attained with an excess of Et_4NCl was 191.8 ppm. The solid compound $\text{Et}_4\text{N}^+\text{PCl}_4^-$ could be isolated by adding PCl_3 to a saturated solution of Et_4NCl in CH_2Cl_2 and cooling to 243 K;³¹ it has a monomeric structure, with one very long P-Cl axial bond (section III). When redissolved in CH_2Cl_2 it produced PCl_3 and Et_4NCl , showing that equilibrium 2 lies well to the left, parallel to that between PBr_3 and PBr_4^- . A solid-state shift of 201.5 ppm was recorded, comparable with the solution value and suggesting that the monomeric structure is retained in both phases. Vibrational spectra were in agreement with C_{2v} symmetry, and ^{35}Cl NQR signals were obtained at 77 K for the equatorial chlorines, at 26.75 and 27.00 MHz, but no lower frequency signals were detected for the axial chlorines.

Addition of Br^- ions to PCl_3 also caused a lower frequency displacement of the single ^{31}P resonance, with limiting shifts of 211.1 ppm for both Bu_4NBr in liquid PCl_3 and Pr_4NBr in MeCN, although no solid product was formed on cooling to 243 K in either case.^{35,36} The results nevertheless indicate the formation of a rather unstable phosphoranide. There was no spectroscopic support, however, for the presence of PCl_3I^- after addition of R_4NI to PCl_3 .³⁵ Unexpectedly, the reaction of PCl_3 with Et_4NCN in MeCN led to the detection of PCl_4^- ($\delta^{31}\text{P}$ 204 ppm) and $\text{P}(\text{CN})_2\text{Cl}_2^-$ ($\delta^{31}\text{P}$ -156.4 ppm) as major products (eq 3), although a small resonance at -9.8 ppm could arise from the $\text{PCl}_3(\text{CN})^-$ ion.³¹ A parallel reaction took place between PBr_3 and



Et_4NCN or [18-crown-6 $\text{Na}]^+\text{CN}^-$ (eq 4).³¹ Weak signals

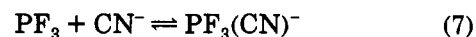


at -1.6 or -2.2 ppm (depending on the cation) could again possibly be due to the $\text{PBr}_3(\text{CN})^-$ ion.

Evidence has also been found for other unstable species. Bright yellow crystals were obtained when a solution of equimolar quantities of PCl_3 and Et_4NNCS in CH_2Cl_2 was cooled to 243 K.³⁵ These were unstable at room temperature, rapidly turning black. The compound was believed to be $\text{Et}_4\text{N}^+\text{PCl}_2(\text{NCS})_2^-$, since on redissolution in CH_2Cl_2 it gave a ^{31}P peak at 112.4 ppm, assigned to $\text{PCl}(\text{NCS})_2$.³⁷ Its IR spectrum (Nujol mull) showed intense absorptions at 2020 and 1930 cm^{-1} , indicating the presence of N-bonded thiocyanato groups. Yellow crystals were similarly produced when a solution of PBr_3 and Et_4NNCS was cooled; these were thought to be $\text{Et}_4\text{N}^+\text{PBr}_3(\text{NCS})^-$, since only one NCS stretching vibration was apparent in their IR spectrum, a strong, broad band at 1970 cm^{-1} .³⁵ (The corresponding band in Et_4NNCS appears at 2060 cm^{-1} .) This conclusion was supported by the ^{31}P NMR of the redissolved material, which displayed a single resonance at 222.2 ppm,^{35,36} ascribed to rapid exchange between PBr_3 and the phosphoranide. Addition of PCl_3 to a solution of Et_4NNCO in CH_2Cl_2 caused a violent exothermic reaction and gave rise to a complex ^{31}P NMR spectrum. Intense resonances at 201.5 and 143.5 ppm were tentatively assigned to $\text{PCl}_3(\text{NCO})^-$ and $\text{PCl}_2(\text{NCO})_2^-$, respectively,^{35,36} since their positions did not correspond to any known three-coordinate species. Reaction of PBr_3 with Et_4NCl in CH_2Cl_2 led to halogen exchange, followed by formation of $\text{Et}_4\text{N}^+\text{PBr}_4^-$, probably according to eqs 5 and 6. There was no evidence for the presence of the PBr_3Cl^- ion.

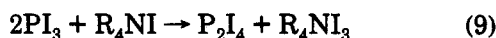
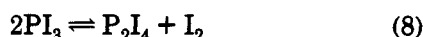


The limiting ^{31}P shift observed when Et_4NNCS was added to a solution of $\text{P}(\text{CN})_3$ in CH_2Cl_2 was -183.8 ppm, attributed to the $[\text{P}(\text{CN})_3(\text{NCS})]^-$ ion.³⁵ The phosphoranide was unstable, and after 1 day only decomposition products were apparent in the spectrum. Lower frequency shifts to 74.4 and 83.8 ppm respectively also occurred on addition of Bu_4NBr or Bu_4NI to a solution of $\text{P}(\text{NCS})_3$ in CH_2Cl_2 , indicating the formation of phosphoranides,³⁵ but in both instances the solutions darkened rapidly with decomposition of the anions. A vigorously exothermic reaction between $\text{P}(\text{NCS})_3$ and Et_4NCN in CH_2Cl_2 gave rise to an intense ^{31}P resonance at -172.6 ppm, together with several smaller peaks from decomposition products. The main signal was tentatively assigned to the $[\text{P}(\text{NCS})_2(\text{CN})_2]^-$ ion,³⁵ by analogy with the reactions of Et_4NCN with PCl_3 and PBr_3 described above. PF_3 did not form adducts with Et_4NCl or Bu_4NBr in CH_2Cl_2 , as evidenced by an unchanged ^{31}P NMR spectrum. Excess PF_3 reacted with Et_4NCN in CH_2Cl_2 to yield a dark solution giving a single ^{31}P resonance at 88.7 ppm, possibly because of rapid exchange (eq 7).³⁵ There was no direct proof for the



presence of a phosphoranide, however. Attempts to synthesize PI_4^- by addition of R_4NI to a solution of PI_3 were unsuccessful, since equilibrium 8 was displaced to

the right by formation of I_3^- ions, the reaction products being P_2I_4 and R_4NI_3 (eq 9).²²



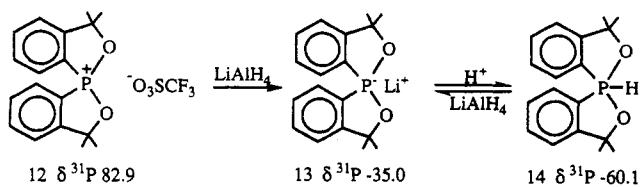
More recent work has shown that several organophosphoranides, particularly of the type $[RP(CN)_2X]^-$, may be prepared by this method.²¹⁻²⁷ This has been demonstrated for $R = Me$,^{21,23} Et ,^{21,23} Ph ,^{21,23} C_6F_5 ,^{21,23} $2-MeC_6H_4$,²⁶ or $4-ClC_6H_4$ ²⁷ and $X = Cl, Br, I, \text{ or } NCS$. The compound $2,4,6-(CF_3)_3C_6H_2P(CN)_2$ also reacts with chloride ion to yield a phosphoranide.²⁵ In most instances the compounds have been isolated as tetraalkylammonium salts, although only one crystal structure has so far been determined,²³ for $Et_4N^+PhP(CN)_2Cl^-$ (section III). A lower frequency (upfield) shift relative to that of the precursor phosphine was detected in each case, the shifts following the sequence $Cl^- > Br^- > NCS^- \approx I^-$ where the whole series of anions X was studied.

In the particular case of the very electronegative R group C_6F_5 , other types of phosphoranides have recently been prepared by Ali and Dillon.^{22,24} These comprise the ions $[P(C_6F_5)_2X_2Y]^-$ ($X = Cl, Y = Cl, Br, \text{ or } I; X = Br, Y = Br \text{ or } I; X = NCS, Y = Cl, Br, I, \text{ or } NCS$), and $[P(C_6F_5)_2XY]^-$ ($X = Cl, Y = Cl, Br, \text{ or } I; X = Br, Y = Br \text{ or } I; X = CN, Y = Cl, Br, I, \text{ or } NCS$).²⁴ It was not possible to synthesize chloride ion adducts of the bromophosphines, or thiocyanato adducts of halophosphines, since substitution occurred in preference to addition. Again characteristic lower frequency NMR shifts were observed on complexation, in the same shift sequence as found for the $RP(CN)_2$ derivatives. Phosphoranide formation thus seems to be favored by the presence of electronegative substituents, probably because the formal negative charge on phosphorus can then be partially delocalized onto the ligands.

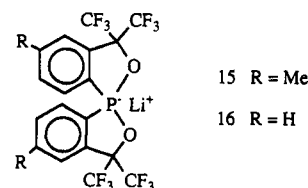
No phosphoranides were obtained from $P(C_6F_5)_2$ (NCS) or $P(CCl_3)Cl_2$.^{22,24} The following phosphines also failed to yield anionic derivatives with $R_4N^+X^-$ salts under the experimental conditions used: $Bu^tP(CN)_2$,²³ $Et_2NP(CN)_2$,²⁵ $(Pr^i_2N)P(CN)_2$,²⁵ $Me_2P(CN)_2$,²³ $Ph_2P(CN)_2$,²³ $(Et_2N)_2P(CN)_2$,²⁵ $(Pr^i_2N)_2P(CN)_2$,²⁵ $PhPCl_2$,^{22,38} $MePCl_2$,^{22,38} $2,4,6-(CF_3)_3C_6H_2PCl_2$,²⁵ $Et_2NP(Cl)_2$,²⁵ $Pr^i_2NP(Cl)_2$,²⁵ $2-MeC_6H_4PCl_2$,²⁶ $C_6F_5PCl_2$,²⁶ $2-CF_3C_6H_4PCl_2$,²⁶ $2,6-(CF_3)_2C_6H_3PCl_2$,²⁶ $2,4,6-Me_3C_6H_2PCl_2$,²⁶ $(Et_2N)_2PCl_2$,²⁵ and $(Pr^i_2N)_2PCl_2$.²⁵

B. Deprotonation

As mentioned in the introduction, work by both Hellwinkel¹⁰ and Savignac et al.¹² had suggested that phosphoranides could be formed by deprotonation of phosphoranides with a P-H bond. The first direct evidence involving this route was reported by Granoth and Martin in 1978.¹⁸ They were able to prepare the lithium derivative 13 either by deprotonation of the phosphorane 14 by $LiAlH_4$, or by $LiAlH_4$ reduction of the triflate salt 12.

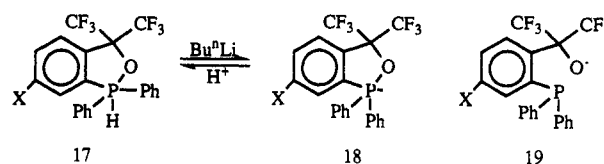


The analogous species 15 ($\delta^{31}P$ -17.9 ppm)³⁹ and 16 ($\delta^{31}P$ -18.5 ppm)⁴⁰ were similarly synthesized from the corresponding phosphoranones ($\delta^{31}P$ -47.6 and -48.2 ppm for $R = Me$ and H , respectively). The chemical shifts

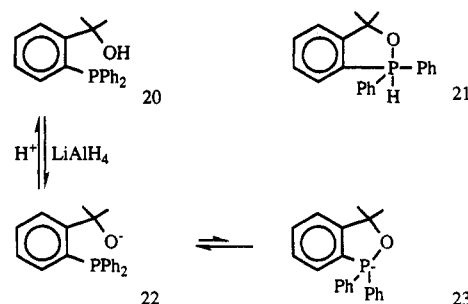


were entirely consistent with phosphoranide structures, rather than open-chain phosphinite forms, for which signals at much higher frequency would have been expected.^{18,39,40}

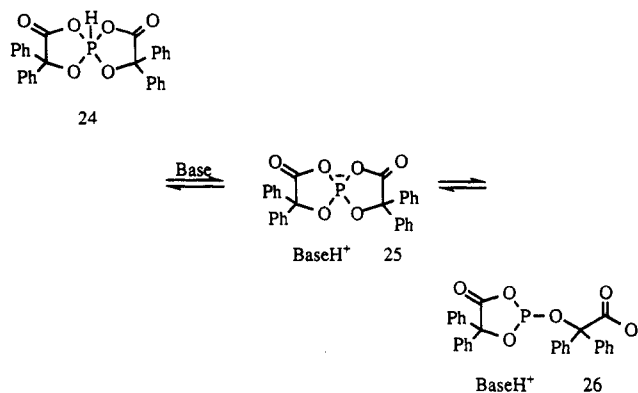
Monocyclic phosphorane 17, with an apical P-H bond and $X = H$, was likewise deduced to form anion 18 on treatment with Bu^tLi ,^{40,41} although in this case NMR data could not distinguish unambiguously between structure 18 and the open chain form 19. Similar



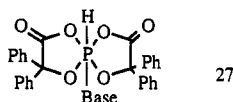
conclusions were reached⁴⁰ for $X = Bu^t$. The analogous compound with CF_3 replaced by Me and $X = H$ was considered to exist primarily in the phosphine form 20 rather than as phosphorane 21.⁴² Addition of $LiAlH_4$ to a solution of this compound in THF led to the relatively slow establishment of an equilibrium between phosphine alkoxide 22 (major component; $\delta^{31}P$ -11.1 ppm) and phosphoranide 23 ($\delta^{31}P$ -30.3 ppm).



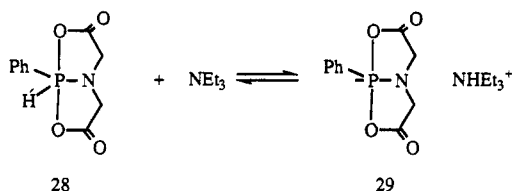
NMR evidence from Garrigues et al. has also supported the presence of the phosphoranide anion 25



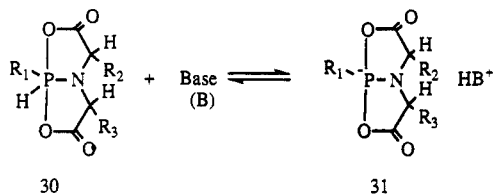
(possibly in equilibrium with the phosphite 26) in the reaction of the spirophosphorane 24 with pyridine or triethylamine in DMF solution.⁴³ A singlet in the ³¹P NMR spectrum between 78 and 87 ppm (depending on base and temperature) was ascribed to the deprotonated species, while signals at much lower frequency were attributed to six-coordinate base adducts such as 27.



The temperature dependence (δ ³¹P 86.4 at 90 °C, 79.2 at -60 °C) of the singlet was compatible with an equilibrium between 25 and 26. Phosphoranide 29, similarly prepared by the action of 2 mol of Et₃N on 1 mol of phosphorane 28, was isolated as its NHEt₃⁺ salt.⁴⁴ The doublet spectrum of 28 (δ -47 ppm, J_{PH} 780

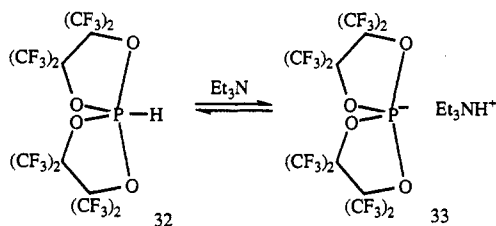


Hz) was replaced by a singlet at -46 ppm on addition of NEt₃, and the above equilibrium was strongly displaced to the right. Similar equilibria, again strongly weighted toward the phosphoranides 31, have been proposed for the action of NEt₃ or DBU on the phosphoranes 30.⁴⁵

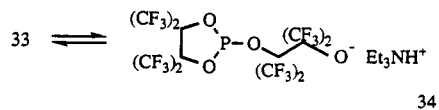


R₁ = Me or Ph R₂, R₃ = Me, Ph

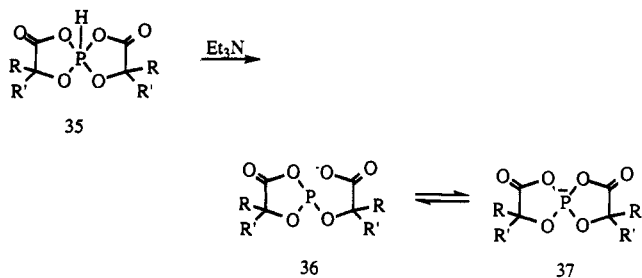
Schomburg et al. isolated spirocyclic phosphoranide 33 from reaction of triethylamine with phosphorane 32, and determined its structure by X-ray crystallography (section III).⁴⁶ The solid compound gave a



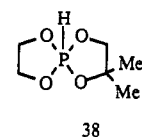
³¹P NMR shift of -5 ppm, while in CDCl₃/Et₂O a 13-line multiplet at 81.5 ppm (⁴ J_{PF} 16.3 Hz) was observed, indicating an equilibrium in solution with the open-chain monocyclic phosphite anion 34.



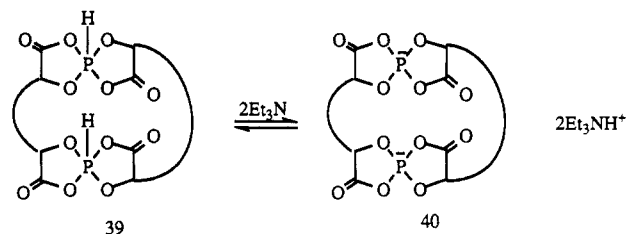
In an extension of earlier work,⁴³ the percentage of phosphoranide form 37 in equilibrium with phosphite 36 after treatment of phosphorane 35 with Et₃N was estimated from the NMR shifts.⁴⁷ Percentages were



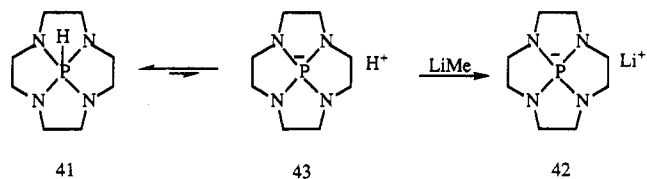
listed as 17 ± 1 for R = H, R' = Prⁱ, 19 ± 1 for R = H, R' = Ph, 32 ± 1 for R = R' = Me, and 33 ± 1 for R = R' = Ph. The anion was deduced to be present exclusively in the phosphite form when derived from phosphorane 38. Diphosphoranide 40 has been ob-



tained from deprotonation of phosphorane 39 by 2 mol of Et₃N.⁴⁸ Treatment of cyclenphosphorane 41 with



LiMe has been reported to yield phosphoranide 42 (cyclen P).⁴⁹ This implies that the hydrophosphorane-phosphoranide acid-base equilibrium, as between 41 and 43, must be taken into account when considering the reactivity of tetracyclic tetraaminophosphoranes, especially when the phosphorane/phosphine tautomeric equilibrium is not operating. The lithiated phospho-



ranide 42 has also been prepared by the action of BuLi on 41, and the compound [Li(THF)cyclen P]_x was isolated.⁵⁰ The structure of this polymeric species has been determined,⁵⁰ and is discussed in section III.

C. Oxidation

The only reports of phosphoranide formation by oxidation of a phosphorus(I) precursor originate from Schmidpeter and co-workers.^{20,51} This route has probably found limited application because of the unavailability of other suitable starting materials. The dicyanophosphide^{52,53} ion P(CN)₂⁻ reacted with X₂ (X = Br or I) to produce P(CN)₂X₂⁻ ions, stable to dissociation

in solution, as shown by their characteristic high-field NMR shifts.^{20,51} Addition of chlorine to $\text{P}(\text{CN})_2^-$ under the same conditions yielded $\text{P}(\text{CN})_2\text{Cl}$ only.^{20,34} Cyanogen bromide or iodide also reacted additively with $\text{P}(\text{CN})_2^-$ to form $\text{P}(\text{CN})_3\text{X}^-$ ($\text{X} = \text{Br}$ or I).^{20,51} Some of these ions have been isolated as salts with large cations; their structures are described in section III.

D. Other Methods

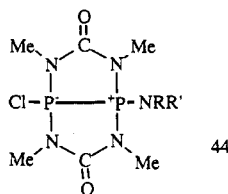
Mass spectrometry has been used by Dillard and Rhyne to show the formation of PF_4^- from reaction of the radical ion SF_6^- with PF_3 at low electron energies and high pressure.^{54,55} PF_4^- was also detected from reactions of SF_6 or SO_2F_2 with PF_3 by ion cyclotron resonance spectroscopy in the gas phase.⁵⁶ More recently, ion cyclotron resonance halide-exchange equilibria have been employed to obtain thermodynamic data such as ΔH_f° for (among others) addition of F^- and Cl^- to PF_3 .⁵⁷ The PF_4^- ion was considered to have a square-pyramidal structure, which is not in accordance with the theoretical studies described earlier.²⁹ AsF_3 exhibited greater Lewis acidity toward both F^- and Cl^- than PF_3 .⁵⁷

A novel way of preparing a salt containing the $\text{P}(\text{CN})_2^-$ ion involved the addition of HCl (2 mol) to $\text{Me}_2\text{NP}(\text{CN})_2$ (1 mol) in $\text{MeCN}/\text{Et}_2\text{O}$ (eq 10).³⁵ A white



precipitate was formed, and although elemental analyses suggested that the product was probably contaminated by $\text{Me}_2\text{NH}_2^+\text{Cl}^-$, it displayed a solid state ^{31}P resonance at -160 ppm, in good agreement with values for the $\text{P}(\text{CN})_2^-$ ion in solution.³¹ The synthesis of phosphoranide 13 by LiAlH_4 reduction of the quasi-phosphonium triflate salt 12 has been mentioned in subsection II.B above.¹⁸

Finally, a series of mixed-valence diphosphorus derivatives with one of the phosphorus atoms in the phosphoranide form has been described by Schmutzler and co-workers.⁵⁸⁻⁶⁰ The compounds were prepared by reaction of 2 mol of N,N' -dimethyl- N,N' -bis(trimethylsilyl)-urea with 3 mol of $\text{RR}'\text{NPCl}_2$, where $\text{R} = \text{R}' = \text{Me}$ or Et , or $\text{RR}' = (\text{CH}_2)_4$, $(\text{CH}_2)_5$, or $\text{O}(\text{CH}_2\text{CH}_2)_2$, and have the general structure 44. $^1J_{\text{PP}}$ in these species is of the



order of 160 Hz.^{58,60} A single-crystal X-ray diffraction study of the derivative with $\text{R} = \text{R}' = \text{Et}$ has revealed the presence of both monomeric molecules, as in 44, and chlorine-bridged dimers;^{58,60} these are described in section III. Substitution of Cl by $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}$ in compound 45 and exchange of Cl^- by BPh_4^- resulted in the formation of phosphoranide 46 (eq 11).⁶¹

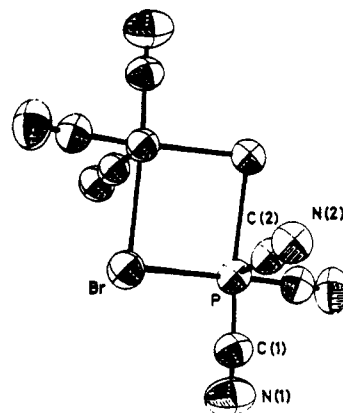
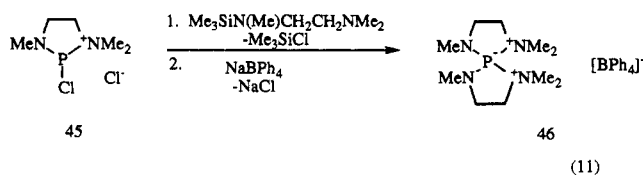


Figure 1. Structure of the anion $[\text{P}_2(\text{CN})_6\text{Br}_2]^{2-}$ in its [18-crown-6 $\text{Na}(\text{THF})_2]^+$ salt. (Reprinted from ref 17. Copyright 1981 The Royal Society of Chemistry.)

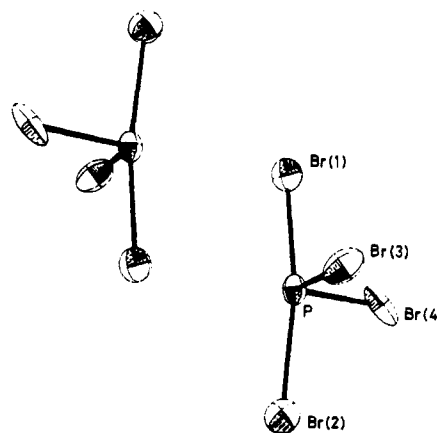


Figure 2. ORTEP plot of PBr_4^- in $[\text{Pr}_4\text{N}]^+[\text{PBr}_4]^-$. (Reprinted from ref 17. Copyright 1981 The Royal Society of Chemistry.)

III. Structures

The first phosphoranides to be characterized by X-ray diffraction contained the ions $\text{P}(\text{CN})_3\text{Br}^-$ or $\text{P}(\text{CN})_3\text{I}^-$ (as their [18-crown-6 $\text{Na}(\text{THF})_2]^+$ salts).⁶² The two compounds crystallized isomorphously, in the form of symmetrical halogen-bridged dimeric anions, with four dimers per unit cell; the structure of the $[\text{P}_2(\text{CN})_6\text{Br}_2]^{2-}$ anion is shown in Figure 1. The bridges display long $\text{P}-\text{X}$ distances [3.058(1) and 3.262(3) Å for $\text{X} = \text{Br}$ and $\text{I} =$ respectively], although these are appreciably shorter than the sum of the van der Waals radii (3.85 and 4.05 Å for $\text{X} = \text{Br}$ and I). Angles $\text{P}-\text{X}-\text{P}$ and $\text{X}-\text{P}-\text{X}$ are 80.1(1)° and 99.9(1)° respectively in the bromo compound and 82.0(1)° and 98.1(1)° in its iodo analogue. As indicated in section II, NMR evidence strongly supports the retention of the dimeric configuration in solution.^{17,20} The structure of the first phosphoranide to be isolated,¹⁶ $\text{Pr}_4\text{N}^+\text{PBr}_4^-$, was reported in 1981¹⁷ and is presented in Figure 2. The anion may be described as having a weak dimeric structure, since the $\text{P}\cdots\text{Br}(1')$ distance of 3.460(4) Å is shorter than the sum of the van der Waals radii, but much longer than the bond distances within the PBr_4^- ions [$\text{P}-\text{Br}_{\text{ax}}$ 2.527(4) and 2.620(4) Å, $\text{P}-\text{Br}_{\text{eq}}$ 2.221(3) and 2.255(3) Å]; the $\text{Br}_{\text{ax}}-\text{P}-\text{Br}_{\text{ax}}$ angle is 170.0(1)°. In this instance the ion probably becomes monomeric in solution, according to the NMR data. More recently the structure of $\text{Et}_4\text{N}^+\text{PBr}_4^-$ has been determined,³² as depicted in Figure 3. The anion is monomeric, with one axial $\text{P}-\text{Br}$

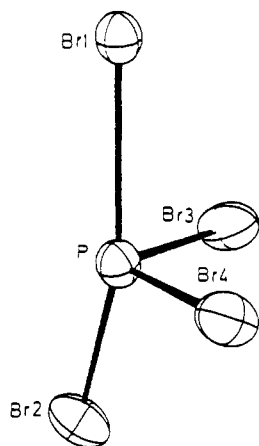


Figure 3. ORTEP plot of PBr_4^- in $[\text{Et}_4\text{N}]^+[\text{PBr}_4]^-$. (Reprinted from ref 32. Copyright 1989 Verlag der Zeitschrift für Naturforschung.)

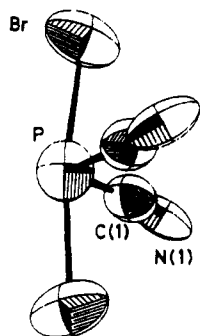


Figure 4. ORTEP plot of $\text{P}(\text{CN})_2(\text{Br})_2^-$ in its [18-crown-6 $\text{Na}(\text{THF})_2$] $^+$ salt. (Reprinted from ref 17. Copyright 1981 The Royal Society of Chemistry.)

bond much longer than the other [2.970(2) and 2.305(2) Å], similar to the structure of $\text{Et}_4\text{N}^+\text{PCl}_4^-$, described below.³¹ A structural correlation of bond distances in halogenophosphoranides indicated that such an asymmetric three-center $\text{X}-\text{P}\cdots\text{X}$ interaction represents an energy minimum for isolated anions.³² The equatorial bond lengths are normal [2.217(2) and 2.233(2) Å], and the $\text{Br}_{\text{ax}}-\text{P}-\text{Br}_{\text{ax}}$ angle is 166.86(8)°. These results suggest that there is only a small energy difference between monomeric and dimeric forms for some phosphoranides, with the cation possibly playing a crucial role; this deduction is supported by the data of Schmutzler et al. for compound 44 ($\text{R} = \text{Et}$),^{58,60} described below.

The structure of [18-crown-6 $\text{Na}(\text{THF})_2$] $^+[\text{P}(\text{CN})_2\text{Br}_2]^-$ is shown in Figure 4;^{17,51} the anion is monomeric, with equal $\text{P}-\text{Br}$ axial bond lengths of 2.496(1) Å and a $\text{Br}-\text{P}-\text{Br}$ bond angle of 171.4(1)°. (This result was included in the correlation of bond distances mentioned above.³²) The geometry of the $\text{P}(\text{CN})_3\text{Cl}^-$ ion in the compound $[(\text{Ph}_3\text{P})_2\text{CH}]\text{P}(\text{CN})_3\text{Cl}-\text{MeCN}$ is presented in Figure 5.^{31,51} This monomeric species has a quite long $\text{P}-\text{Cl}$ axial bond of 2.625(1) Å, and a $\text{Cl}-\text{P}-\text{C}$ (of the axial CN group) angle of 168.2(1)°. The PCl_4^- anion in $\text{Et}_4\text{N}^+\text{PCl}_4^-$ is also monomeric (Figure 6),³¹ with a very asymmetric structure, similar to that of the PBr_4^- ion in $\text{Et}_4\text{N}^+\text{PBr}_4^-$. The axial bond lengths are 2.850(4) and 2.118(4) Å, while the equatorial chlorines have normal $\text{P}-\text{Cl}$ bond distances of 2.049(4) and 2.044(4) Å; angle $\text{Cl}_{\text{ax}}-\text{P}-\text{Cl}_{\text{ax}}$ has a value of 171.4(2)°.

As yet only two cyclic organophosphoranides have had their structures determined by X-ray diffraction;

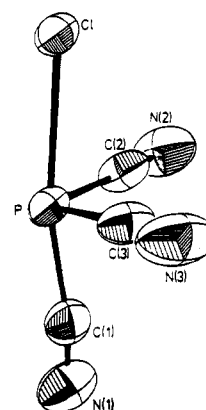


Figure 5. Geometry of the anion $\text{P}(\text{CN})_3\text{Cl}^-$ in its $[\text{Ph}_3\text{P}=\text{CHPh}_3]^+$ salt. (Reprinted from ref 31. Copyright 1982 Barth Verlagsgesellschaft mbH.)

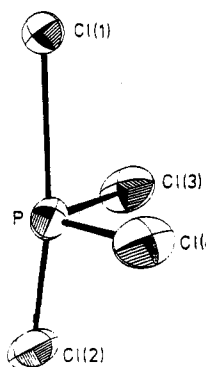


Figure 6. Geometry of the anion PCl_4^- in its $[\text{Et}_4\text{N}]^+$ salt. (Reprinted from ref 31. Copyright 1982 Barth Verlagsgesellschaft mbH.)

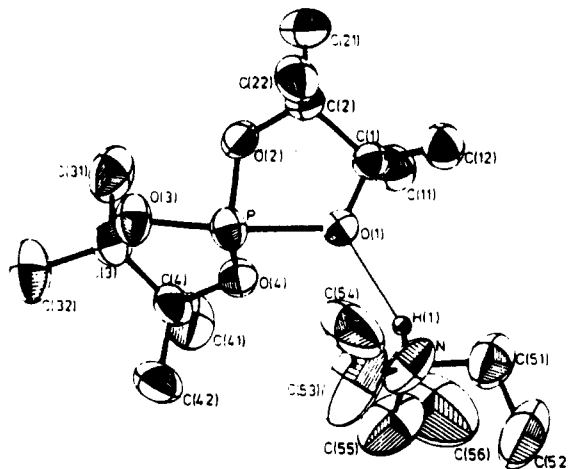


Figure 7. Perspective view of the molecular structure of compound 33; the fluorine atoms are omitted for clarity. (Reprinted from ref 46. Copyright 1983 VCH Verlagsgesellschaft mbH.)

that of compound 33 (section II) is represented in Figure 7.⁴⁶ The monomeric anion structure is again based on a trigonal bipyramid with an equatorial lone pair, and one of the $\text{P}-\text{O}$ axial bonds is appreciably longer than the other [2.019(4) and 1.772(4) Å]. The equatorial $\text{P}-\text{O}$ bond lengths are 1.675(4) and 1.687(4) Å, while angle $\text{O}_{\text{ax}}-\text{P}-\text{O}_{\text{ax}}$ is 165.3(2)°. The structure of $[\text{Li}(\text{THF})\text{cyclen P}]_x$ is polymeric, with each $\text{Li}(\text{THF})$ unit bridging two cyclen P units via coordination of the axial nitrogen.⁵⁰ Each lithium has approximately trigonal planar geometry, while the phosphorus is in a distorted

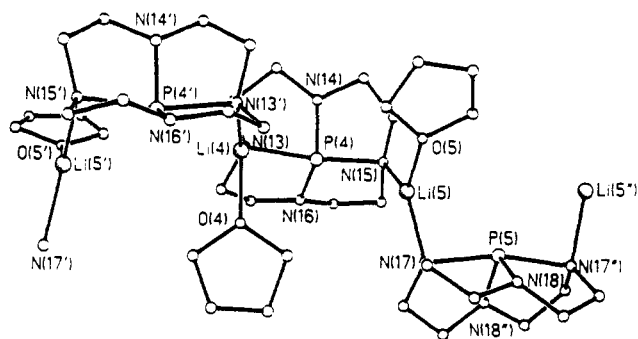


Figure 8. Computer-generated drawing of $[\text{Li}(\text{THF})\text{cyclen P}]_x$, showing a portion of one of the polymeric chains. (Reprinted from ref 50. Copyright 1988 American Chemical Society.)

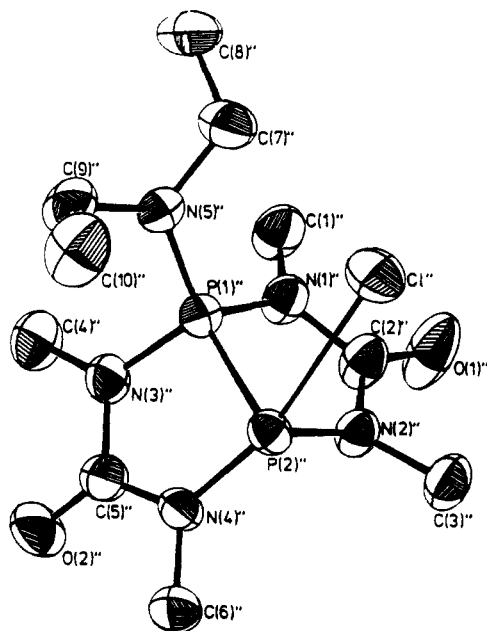


Figure 9. Molecular structure of the monomeric form of compound 44 ($R = R' = \text{Et}$). (Reprinted from ref 60. Copyright Prof. Dr. R. Schmutzler.)

ψ -tbp arrangement, with the lone pair equatorial; the $\text{P}-\text{N}_{\text{ax}}-\text{Li}$ angle is only 94° , possibly due to a weak bonding interaction between the phosphorus lone pair and lithium. The asymmetric unit contains 4.5 $[\text{Li}(\text{THF})\text{cyclen P}]$ moieties, forming two parallel, spiral noninteracting chains propagating in the c direction. One chain comprises 3 $[\text{Li}(\text{THF})\text{cyclen P}]$ units that propagate by translation along the c axis, while a computer-generated drawing of a portion of the chain containing the remaining 1.5 units is illustrated in Figure 8. The $\text{P}-\text{N}_{\text{eq}}$ distances in the polymer range from 1.717(7) to 1.761(7) (mean 1.74) Å, and $\text{P}-\text{N}_{\text{ax}}$, from 1.937(6) to 2.014(6) (mean 1.98) Å; the mean $\text{N}_{\text{eq}}-\text{P}-\text{N}_{\text{eq}}$ and $\text{N}_{\text{ax}}-\text{P}-\text{N}_{\text{ax}}$ angles are 112° and 165° , respectively.

Crystal structure determination for the mixed-valence compound 44 ($R = R' = \text{Et}$) interestingly showed the presence of monomers (Figure 9) and chlorine-bridged dimers (Figure 10). The monomeric species has a long $\text{P}-\text{Cl}$ axial bond of 2.815 Å, while in the dimer the two phosphorane phosphorus atoms and two chlorine atoms form a planar ring, with bond angles near 90° .^{58,60} In the latter the $\text{P}-\text{Cl}$ distances range from 2.998 to 3.103 Å, shorter than the sum of the van der Waals

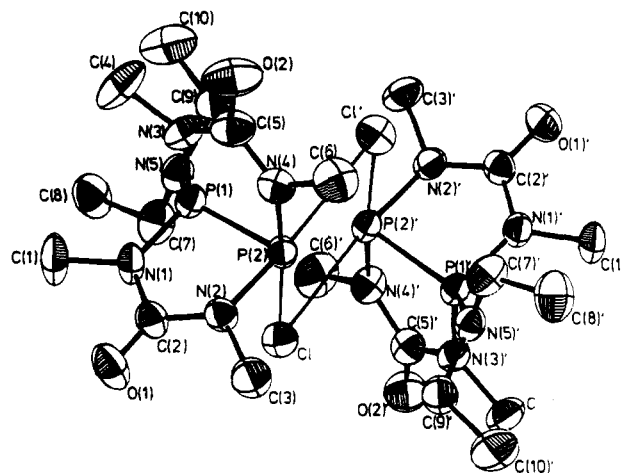


Figure 10. Molecular structure of the chlorine-bridged dimer of compound 44 ($R = R' = \text{Et}$). (Reprinted from ref 60. Copyright Prof. Dr. R. Schmutzler.)

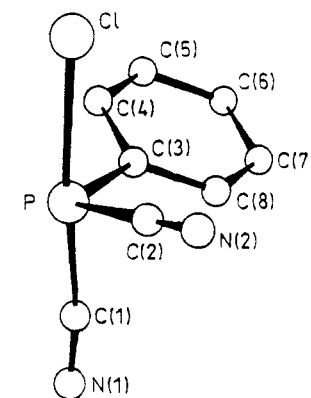


Figure 11. The geometry of the anion in $[\text{Et}_4\text{N}][\text{PhP}(\text{CN})_2\text{Cl}]$. (Reprinted from ref 23. Copyright 1990 The Royal Society of Chemistry.)

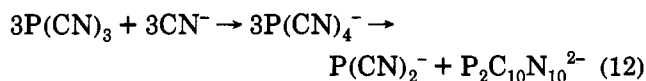
radii (3.56 Å), but indicating weak bonding.⁶⁰

Only one organophosphorane of the type $\text{RP}(\text{CN})_2\text{X}$ has had its structure determined so far, namely the $\text{PhP}(\text{CN})_2\text{Cl}^-$ ion (as its Et_4N^+ salt).²³ This anion likewise has a structure based on a tbp , with an equatorial lone pair (Figure 11), a long $\text{P}-\text{Cl}$ axial bond of 2.810(1) Å, and the phenyl substituent in an equatorial site; angle $\text{Cl}-\text{P}-\text{C}(1)$ has a value of $172.1(1)^\circ$. Such structures have been interpreted as representing "frozen" intermediates⁶² along the reaction pathway for nucleophilic addition to a phosphorus(III) center.^{23,31}

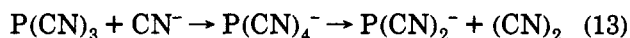
IV. Reactivity

Most of the reactions described in the literature concern cyclic organophosphoranes or mixed-valence compounds, and comparatively few have been reported for halogeno or pseudohalogeno derivatives. There are some important exceptions, however. In view of the stability conferred on phosphoranes by the presence of cyano groups, the $\text{P}(\text{CN})_4^-$ ion might conceivably have been predicted as particularly stable, but this is not the case. While this anion can be detected by solution NMR from the addition of a suitable cyanide to $\text{P}(\text{CN})_3$ ($\delta^{31}\text{P}$ -242 ppm for $[\text{18-crown-6 Na}]\text{P}(\text{CN})_4$ in THF, -238.6 ppm for $\text{Bu}_4\text{NP}(\text{CN})_4$ in CH_2Cl_2), it rapidly decomposes above -10°C , with formation of $\text{P}(\text{CN})_2^-$ ($\delta^{31}\text{P}$ -193 ppm in THF, -193.5 ppm in CH_2Cl_2).^{17,51} With $[\text{18-crown-6 Na}]\text{CN}$ as the cyanide

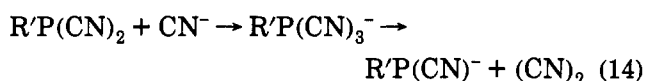
ion source in THF, a second salt containing the $P_2C_{10}N_{10}^{2-}$ ion was isolated after reaction, which thus appeared to follow eq 12.⁵¹ There was no evidence for



this second product when Bu_4NCN was used, and the transformations shown in eq 13 were deduced to occur.^{17,35} A similar reaction to eq 13 has been observed

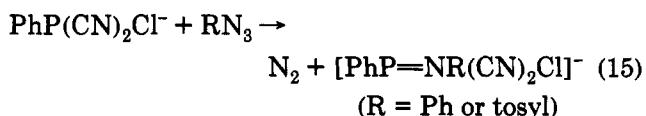


on addition of R_4NCN to $R'P(CN)_2$ ($R' = Me$,⁶⁴ Et,⁶⁴ Ph⁶⁴ or CF_3 ²⁵), leading to organocyanophosphides, $R'P(CN)_3^-$, eq 14. In these reactions the intermediate



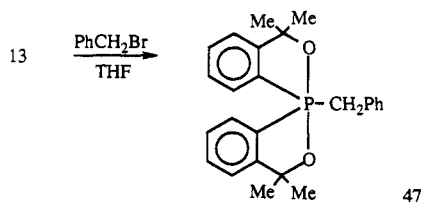
$R'P(CN)_3^-$ ions were not detected.

Addition of phenyl azide or tosyl azide to the phosphoranide $Et_4N^+PhP(CN)_2Cl^-$ in MeCN solution resulted in a Staudinger reaction, with evolution of nitrogen and formation of novel anionic phosphorus(V) species, as shown in eq 15.⁶⁵ The reaction products

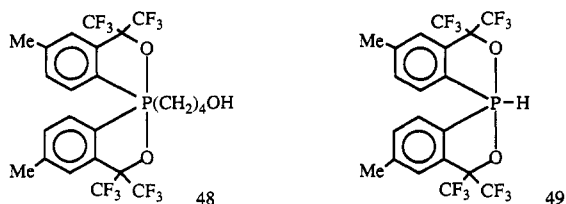


were extremely moisture-sensitive and could not be isolated in a pure state, but were characterized by their ³¹P NMR shifts (-91.5, -90.9 ppm for $R = Ph$ or tosyl respectively), and solution chemistry.⁶⁵

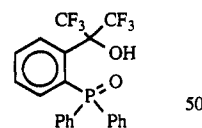
Most of the reactions reported for cyclic organophosphoranides demonstrate their nucleophilic properties. This is in accordance with the work of Hellwinkel,¹⁰ and Savignac et al.,¹² described in section I, where phosphoranides were postulated as intermediates in nucleophilic substitution reactions. Phosphoranide 13 was thus alkylated by benzyl bromide in THF at ambient temperature within 3 days to produce phosphorane 47.³⁹ Phosphoranide 15 either reacted with



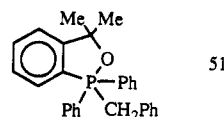
the solvent (THF) via a nucleophilic attack at C- α to give 48, or acted as a base to abstract a proton from the solvent and form phosphorane 49; both of these products were isolated and characterized.³⁹ Exposure of phos-



phoranide 18 to oxygen yielded the phosphine oxide 50.⁴¹ Phosphoranide 23 (in equilibrium with phosphine

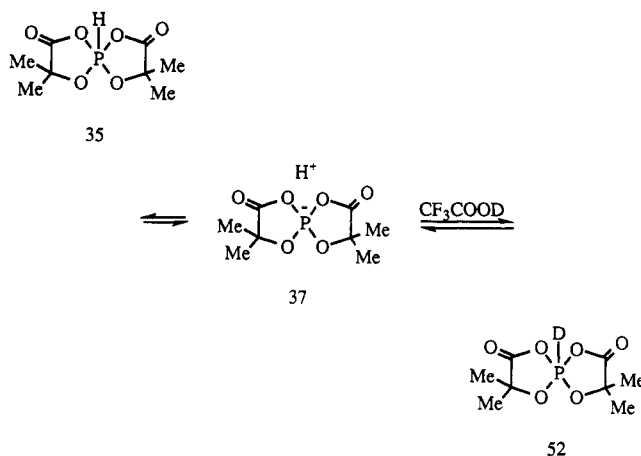


alkoxide 22) was alkylated at phosphorus by benzyl bromide, leading to the corresponding phosphorane 51.⁴²

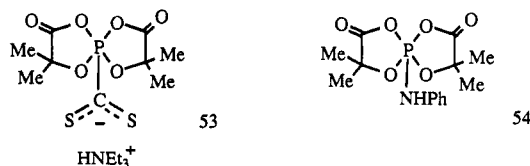


Alkylation of phosphoranide 25 by MeI similarly resulted in the analogous phosphorane with a methyl group on phosphorus.⁴³

There was evidence for the presence of a small quantity of the six-coordinate adduct 27 in equilibrium with phosphoranide 25 and its (base-H)⁺ counterion.⁴³ Separate NMR signals from the phosphorane 24, phosphoranide 25, open-chain (phosphite) form 26, and adduct 27 could be detected on cooling to -50 °C, showing that the exchange rate was slow on the NMR time scale. Deuterium exchange (using CF_3COOD) at the P-H bond in phosphorane 35 ($R = R' = Me$) was also considered to proceed via phosphoranide 37, giving 52.⁴³ Phosphorane 35 ($R = R' = Me$) in the presence



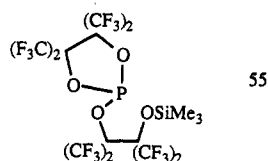
of Et_3N reacted with CS_2 to produce 53,^{44,66} the crystal structure of which was subsequently determined.⁶⁷ N_2 was evolved when 35 ($R = R' = Me$) and an equimolar quantity of Et_3N reacted with PhN_3 , yielding compound 54.^{44,66} Both of these reactions were thought to involve



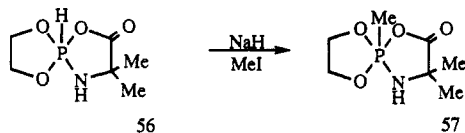
phosphoranide 37, since base was necessary in each case. Phosphoranide 29 did not react with MeI in DMF, but was alkylated at phosphorus by $PhCH_2Br$.^{44,66} With 29, CS_2 and PhN_3 formed analogous reaction products to those described above for 37 ($R = R' = Me$).

Phosphoranide 33, which was stable enough to have its crystal structure determined (section III), was

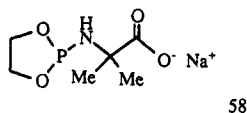
methylated at phosphorus by MeI, but with Me₃SiI yielded the derivative **55** of the open-chain (phosphite) form.⁴⁶ Simultaneous addition of NaH and MeI to



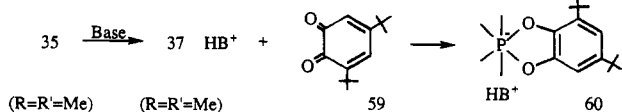
phosphorane **56** led to the P-methylated product **57**.⁶⁶



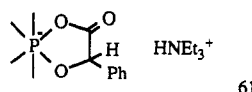
Base was again a necessary requirement for the occurrence of reaction, which was considered to proceed via the phosphoranide as the kinetic product. If the base was added first, amidophosphite **58** was formed, and could be isolated; the latter gave a complex mixture when treated with MeI. The family of phosphoranides



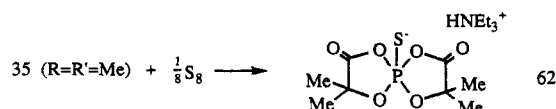
37 (R = R' = H; R = H, R' = Prⁱ; R = H, R' = Ph; R = R' = Me; R = R' = Ph) was all methylated at phosphorus by MeI.⁶⁶ For R = R' = Me, reaction of phosphorane **35** in the presence of base with di-*tert*-butyl-benzoquinone (**59**) in DMF or DMSO led to the six-coordinate anion **60** as the final product.⁶⁶ (The



other substituents on phosphorus in structures **60** and **61** are as shown in **37**, with R = R' = Me.) Phosphorane **35** (R = R' = Me) also reacted in the presence of Et₃N with benzoylformic acid to give a solution-stable six-coordinate species, which decomposed when isolation was attempted. Structure **61** was proposed for the product, and reaction mechanisms involving phosphoranide **37** (R = R' = Me) were suggested in each of the above transformations.

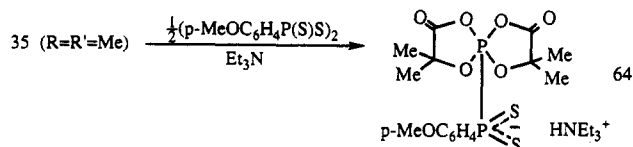


Further reactions of **35** in the presence of Et₃N with electrophilic reagents were subsequently investigated.^{48,68} For R = R' = Me, elemental sulfur formed the phosphoranethiolate **62**.⁶⁸ The structure of **62** was

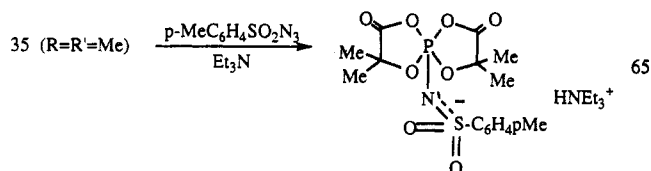


deduced from IR and NMR studies, and alternative isomeric configurations could be discounted. Analogous

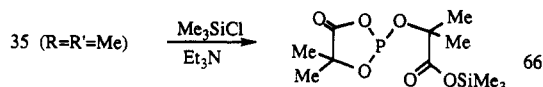
products were obtained with sulfur for **35** (R = R' = Ph) and with selenium for **35** (R = R' = Me or R = R' = Ph).⁴⁸ Diphosphoranide **40** reacted similarly with ^{2/8}S₈ or Se₈ to produce the bis salts.⁴⁸ Compound **35** (R = R' = Me) yielded a P-P bonded species **64** with Lawesson's reagent (*p*-MeOC₆H₄P(S)S)₂ (**63**). Tosyl



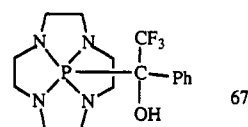
azide interacted under similar conditions with loss of N₂ and formation of salt **65**. With Me₃SiCl, however,



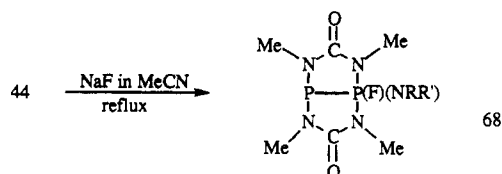
reaction took place with the open-chain (phosphite) form of the anion to yield **66**. Phosphoranide **43** reacted



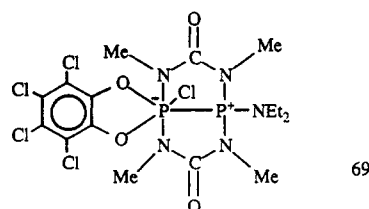
instantaneously with CF₃COPh to produce (after hydrolysis) compound **67**.⁴⁹



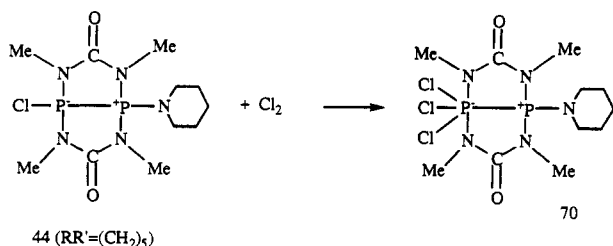
The mixed-valence species **44** underwent fluorine-chlorine exchange when refluxed with NaF in MeCN, but the fluorine was transferred to the other phosphorus atom, giving λ³λ⁵ derivatives **68**.⁵⁸⁻⁶⁰ For compound **44**



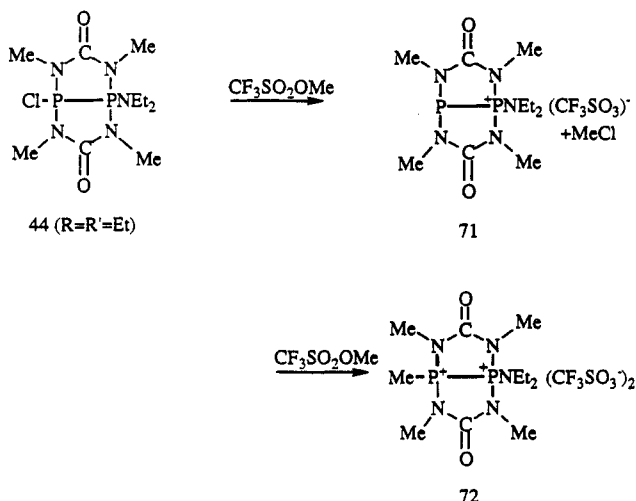
with R = R' = Et, oxidative addition occurred with 2,3,4,5-tetrachloro-*o*-benzoquinone to form **69**, with one six-coordinate P atom;⁵⁸⁻⁶⁰ the X-ray crystal structure of this species has been determined.⁶⁰ A similar reaction



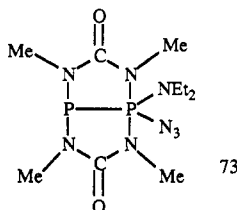
took place⁶⁰ with 3,5-*tert*-butyl-*o*-benzoquinone. Compound **44** with RR' = (CH₂)₅ was oxidized by chlorine to derivative **70**,^{59,60} again with one six-coordinate P atom. Two moles of CF₃SO₂OMe reacted with **44** (R



= R' = Et), leading first to a monocationic derivative 71 and then to a dicationic phosphorus species 72.^{59,60}



The first stage was also observed for RR' = (CH₂)₅.⁶⁰ Clear NMR evidence was obtained for the products in all the above reactions. Compound 44 (R = R' = Et) gave rise to a complex mixture of products when treated with NaN₃, probably involving 73 as an intermediate species, since two doublets at 38.9 and -66.3 ppm were detected, ¹J_{PP} 57 Hz.⁶⁰ Finally, the action of 2 mol of



44 (R = R' = Et) upon 2 mol of (C₂H₄)Pt(PPh₃)₂ resulted in a novel binuclear platinum complex, the crystal structure of which has been determined,^{59,69} this complex does not contain phosphoranide ligands, however.

V. Metal Derivatives

Availability of a lone pair of electrons on the phosphorus atom enables phosphoranides to act as ligands toward transition metals; the first such compound was reported by Riess and co-workers in 1981.⁷⁰ They treated cationic complex 74 (R = Ph, M = Mo, n = 2), as its PF₆⁻ salt, with LiMe at 60 °C, to yield complex 75. Its ³¹P NMR shift of 23.8 ppm was at a

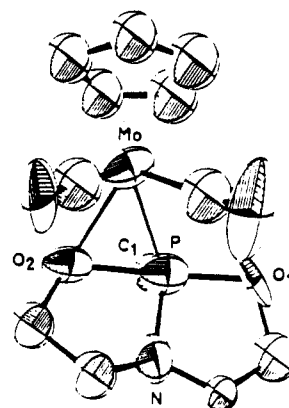
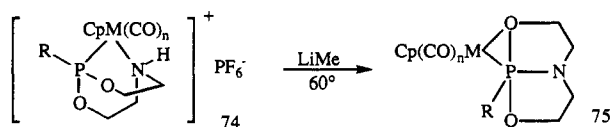


Figure 12. Molecular structure of complex 75 in the crystal; only the C-1 atom of the phenyl group bonded to phosphorus is included, for clarity. (Reprinted from ref 70. Copyright 1981 VCH Verlagsgesellschaft mbH.)

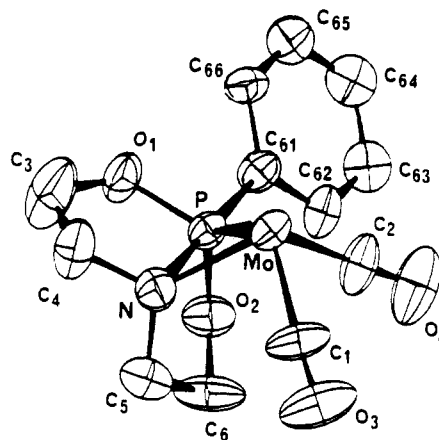
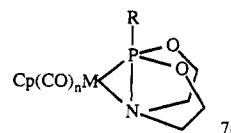


Figure 13. Molecular structure of Cp(CO)₂Mo[PhP-(OCH₂CH₂)₂N], complex 76; the Cp ring has been omitted for clarity. (Reprinted from ref 71. Copyright 1981 American Chemical Society.)

much lower frequency than for phosphane complexes. The crystal structure of this compound is shown in Figure 12; the P-O distance to the Mo-bound oxygen is quite long [1.893(4) Å] compared with the other P-O bond (1.653 Å), while a P-N bond length of 1.69(5) Å is as expected for P-N_{eq}. The ligand has the oxygen atoms in the more favorable apical positions around phosphorus, with the phenyl group occupying an equatorial site. Interestingly, similar reactions of 74 (M = Mo or W) with 1 molar equiv of LiMe in THF/ether at -20 °C led to the kinetic, but thermodynamically less stable, product 76 (M = Mo or W; R = Ph; n = 2), an isomeric phosphoranide complex with N instead of O bound to the metal (δ ³¹P 43.9 ppm for M = Mo; 26.4 ppm, ¹J_{PW} 232 Hz for M = W).^{71,72} This structure was confirmed for M = Mo by X-ray diffraction (Figure 13), the N atom [P-N 1.908(12) Å] and phenyl substituent occupying axial positions in the tbp.⁷¹ When the Mo complex 76 was heated for 4 h in



THF at 60 °C, it isomerized to compound 75 (R = Ph, M = Mo, n = 2).

Table 2. $\delta^{31}\text{P}$ (ppm) for Metal Phosphoranide Complexes 76

M	n	R	$\delta^{31}\text{P}$	solvent	ref(s)
Mo	2	Ph	43.9	CDCl_3/THF	71
Mo	2	PhCH_2	52	THF	75
Mo	2	$\text{CH}_2\text{CH}=\text{CH}_2$	49	THF	75
Mo	2	$\text{CH}=\text{CH}_2$	43	THF	75
W	2	Ph	26.4	CDCl_3	71
Fe	1	Me	90	THF	19
Fe	1	Ph	69	THF, -100°C	76
Fe	1	Ph	73	THF, 20°C	75, 76
Fe	1	PhCH_2	82	THF	75
Fe	1	$\text{CH}_2\text{CH}=\text{CH}_2$	80	THF	74
Fe	1	$\text{CHMeCH}=\text{CH}_2$	83.4, 83.3	THF	75
Fe	1	$\text{CH}=\text{CH}_2$	74	THF	75
Fe	1	3,4,5-trimethylphenyl	74	THF, -100°C	76
Fe	1	3,4,5-trimethylphenyl	80	THF, 20°C	76
Ru	1	Ph	69	THF	76

An attempt to prepare a similar iron complex starting from 74, with $\text{M} = \text{Fe}$, $\text{R} = \text{Ph}$, $n = 1$, led to the unexpected (and reversible) migration of a phenyl group from phosphorus to iron, with formation of $(\eta^5\text{-Cp})(\eta^1\text{-Ph})(\text{CO})\text{Fe}[\text{P}(\text{OCH}_2\text{CH}_2)_2\text{N}]$ (77), which does not contain a phosphoranide ligand.^{72,73} A more detailed ^{31}P NMR study of this reaction was carried out, with BPh_4^- as the counterion to the cationic precursor and utilizing a chemically-labeled phenyl group.⁷⁴ This demonstrated that the iron phosphoranide 76 ($\text{M} = \text{Fe}$, $\text{R} = \text{Ph}$, $n = 1$) was formed initially, followed by a 1,2-nucleophilic transfer of the phenyl group. When an allyl group R was introduced into 74, the latter was converted quantitatively into phosphoranide 76 ($\text{M} = \text{Fe}$, $n = 1$, $\text{R} = \text{CH}_2\text{CH}=\text{CH}_2$) after treatment with LiMe at -60°C ($\delta^{31}\text{P}$ 80 ppm). This complex was only stable in solution below 0°C , and at higher temperatures the allyl group attached to phosphorus rearranged and migrated to give an iron-bound vinyl group, with concomitant formation of an amidophosphane ligand.⁷⁴ A series of complexes of type 76, including Mo ,⁷⁵ Fe ,^{75,76} and Ru ⁷⁶ derivatives, has subsequently been prepared; these may be readily recognized as phosphoranides from their ^{31}P solution shifts, as listed in Table 2.

The Mo complexes with $\text{R} = \text{PhCH}_2$, $\text{CH}_2\text{CH}=\text{CH}_2$, or $\text{CH}=\text{CH}_2$ yielded a complex mixture of products on heating in THF, as shown by ^{31}P NMR, although the presence of a resonance 10–20 ppm upfield of those quoted in Table 2 suggested that the isomeric phosphoranides 75 could be present.⁷⁵ Both P -benzyl and P -vinyl iron phosphoranides also gave rise to several compounds when refluxed in THF, while the α -Me allyl derivative was converted after 10 h of reflux into an iron vinylic species with an amidophosphane ligand, analogous to the behavior of the allyl compound. The mechanism and stereochemistry of this rearrangement have been established.^{75,77} Ruthenium cationic species 74 ($\text{R} = \text{Ph}$; $n = 1$) when treated with LiMe at -80°C formed an amidophosphane complex ($\delta^{31}\text{P}$ 181 ppm) as the initial product; this was unstable at room temperature both in the solid state and in solution, and converted slowly into phosphoranide complex 76 ($\text{M} = \text{Ru}$; $\text{R} = \text{Ph}$; $n = 1$), $\delta^{31}\text{P}$ 69 ppm (Table 2).⁷⁶

The above approach was successfully extended to generate molybdenum and tungsten phosphoranides from cyclamphosphorane, 78 (cyclam PH), which is in equilibrium with the open form 79.⁷⁸ Cationic complexes $[\text{Cp}(\text{CO})_2\text{Mo}(\text{cyclam PH})]^+\text{X}^-$ ($\text{X} = \text{Cl}$, $\delta^{31}\text{P}$

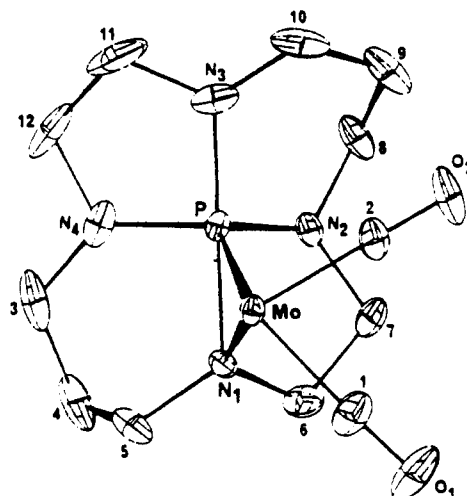
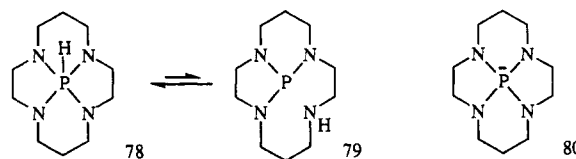


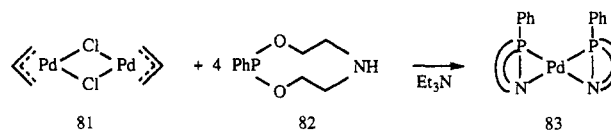
Figure 14. View of the N-Mo-P bridge and pentacyclic structure for $[\text{Cp}(\text{CO})_2\text{Mo}(\text{cyclam P})]$; the Cp ring has been omitted for clarity. (Reprinted from ref 78. Copyright 1982 American Chemical Society.)

144.6; $\text{X} = \text{BPh}_4$, $\delta^{31}\text{P}$ 144.8 ppm), with the ligand in the open configuration 79, were treated by LiMe in



THF to yield $[\text{Cp}(\text{CO})_2\text{Mo}(\text{cyclam P})]$, $\delta^{31}\text{P}$ -31.0 ppm, containing phosphoranide ligand 80, the structure of which was confirmed by X-ray crystallography (Figure 14).^{78,79} The $\text{P}-\text{N}_1$ bond distance [1.854(5) Å] is appreciably longer than the others [1.697(6), 1.696(7), 1.670(7) Å]. The tungsten analogue was similarly obtained from its BPh_4^- salt ($\delta^{31}\text{P}$ -52 ppm, $^1J_{\text{PW}}$ 250 Hz).

Tkatchenko reacted the allylpalladium complex 81 with 4 equiv of phosphine 82 in the presence of Et_3N to produce an unstable material, with a multiplet ^{31}P signal at -14 ppm (-20°C), which could be assigned to the diphosphoranide complex 83.⁸⁰ An iridium complex



with PCl_4 as a ligand was prepared by Ebsworth et al. by oxidation of a solution of $\text{Ir}(\text{CO})\text{Cl}_2(\text{PETe}_3)_2(\text{PCl}_2)$ ($\delta^{31}\text{P}$ for the PCl_2 ligand 304 ppm) with dichlorine in CHCl_3 .⁸¹ The product was formulated as $\text{Ir}(\text{CO})\text{Cl}_2(\text{PETe}_3)_2\text{PCl}_4$ on the basis of elemental analysis, dissolution in MeNO_2 to give a nonconducting solution, and its ^{31}P spectrum which displayed a triplet at 7.6 ppm ($^2J_{\text{PP}}$ 17.7 Hz) and a doublet at -8.6 ppm ($^2J_{\text{PP}}$ 17.7 Hz). The complex reacted with Et_3P to produce the Ir-containing starting material and Et_3PCl_2 . A similar complex with PF_4 as a ligand was subsequently synthesized from $\text{Ir}(\text{CO})\text{Cl}_2(\text{PETe}_3)_2\text{PF}_2$ and XeF_2 in CH_2Cl_2 at 280 K.⁸² The presence of the PF_4 ligand in $\text{Ir}(\text{CO})\text{Cl}_2(\text{PETe}_3)_2\text{PF}_4$ was unequivocally confirmed by its ^{19}F and ^{31}P NMR spectra. Complex 85 was obtained

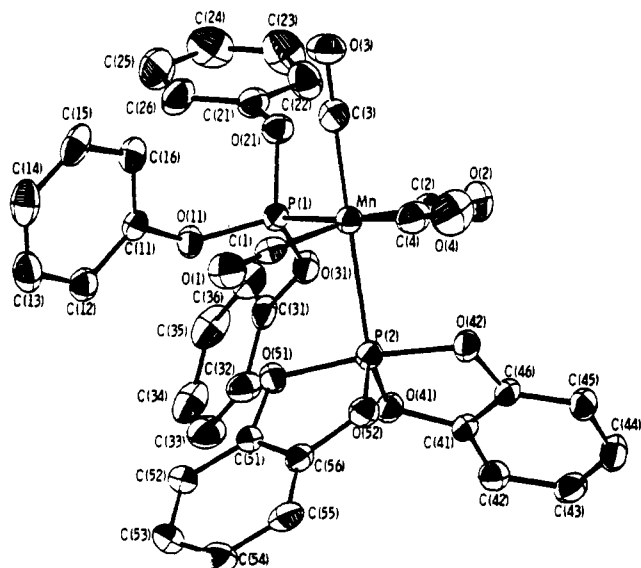
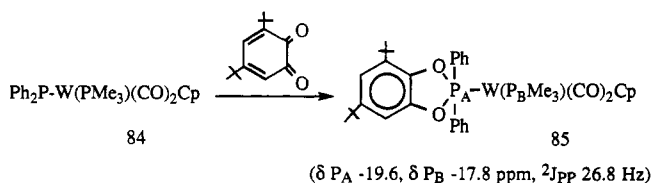
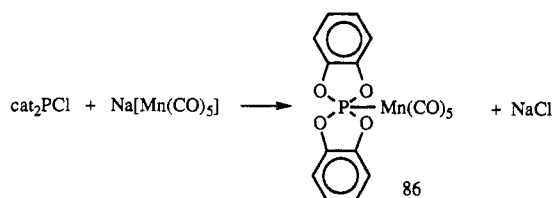


Figure 15. Drawing of *cis*-cat₂PMn(CO)₄P(OPh)₃. (Reprinted from ref 86. Copyright 1985 Elsevier Sequoia S.A.)

by Malisch from oxidative addition of the appropriate quinone to metal-substituted phosphine 84.⁸³



Several other transition metal derivatives have been prepared in recent years by Lattman and co-workers.⁸⁴⁻¹⁰¹ Chlorophosphorane (C₆H₄O₂)₂PCl (*cat*₂PCL) reacted with Na[Mn(CO)₅] in THF at -60 °C to give complex 86, *cat*₂PMn(CO)₅.^{84,85} This compound



can be considered either as a metal-substituted phosphorane or a phosphoranide coordinated to a metal, depending on the electron count.^{84,85} *Cat*₂PMn(CO)₅ underwent carbonyl substitution reactions with the phosphorus ligands L [L = PPh₃, P(OMe)₃, or P(OPh)₃] to form *cis* derivatives *cat*₂PMn(CO)₄L; the crystal structure of the P(OPh)₃ species is shown in Figure 15.⁸⁶ Each *cat* group had one shorter and one longer P-O bond [1.650(3) and 1.768(3) Å in one ring, 1.660(4) and 1.784(3) Å in the second]. The PPh₃ complex rearranged to the *trans* isomer in THF, conversion being ~95% complete after 9 days at ambient temperature. Free PPh₃ was detected in the ³¹P spectrum, indicating a possible dissociative mechanism for isomerization. The *trans* isomer could be isolated by stirring *cat*₂PMn(CO)₅ with an equimolar quantity of PPh₃ in toluene at 50–55 °C for 16 h, since it was insoluble in this solvent. A similar reaction between *cat*₂PCL and Na[Co(CO)₃PPh₃] led to the isolation of *cat*₂PCo-

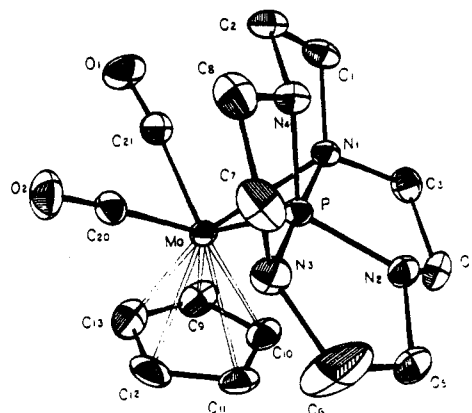
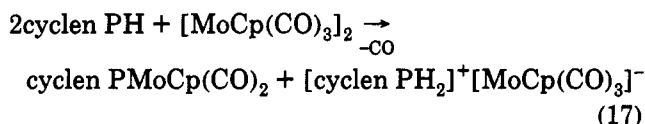
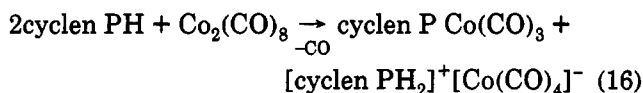


Figure 16. ORTEP plot of cyclen PMoCp(CO)₂. (Reprinted from ref 88. Copyright 1986 American Chemical Society.)

(CO)₃PPh₃, the structure of which was determined by X-ray diffraction.⁸⁷

The majority of more recent investigations has involved derivatives of cyclenphosphorane 41 (cyclen PH). Phosphoranide complexes, together with ionic species, were obtained from reaction of cyclen PH with Co₂(CO)₈ and [MoCp(CO)₃]₂ (eqs 16 and 17).^{88,89} The



ionic product from the Co₂(CO)₈ reaction reverted to the phosphoranide at high temperature, with loss of H₂ and CO, but the analogous Mo compound was not converted, even under refluxing conditions. From the crystal structure of the Mo complex (Figure 16), the P-N₁ distance of 1.852(2) Å is appreciably longer than the other P-N bond lengths [1.699(3), 1.733(2) and 1.698(2) Å]. Ionic species only, with no phosphoranides, were obtained from cyclen PH and Mn₂(CO)₁₀ or HWCp(CO)₃, while [FeCp(CO)₂]₂ did not react with cyclen PH under the experimental conditions.⁸⁸ The crystal structure of cyclen PCo(CO)₃ was subsequently determined,^{89,90} again the P-N₁ bond distance is longer than the others.

Cyclen PH reacted with ClRh(PPh₃)₃ with loss of two PPh₃ residues to yield initially a complex containing the open form of the incoming ligand.⁹¹ This species underwent a three-fragment oxidative addition of CH₂Cl₂, leading to a novel phosphoranide-rhodium(III) complex, the geometry of which is indicated in Figure 17. The equatorial P-N bonds in the cyclen ligand are shorter [1.661(6) and 1.677(7) Å] than the axial ones [1.931(7) and 1.911(8) Å], as expected.

cis-Cl₂Pt(PPh₃)₂ reacted in a 1:1 molar ratio with cyclen PH in THF to give two different platinum-containing complexes, deduced from various physical measurements to be (cyclen P)PtCl(PPh₃) and [*cis*-(H₂ cyclen P)PtCl₂(PPh₃)]⁺Cl⁻. From their ³¹P NMR shifts, both of these species appeared to contain phosphoranide ligands.^{89,92} This was confirmed for (cyclen P)PtCl(PPh₃) by X-ray crystallography (Figure 18), which indicated one long P-N bond of 1.872(11)

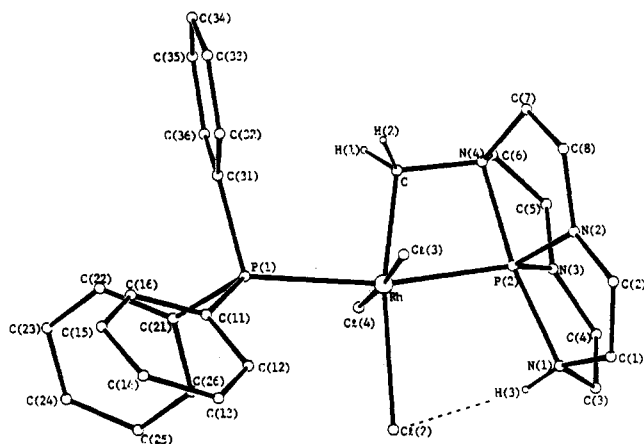


Figure 17. Geometry of the Rh(III) complex; all H atoms are excluded for clarity except H(1) and H(2) belonging to the bridging CH₂ group, and H(3), involved in an intramolecular H bond. (Reprinted from ref 91. Copyright 1986 American Chemical Society.)

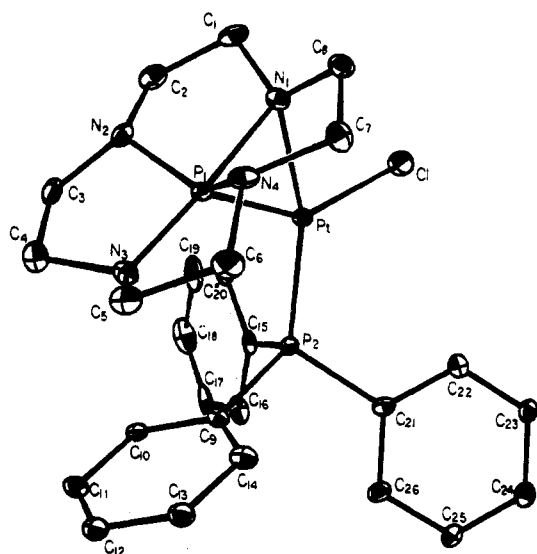


Figure 18. ORTEP view of (cyclohexylphosphorane)PtCl(PPh₃) showing the atom-numbering scheme. (Reprinted from ref 92. Copyright 1987 American Chemical Society.)

Å in the cyclen ligand, the other three ranging between 1.68 and 1.70 Å. Addition of HCl converted this complex to the ionic product, and the reverse process could be achieved by deprotonation with NaOH in CH₂Cl₂.⁹³ The crystal structure of the cationic species, subsequently determined,⁹³ confirmed that the ligand was coordinated in the phosphoranide form, as deduced previously. Interestingly, protonation of (cyclohexylphosphorane)PtCl(PPh₃) by an equimolar quantity of HBF₄ resulted in a derivative where one of the P–N bonds was cleaved, thus removing the phosphoranide character.

The Cl ligand in (cyclohexylphosphorane)PtCl(PPh₃) could be substituted by Br via reaction with BuBr; this was confirmed by X-ray crystallography of the product.^{94,95} Further exchange reactions occurred with Co(CO)₄⁻, SMe⁻, I⁻, and Br⁻, the ligands replacing Cl in (cyclohexylphosphorane)PtCl(PPh₃), while Ph₂PCH₂PPh₂ (dppm) displaced PPh₃, with only one P site of dppm bound to platinum.^{95,96} MeI produced the iodo derivative, which was also formed, together with Me₃SiCo(CO)₄, by treatment of the Co(CO)₄ complex with Me₃SiI. Crystal structures of the Co(CO)₄ and I derivatives displayed the usual

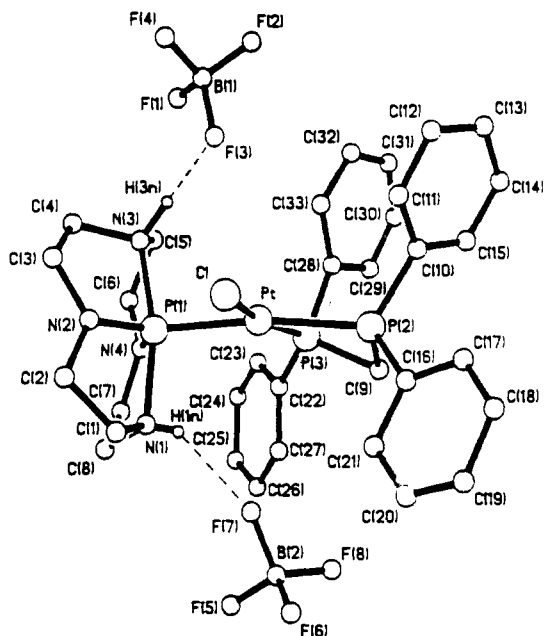


Figure 19. Computer-generated drawing of [(H₂ cyclen P)PtCl dppm]²⁺(BF₄⁻)₂; H atoms (except those involved in H bonding) are omitted for clarity. (Reprinted from ref 97. Copyright 1992 American Chemical Society.)

cyclen P geometry in phosphoranide complexes, with one long P–N bond in each case [1.876(9) and 1.854(9) Å respectively].⁹⁵ (Cyclen P)PtCl(PPh₃) with Ph₂CH₂CH₂PPh₂ (dppm) yielded the ionic complex [(cyclohexylphosphorane)PtCl dppm]⁺Cl⁻, by displacement of PPh₃; the chloride could be converted to the corresponding PF₆⁻ salt by NaPF₆.⁹⁷ Displacement of chloride from (cyclohexylphosphorane)PtCl (dppm) by addition of NaBPh₄ led to a mixture of products, one of which was identified as the bischelate species [(cyclohexylphosphorane)Pt dppm]⁺BPh₄⁻, from NMR evidence. The complex (cyclohexylphosphorane)PtCl (dppm) reacted in a 1:2 molar ratio with HBF₄ in THF to give [(H₂ cyclen P)PtCl dppm]²⁺(BF₄⁻)₂, and with Na[Co(CO)₄] to yield [(cyclohexylphosphorane)PtCo(CO)₃ (μ-dppm)]; the crystal structures of the two Pt derivatives are depicted in Figures 19 and 20.

The species [(H₂ cyclen P)Mo(CO)₅]BF₄ has been synthesized by treatment of the open-chain complex (H cyclen P)Mo(CO)₅ with HBF₄, causing an upfield ³¹P NMR shift from 116 to 35 ppm.⁹⁸ X-ray crystallography of the open-chain precursor revealed a transannular P–N distance of 2.356(23) Å, ca. 0.4 Å longer than P–N axial bonds in related cyclen P complexes, but still within the sum of the van der Waals radii. In view of the geometry about phosphorus, the authors considered that the electronics of H cyclen P might best be described by regarding it as a zwitterionic phosphoranide ligand. (H cyclen P)Mo(CO)₅ reacted with Me₃O⁺BF₄⁻ to give a species thought to be [H(Me) cyclen P]Mo(CO)₅]BF₄ from its ³¹P shift of 40 ppm.⁹⁹ In a 2:1 molar ratio reaction with CF₃SO₃Me, (H cyclen P)Mo(CO)₅ yielded two products, Me cyclen P]Mo(CO)₅ (not a phosphoranide) and [H₂ cyclen P]Mo(CO)₅]CF₃SO₃, containing the same cation as the tetrafluoroborate mentioned above.¹⁰⁰ The complex formed on treatment of (H cyclen P)Mo(CO)₅ with BuLi was formulated as Li⁺[(cyclohexylphosphorane)Mo(CO)₄]⁻; its ³¹P NMR shift of 20 ppm indicated a full P–N bond rather than a transannular interaction, characterizing it as the first anionic transition metal phosphoranide complex.¹⁰¹

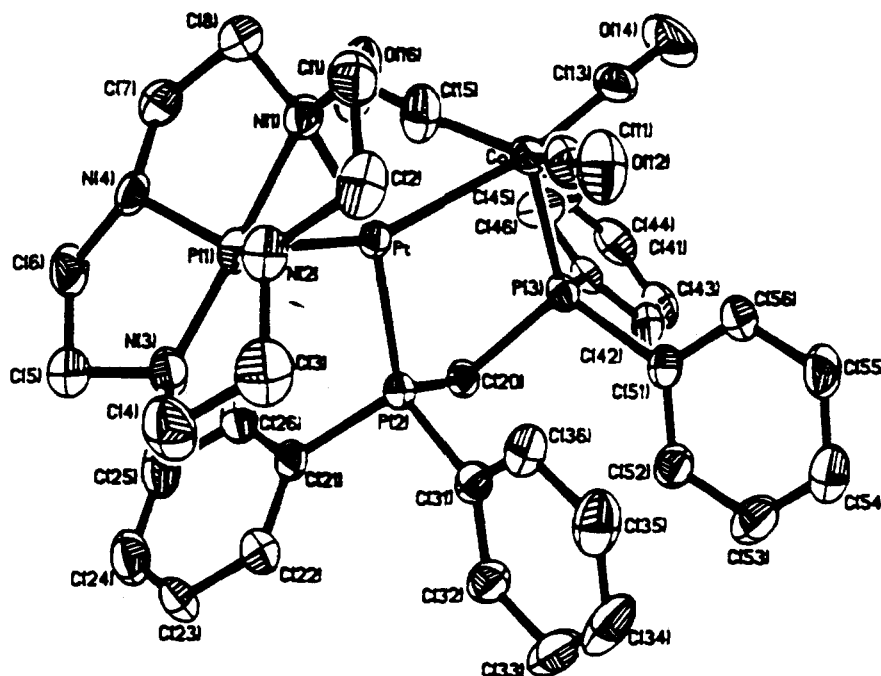


Figure 20. Computer-generated drawing of $[(\text{cyclo-P})\text{PtCo}]_3(\mu\text{-dppm})$; H atoms are omitted for clarity. (Reprinted from ref 97. Copyright 1992 American Chemical Society.)

In conclusion, the chemistry of phosphoranides has developed considerably in recent years, and the range of species stable to isolation has been greatly extended, particularly in the area of transition metal complexes. The synthesis of simple noncyclic phosphoranides with one or two organo groups on phosphorus further increases the likelihood that such species play a pivotal role in nucleophilic substitution reactions at phosphorus(III) centers. The stability of these compounds is evidently enhanced by the presence of strongly electron-withdrawing substituents, such as CN or C_6F_5 , leading to the possibility of synthesizing a more extended range of derivatives using CF_3 groups, for example, as substituents on phosphorus. As yet little if any use has been made of low-temperature ^{31}P NMR spectroscopy; in view of the marked shift differences between neutral phosphorus(III) species and phosphoranides, this technique could be particularly valuable for detecting organophosphoranides, where the species are unlikely to be isolable at room temperature. No transition metal complexes have been reported involving simple noncyclic phosphoranides, which have lone pairs available for donation, and this area remains open to investigation. The metal fragment would need to be carefully chosen, however, to avoid breakdown of the ligand into a phosphine and halide (or pseudohalide), which could then coordinate separately to the metal. For the cyclic species, encompassing both phosphoranides themselves and their transition metal derivatives, the atoms bound to phosphorus are invariably O or N donors in the species studied so far. Potential extension to other donor atoms, such as S or even P, may be possible, although their lower electronegativity would tend to decrease stability compared with that of presently-known compounds. Low-temperature studies could again prove invaluable for identifying such species. Detailed mechanistic investigations, for example using isotopically-labeled materials, on the formation of phosphoranides and their role in nucleophilic substitution reactions, would also be worth pursuing. It is

evident that there is considerable scope for expansion of research in this important and interesting area of phosphorus chemistry.

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