Aspects of the chemistry of some phosphorus halides and pseudohalides

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ASPECTS OF THE CHEMISTRY OF SOME PHOSPHORUS HALIDES AND PSEUDOHALIDES

BY

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To my parents and Em and J.P.

" .. I tell you I do not see the signal."

- H. Nelson on being shown an n.q.r spectrum at the Battle of Copenhagen.

Declaration

The work described in this thesis was carried out in the University of Durham between October 1977 and October 1980. This work has not been submitted, either completely or in part, for a degree in this or any other university and is the original work of the author except where acknowledged by reference.

Some aspects of this work have been published in the following papers.

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Abstract

The preparation of pseudohalogeno derivatives of the simple phosphorus(V) species PCl_4^+, PCl_5 and PCl_6^- has been attempted. In the case of the tetrachlorophosphonium ion only azido-derivatives are observable in normal organic solvents, cyano and thiocyanato derivatives being more stable in liquid halogen media. Isolation of these compounds was not possible.

Molecular derivatives based on PCl_5 seem to be particularly unstable and are only readily observable under forcing conditions for cyanide.

The derivatives of the hexachlorophosphate ion are all observable, PX_6^- being readily formed for X = N_3, NCS, NCO and OCN although these and the intermediate species are all unstable. The series of cyanides $PCl_{6-n}(CN)_n^-$ ($0 \leqslant n \leqslant 3$) have been isolated as solids and fully characterised, and the presence of isomers for n = 2 and 3 has been clearly established.

The six-coordinate fluorochlorophosphates $PF_3Cl_3^-$, $PF_2Cl_4^-$ and $PFCl_5^-$ have been isolated as pure tetraalkylammonium salts and the reactions of these anions studied with respect to substitution by pseudohalides.

The observation of $PF_{6-n}X_n^-$ (X = pseudohalogen) has been carried out by ligand exchange between PF_6^- and PX_6^- (where known) or PX_3 and attempts have been made to isolate compounds, where feasible, by other reactions such as the addition of pseudohalide ions to PF_5.

The use of pairwise interactions has proved invaluable in assigning formulae in the tetrahedral systems, and in both assigning formulae and identifying specific isomers in many of the six-coordinate systems. The substitution patterns in the six-coordinate systems can be rationalised in terms of a simple steric model, or on the basis of ligand field theory for the cyanides.

Other six-coordinate systems have been studied with respect to substitution by azide and several new species have been identified.

The acceptor properties of phosphorus(III) halides and pseudohalides have also been studied and the crystal structures of PCl_4^- and PBr_4^- salts prepared during the course of this work have been determined by Dr. W.S. Sheldrick. Phosphorus tricyanide was found to have relatively extensive acceptor properties towards halide ions and pyridine donors. $P(NCS)_3$ appears to have limited Lewis acidity, forming unstable adducts only.

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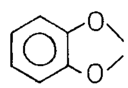
The following abbreviations are used in this work:

Et	=	C_2H_5-
Pr	=	$n-C_3H_7-$
Bu	=	$n-C_4H_9-$
Pe	=	$n-C_5H_{11}-$
R	=	any alkyl group
Py	=	pyridine
dipy	=	2,2'-dipyridyl
Cat	=	catechyl 

Chapter 1

Introduction

Many pseudohalogen derivatives of both phosphorus(III) and phosphorus(V) have been characterised. The simple tripseudohalo-compounds, PX_3 (X = CN[1], NCO[2], NCS[3] and N_3[4]), have all been reported and are conveniently prepared by addition of the appropriate metal salt (Ag where X = CN, NCO and NCS, and Na for X = N_3) to a solution of PCl_3 in an anhydrous organic solvent.

Many of the possible mixed halogen-pseudohalogen species have also been characterised. $PF_{3-n}X_n$ (X = NCS and NCO, $0 \leqslant n \leqslant 3$) are obtained by the reaction of the corresponding tripseudohalide with SbF_3[5]. PF_2CN has been prepared by addition of CuCN to PF_2I[6]. PCl_2X (X = NCS[7] and NCO[8]) and $PCl(NCO)_2$[7] can be isolated by reacting the theoretical mole ratio of silver salt with PCl_3 followed by distillation of the crude product.

^{31}P n.m.r. spectroscopy has proved to be a powerful means of identifying species which have proved difficult to isolate and characterise by normal methods. Thus the species $PY_{3-n}(NCO)_n$ (Y = F, Cl, Br, $0 \leqslant n \leqslant 3$)[9], $PY_{3-n}(NCS)_n$ (Y = Cl, Br, $0 \leqslant n \leqslant 3$)[9] and $PY_{3-n}(CN)_n$ (Y = Cl, Br, I, $0 \leqslant n \leqslant 3$)[10] have all been unambiguously identified in solution.

Many of the isolable compounds are unstable. Of the tripseudo-halides, $P(NCS)_3$ and $P(NCO)_3$ both decompose to give as yet uncharacterised polymeric materials, while $P(N_3)_3$ is explosive. Only $P(CN)_3$ is stable, and may itself be considered polymeric with close N - P interactions between adjacent molecules[11]. Most of the mixed species are unstable with respect to disproportionation to the corresponding trihalide and tripseudohalide, $PF(NCO)_2$ and $PCl_2(NCO)$ being the only exceptions.

Pseudohalogen derivatives of phosphoryl and thiophosphoryl compounds have been identified by ^{31}P n.m.r. spectroscopy and in many cases isolated and characterised by physical measurements. POX_3 (X = NCS, NCO) can be prepared by reacting AgX with $POCl_3$ in an inert solvent[12]. $PS(NCO)_3$ is best synthesised by heating $P(NCO)_3$ with sulphur in a sealed tube, since reaction between $PSCl_3$ and AgNCO is very slow[13]. $PO(N_3)_3$ can be prepared by treating $POCl_3$ with NaN_3 in acetonitrile[14]. Of the mixed species only $POCl_2(NCS)$, $POCl_2(NCO)$ and $POF_2(NCO)$ have been isolated. $POCl_2(NCS)$ was prepared by reacting equimolar quantities of $POCl_3$ and AgNCS, followed by distillation of the crude product[8]. $POCl_2(NCO)$ was obtained by the reaction of PCl_5 with ethylcarbamate[15]. $POF_2(NCO)$ was prepared by treating $POCl_2(NCO)$ with SbF_3[16]. Whereas many of the possible mixed halogeno-pseudohalogeno intermediate species have not been isolated, several have again been unambiguously identified by means of ^{31}P solution n.m.r. spectroscopy. These include $POCl_{3-n}X_n$ (X = NCO, NCS, $0 \leqslant n \leqslant 3$), $PSBr_{3-n}(NCS)_n$ ($0 \leqslant n \leqslant 3$)[17] and $PS(NCO)_3$[18], but rather interestingly no cyano-derivatives.

$P_2O_3(NCS)_4$ is prepared from the reaction of pyrophosphoryl chloride with KNCS in acetonitrile[19]. The anion $PO_2(N_3)_2^-$ [20] has been prepared by partial hydrolysis of the $P(N_3)_6^-$ anion. $POS(N_3)_2^-$ and $PS_2(N_3)_2^-$ were isolated from the reaction of $P_4S_4O_6$ with NaN_3 while $PS_2(N_3)_2^-$ and $PS_2(CN)_2^-$ were prepared by reaction of P_4S_{10} with NaN_3 and KCN respectively[21].

Reports of other phosphorus(V) pseudohalogen containing species are less abundant. Evidence for the existence of $P(CN)_5$ was obtained from vapour pressure measurements on the $P(CN)_3$-cyanogen system[22]. $PCl_2(NCO)_3$ has been postulated as the product of the reaction between chlorine and $P(NCO)_3$ on the basis that hydrolysis gave no indication of phosphorus(III) species in solution[23]. No other molecular species based on PCl_5 have been reported. The hexaazidophosphate ion has been prepared by the reaction of NaN_3 with PCl_5 in acetonitrile followed by addition of R_4NCl, R_4NN_3 or R_4PCl (R = alkyl group) to obtain the ion as its tetraalkylammonium or phosphonium salt[24,25]. $P(N_3)_4^+$ was obtained by the reaction between PCl_3 and $(SbCl_4N_3)_2$[26,27]. $PCl_4(CN)_2^-$ has been prepared as a tetrachlorophosphonium salt by reaction of PCl_5 with AgCN in acetonitrile[28], or as a tetraalkylammonium salt by treating the reaction mixture with a solution of a tetraalkylammonium chloride[29]. PCl_5CN^- was synthesised by the reaction of PCl_5 with AgCN in a 2:1 ratio in CH_3CN, again as the tetrachlorophosphonium salt[28].

Phosphorus(V) pseudohalogen containing species are generally unstable, decomposing to give uncharacterised polymeric materials in the case of cyanates and thiocyanates, the only exception being $PO(NCS)_3$. Azide-containing species are all explosive. PCl_5CN^- and $PCl_4(CN)_2^-$ readily decompose when prepared as tetrachlorophosphonium salts, but $PCl_4(CN)_2^-$ is, however, stable with a tetraalkylammonium counterion. $P(CN)_5$ appears only to be stable under a pressure of cyanogen, dissociation to $P(CN)_3$ and $(CN)_2$ occurring at normal pressure.

There are very few reports of phosphorus(III) compounds acting as Lewis acids. $P(NCS)_3$ forms a well-defined 1:1 adduct with aniline which precipitated from a benzene solution[30]. $PCl_3.3Et_3N$ has been reported from vapour pressure measurements on the PCl_3-triethylamine system[31]. Adducts of PCl_3 and PBr_3 with pyridines and amides have also been reported, but no structural data were available[32-36]. The compounds $PCl_3.NMe_3$[37] and $PBr_3.NMe_3$[38] have been characterised, the P - N bond energies indicating that PCl_3 is a better acceptor than PBr_3. Salts of the PBr_4^- anion have been prepared by the reaction between PBr_3

and tetraalkylammonium bromides[39]. Adducts of PCl_3[40] and PI_3[41] with pyridine have been detected by ^{31}P n.m.r. measurements, and a four-coordinate anion has been identified by deprotonation of a hydrido-spirophosphorane[42].

The present work was aimed at extending investigations into the Lewis acidic properties of phosphorus(III) halides and pseudohalides towards halide and pseudohalide ions. The identification and, where possible, characterisation of phosphorus(V) pseudohalogen containing compounds based on the simple PCl_4^+, PCl_5, PCl_6^- and PF_6^- species have also been carried out. The main technique used for investigating reactions was ^{31}P n.m.r., and where applicable ^{19}F n.m.r. spectroscopy. Where compounds have been isolated standard techniques such as elemental analysis, vibrational spectroscopy, and occasionally ^{35}Cl n.q.r. have been used.

Whilst the acceptor properties of phosphorus(III) compounds were being investigated reports of the synthesis of $PY_2(CN)_2^-$ (Y = Br, I) and $PY(CN)_3^-$ (Y = Cl, Br, I) were published[43,44] duplicating some of the work on these systems, as described subsequently.

Chapter 2

Experimental

1. The Dry Box

Due to the moisture-sensitive nature of many of the compounds studied, manipulation of materials was carried out under an atmosphere of dry nitrogen. The dry box was equipped with two ports. The large port, for sizeable apparatus, was purged for at least 30 minutes before opening to the box. A smaller "quick entry" port, suitable for removal of n.m.r. sample tubes and other small apparatus, was purged by excess internal pressure. The laboratory supply of piped nitrogen was further dried by passage through a tower packed with P_2O_5 about 1m in length. When not in use the atmosphere of the box was recirculated by means of a pump through a trap cooled to 194K in acetone/CO_2. This removed solvent vapours and any small trace of water from the atmosphere which may have accumulated during the day. The external water pump, used for filtering solutions in the box, was protected by a trap cooled in liquid N_2 to prevent any water vapour diffusing into the dry box. In addition to these precautions a large dish of P_2O_5 was kept exposed in the box to remove any traces of water admitted through the entry ports.

2. The ^{31}P n.m.r. Spectrometer

The Fourier Transform spectrometer was constructed in this department by Dr. A. Royston and has been described in detail elsewhere[40]. The spectrometer utilises a 1.4T magnet from a Perkin-Elmer R10 and is controlled by a Varian 620/L computer. This stores and accumulates the free induction decay produced by a powerful R.F. pulse. After the required number of scans have been completed the computer processes the accumulated F.I.D.s to give the spectrum. The sweep width can be varied from 40 to 800 ppm to observe resonances in the range -400 to +1100 ppm.

Spectra were run at 307.2K, the stationary samples being contained in 8.4 mm external diameter tubes. Chemical shifts were measured relative to external 85% H_3PO_4 with the upfield direction taken as positive.

3. Preparation of Starting Materials

i Anhydrous hydrogen cyanide

Methods of preparation of anhydrous HCN involving treatment of a metal cyanide with concentrated sulphuric acid were found to be extremely violent and gave rise to the formation of much black polymeric HCN. A more controlled method of production involved treatment of KCN with glacial acetic acid. In a typical preparation KCN (40 g) was placed in a flask which was purged with dry nitrogen. Glacial acetic acid was then added from a dropping funnel. The gas formed was passed through a short air condenser and collected at 194K in a flask cooled in acetone/CO_2. After excess acetic acid had been added the solution was warmed to 350K to volatilise as much HCN as possible. The white crystals of HCN were then condensed into a graduated rotaflo on the vacuum line. 17 mls were obtained in this way. The purity of the gas was checked by recording its infrared spectrum.

ii Anhydrous tetraalkylammonium cyanides

Tetra-ethyl, -n-propyl and -n-butylammonium cyanides were prepared by an adaptation of the method of Norris[45].

In a typical preparation of $(C_2H_5)_4NCN$, 50 mls of a 25% aqueous solution of Et_4NOH were placed in a flask with 50 mls CH_3OH. HCN (3.5 mls) was condensed onto the solution frozen under vacuum at 77K. The solution was allowed to warm to room temperature and the solvent was evaporated under vacuum. The resulting solid was still moist and was dried by stirring with benzene for 10 minutes and removing the solvent under vacuum. The solid was then completely dried by heating at 373K under vacuum for 3 h . 11.9 g dry Et_4NCN were obtained in this way.

Analysis	Et_4NCN requires	C 69.23%	H 12.82%	N 17.95%
	found	C 68.81%	H 12.73%	N 17.98%.

iii Anhydrous tetraethylammonium thiocyanate was either purchased and used as such or prepared by the reaction of equimolar amounts of $(C_2H_5)_4NBr$ and NH_4NCS in methanol. The white precipitate of NH_4Br which immediately forms was filtered off and the solution evaporated to dryness. The solid thus obtained was extracted with CH_2Cl_2 several times. The resulting solution was evaporated under reduced pressure and the solid heated to 373K under vacuum for one hour.

Analysis	$(C_2H_5)_4NNCS$ requires	C 57.44%	H 10.64%	N 14.89%	S 17.02%
	found	C 52.48%*	H 10.90%	N 14.47%	S 17.62%.

* This low carbon analysis was reproducible and is thought to arise from incomplete combustion of the sample.

iv Cyanogen chloride was prepared by the method of Jennings and Scott[46]. NaCN (16 g) was powdered and made into a suspension with 50 mls CCl_4. This was cooled to 253K and 3 mls glacial acetic acid were added. Chlorine was then slowly passed through the stirred solution. The reaction mixture was kept between 258K and 268K. When excess chlorine had been added the chlorination was stopped and the solution warmed to 313K. The gases evolved were collected in a trap cooled to 243K. The white crystals formed were then warmed to 273K to remove impurities such as HCl and Cl_2. The remaining liquid was transferred to a rotaflo under vacuum. The infrared spectrum of the gas shows small traces of HCN as the only impurity. 9.8 g gas were obtained.

v Anhydrous lithium cyanide

This was prepared by the method adopted by Ludman[47].

Lithium metal was cut into small lumps under hexane and small quantities of HCN were condensed onto the metal under vacuum. The reaction vessel was allowed to warm towards room temperature, visible reaction occurring when the HCN melted. This process was repeated until a reasonable amount of the white solid had been produced. It was found to be impossible to react all the metal in this way and the unreacted lumps of lithium had to be removed mechanically in the dry box. Use of lithium powder (obtained from the metal dispersed in oil) led to an extremely exothermic reaction producing large amounts of polymeric HCN. Similarly if large amounts of HCN were condensed onto the lumps of lithium the reaction became violent.

LiCN is extremely hygroscopic and cannot be dried even by prolonged heating under vacuum once it is hydrated. Thus methods of preparing the anhydrous salt from aqueous media are not feasible.

vi Anhydrous lithium azide was prepared by the method of Hoffman-Bang[48]. $Li_2SO_4.H_2O$ (5.6 g) was dissolved in 30 mls water and NaN_3 (5.2 g) was added. The resulting solution was treated with 150 mls absolute alcohol. A white precipitate was formed, this was filtered and the remaining solution was evaporated to dryness on a water bath. The crude LiN_3 was digested with 20 mls alcohol for 2 minutes and the resulting solution was filtered and evaporated to give pure LiN_3.

Analysis LiN_3 requires Li 14.2% N 85.8%

found Li 14.6% N 82.9%.

vii Phosphorus tricyanide was prepared by an adaptation of the method of Maier[49]. The reflux was found to be unnecessary and diethyl ether was preferred as solvent since the silver salts are insoluble in it and it is easier to remove. In a typical preparation AgCN (19 g) was placed in a beaker inside the dry box and covered with 50 mls diethyl ether. PBr_3 (4 mls) was diluted to 10 mls with Et_2O and slowly added in 1 ml portions. Successive additions caused rapid reaction accompanied by boiling of the solvent. After complete addition the solution was filtered and the remaining silver bromide extracted ten times with Et_2O. The washings were combined and evaporated under reduced pressure to give a white crystalline solid (3.5 g).

Analysis	$P(CN)_3$ requires	C 33.02%	N 38.52%
	found	C 34.20%	N 38.32%.

^{31}P n.m.r. of a solution of the product in CH_2Cl_2 showed a single sharp resonance at + 125 ppm.

viii Tetraethylammonium hexachlorophosphate was prepared from the reaction of PCl_5 with Et_4NCl. PCl_5 (7.5 g) was completely dissolved in CH_2Cl_2. (It is important that no solid remains as this will be coated with an insoluble layer of the hexachlorophosphate which will prevent it from reacting further.) To this was added a solution of Et_4NCl (6.0 g) in CH_2Cl_2. A thick white precipitate immediately formed. This was filtered, washed with CH_2Cl_2 and dried at the pump to give a quantitative yield of Et_4NPCl_6.

Analysis	Et_4NPCl_6 requires	C 25.7%	H 5.3%	N 3.7%	P 8.29%	Cl 57.0%
	found	C 26.0%	H 5.8%	N 3.4%	P 8.12%	Cl 54.3%.

Solid state n.m.r. showed a single broad peak centred at + 300 ppm.

ix Tetra-n-pentylammonium hexachlorophosphate was prepared by the reaction of equimolar amounts of $(C_5H_{11})_4NCl$ and PCl_5. Pe_4NCl (6.5 g) and PCl_5 (4.0 g) were dissolved in 50 mls CH_2Cl_2. The solution was stirred until all the solids had dissolved. The solvent was then removed under vacuum to leave 10 g white/green solid.

Analysis Pe_4NPCl_6	requires	C 44.3%	H 8.2%	N 2.6%	P 5.7%	Cl 39.3%
	found	C 45.8%	H 9.0%	N 2.1%	P 5.7%	Cl 38.7%.

The n.m.r. of a solution of the solid in CH_2Cl_2 showed a single resonance at + 298.2 ppm.

x Tetraalkylammonium halides were purchased in the best commercially available grade. Bromides and iodides were used without further treatment as they were found to be dry and not hygroscopic. $(C_2H_5)_4NCl$ and $(n\text{-}C_3H_7)_4NCl$ were dried by heating to 433K for 6 - 7 hours under vacuum. $(n\text{-}C_5H_{11})_4NCl$ was dried by heating to 373K for 5 hours under vacuum.

xi Other chemicals were purchased in the best form commercially available and used as such.

Phosphorus compounds were checked for impurities by ^{31}P n.m.r. spectroscopy before use.

4. Analyses

C, H and N were determined by microcombustion with a Perkin-Elmer 240 instrument. The reliability of the machine was found to be variable.

Phosphorus and halogen analyses were carried out by R. Coult. For phosphorus and chlorine a weighed sample was decomposed by fusing in a nickel Parr bomb. The residue was acidified with concentrated nitric acid and made up to 100 mls with distilled water. For phosphorus a suitable aliquot was treated with ammonium molybdate/ammonium vanadate reagent and the absorbance measured at 420μ using a Unicam SP500 spectrophotometer. Chlorine was determined by potentiometric titration against N/100 silver nitrate solution using Ag/AgCl electrodes in an acetone medium.

Bromine and iodine were determined iodometrically following a Schoniger oxygen flask combustion.

5. Solvents

Generally solvents of the best commercially available grade were used. Chlorocarbons were dried over 4A mesh molecular sieve and stored under nitrogen. Hydrocarbon solvents were first dried over sodium wire and then stored under nitrogen over freshly activated molecular sieve.

Nitrobenzene was distilled from P_2O_5 and stored over molecular sieve before use.

Pyridine was distilled from KOH pellets and stored under dry nitrogen before use.

6. Vibrational Spectra

Infrared spectra were recorded on a Perkin-Elmer 577 instrument, as nujol mulls between CsI plates for solids or in a 0.05 mm solution cell with KBr windows for solution spectra. Gas phase spectra were obtained using a 10 cm cell with KBr windows.

Raman spectra were recorded by Mrs. J. Slegrova on a Cary 82 spectrometer using an argon laser.

7. Other Radio Frequency Measurements

^{35}Cl n.q.r. spectra were recorded on a mid-range Decca spectrometer operating in a range of 5 - 55 MHz using Zeeman modulation. The resonances (where observable) were measured at 77K in glass containers of 13 mm external diameter.

^{19}F n.m.r. spectra were recorded on either a Varian A 56/60 operating at 56.4 MHz for continuous wave spectra, or by Dr. R.S. Matthews on a Brucker HX90E Fourier transform spectrometer operating at 84.658 MHz. 5 mm external diameter spinning sample tubes were used. Chemical shifts were measured relative to external $CFCl_3$, with the upfield direction taken as positive.

8. Sealed Tube Reactions

For reactions involving particularly noxious reagents such as HCN, $(CN)_2$, ClCN and PF_3 which have a high volatility, and for reactions involving the use of liquid chlorine as a solvent, sealed tube systems were used. The 8 mm outside diameter silica tube was fitted with an S 19 cup joint by which it could be attached to the vacuum line by means of a suitable tap adaptor, and evacuated. If all the reactants were volatile they could be condensed directly into the tube by cooling in liquid nitrogen. The tube would then be sealed under vacuum. For solids and non-volatile reagents the tube was first evacuated and then opened to a supply of dry nitrogen and removed to the dry box where it could be charged with solid materials. The tube would then be attached to the vacuum line and the procedure outlined above followed.

Chapter 3

Azido-derivatives of Phosphorus(III) and (V)

i Introduction

Although several fully-substituted azido-species have been characterised, no detailed studies of the likely mixed species or of decomposition products have been carried out. The reaction of excess PBr_3 with NaN_3 at 438 - 440K gave a mixture of phosphonitrilic bromide polymers[50], while photolytic reaction of HN_3 with PCl_3 between 195 and 206K yielded a tetrameric product of composition $(P_5N_8Cl_9)_4$[51]. In neither case were any azido-substituted phosphorus(III) compounds detected, although PCl_2N_3 was postulated as an intermediate in the formation of the tetramer.

Previous work on the decomposition of compounds of the type R_2PN_3, where R = CF_3[52,53], C_3F_7[53] and C_6H_5[54], which often required elevated temperatures, has shown that the reaction products are phosphonitrilic polymers $(R_2PN)_n$. Similarly decomposition of $PCF_3CH_3N_3$ gave $(NPCF_3CH_3)_n$[53], while reaction of $C_6H_5PCl_2$ with $(C_6H_5)_3SiN_3$ or $(CH_3)_3SiN_3$ produced $(NP(C_6H_5)Cl)_n$[55], and the action of NaN_3 on a $(C_6H_5)_2PCl$ - $(C_6H_5)PCl_2$ mixture led to the isolation of $N_4P_4(C_6H_5)_6Cl_2$[56].

The series of azido-containing cations $(CH_3)_{4-n}P(N_3)_n^+$ [26] and $(C_6H_5)_{4-n}P(N_3)_n^+$ [27] ($0 \leqslant n \leqslant 4$) have been characterised and their ^{31}P n.m.r. chemical shifts measured[27].

ii Azido-derivatives of phosphorus(III) halides and their decomposition products

a. $PCl_{3-n}(N_3)_n$ $(0 \leqslant n \leqslant 3)$

PCl_3 was treated with NaN_3 in CH_3CN, and the ^{31}P n.m.r. spectrum run immediately after preparation indicated the presence of three new species, giving resonances upfield from PCl_3. These were readily assigned to the compounds PCl_2N_3, $PCl(N_3)_2$ and $P(N_3)_3$. In other less polar solvents no reaction was observed with NaN_3, but LiN_3 was found to react. The shifts for the $PCl_{3-n}(N_3)_n$ species $(0 \leqslant n \leqslant 3)$ in various solvents are shown in Table 3.1. During the course of the

Table 3.1 The solvent dependence of chemical shifts of $PCl_{3-n}(N_3)_n$

Solvent	PCl_3	PCl_2N_3	$PCl(N_3)_2$	$P(N_3)_3$
CH_3CN	-220.0	-164.4	-149.1	-134.6
CH_2Cl_2	-219.6	-161.6	-144.6	-130.2
$C_6H_5NO_2$	-220.8	-162.1	-145.7	-131.2
CS_2	-219.3	-160.4	-143.3	-

reaction further upfield resonances were observed at 6.2 and 16.2 ppm, the latter being more intense. A colourless gas was continuously evolved from the solution and is almost certainly nitrogen.

The substitution of PCl_3 could be driven to completion before any significant decomposition occurred. Thus it was possible to study the decomposition of $P(N_3)_3$. Triazidophosphine decomposes smoothly in all the solvents used, evolving nitrogen gas. The decomposition was complete within one day, the ^{31}P n.m.r. spectrum showing an intense resonance at 16.2 ppm with a less intense peak at 6.2 ppm. This spectrum is identical to that quoted for $(P_5N_8Cl_9)_4$[51]. The product from the decomposition of $P(N_3)_3$ cannot contain chlorine, however, the expected material being $(NP(N_3)_2)_n$ by analogy with the R_2PN_3 species mentioned above. After complete decomposition the solvent was allowed to evaporate slowly, leaving a creamy viscous oil. This could be handled if care was taken to avoid any violent mechanical agitation. A sample submitted for micro-analysis exploded during combustion and no estimation of nitrogen content could be obtained. The phosphorus content was determined as 22.6%; $NP(N_3)_2$ requires 24.0%, but the presence of end groups in the polymer would lower this figure, the exact value depending on the length of the polymer chain, if a linear rather than a cyclic polymer is formed. Its infrared spectrum was obtained as a contact film and in CH_3CN solution, both spectra clearly showing the presence of coordinated azido-groups with vibrations at 2150 and 2165 cm^{-1} respectively[57,58].

The decomposition of PCl_2N_3 could also be followed as it could be prepared in isolation from higher substituted azido-species by the addition of a small quantity of LiN_3 to a strong solution of PCl_3 in CH_2Cl_2. Dichloroazidophosphine is much more stable than the fully substituted species, taking up to several weeks to decompose completely. The expected decomposition product is $(NPCl_2)_n$, but the ^{31}P n.m.r. spectrum was identical to that obtained from the decomposition of $P(N_3)_3$. The infrared spectrum of a solution in CH_2Cl_2 clearly showed the presence of coordinated azido-groups with a band at 2165 cm^{-1}, although the rest of the spectrum indicated that the product was not the same as that obtained from $P(N_3)_3$. The presence of azido-groups implies that the equilibrium (1) occurs to some extent. The rate of

$$2PCl_2N_3 \rightleftharpoons PCl_3 + PCl(N_3)_2 \qquad \ldots (1)$$

decomposition in mixtures of phosphorus(III) chloro-azides was always found to be $P(N_3)_3 > PCl(N_3)_2 > PCl_2N_3$, (decomposition of a solution containing all three compounds giving rise to an identical ^{31}P n.m.r. spectrum to that obtained from PCl_2N_3 and $P(N_3)_3$). Thus removal of a small amount of $PCl(N_3)_2$ by decomposition would cause more PCl_2N_3 to disproportionate. The alternative possibility of direct substitution by LiN_3 into the polymer can be discounted, since the large excess of PCl_3 used would have reacted with all the azide long before the formation of the polymer.

From the above discussion it would appear that substitution of chloride by azide ligands has very little effect on the chemical shifts of the decomposition products. Such a situation is also observed in the $POCl_3$ - $PO(N_3)_3$ system with a difference of less than 3 ppm between the chemical shifts of starting material and final product[59]. Further support for this can be obtained from the smaller differences in shift with 1. increasing ring size and 2. chloride-azide substitution in phosphonitrilic ring systems, as shown in Table 3.2. Thus it seems reasonable to assume that the decomposition

Table 3.2 The variation in ^{31}P n.m.r. chemical shift with ring size and $Cl - N_3$ substitution in cyclic phosphazenes

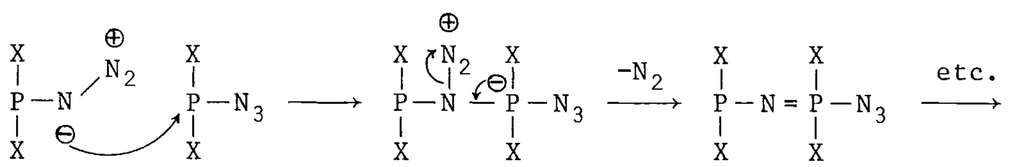
	$(NPCl_2)_x$	$(NP(N_3)_2)_x$
x	δ ppm[60]	δ ppm*
3	-19.8	-11.4
4	5.8	8.5
5	17.5	-
6	16.0	-
7	18.0	-
8	18.0	-

* see section iii

products of PCl_2N_3 and $P(N_3)_3$ are predominantly $(NPCl_2)_n$ and $(NP(N_3)_2)_n$ respectively, the difference in the ^{31}P n.m.r. chemical shifts being undetectable. The low phosphorus analysis obtained from the $P(N_3)_3$ decomposition product and the observation of resonances assigned as end groups in a polymer chain indicate the formation of linear rather than cyclic polymeric materials. A possible mechanism for the decomposition is shown in Scheme 3.1 below. Although P - P coupling might be expected it is not observed in these systems. This could be due to distance between the inequivalent nucleii making the

Scheme 3.1

A mechanism for the decompositions of azido phosphines



coupling small. The probability that more than one type of end group is present would also tend to broaden the signal, making observation of the coupling difficult.

b. $PBr_{3-n}(N_3)_n$ $(0 \leqslant n \leqslant 3)$

PBr_3 was found to react in a similar manner to PCl_3 with NaN_3 in CH_3CN, and with LiN_3 in other solvents. The chemical shifts are shown in Table 3.3. From this and Table 3.1 it can be seen that the shifts for the higher azido-substituted species are considerably higher in non-polar solvents, suggesting specific solvent-solute interactions. Similar solvent effects have been noted for PI_3[61] and the $PY_{3-n}(CN)_n$ $(0 \leqslant n \leqslant 3;\ Y = Cl, Br, I)$[10] series.

Table 3.3 The solvent dependence of the chemical shifts of $PBr_{3-n}(N_3)_n$ $(0 \leqslant n \leqslant 3)$

Solvent	PBr_3	PBr_2N_3	$PBr(N_3)_2$	$P(N_3)_3$
CH_3CN	-230.1	-170.0	-157.1	-134.6
CH_2Cl_2	-228.9	-169.3	-158.0	-
$C_6H_5NO_2$	-228.2	-168.6	-155.2	-
CS_2	-227.2	-167.8	-150.2	-126.9

The decomposition of PBr_2N_3 was followed by the same method as for PCl_2N_3. Decomposition again occurred very slowly with liberation of N_2 to give three new resonances in the ^{31}P n.m.r. spectrum at 38.7, 71.0 and 80.0 ppm. The signal at 71 ppm is readily assignable to $(NPBr_2)_4$ [56], but the remaining two resonances cannot be readily assigned to simple known bromophosphazenes. Nevertheless from the magnitudes of their chemical shifts they may be reasonably ascribed to $\left(\overset{Br}{\underset{N_3}{P}} = N \right)$ (δ 38.7 ppm) and $\left(\overset{Br}{\underset{Br}{P}} = N \right)$ (δ 80.0 ppm) units in a polymer chain. As in the chloro-azidophosphine system, an equilibrium between PBr_2N_3 and more highly substituted species must be postulated to account for the presence of azido-groups in the product. The resonance at 80 ppm was always the most intense, however, (apart from that due to excess PBr_3) suggesting that the equilibrium plays only a minor role in this decomposition. It is also possible that the resonance at 38.7 ppm could be due to an end group in a polymer chain comprising mainly $-NPBr_2-$ units.

The decomposition of $P(N_3)_3$ obtained by the reaction of PBr_3 with LiN_3 led to a ^{31}P n.m.r. spectrum identical to that obtained from the chloro-system, confirming that no halogen is present in the phosphorus-containing products.

c. $PI_{3-n}(N_3)_n$ $(0 \leqslant n \leqslant 3)$

Attempts to identify iodoazidophosphines were only partially successful. PI_3 reacted vigorously with NaN_3 in CH_3CN to give $P(N_3)_3$ with rapid evolution of N_2. In addition to the decomposition products from $P(N_3)_3$ a new high field resonance at 178.9 ppm was observed. In nitrobenzene, LiN_3 reacted with PI_3, the ^{31}P n.m.r. spectrum showing a new resonance in the phosphorus(III) region at -162.0 ppm assigned as PI_2N_3. No further substitution appeared to take place and a complex spectrum was observed at higher field with peaks at 2.2, 12.9, 31.8, 55.8, 64.1 and 83.1 ppm. Evolution of N_2 continued even after no phosphorus(III) species remained in solution. After 3 days the spectrum had simplified somewhat, showing just three signals at 2.2, 12.9 and 83.3 ppm.

The reaction of PI_3 with LiN_3 in 1-iodopropane was much slower. The resonance at -162.2 ppm, assigned as PI_2N_3, was present after a few hours and after a day a peak at 87.1 ppm due to decomposition was seen. Addition of more LiN_3 caused an increase in concentration of PI_2N_3, but no evidence of further substitution could be obtained. The solution slowly evolved N_2, the ^{31}P n.m.r. spectrum showing a corresponding increase in the concentration of the decomposition products at 14.5 and 85.1 ppm (both resonances of approximately equal intensity). No small end group resonance was apparent, suggesting that the peak at 14.5 ppm arises from either a cyclic system or a long-chain polymer, where the concentration of end groups would be low.

In CS_2 the reaction of PI_3 with LiN_3 was extremely slow, producing small amounts of PI_2N_3 (δ -161.3 ppm) after several days. The substitution could be driven no further, even by the addition of a large excess of the azide.

In view of the ability of LiN_3 to replace the chloride lignands of PCl_3 in CS_2, and its apparent reluctance to displace iodide from PI_3 in the same solvent, a system containing PCl_3, PCl_2I, $PClI_2$ and PI_3 [62] was prepared by mixing PCl_3 and PI_3 in CS_2. This solution was treated with LiN_3 in the hope that the following reactions would take place:-

$$PCl_2I \xrightarrow{LiN_3} PIClN_3 \longrightarrow PI(N_3)_2 \qquad \ldots (2)$$

$$PClI_2 \xrightarrow{LiN_3} PI_2N_3 \qquad \ldots (3)$$

Only the known $PCl_{3-n}(N_3)_n$ series was observed apart from a new signal at -170.9 ppm tentatively assigned as $PIClN_3$. No resonances were seen which could be unambiguously assigned as $PI_{3-n}(N_3)_n$ species. This is perhaps not surprising as the shifts of PI_2N_3 and PCl_2N_3 are identical in CS_2, so it is possible that $PI(N_3)_2$ has the same shift as $PCl(N_3)_2$, making it unobservable. In addition to a peak at 17.8 ppm, strong resonances were observed at 87.1 and 114.6 ppm, suggesting that some mixed phosphorus(V) iodine-containing derivatives are formed.

One further attempt to produce the mixed iodoazidophosphines was made by adding LiI to a solution containing PCl_3, PCl_2N_3, $PCl(N_3)_2$ and $P(N_3)_3$. Rapid decomposition occurred giving rise to resonances at 10.7 and 17.8 ppm, and no evidence for substitution was found.

Identification of the decomposition products is by no means certain, but from the magnitudes of the chemical shifts some structural assignments may be made. Species giving resonances between 0 - 20 ppm may be assumed to contain no iodine, and are ascribed to $\text{(}NP(N_3)_2\text{)}$

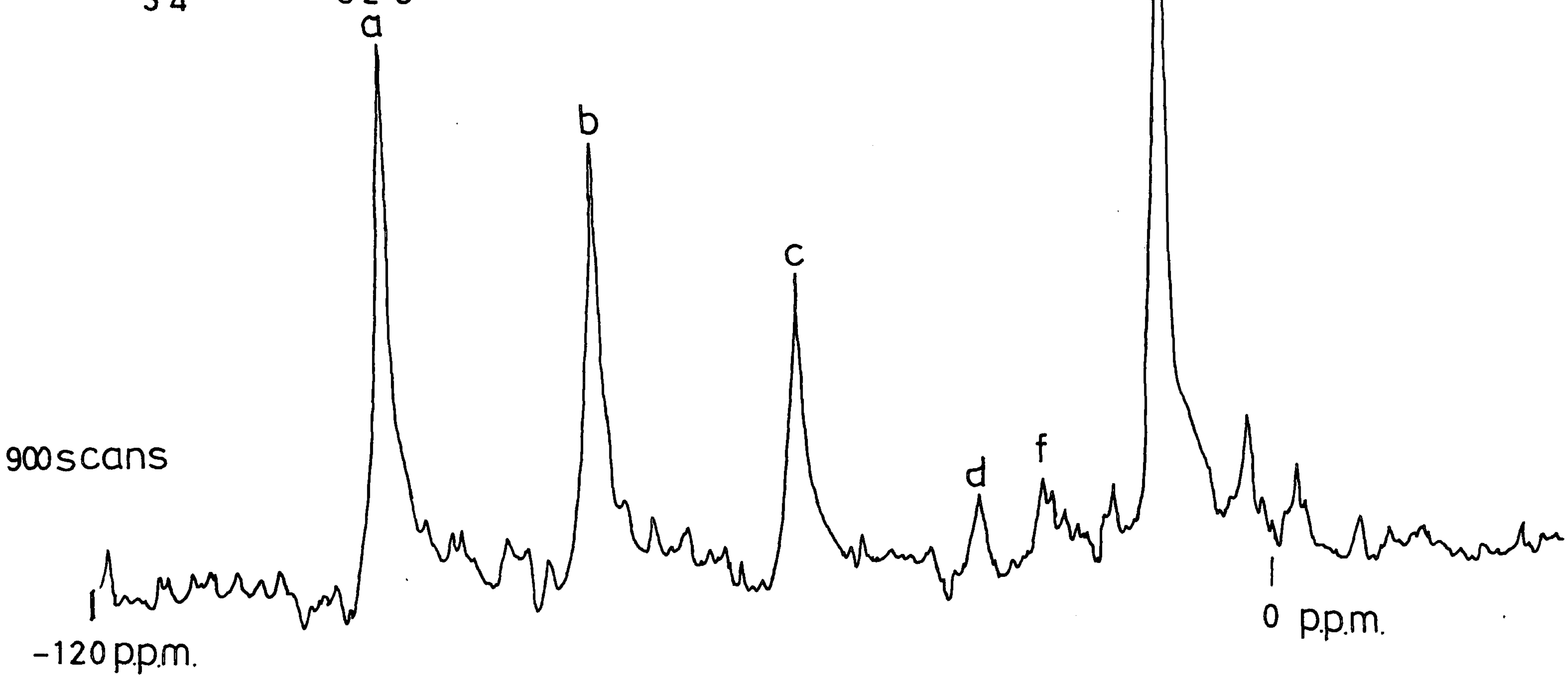
Figure 3.1

A spectrum from the $PCl_4^+ - LiN_3$ system

$a = PCl_4^+$ $b = PCl_3(N_3)^+$

$c = PCl_2(N_3)_2^+$ $d = PCl(N_3)_3^+$

$e = P(N_3)_4^+ - (NP(N_3)_2)_3$ $f = (NPCl_2)_3$



units in a polymer chain. Resonances between 83 - 87 ppm, at 114.6 (from the mixed Cl - I system) and at 178.9 ppm (from the PI_3 - NaN_3 reaction in CH_3CN) almost certainly contain iodo-groups, and are assigned to $\leftarrow NPIN_3 \rightarrow$, $\leftarrow NPICl \rightarrow$ and $\leftarrow NPI_2 \rightarrow$ units respectively in polymeric phosphazenes. The signal at 87.1 ppm clearly arises from a group which contains no chlorine since it occurs in the spectrum of the decomposition products from the PI_3 - LiN_3 reaction. Phosphonitrilic iodides do not seem to have been reported, but the shift difference for replacement of chlorine by iodine in a phosphorus(V) compound looks reasonable by comparison with the results from the $PCl_nI_{3-n}OH^+$ [63] and $PSCl_{3-n}I_n$ [64] series.

iii <u>Azido-derivatives of tetrahalophosphonium ions and their decomposition products</u>

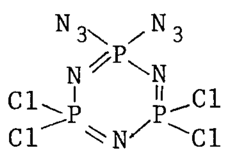
Treatment of PCl_4SbCl_6 with NaN_3 or LiN_3 in CH_3CN led to rapid decomposition with evolution of N_2, in agreement with the work of Schmidt[26]. Resonances from the decomposition products were seen at -21.1, -15.0, -11.4, 5.8 and 8.9 ppm. Addition of LiN_3 to a nitromethane solution of PCl_4SbCl_6 caused the appearance of new peaks upfield of PCl_4^+, which can readily be assigned as $PCl_{4-n}(N_3)_n^+$ species. Typical spectra are shown in Figure 3.1 and the chemical shifts are given in Table 3.4. The only uncertainty in the assignments is that of $P(N_3)_4^+$, since one of the major decomposition products

<u>Table 3.4</u> <u>Chemical shifts for $PCl_{4-n}(N_3)_n^+$ $(0 \leq n \leq 4)$ in CH_3NO_2</u>

n	0	1	2	3	4
δ	-87.1	-66.9	-46.7	-27.5	-11.4

also gives a resonance at -11.4 ppm as described below. This shift is in good agreement with the literature value[26] however, so the signal may well be a composite with contributions from both sources. In addition to the above, resonances were seen corresponding to the decomposition products observed in the reaction in CH_3CN.

The peaks at -21.1 and 5.8 ppm agree well with previous results for $(NPCl_2)_3$ and $(NPCl_2)_4$[60], suggesting that these species and possibly their azido-substituted derivatives are present in the decomposition products. $(NP(N_3)_2)_3$ has been prepared previously[65], and its infrared and ultraviolet spectra recorded[57,58], but no ^{31}P n.m.r. data were given. This compound was prepared in CH_3CN solution as described[58,65] and gave a single resonance at -11.4 ppm, in excellent agreement with one of the decomposition products. This material was found to be quite stable in solution, but when isolated as a neat liquid it is dangerously explosive[57]. $(NPCl_2)_4$ was similarly treated with excess NaN_3 in CH_3CN, and the ^{31}P n.m.r. spectrum showed a single resonance at 8.9 ppm, agreeing well with the highest field peak from the decomposition of the cations. No peaks between those of starting material and final product were observed in either case, suggesting that geminal substitution occurs. This conclusion was strongly supported by the results from the reaction of $(NPCl_2)_3$ and NaN_3 in a 1:2 mole ratio, where only two resonances at -21.1 and 11.4 ppm in a ratio of 2:1 were observed. This is consistent with either a 2:1 mixture of $(NPCl_2)_3$ and $(NP(N_3)_2)_3$ or the presence of



(although P - P coupling might be expected here), but either possibility requires geminal substitution. This probably arises because the azide group is more electronegative than chloride and will activate the phosphorus atom to which it is attached to further substitution. The results are consistent with substitution of Cl by F in cyclic phosphazenes where only the products of geminal substitution can be isolated[66].

The resonance at -15 ppm observed in the decomposition of the cations could be due to an $\leftarrow NPClN_3 \rightarrow$ unit in a trimer molecule. This is not inconsistent with the suggested pattern of substitution, as this is formed by decomposition involving loss of N_2 rather than by direct substitution.

Final confirmation of the assignments of the decomposition products was obtained by the reaction of $(NPBr_2)_n$ with NaN_3 in CH_3CN. The mixture of bromophosphazenes contained $(NPBr_2)_3$ (δ 43.6 ppm), $(NPBr_2)_4$ (δ 75.8 ppm)[56] and probably a higher cyclic polymer (δ 95.1 ppm). When the solution was treated with NaN_3, the ^{31}P n.m.r. spectrum showed three resonances at -11.4 ppm, 8.9 ppm and 16.2 ppm assigned as the fully azido-substituted trimer, tetramer and higher cyclic polymer respectively.

Attempts to obtain azido-derivatives of the PBr_4^+ ion were hampered by the instability of this ion in normal organic solvents. Reaction of PBr_5 and LiN_3 in liquid bromine led to an explosion, presumably due to formation of BrN_3, rather than instability of any $PBr_{4-n}(N_3)_n^+$ species which may have been formed.

iv Azido-derivatives of phosphoryl and thiophosphoryl chlorides and bromides

Addition of NaN_3 to acetonitrile solutions of $POBr_3$, $PSBr_3$ or $PSCl_3$ produced resonances downfield from the starting material, readily assigned to the azido-substituted species. The chemical shifts are shown in Table 3.5. The shift observed for $PO(N_3)_3$ is

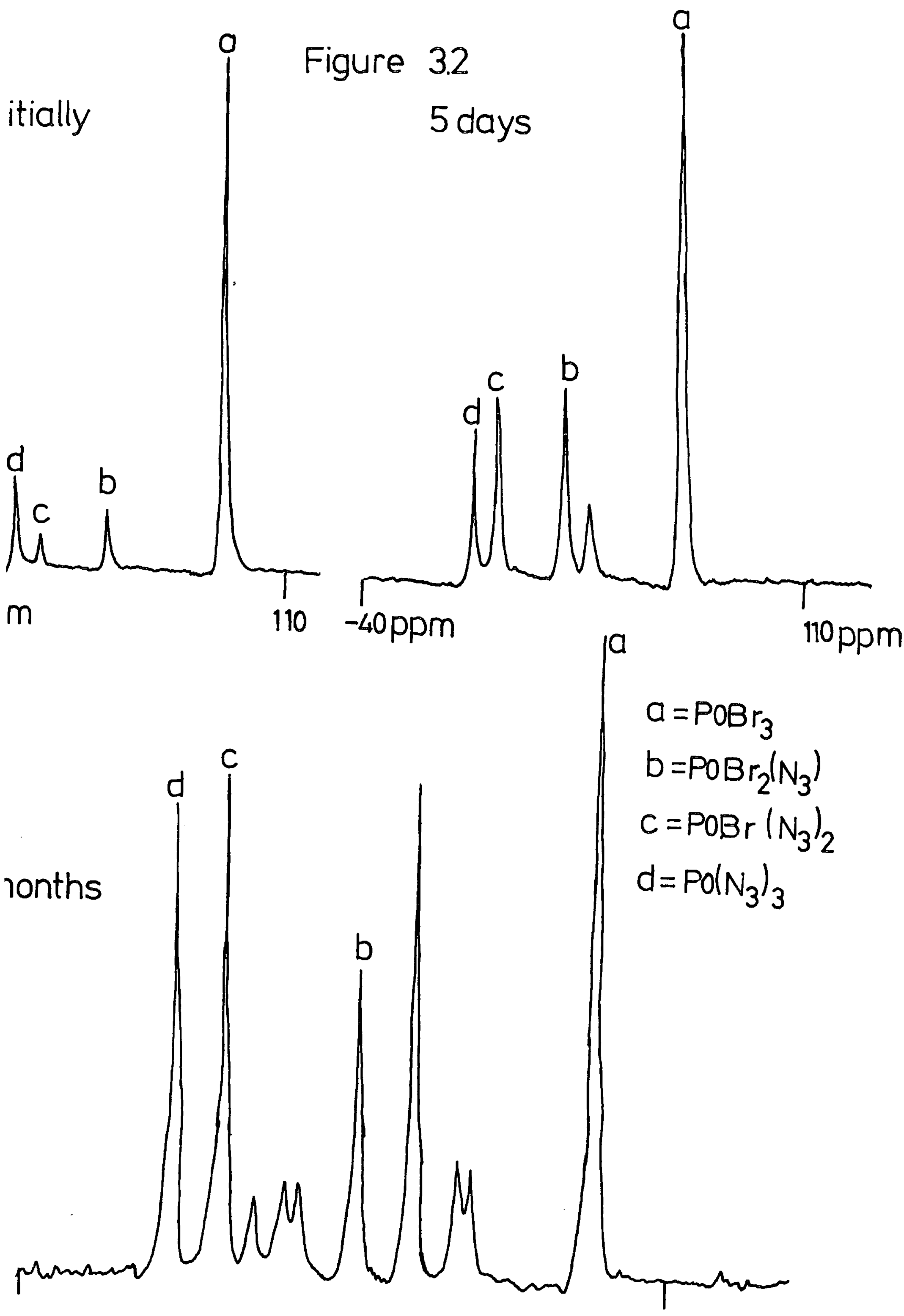
Table 3.5 Chemical shifts of $POX_{3-n}(N_3)_n$ and $PSX_{3-n}(N_3)_n$ (X = Cl, Br; $0 \leq n \leq 3$) in CH_3CN

X	PSX_3	PSX_2N_3	$PSX(N_3)_2$	$PS(N_3)_3$
Br	108.0	19.4	-35.5	-62.9
Cl	-34.0	-51.0	-61.1	-63.0
X	**POX_3**	**POX_2N_3**	**$POX(N_3)_2$**	**$PO(N_3)_3$**
Br	101.6	44.4	12.2	- 0.5
Cl	- 4.3	-	-	0.3

in reasonable agreement with the literature value of -0.8 ppm[4]. Upon reaction of $POCl_3$ with NaN_3 no intermediate species could be detected and only a discrete resonance assignable to $PO(N_3)_3$ was resolved from the $POCl_3$ signal. This is almost certainly because the shifts for the remaining species are close to those of $POCl_3$ or $PO(N_3)_3$. $PS(N_3)_3$ was found to be stable in solution for at least three weeks, although a brown solid was slowly deposited around the sides of the n.m.r. sample tube. $PO(N_3)_3$ showed significant decomposition after two weeks, giving an additional resonance in the ^{31}P n.m.r. spectrum at 6.5 ppm.

Decomposition of a solution containing $POBr_{3-n}(N_3)_n$ $(0 \leq n \leq 3)$ occurred slowly. After four days a new resonance at 53.3 ppm had

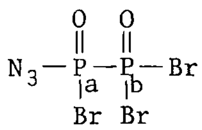
Figure 3.2

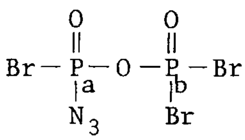


pectra showing the stages of the $POBr_{3-n}(N_3)_n$

decomposition

become apparent. After two months the spectrum showed, in addition to the phosphorylbromoazides, the presence of PBr_3, and two doublets, δ 26.8 and 65.7 ppm J_{PP} 69 Hz, with other resonances at 53.3 and 18.5 ppm. The course of this decomposition is shown in Figure 3.2. The signal due to $POBr_3$ was greatly reduced in intensity, indicating that it was participating in the decomposition. Assignment of these signals from decomposition products is not easy. Simple phosphonitrilic derivatives would not be expected, and indeed no resonances assignable to bromophosphazenes could be seen. The two doublets certainly arise from coupling between two adjacent phosphorus atoms, possibly in compounds of the type I, II or III.


(I)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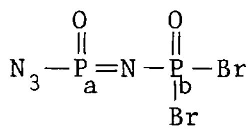

(III)

The resonance at 26.8 ppm is assigned to P_a whilst that at 65.7 ppm is assigned to P_b in all the above structures. Structure (II) seems unlikely in view of the large coupling constant, since values of around 20 Hz are normally observed for P - O - P coupling[66]. (III) is possible but again the coupling is rather large for - P = N - P - systems[66] (no coupling could be detected in the phosphonitrilic polymers produced in section ii). It is also interesting to note that the decomposition product of $PO(N_3)_3$ which gave a resonance at 6.5 ppm is absent from this system, even though $PO(N_3)_3$ is present. This implies that a different decomposition route occurs, presumably due to the other species present in solution.

v Azido-derivatives of the hexachlorophosphate ion

In CH_3CN NaN_3 reacted slowly with tetra-n-pentylammonium hexachlorophosphate to give only decomposition products, mainly polymeric phosphazenes (δ 16.2 ppm) and N_2. Smaller peaks were also observed at -21.1 and -9.8 ppm, possibly due to $(NPCl_2)_3$ and $(NP(N_3)_2)_3$. Addition of LiN_3 to a CH_2Cl_2 solution of Pe_4NPCl_6 gave rise to several resonances downfield from that of PCl_6^-, as well as some due to decomposition products. Careful addition of small quantities of LiN_3 to a solution of the hexachlorophosphate in CH_2Cl_2 allowed observation of the various stages of the substitution reaction, and from the changes in relative intensities as the reaction proceeded the resonances could be assigned to particular members in the $PCl_{6-n}(N_3)_n^-$ series. Some typical spectra are shown in Figure 3.3, and the chemical shifts in Table 3.6.

Table 3.6 Chemical shifts for the $PCl_{6-n}(N_3)_n^-$ ions ($0 \leqslant n \leqslant 6$) in CH_2Cl_2

n	0	1	2	3	4	5	6
δ	298.2	243.5	206.4	183.4	171.2	167.7	180.0

The shift for the hexaazidophosphate ion has been reported as 184.1 ppm in CH_3CN[25], which is in reasonable agreement with the observed value in this work.

During the substitution reaction decomposition took place, approximately 50% of the phosphorus being in the form of polymeric phosphazenes by the time complete substitution to $P(N_3)_6^-$ had been achieved. The solution turned green during this process, indicating the presence of Cl_2 as a decomposition product. To test this hypothesis a solution containing $PCl_{6-n}(N_3)_n^-$ ($0 \leqslant n \leqslant 3$) was allowed to decompose so that no six-coordinate species remained in solution. The resulting green solution was treated with a few drops of PCl_3, and was immediately decolourised. The ^{31}P n.m.r. spectrum of the resulting clear solution showed the presence of PCl_6^- and $PCl_5N_3^-$. This strongly suggests the presence of Cl_2,Pe_4NCl and possibly ClN_3 in solution. The reactions for the re-formation of the six-coordinate species would be

$$PCl_3 + Cl_2 + Cl^- \longrightarrow PCl_6^- \qquad \ldots (4)$$

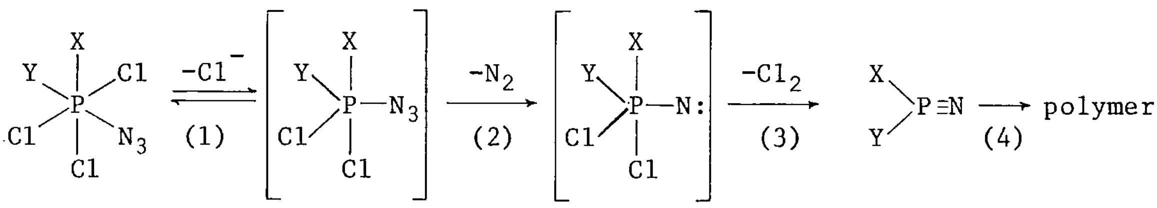
$$PCl_3 + ClN_3 + Cl^- \longrightarrow PCl_5N_3^- \qquad \ldots (5)$$

The formation of $PCl_5N_3^-$ by substitution into PCl_6^- is unlikely since excess LiN_3 would not be expected in the mixture at this stage.

Members of the series $PCl_{6-n}(N_3)_n^-$ $(0 \leqslant n \leqslant 4)$ decomposed readily in solution, but $PCl(N_3)_5^-$ and $P(N_3)_6^-$ showed a considerable increase in stability, $P(N_3)_6^-$ being indefinitely stable in solution. A plausible mechanism for the decomposition is shown in Scheme 3.2.

Scheme 3.2

Mechanism for the decomposition of $PCl_{6-n}(N_3)_n^-$



X = Cl or N_3

Y = Cl or N_3

In more highly-substituted species the loss of Cl_2 in step (3) could be replaced by loss of chlorine azide, and similarly the initial equilibrium (1) would produce more highly substituted (and hence more unstable) molecular species. Thus for $PCl(N_3)_5^-$ and $P(N_3)_6^-$ the equilibrium must be well to the left, providing some kinetic stability for these ions.

Since only six resonances downfield of PCl_6^- were seen in the six-coordinate region of the spectrum, the last of which is readily assignable as $P(N_3)_6^-$, it must be assumed that only one isomer is formed preferentially for the *bis*, *tris*, and *tetrakis*-azido-derivatives, where two are possible in each case. Structures can be assigned to each of the ions on the basis of pairwise interactions[68,69]. This treatment considers the chemical shift to arise from interactions between adjacent ligands attached to the central atom, which act along the edges of the coordination polyhedron. For an octahedron there are thus twelve terms of three types, corresponding to Cl:Cl, $Cl:N_3$ and $N_3:N_3$ interactions. The Cl:Cl term is taken as 24.9 ppm from the shift of PCl_6^-. The $Cl:N_3$ term can be obtained from the observed chemical shift for $PCl_5N_3^-$. Here the shift

$$\delta = 4Cl:N_3 + 8Cl:Cl = 243.5 \text{ ppm},$$

giving the $Cl:N_3$ term as 11.2 ppm. This allows the calculation of the chemical shift for *trans*-$PCl_4(N_3)_2^-$ as there are no $N_3:N_3$ interactions to be considered. This is evaluated as

$$\delta\ (trans\text{-}PCl_4(N_3)_2^-) = 8Cl:N_3 + 4Cl:Cl = 189.2 \text{ ppm},$$

which is considerably lower than the experimental value of 206.4 ppm. Thus it seems reasonable to suppose that the observed shift is due to *cis*-$PCl_4(N_3)_2^-$, and from this the calculation of the $N_3:N_3$ term is possible:-

$$\delta\ (cis\text{-}PCl_4(N_3)_2^-) = 206.4 = N_3:N_3 + 5Cl:Cl + 6Cl:N_3$$

This gives the $N_3:N_3$ term as 14.7 ppm. As all three terms have now been found it is possible to calculate the shifts of the remaining compounds. Alternatively the $N_3:N_3$ term may be taken from the observed shift of $P(N_3)_6^-$, giving $N_3{:}N_3$ = 15.0 ppm. The results are shown in Table 3.7. The data agree well with the estimated shifts produced by a pattern of *cis* substitution, that is formation of *fac*- as opposed to *mer*-$PCl_3(N_3)_3^-$ and *cis*- as opposed to *trans*-$PCl_2(N_3)_4^-$. Once assignments have been made the data can be refined by a least squares method and better estimations of the shifts for all species calculated. The least squares best fit interaction terms obtained from the observed data are Cl:Cl = 24.8, $Cl{:}N_3$ = 11.3 and $N_3{:}N_3$ = 15.1 ppm. The chemical shifts evaluated on this basis are shown in column c of Table 3.7 and in general compare well with the experimental data.

Table 3.7 Calculated and observed shifts for $PCl_{6-n}(N_3)_n^-$ ions

Ion	Calculated			Observed
	a*	b*	c†	
PCl_6^-	-	-	297.4	298.2
$PCl_5N_3^-$	-	-	243.4	243.5
cis $PCl_4(N_3)_2^-$	-	206.7	206.7	206.4
trans $PCl_4(N_3)_2^-$	189.2	189.2	189.4	
fac $PCl_3(N_3)_3^-$	186.0	186.9	187.4	183.4
mer $PCl_3(N_3)_3^-$	168.8	169.4	170.0	
cis $PCl_2(N_3)_4^-$	165.6	167.1	168.0	171.2
trans $PCl_2(N_3)_4^-$	148.4	149.6	150.7	
$PCl(N_3)_5^-$	162.4	164.8	166.0	167.7
$P(N_3)_6^-$	176.4	-	181.3	180.0

*a $N_3{:}N_3$ term from *cis* $PCl_4(N_3)_2^-$

b $N_3{:}N_3$ term from $P(N_3)_6^-$

†c Calculated from least squares fit of observed shifts assuming *cis* substitution.

Whichever method is used to predict the n.m.r. shifts, the conclusions as to the general pattern of substitution remain the same. This, together with the successful prediction of the upfield shift of $P(N_3)_6^-$ from $PCl(N_3)_5^-$ gives some confidence in this method. Pairwise interactions have previously been used to predict the shifts in the $NbCl_{6-n}Br_n^-$[70], $SbCl_{6-n}Br_n^-$[71] and $PF_{6-n}Cl_n^-$[72] ($0 \leqslant n \leqslant 6$) species. In each case *cis*- rather than *trans*-isomers seem to be preferentially formed. In the case of the $PF_{6-n}Cl_n^-$ series the assignments were amply confirmed by observation of characteristic splitting patterns in the ^{31}P and ^{19}F n.m.r. spectra[72].

vi Azido-derivatives of PCl_5 and PCl_5.pyridine

Reactions of PCl_5 with both lithium and sodium azide in $C_6H_5NO_2$ led only to the observation of decomposition products. Thus when a solution of PCl_5 in nitrobenzene was treated with a small amount of LiN_3, effervescence was noted. The spectrum was obtained after this reaction had subsided and showed only $(NPCl_2)_3$ (δ -21.1 ppm) in addition to a small amount of unreacted PCl_5. If larger amounts of the azide were added the reaction became violently exothermic and the resulting ^{31}P n.m.r. spectrum was more complex with major peaks visible at -8.2 and 12.2 ppm, possibly with fine structure. The observed resonances are almost certainly due to phosphonitrilic polymers, the fine structure arising from long range coupling between phosphorus nucleii. The reactivity of PCl_5 towards azides tends to confirm the view that molecular azido-containing species are especially unstable.

As the hexachlorophosphate ion reacted to give substitution products with LiN_3 it seemed reasonable to attempt the reaction of the six-coordinate PCl_5.pyridine complex, which might be expected to form more stable molecular species. The reaction of $PCl_5.py$ with LiN_3 in CH_2Cl_2 was accompanied by gentle effervescence, the n.m.r. spectrum showing a small resonance downfield from that of $PCl_5.py$ (δ 231.3 ppm) at 197.5 ppm. The main products of the reaction were again phosphazene derivatives, giving resonances at -3.3, 5.8 ($(NPCl_2)_4$), 8.9 ($(NP(N_3)_2)_4$) and 12.9 ppm. Although some substitution is apparent decomposition is quite rapid, possibly due to the dissociation of the complex. To suppress this dissociation

$$PCl_{5-n}(N_3)_n.py \rightleftharpoons py + PCl_{5-n}(N_3)_n \longrightarrow \text{rapid decomposition} \quad ... \quad (6)$$

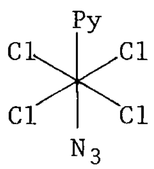
the reaction was carried out in neat pyridine. LiN_3 dissolved in the pyridine solution of PCl_5 giving a mildly exothermic reaction, but no evolution of N_2. The ^{31}P n.m.r. spectrum clearly showed the presence of peaks to lower field of the $PCl_5.py$ resonance with no initial formation of decomposition products. By addition of small amounts of LiN_3 the resonances could be assigned to particular species as in the case of $PCl_{6-n}(N_3)_n^-$. The results are shown in Table 3.8. The final product gave a resonance at 178.9 ppm which is

Table 3.8 Chemical shifts for the $PCl_{5-n}(N_3)_n.py (0 \leqslant n \leqslant 5)$ species in pyridine

n	0	1	2	3	4	5
δ	231.3	199.6	159.7	165.5	171.9	-

in good agreement with the shift for $P(N_3)_6^-$, suggesting that at some stage in the reaction the coordinated pyridine is replaced by azide. The assignment for the n = 4 complex is ambiguous since the shift agrees well with that observed for $PCl_2(N_3)_4^-$.

In this series there is again a possibility of isomerism. If the parameters obtained from the octahedral system $PCl_{6-n}(N_3)_n^-$ are independent of the charge of the complex, evaluation of the py:N_3 and py:Cl terms should allow calculation of the shifts of the other species. The py:Cl term can be readily obtained from the shift of PCl_5.py as 8.2 ppm, on the assumption that the Cl:Cl term can be transferred from the anionic system. This allows the calculation of the shift of the *trans* isomer (IV). This value is considerably different

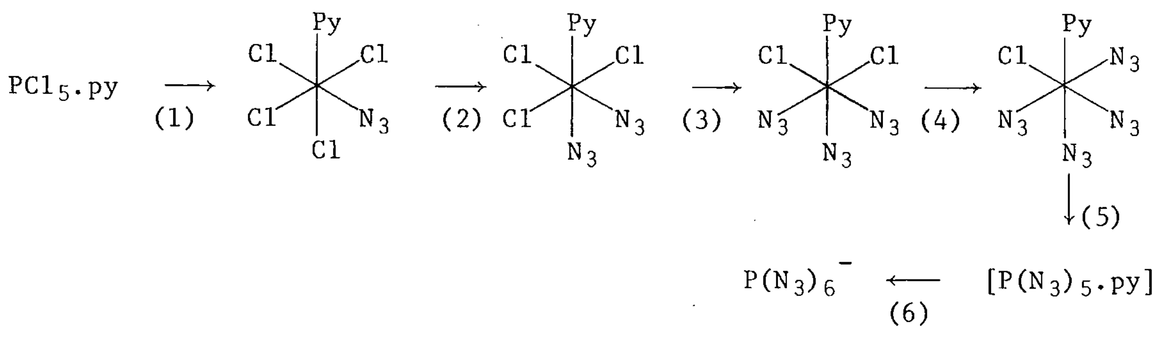


$\delta = $ 4py:Cl + 4N_3:Cl + 4Cl:Cl = 177.2 ppm.

(IV)

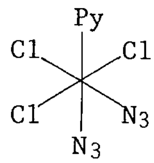
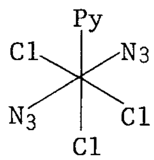
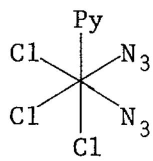
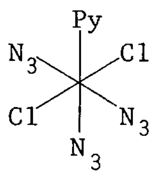
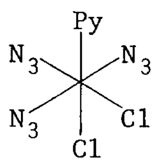
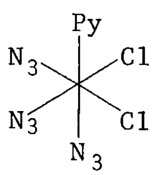
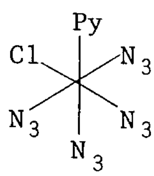
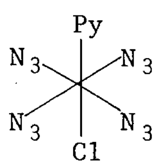
from the observed shift of PCl_4N_3.py, which is presumably the *cis* isomer. By assuming that PCl_4N_3.py exists as the isomer with the *cis* pyridine - azide configuration, the py:N_3 term can be calculated as 17.1 ppm, giving sufficient information to calculate the chemical shifts of all the other species. These are shown in Table 3.9, and from this the course of the reaction seems to be as indicated in Scheme 3.3. Step (4) is more ambiguous since the observed shift for

Scheme 3.3

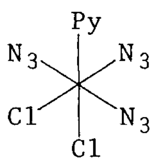


$PCl(N_3)_4$.py lies between the two calculated values. If the assignment of $PCl_2(N_3)_3$.py is correct then clearly only the isomer with a

Table 3.9 The calculated and observed shifts for $PCl_{5-n}(N_3)_n.py$ ($0 \leq n \leq 5$) species

Formula	Structure	Calculated	Observed
$PCl_3(N_3)_2.py$		163.0	159.6
		168.0	
		185.3	
$PCl_2(N_3)_3.py$		148.6	165.5
		171.0	
		166.2	
$PCl(N_3)_4.py$		168.9	171.9
		174.0	
$P(N_3)_5.py$	one isomer	189.2	-

cis pyridine - chlorine arrangement of ligands can be formed, as shown in the scheme. The situation is further complicated by the fact that the shift assigned to $PCl(N_3)_4.py$ is very close to that of $PCl_2(N_3)_4^-$ (δ 171.2 ppm in CH_2Cl_2). No resonance assignable to $PCl(N_3)_5^-$ was seen, however, (although this would be close to that assigned to $PCl_2(N_3)_3.py$ there is no ambiguity here as the resonance at 165.5 ppm was much more intense than that at 171.9 ppm), suggesting that $PCl(N_3)_4.py$ is formed, but reacts rapidly (hence the consistently low intensity of the resonance) with more azide to form $P(N_3)_5.py$. This itself then reacts rapidly to displace the pyridine molecule, yielding the observed $P(N_3)_6^-$ ion. Another possibility is the formation of



, the calculated shift of which at 171.0 ppm is in good agreement with that observed, but this is difficult to rationalise on a chemical basis. Whatever the identity of the 171.9 ppm resonance, the stability of the adducts appears to decrease with the azide content. This is possibly due to azido-groups activating the complex toward further substitution.

During the reaction, only comparatively small amounts of decomposition products were observed. These were identified as phosphonitrilic azide tetramer (δ 8.2 ppm) and polymeric phosphonitrilic chloride and/or azide (δ 14.5 ppm). This reaction would thus provide a better route to the $P(N_3)_6^-$ ion, as less decomposition occurs than in the direct substitution of PCl_6^- salts. The pyridine solution remained clear throughout the experiment, indicating that the solvated lithium cations[73] provide a suitable counter-ion for the $P(N_3)_6^-$ eventually formed.

vii Reactions of LiN_3 with catechyl derivatives of phosphorus(V)

The catechylphosphoranes, $CatPCl_3$ and Cat_2PCl, form the anionic species $CatPCl_4^-$ and $Cat_2PCl_2^-$ [74] with chloride ion donors. Thus a study of the reactions of these species with LiN_3 should provide an interesting comparison with the PCl_5 and $PCl_6^- - N_3^-$ reactions.

a. Azido-derivatives of *bis* catechylphosphorus monochloride

Addition of LiN_3 to a solution of *bis* catechylphosphorus monochloride in CH_2Cl_2 gave rise to a single new resonance at 26.7 ppm as well as that of the starting material at 8.6 ppm. This is assigned to Cat_2PN_3. No evolution of gas occurred indicating that this species is stable in solution.

The acceptor properties of this compound towards chloride ion were briefly investigated by addition of tetra-n-pentylammonium chloride to the solution. This caused the appearance of a new resonance at 112.9 ppm which increased in intensity with the addition of more chloride ion, and is assigned as $Cat_2PClN_3^-$. There was no sign of any resonance due to decomposition, the only other peak present arising from Cat_2POH at 30.7 ppm[75] formed by partial hydrolysis of Cat_2PCl. This resonance shifted to 83.1 ppm upon the addition of chloride, presumably due to the formation of Cat_2POHCl^- [74].

b. Azido-derivatives of the *bis* catechyldichlorophosphate ion

The compound $Pe_4NCat_2PCl_2$ was prepared by addition of excess Pe_4NCl to a solution of Cat_2PCl in CH_2Cl_2. The shift observed (61.3 ppm) was not the limiting shift of 66.2 ppm[74], but indicated that more than an equimolar amount of chloride had been added. Addition of LiN_3 to this solution caused the appearance of three peaks in the ^{31}P n.m.r. spectrum at 27.5, 82.2 and 111.3 ppm. The high field resonance is due to $Cat_2PClN_3^-$ as observed previously, the remaining two signals being readily assigned to Cat_2PN_3 and Cat_2POHCl^- respectively. The substitution of the anion could be driven no further with addition of excess azide, and no evidence for the formation of the fully-substituted $Cat_2P(N_3)_2^-$ species could be obtained.

c. Azido-derivatives of catechylphosphorus trichloride

Violent reaction, with evolution of N_2, occurred when LiN_3 was added to a nitrobenzene solution of $CatPCl_3$. The ^{31}P n.m.r. spectrum clearly showed the presence of Cat_2PCl (δ 8.9 ppm), $(NPCl_2)_3$ (δ -21.1 ppm), $(NP(N_3)_2)_3$ (δ -11.4 ppm) and $(NPCl_2)_4$ (δ 5.8 ppm) with an unassigned resonance at -3.5 ppm. No peaks were seen which could be assigned to direct substitution products of $CatPCl_3$. Addition of a small amount of LiN_3 to a solution of $CatPCl_3$ in CH_2Cl_2 again caused effervescence, the ^{31}P n.m.r. spectrum showing, in addition to starting material, Cat_2PCl with unassigned resonances at -4.9 and 35.5 ppm. The latter rapidly disappeared and signals due to $(NPCl_2)_3$ and $(NP(N_3)_2)_3$ were observed. To confirm the assignment of Cat_2PCl, which gives a resonance close to that of $(NP(N_3)_2)_4$, the solution was treated with more LiN_3, which caused the appearance of the expected resonance upfield at 26.7 ppm due to Cat_2PN_3.

Thus it seems that the main route for decomposition of $CatPCl_{3-n}(N_3)_n$ species is to *bis* catechyl compounds and presumably $PCl_{5-n}(N_3)_n$ species which rapidly decompose giving the phosphonitrilic derivatives observed. In CH_2Cl_2 the reaction initially produced an upfield resonance which could possibly arise from $CatPCl_2N_3$ (δ 35.5 ppm). The peak at -4.9 ppm cannot be assigned to any simple phosphazene derivative. It could be due to a catechyl derivative such as $(NPCat)_3$. Although there seem to be no reports of such compounds in the literature, and attempted preparation by reaction of $(NPCl_2)_3$ with catechol in refluxing benzene failed, the chemical shifts of $(NP(OEt)_2)_3$ at 0.6 ppm[76] and $(NP(OC_6H_5)_2)_3$ at -9.0 ppm[77] are quite close to that observed, indicating the possible presence of $(NPCat)_3$ amongst the decomposition products. This was only a minor product, however, as the signal was always of low intensity. The main course of the reaction is summarised in Scheme 3.4.

Scheme 3.4

The decomposition of $CatPCl_2N_3$

$$2CatPCl_2N_3 \longrightarrow Cat_2PCl \; + \; [PCl_3(N_3)_2] \longrightarrow \text{phosphonitrilic derivatives}$$

d. Azido-derivatives of the catechyltetrachlorophosphate ion

A solution of $Pe_4NCatPCl_4$ was prepared by the addition of Pe_4NCl to a solution of $CatPCl_3$ in CH_2Cl_2 until the limiting shift of 156.1 ppm[74] was observed. Addition of LiN_3 to this solution caused downfield resonances characteristic of substitution. The reaction of successive small quantities of the azide with the solution allowed assignments of formulae to be made. These are shown in Table 3.10.

Table 3.10 Chemical shifts of $CatPCl_{4-n}(N_3)_n^-$ $(0 \leqslant n \leqslant 4)$ in CH_2Cl_2

n	0	1	2	3	4
δ	156.7	130.6	117.9	122.2	143.8

The observation of the $CatPCl(N_3)_3^-$ ion was always difficult, as it seems very activated towards further substitution, and its presence in solution was always transient. The fully azido-substituted ion seems indefinitely stable in solution, while the lower members of the series decompose only slowly, in contrast with the $PCl_{6-n}(N_3)_n^-$

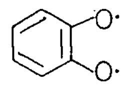
(0 ≤ n ≤ 4) species and only relatively small amounts of decomposition products, readily assigned as phosphonitrilic chlorides and azides (mainly trimer and tetramer) and Cat_2PN_3 were observed. Small amounts of $Cat_2PClN_3^-$ were also seen, presumably due to the excess chloride ion present reacting with Cat_2PN_3 formed by decomposition. A reasonable mechanism for the decomposition is shown in Scheme 3.5. This mechanism

Scheme 3.5

Mechanism for the decomposition of $CatPCl_3N_3^-$

$$2CatPCl_3N_3^- \underset{(1)}{\overset{-Cl^-}{\rightleftharpoons}} 2CatPCl_2N_3 \xrightarrow[(2)]{} Cat_2PN_3 + PCl_4N_3 \xrightarrow[(3)]{} \text{phosphonitrilic polymers}$$

could account for the stability of the fully-substituted anion since the highly azido-substituted molecular species would be particularly unstable, imparting kinetic stability to the anion as observed for the $P(N_3)_6^-$ ion. Although the possibility of isomerism occurs here only four new resonances were seen, again implying that either one isomer of each species is preferentially formed or the shift differences are too small to be resolved. Unfortunately the application of pairwise interactions to this system is not possible due to the many unknown terms such as internal O:O terms from the catechyl group which are difficult to estimate. Thus it is impossible to predict which isomers are preferentially formed in this system.

Compared with the corresponding $PCl_5 - LiN_3$ and $PCl_6^- - LiN_3$ systems the catechyl systems $Cat_2PCl - LiN_3$ and $Cat_2PCl_2^- - LiN_3$ show a much greater stability, their azido-derivatives showing no detectable decomposition. Pathways of decomposition analogous to the PCl_5 system would involve the formation of intermediate species such as CatP≡N involving loss of a catechyl group. This seems to be a particularly unfavourable step judging by the stability of Cat_2PN_3, possibly because it would necessitate the formation of the  radical (the analogous step in the $PCl_5 - LiN_3$ decomposition involves loss of chlorine).

Monocatechyl systems do show some decomposition, although here one molecular species based on $CatPCl_3$ has been tentatively identified, mainly to *bis* catechyl systems and products derived from the $PCl_5 - N_3^-$ system. The observed stability of the lower members of the $CatPCl_{4-n}(N_3)_n^-$ series may well be due, in part, to the excess chloride ion present suppressing the initial dissociation into molecular species.

viii Reactions of other organo-phosphorus(V) species with LiN_3

a. Azido-derivatives of monomethyl- and monophenyl-trichlorophosphonium salts

The compounds $CH_3PCl_3^+SbCl_6^-$ and $(C_6H_5)PCl_3^+BCl_4^-$ when treated with LiN_3 in CH_3NO_2 solution showed downfield resonances which could readily be assigned to cationic species as shown in Table 3.11. The values for the fully-substituted cations are in good agreement with those obtained by Schmidt et al.[26,27].

Table 3.11 The chemical shifts of $CH_3PCl_{3-n}(N_3)_n^+$ and $(C_6H_5)PCl_{3-n}(N_3)_n^+$ $(0 \leqslant n \leqslant 3)$ cations in CH_3NO_2

n	0	1	2	3
δ $CH_3PCl_{3-n}(N_3)_n^+$	-120.9	-90.4	-67.8	-51.6
δ $C_6H_5PCl_{3-n}(N_3)_n^+$	-101.6	-72.6	-51.6	-37.1

The decomposition products of these systems gave rise to complex spectra with much P - N - P coupling apparent in the unresolved fine structure of the peaks. The chemical shifts of the decomposition products at -30.7, -29.1, -21.5, -13.4 and 8.5 ppm from the phenyl system are in the right region for phenyl-substituted phosphonitrilic trimer derivatives[78]. It is reasonable to assume that these, and their azido-substituted derivatives, are the main decomposition products in this case, although the presence of many possible isomeric forms precludes unambiguous identification.

b. Azido-derivatives of the PCl_4dipyridyl$SbCl_6$ complex

A sample of $PCl_4dipy^+SbCl_6^-$ in nitromethane gave no reaction when LiN_3 was added and the only resonance in the ^{31}P n.m.r. spectrum was at 192.6 ppm due to PCl_4dipy^+. When 2,2'-dipyridyl was added to a solution containing $PCl_{4-n}(N_3)_n^+$ (section iii), however, new resonances appeared in the six-coordinate region of the spectrum. A solution containing predominantly less substituted species gave rise to a spectrum containing a signal due to PCl_4dipy^+, together with lower field resonances. This is shown schematically in Figure 3.4. When the more highly-substituted cations were similarly treated, new resonances at slightly lower field were seen. Assignments of formulae are made on the basis of the ratio of intensities of the known cations compared with the intensities of the resulting signals in the six-coordinate region. The chemical shifts are shown in Table 3.12.

Table 3.12 The chemical shifts of the $PCl_{4-n}(N_3)_ndipy^+$ ions in CH_3NO_2 $(0 \leqslant n \leqslant 4)$

n	0	1	2	3	4
δ	192.6	166.9	156.9	142.7	150.9

These complexes showed no sign of decomposition over a period of a few hours. This is perhaps not surprising as dissociation to a five-coordinate species, involving loss of chloride ion from the positively charged complex and formation of a doubly charged species, would be improbable. The other reasonable route to decomposition would be dissociation into the four-coordinate cations by loss of dipyridyl

$$PCl_{4-n}(N_3)_n{}^{+}dipy \rightleftharpoons PCl_{4-n}(N_3)_n{}^{+} + dipy,$$

followed by decomposition of the cationic species. As can be seen from the initial reaction this equilibrium lies well to the left.

The reaction of dipyridyl with the solution containing the more highly azido-substituted cations resulted in a ^{31}P n.m.r. spectrum containing no resonance at -11.4 ppm. This implies that little decomposition to $(NP(N_3)_2)_3$ has occurred at this stage.

ix Experimental

All solutions containing azide were destroyed by treating with an aqueous solution of sodium nitrite and dilute acetic acid.

Isolation of azido-containing compounds was in general not attempted due to the potential explosive nature of the compounds. Reactions were usually studied by placing a small quantity of the phosphorus compound (solid or liquid) directly into the n.m.r. sample tube. The minimum of solvent was then added to facilitate the rapid accumulation of the spectrum which was required for observation of some of the more transient species. Lithium azide was then added in the desired quantity depending on the requirements of the experiment. If violent reaction occurred on this addition the reaction was allowed to subside before sealing the tube and obtaining the spectrum. All the manipulations were carried out inside the dry box.

For the reaction of $(NPCl_2)_3$ and NaN_3 in the ratio 1:2 in CH_3CN, $(NPCl_2)_3$ (0.285 g 8.2×10^{-4} moles) was placed in an n.m.r. tube and dissolved in CH_3CN. NaN_3 (0.107 g 16.4×10^{-4} moles) was added and the solution vigorously agitated. After 6 days the ^{31}P n.m.r. spectrum showed two peaks in approximately a 2:1 ratio at -20.3 and -11.7 ppm.

The mixture of bromophosphazenes was prepared by the method of Bode[79]. PBr_3 was dissolved in tetrachloroethylene, equimolar amounts of Br_2 and NH_4Br were added and the mixture was refluxed for 20 hours. Bromine was added to the reaction mixture from time to time as it tends to distil out of the system. The solvent was distilled off to leave the phosphazene mixture which was used as such.

Catechylphosphoranes were prepared by methods described previously[74], the samples of $C_6H_5PCl_3BCl_4$ and $PCl_4dipySbCl_6$ were donated by J. Lincoln, and $CH_3PCl_3SbCl_6$ was donated by R.M.K. Deng.

Chapter 4

Preparations of Simple Phosphorus(V) Species Containing the Cyanide Group

i Introduction

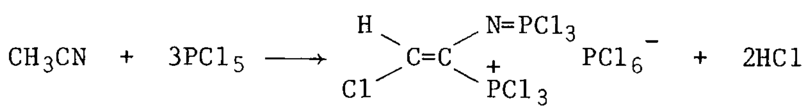
There are several possible methods of introducing cyano-groups into phosphorus(V) compounds. The simplest of these is direct substitution by a metal cyanide into a suitable phosphorus(V) compound.

$$PCl_4^+X^- \ + \ MCN \longrightarrow PCl_{4-n}(CN)_n^+X^- \ + \ MCl \qquad \ldots (1)$$

$$PCl_5 \ + \ MCN \longrightarrow PCl_{5-n}(CN)_n \ + \ MCl \qquad \ldots (2)$$

$$R_4N^+PCl_6^- \ + \ MCN \longrightarrow R_4N^+PCl_{6-n}(CN)_n^- + \ MCl \qquad \ldots (3)$$

In CH_3CN equation (2) has been shown to lead to anionic chlorocyanides[28,29] presumably due to the reaction of PCl_5 with the solvent to give hexachlorophosphate[80].



... (4)

The oxidation of phosphorus(III) compounds provides another potentially useful method of preparing cyanide-containing phosphorus(V) species. The cyano-group could be incorporated in the oxidising agent (equation (5)).

$$PCl_3 \ + \ YCN \longrightarrow PCl_3YCN \qquad Y = CN, Cl, Br, I \qquad \ldots (5)$$

In the presence of Lewis acids this reaction might be expected to give cations, whilst anions could be produced in the presence of Lewis bases. The cyano-group could also be incorporated in the phosphorus(III) compound (equations (6) and (7)). Again anions or cations might

$$P(CN)_3 + YCN \longrightarrow P(CN)_4Y \qquad Y = CN, Cl, Br, I \qquad \ldots (6)$$

$$P(CN)_3 + Y_2 \longrightarrow P(CN)_3Y_2 \qquad Y = Cl, Br \qquad \ldots (7)$$

be produced in the presence of Lewis bases or acids. The oxidation of phosphines by $SbCl_5$ has been shown to lead to the formation of cationic species[81] (equation (8)). Liquid hydrogen bromide reacts

$$R_3P + 2SbCl_5 \longrightarrow R_3PCl^+SbCl_6^- + SbCl_3 \qquad \ldots (8)$$

with PCl_3 as shown in equation (9), while PBr_3 reacts with liquid

$$PCl_3 \xrightarrow{\text{liq. HBr}} PCl_2Br, PClBr_2, PBr_3 + HCl \qquad \ldots (9)$$

hydrogen chloride in a similar manner[61] (equation (10)). Thus exchange

$$PBr_3 \xrightarrow{\text{liq. HCl}} PBr_2Cl, PBrCl_2, PCl_3 + HBr \qquad \ldots (10)$$

reactions involving HCN might be expected to yield cyano-containing species (equation (11)).

$$PCl_4^+ \xrightarrow{\text{liq. HCN}} PCl_{4-n}(CN)_n^+ + HCl \qquad \ldots (11)$$

Results and Discussion

ii Oxidations of phosphorus(III) compounds to produce cationic species

a. Phosphorus tricyanide

The reaction of $P(CN)_3$ with $SbCl_5$ in a 1:2 mole ratio in CH_2Cl_2 was carried out in an attempt to prepare the $P(CN)_3Cl^+SbCl_6^-$ species[81]. The ^{31}P n.m.r. spectrum of the resulting solution showed a new resonance at 24.2 ppm in addition to unreacted $P(CN)_3$ (δ 125 ppm). This resonance is in reasonable agreement with that of $PCl(CN)_2$[10], and cannot be unambiguously assigned as $P(CN)_3Cl^+$, implying that exchange may occur rather than oxidation. When the reaction was repeated using nitrobenzene as the solvent oxidation was observed. After one day the ^{31}P n.m.r. spectrum showed unreacted starting material and a peak at -87.1 ppm readily assigned as PCl_4^+. The reaction continued slowly, and after nine days only PCl_4^+ was apparent in the spectrum.

A similar reaction was attempted using PCl_5 as the oxidising agent. With a 1:2 ratio of $P(CN)_3$ to PCl_5 in CH_2Cl_2 reaction occurred rapidly. The ^{31}P n.m.r. spectrum run immediately on mixing the reagents showed resonances at -219.7, -96.7 and 24.2 ppm readily assignable as PCl_3, $PCl_2(CN)$ and $PCl(CN)_2$ respectively[10]. In addition, signals were seen at -87.1 ppm and to higher field of PCl_6^-. These are assigned as PCl_4^+ and $PCl_{6-n}(CN)_n^-$ species respectively (see section vi). The peaks due to phosphorus(V) species rapidly reduced in intensity and after one day only PCl_3 and $PCl_2(CN)$ could be detected in solution. With a 1:1 ratio of $P(CN)_3$ to PCl_5 in CH_2Cl_2 the ^{31}P n.m.r. spectrum initially showed the presence of $PCl_4^+PCl_3(CN)_3^-$ (δ -87.1 and 340.0 ppm), possibly $PCl(CN)_2$ (δ 24.2 ppm) and a small amount of unreacted $P(CN)_3$. Again the $PCl_4^+PCl_3(CN)_3^-$ decomposed quite rapidly to give PCl_3 and $PCl_2(CN)$. The peak at 24.2 ppm was also reduced in intensity. PCl_3,

$PCl_2(CN)$ and a small concentration of PCl_4^+ (presumably with Cl^- or CN^- as counterion, as no resonances were seen in the six-coordinate region of the spectrum) were also present.

As PCl_3 is not produced initially the analogous reaction to the $SbCl_5$ oxidation (equation (12)) cannot be occurring. In the initial

$$2PCl_5 + P(CN)_3 \longrightarrow PCl(CN)_3^+PCl_6^- + PCl_3 \qquad \ldots (12)$$

stages of the reactions the only phosphorus(III) compound seems to be $PCl(CN)_2$ (apart from unreacted starting material in small amounts) whilst the phosphorus(V) is present as $PCl_4^+PCl_3(CN)_3^-$. This indicates that the reaction could have the stoichiometry indicated in equation (13).

$$2PCl_5 + 3P(CN)_3 \longrightarrow 3PCl(CN)_2 + PCl_4^+PCl_3(CN)_3^- \qquad \ldots (13)$$

With this in mind the reaction was repeated with a 3:2 ratio of $P(CN)_3$ to PCl_5. The ^{31}P n.m.r. spectrum showed resonances assignable to PCl_3, $PCl(CN)_2$, unreacted $P(CN)_3$ and $PCl_4^+PCl_3(CN)_3^-$. The phosphorus(V) compounds once again readily decompose, giving only $PCl_{3-n}(CN)_n$ $(0 \leqslant n \leqslant 3)$ species in solution. The exact stoichiometry of the reaction remains unconfirmed. With all of the ratios of reactants used no PCl_5 remained after the initial reaction. The reaction is probably a composite of (12) and (13). The $PCl(CN)_3^+PCl_6^-$ initially produced in equation (12) could rapidly rearrange to give the observed species as shown in equation (14).

$$PCl(CN)_3^+PCl_6^- \longrightarrow PCl_4^+PCl_3(CN)_3^- \qquad \ldots (14)$$

Oxidation of $P(CN)_3$ with bromine was carried out using a 1:1 mole ratio of the reactants. Upon addition of Br_2 to a CH_2Cl_2 solution of $P(CN)_3$ violent reaction occurred to give a red solution with a yellow solid in the bottom of the tube. The ^{31}P n.m.r. spectrum of the resulting solution showed mainly PBr_3 (δ -230.6 ppm) with peaks at 51.6, 80.7 and 100.0 ppm of much lower intensity. After one day only PBr_3 could be seen in the spectrum. The reaction was repeated on a larger scale at 194K, in the hope that these conditions might favour the oxidation as opposed to the exchange reaction. After the addition of Br_2 was complete the reaction mixture was slowly evaporated at 194K under vacuum to leave a pale orange solid. The solid state n.m.r. showed mainly PBr_3 with other resonances at -72.6, 79.1 and 101.6 ppm. This solid was dissolved in CH_2Cl_2, the solution n.m.r. showed PBr_3 (δ -230.6 ppm), $PBr_2(CN)$ (δ -64.5 ppm), $PBr(CN)_2$ (δ 54.9 ppm), a small amount of either PBr_4^+ or $POBr_3$ (δ 101.6 ppm), unreacted $P(CN)_3$ (δ 120.9 ppm) and an unassigned resonance at 80.7 ppm. Thus it would seem that if the reaction does follow the desired course (equation (15)) the product decomposes rapidly back to phosphorus(III) species. The reaction of $P(CN)_3$ with BrCN was studied

$$P(CN)_3 + Br_2 \longrightarrow P(CN)_3Br^+Br^- \qquad \ldots (15)$$

by mixing the solids in an n.m.r. sample tube. No reaction occurred so the tube was gently warmed to melt the BrCN. This caused a vigorous reaction and the ^{31}P n.m.r. spectrum showed PBr_3 with small amounts of $PBr_2(CN)$ and $PBr(CN)_2$ and some unreacted $P(CN)_3$, together with two unassigned resonances at 30.3 and 42.0 ppm. These could be due to $PBr_{4-n}(CN)_n^+$ ions. They rapidly diminished in intensity, however, leaving only the known $PBr_{3-n}(CN)_n$ species with an additional resonance at 99.1 ppm, assignable as PBr_4^+ or $POBr_3$ (formed by hydrolysis or oxidation).

In an attempt to prepare $P(CN)_4^+I^-$ (or $P(CN)_3I^+CN^-$) $P(CN)_3$ and ICN were reacted in a 1:1 mole ratio in CH_2Cl_2. Although the solution turned pink, possibly due to the liberation of free iodine, no reaction could be detected, the ^{31}P n.m.r. spectrum showing only $P(CN)_3$. The iodine could presumably be liberated by the reaction shown in equation (16) which may be catalysed to some extent by $P(CN)_3$.

$$2ICN \rightleftharpoons I_2 + (CN)_2 \quad \ldots (16)$$

Thus it can be seen that while $P(CN)_3$ reacts readily with most of the oxidising agents, the products are consistent with ligand exchange. Only the BrCN reaction led to any evidence of phosphorus(V) species being produced. It was decided that oxidations of phosphorus tricyanide were of no synthetic value in preparing cyano-derivatives of PCl_4^+ and PBr_4^+.

b. Phosphorus trichloride

The oxidation of PCl_3 by cyanogen chloride was undertaken in the presence of BCl_3 and $SbCl_5$ as Lewis acids in an attempt to prepare $PCl_3(CN)^+BCl_4^-$ and $PCl_3(CN)^+SbCl_6^-$. Equimolar amounts of PCl_3, ClCN and BCl_3 were condensed into the reaction vessel and the mixture was allowed to warm to room temperature. A sample was removed and its ^{31}P n.m.r. spectrum indicated little reaction, showing in addition to PCl_3 (δ -219.7 ppm) small resonances at -42.0 and -9.0 ppm. These are tentatively assigned as $PCl_3(CN)^+$ and $PCl_2(CN)_2^+$. With $SbCl_5$ as the Lewis acid little initial reaction occurred, but gradually a fine white precipitate formed. The solid state n.m.r. showed a broad peak at -87 ppm due to PCl_4^+, and the infrared spectrum showed an intense absorption at 350 cm^{-1}, indicating the presence of the $SbCl_6^-$ ion. This is, perhaps, not surprising, the $SbCl_5$ oxidising the PCl_3 [81] with ClCN taking no part in the reaction.

The mixing of PCl_3 with BrCN in CH_2Cl_2 gave little initial reaction, the ^{31}P n.m.r. spectrum showing small resonances at -40.4, -4.9 and 27.4 ppm . After two days the presence of $PBrCl_2$ was apparent, together with low intensity signals assigned as PCl_3Br^+ (δ -46.7 ppm), $PCl_3(CN)^+$ (δ -40.4 ppm), $PCl_2Br_2^+$ (δ -4.9 ppm) and $PClBr_3^+$ (δ 27.4 ppm), as shown in Figure 4.1. A vigorous reaction took place on the addition of a few drops of PCl_3 onto solid BrCN. The ^{31}P n.m.r. spectrum showed a resonance at -230.2 ppm (PBr_3), together with strong signals at 25.8, 30.7, 59.6 and 98.4 ppm. The signal due to PBr_3 became less intense indicating further reaction, but no new peaks were observed corresponding to this decrease in intensity. The resonance at 98.4 ppm can be assigned as either PBr_4^+ or $POBr_3$. Of the lower field resonances those at 59.6 and 25.8 ppm may be assigned as $PBr(CN)_2$ and $PCl(CN)_2$ respectively[10] while the peak at 30.7 ppm can be ascribed to $PClBr_3^+$.

Addition of PCl_3 to a solution of ICN in CH_2Cl_2 caused the formation of a pink solution. The ^{31}P n.m.r. spectrum showed that very little reaction had occurred, but small resonances were apparent at -42.0 and -4.9 ppm . The first may reasonably be assigned as $PCl_3(CN)^+$ and the second as either $PCl_2(CN)_2^+$, PCl_3I^+ [82] or possibly $POCl_3$. PCl_3 was also added to solid ICN and gently warmed to melt the solid which turned a violet colour in the process. The ^{31}P n.m.r. spectrum again indicated very little reaction, small resonances being observed at 0.0, 114.6, 125.8 and 146.7 ppm . After one hour the high field resonances were no longer present, being replaced by a broad signal at 133.8 ppm. The peak at 0 ppm is tentatively assigned as PCl_3I^+ whilst those at 114.6 and 125.8 are probably due to $PI(CN)_2$ and $P(CN)_3$ respectively[10]. The resonance at 146.7 ppm could be due to a cationic species of the type $PCl_xI_y(CN)_z^+$ (x+y+z = 4), the magnitude of the shift suggesting that two iodine atoms are present, and giving possible formulae of $PI_2(CN)_2^+$ or $PI_2Cl(CN)^+$. After four days the high field resonances were undetectable, while the signal due to PCl_3 was still by far the most intense, but other fairly strong resonances were seen due to $PCl_3(CN)^+$ (δ -40.4 ppm), PCl_3I^+ or $PCl_2(CN)_2^+$ (δ -3.3 ppm) and an unassigned peak at -21.1 ppm.

Only the oxidation with BrCN gave any significant reaction. In general little reaction seems to occur with cyanogen halides, and certainly its extent is too small to be of synthetic value.

c. Phosphorus tribromide

When PBr_3 was added to a solution of BrCN in CH_2Cl_2 new resonances upfield from PBr_3 were seen at 43.6 and 100.0 ppm. The latter may be assigned as PBr_4^+ whilst the lower field peak is presumably a cyano-containing cation. After one day only PBr_3 and PBr_4^+ were apparent in the ^{31}P n.m.r. spectrum. In the absence of a solvent violent reaction occurred when the BrCN - PBr_3 mixture was melted. The ^{31}P n.m.r. spectrum showed a new resonance at 101.6 ppm (PBr_4^+) in addition to PBr_3. After one day further small peaks could be seen at -79.1, 22.7 and 43.6 ppm. The addition of more BrCN caused further vigorous reaction, and the ^{31}P n.m.r. spectrum showed that the new resonances had increased in intensity relative to PBr_3 (except that at -79.1 ppm which was no longer present). The assignment of these new resonances is by no means certain; the -79.1 ppm peak could be due to $PBr_2(CN)$ but the shift is rather low for this compound[10], while the signals at 22.7 and 43.6 ppm could be due to cations of the $PBr_{4-n}(CN)_n^+$ series. As will be seen in section iii 22.7 ppm is a rather low shift for any of these species, and no definite assignment can be made.

The reaction of ICN with PBr_3 in CH_2Cl_2 led to the formation of a violet solution presumably due to the presence of free iodine. No sign of oxidation of PBr_3 could be detected in the ^{31}P n.m.r. spectrum. Without a solvent reaction slowly occurred with apparent liberation of iodine. In addition to excess PBr_3, the n.m.r. spectrum showed two equal intensity resonances at -59.4 and 104.1 ppm, assigned as $PBr_2(CN)$ and PBr_4^+ respectively, suggesting that the reaction follows the course indicated in equations (17) and (18).

$$2PBr_3 + 2ICN \rightarrow 2PBr_2(CN) + I_2 + BrCN \qquad \ldots (17)$$

$$PBr_3 + BrCN \rightarrow PBr_4^+CN^- \qquad \ldots (18)$$

Although the oxidation of phosphines led to no synthetically useful reactions some tentative identifications of cyano-containing species based on PCl_4^+ were possible. The most reasonable assignment is that of $PCl_3(CN)^+$ between -45 and -40 ppm which has been observed in a number of reactions.

iii Attempts to produce $PY_{4-n}(CN)_n^+$ (Y = Cl, Br; $0 < n < 4$) by direct substitution

PCl_4SbCl_6 reacted slowly with AgCN in nitrobenzene. After three weeks a broad solid state resonance at 343 ppm was the only feature in the n.m.r. spectrum. This is assigned as $PCl_3(CN)_3^-$ and is presumably present as its silver salt. The solution was filtered and the solid washed with CH_2Cl_2 to remove the remaining nitrobenzene. The n.m.r. of the resulting solid showed a broad resonance at 26 ppm. Although this shift is in good agreement with that of $PCl(CN)_2$, assignment as the phosphine can be ruled out as it would be soluble in CH_2Cl_2, whereas the solid is not. A possible assignment is to $PCl(CN)_3^+$, the presence of which can be rationalised as shown in equation (19).

$$\underset{\delta\ -87}{PCl_4SbCl_6} + 3AgCN \xrightarrow{C_6H_5NO_2} AgCl + AgSbCl_6 + \underset{\delta\ 343}{Ag^+PCl_3(CN)_3^-} \quad \ldots (19)$$

$$Ag^+PCl_3(CN)_3^- \xrightarrow{CH_2Cl_2} 3AgCl + \underset{\delta\ 26}{PCl(CN)_3^+SbCl_6^-}$$

The reaction of PCl_4BCl_4 with AgCN in $C_6H_5NO_2$ led only to the formation of PCl_3, as did the reaction between PCl_4SbCl_6 and LiCN in the same solvent.

The addition of AgCN to PCl_4SbCl_6 in CH_3CN yielded $PCl_3(CN)_3^-$ as the only phosphorus-containing reaction product. As the ratio AgCN:PCl_4SbCl_6 was increased the intensity of the resonance assigned to $PCl_3(CN)_3^-$ increased. At the 3:1 ratio all the tetrachlorophosphonium ion reacted to give $PCl_3(CN)_3^-$.

The above reactions indicated that, in general, simple cationic species could not be produced in normal organic solvents. Because of this it was decided to attempt direct substitution reactions in liquid halogen solvents. PCl_5 is known to dissolve in bromine to give the PCl_4^+ cation, so use of solvents such as Br_2 and Cl_2 could suppress the formation of molecular species which could provide a route to the decomposition to phosphorus(III) compounds observed in some of the above reactions. Certainly in such strongly oxidising media any phosphorus(III) compound would be instantly oxidised back to phosphorus(V). One obvious disadvantage of this method was the possibility of side reactions involving the metal cyanide and the halogen. Although this was apparent it was not always rapid and the reaction with the phosphorus compound often seemed to occur at a faster rate.

PCl_4SbCl_6 and $Zn(CN)_2$ were placed in a silica tube and Cl_2 was condensed into the reactants under vacuum. The tube was sealed and allowed to warm to room temperature. No visible reaction was apparent and the spectrum initially showed only a solid state resonance at -85 ppm from PCl_4^+ with a less intense peak at -1.6 ppm due to a small amount of $POCl_3$, presumably caused by hydrolysis. Gradually a new solid state signal appeared at -44 ppm readily assigned as $PCl_3(CN)^+$, and after 3 weeks the spectrum showed another solid state peak at -11 ppm assigned as $PCl_2(CN)_2^+$ (Figure 4.2). When PCl_5 was dissolved in chlorine with $Zn(CN)_2$ in the same way a solid state resonance was initially seen due to PCl_4^+. Gradually a new solid state peak corresponding to $PCl_3(CN)^+$ (δ -44 ppm) appeared and became quite intense although no further substitution occurred.

PCl_5 dissolved in Br_2 to give PCl_4^+ (δ -83.2 ppm). Addition of $Zn(CN)_2$ to this solution caused upfield resonances to appear in the ^{31}P n.m.r. spectrum at -47.2 (PCl_3Br^+), -44.2 ($PCl_3(CN)^+$), -8.5 ($PCl_2Br_2^+$), 32.9 ($PClBr_3^+$) and 76.5 ppm (PBr_4^+). In addition, small resonances were seen at -29.8 and -15.8 ppm. The main reaction appears to be attack of the solvent on $Zn(CN)_2$ to yield $ZnBr_2$, which reacts rapidly with PCl_4^+ giving the observed $PCl_{4-n}Br_n^+$ series. This hypothesis was verified by the reaction of PCl_5 with $ZnBr_2$ in Br_2 which proceeded as shown in equation (20). $Zn(CN)_2$ was added in small portions to a solution of PCl_5 in Br_2 and the ^{31}P n.m.r. spectrum was recorded after each addition. The predominant reaction was the formation

$$PCl_4^+ + ZnBr_2 \xrightarrow{Br_2} PCl_{4-n}Br_n^+ + ZnCl_2 \qquad \ldots (20)$$

of the $PCl_{4-n}Br_n^+$ cations, but several lower intensity resonances were seen presumably corresponding to $PCl_xBr_y(CN)_z^+$ species (x+y+z = 4). Two typical spectra are shown in Figure 4.3.

Assignment of all the new resonances observed from this system was aided by observation of $PBr_{4-n}(CN)_n^+$ cations from the reaction between PBr_5 and $Zn(CN)_2$ in bromine. Four new resonances downfield of that due to PBr_4^+ were seen. On the basis of relative intensities, and the reaction between $P(CN)_3$ and $(CN)_2$ to give the shift of $P(CN)_4^+$ (see section v) assignments could be made. These are shown in Table 4.1 and a typical spectrum is illustrated in Figure 4.4.

Table 4.1 Chemical shifts of $PBr_{4-n}(CN)_n^+$ ions in Br_2

n	0	1	2	3	4
δ	76.5	49.3	40.3	33.3	41.9

By using the pairwise interaction method on this and the $PCl_{4-n}Br_n^+$ series, values for the Cl:Cl, Cl:Br, Br:Br, Br:CN and CN:CN parameters can be obtained from the least squares method. This gave best fit values of Cl:Cl = -13.87, Cl:Br = -1.84, Br:Br = 12.70, Br:CN = 4.54 and CN:CN = 6.96 ppm. Only the Cl:CN term is required to enable the calculation of the shifts of all the possible $PCl_xBr_y(CN)_z^+$ cations. The results from the $PCl_5 - Zn(CN)_2 - Br_2$ reaction together with assignments and calculated values are shown in Table 4.2. The Cl:CN parameter was calculated from the observed shift of $PCl_3(CN)^+$. In general the agreement between calculated and observed shift is very good, although the presence of unassignable

Table 4.2 Chemical Shifts and Assignments for the PCl_5-$Zn(CN)_2$-Br_2 system

Observed shift	Assignment	Calculated shift	δ calc-obs
-83.2	PCl_4^+	-83.2	0.0
-47.2	PCl_3Br^+	-47.1	0.1
-44.2	$PCl_3(CN)^+$	-	-
-29.2	-	-	-
-15.4	$PBrCl_2(CN)^+$	-14.7	0.7
- 8.5	$PCl_2Br_2^+$	- 8.5	0.0
- 1.1	-	-	-
1.0	-	-	-
17.4	$PBr_2Cl(CN)^+$	17.2	-0.2
19.6	$PCl(CN)_3^+$	18.3	1.3
32.9	$PClBr_3^+$	32.6	-0.3
45.7	$P(CN)_4^+$	41.8	-3.9
52.7	$PBr_3(CN)^+$	51.7	-1.0

resonances at -29.2, -1.1 and 1.0 ppm is puzzling. $PCl_2(CN)_2^+$ was not observed in this system; its calculated shift of -10.4 ppm, in good agreement with the observed value of -11.4 ppm in liquid chlorine, may well mean that the signal is submerged beneath the intense $PCl_2Br_2^+$ resonance. No peak was observed which could be assigned as $PClBr(CN)_2^+$; the calculated value is 12.5 ppm so a resonance from this cation would be observable as there are no intense signals due to $PCl_{4-n}Br_n^+$ species in this region. Presumably $PClBr(CN)_2^+$ is not formed in any detectable concentration.

The reaction between PCl_5 and cyanogen might be expected to follow a similar course producing only $PCl_{4-n}(CN)_n^+$ cations. On dissolving PCl_5 in liquid cyanogen in a sealed tube, reaction occurred giving rise to a complex ^{31}P n.m.r. spectrum. Initially resonances were seen at -46.7, -8.2, 309.5 and 330.2 ppm assigned as $PCl_3(CN)^+$, $PCl_2(CN)_2^+$, $PCl_5(CN)^-$ and $PCl_4(CN)_2^-$ respectively. There were unassigned resonances at -22.7, -14.5, 93.5, 103.3, 212.8 and 220.8 ppm , all of lower intensity, with a stronger resonance at -38.7 ppm . After 3 days some decomposition to PCl_3 had occurred. The concentration of $PCl_3(CN)^+$ had decreased, corresponding to an increase in intensity of the peak at -38.7 ppm , as shown in Figure 4.5. Clearly the initial reaction is the desired exchange of cyanogen with solid PCl_5 in the form $PCl_4^+PCl_6^-$ to give cyano-containing derivatives of both ions, and resonances in the range 90 - 105 ppm are probably due to molecular species (section v). While the signals at 212.8 and 220.8 ppm are in the right region of the spectrum for 6-coordinate derivatives they are certainly not due to any of the $PCl_{6-n}(CN)_n^-$ species (section vi), and could arise from iso-cyanides.

iv <u>Reactions of PCl_5 and PBr_5 with liquid HCN</u>

The reaction of PCl_5 with HCN was carried out by stirring the solid with excess liquid hydrogen cyanide at 273K. After 2½ hours the solid had turned from the green-yellow colour of PCl_5 to white. The HCN was removed under vacuum and the solid state ^{31}P n.m.r. spectrum obtained. This showed three resonances upfield from PCl_4^+ (δ -92 ppm) at -46.7, -6.5 and 12.9 ppm , together with a strong signal at 293 ppm due to PCl_6^- (Figure 4.6). The ratio of PCl_6^- to the remaining signals was approximately 1:1. The resonances upfield from PCl_4^+ can reasonably be assigned as $PCl_3(CN)^+$, $PCl_2(CN)_2^+$ and $PCl(CN)_3^+$. The chemical shifts of these cations vary with the counterion and solvent. This is particularly noticable for the $PCl(CN)_3^+$ ion, the shift of which varies from 26 ppm as the $SbCl_6^-$ salt to 12.9 ppm as the PCl_6^- salt. Further reaction of PCl_5 and HCN at 273K for a day gave a solid, the n.m.r. of which gave two broad resonances centred at -27 and 316 ppm . The latter is readily assigned as $PCl_5(CN)^-$ (section vi). The lower field resonance is not readily assignable to a simple cation, but may well be a composite resonance from $PCl_3(CN)^+$ and $PCl_2(CN)_2^+$. On dissolving this solid in CH_3NO_2 a complex spectrum was obtained with strong resonances at -48.4 ($PCl_3(CN)^+$) and 312.8 ppm ($PCl_5(CN)^-$) and less intense signals at -40.4 (unassigned), -12.9 ($PCl_2(CN)_2^+$), 24.2 ($PCl(CN)_3^+$) and -4.9 ppm .

The reaction of PBr_5 with HCN was carried out in a sealed tube. The ^{31}P n.m.r. spectrum showed the formation of PBr_3 only.

v Attempts to produce $PCl_{5-n}(CN)_n$ species ($0 \leqslant n \leqslant 5$)

a. By oxidation of phosphorus(III) compounds

1. $P(CN)_3$

As has previously been noted, vapour pressure measurements on the $P(CN)_3$-$(CN)_2$ system suggested the formation of $P(CN)_5$[22]. This system was therefore studied by ^{31}P n.m.r. spectroscopy. Cyanogen was condensed into a tube containing $P(CN)_3$ and the tube was sealed under vacuum. The $P(CN)_3$ did not dissolve completely in the liquid cyanogen at room temperature but the ^{31}P n.m.r. spectrum showed three resonances at 130.6, 98.4 and 43.6 ppm . These are assigned as $P(CN)_3$, $P(CN)_5$ and $P(CN)_4^+$ respectively. If a smaller quantity of cyanogen was used, the resulting n.m.r. showed relatively more $P(CN)_4^+$, so presumably the equilibrium $P(CN)_4^+CN^- \rightleftharpoons P(CN)_5$ lies further to the right in the presence of more cyanogen. The reaction of $P(CN)_3$ with ClCN gave mainly $P(CN)_4^+Cl^-$ (δ 43.6 ppm), together with resonances at 98.4, 108.0 and 32.5 ppm in addition to $P(CN)_3$. The resonance at 98.4 ppm is in good agreement with that observed for $P(CN)_5$, while the signal at 108.0 ppm is presumably due to an isomer of $PCl(CN)_4$; the shift value of 32.5 ppm is rather high for $PCl(CN)_3^+$, although with a different counterion and solvent the shift may vary. With a large excess of ClCN the spectrum showed mainly $P(CN)_3$ and $P(CN)_5$. The reaction of $P(CN)_3$ in cyanogen chloride is summarised in equations (21) and (22).

$$P(CN)_3 + ClCN \longrightarrow P(CN)_4^+Cl^- + PCl(CN)_3^+CN^- + PCl(CN)_4 \quad \ldots (21)$$

$$P(CN)_4^+ + CN^- \longrightarrow P(CN)_5 \quad \ldots (22)$$

The tube containing $P(CN)_3$ with a small amount of cyanogen was cooled in liquid nitrogen and opened in the dry box. The remaining cyanogen was allowed to evaporate and the resulting solid was dissolved in CH_2Cl_2. The ^{31}P n.m.r. spectrum showed mainly $P(CN)_3$ with a smaller resonance at 100.0 ppm due to $P(CN)_5$, which rapidly decreased in intensity. This result indicates that in the absence of a high pressure of cyanogen dissociation back to $P(CN)_3$ and $(CN)_2$ occurs.

2. $\underline{PCl_3}$

As $P(CN)_3$ was oxidised by $(CN)_2$ and ClCN it was hoped that PCl_3 would react similarly to give $PCl_4(CN)$ and $PCl_3(CN)_2$. PCl_3 and ClCN were reacted in a 1:1 mole ratio in a sealed tube at 418K for 1 day. After this time the solution had turned black, but the ^{31}P n.m.r. spectrum showed no significant reaction. Small resonances were observed at -67.8 and 0.0 ppm but cannot be readily assigned. (The peak at -67.8 ppm may be due to the reaction of PCl_3 with the small amount of HCN impurity in the ClCN. See Appendix 2). Under less forcing conditions at 303K for 3 days no reaction was observed. Very little reaction occurred when PCl_3 was heated in a sealed tube with $(CN)_2$ at 343K for 4 hours. Two small resonances were observed at -50.0 and -3.2 ppm which can be assigned to the cationic derivatives $PCl_3(CN)^+$ and $PCl_2(CN)_2^+$.

b. By direct substitution into PCl_5

The reaction of PCl_5 with AgCN in a 1:1 mole ratio in CH_2Cl_2 slowly produced PCl_3. No substitution into molecular PCl_5 was observed and after 5 days all the phosphorus was present as PCl_3. The reaction was repeated using the more polar nitrobenzene as solvent. After one hour the spectrum showed in addition to unreacted PCl_5 (δ 82.2 ppm), resonances readily assigned to the $PCl_4^+PCl_{6-n}(CN)_n^-$ species (δ -88.7 ppm (PCl_4^+); δ 309.4, 315.0, 332.0 and 340.0 ppm for $PCl_{6-n}(CN)_n^-$. See section vi). Slow decomposition to PCl_3 was observed after a few hours.

The course of the reaction between PCl_5 and AgCN is influenced by the polarity of the solvent. Presumably in each case $PCl_{5-n}(CN)_n$ species are formed (though in such a small concentration as to remain undetectable). In polar solvents these rapidly rearrange to give the ionic $PCl_4^+PCl_{6-n}(CN)_n^-$ species, whereas in less polar media the molecular species decompose directly to PCl_3 and ClCN. The presence of ClCN was confirmed by heating the reaction mixture in nitrobenzene under vacuum at 373K for 2 hrs and collecting the gases evolved in a cold finger attached to the vacuum line cooled in liquid nitrogen. This gas was allowed to evaporate into a gas cell and the infrared spectrum clearly shows the presence of ClCN with bands at 2220, 794, 712 and 380 cm^{-1} [83].

These experiments suggest that molecular cyano-containing species based on PCl_5 are unstable. Higher members of the series seem to have some stability in solvents such as cyanogen or cyanogen chloride where dissociation back to the phosphorus(III) compound will be suppressed. The lower members of the series appear to adopt a cationic form in cyanogen (equation (23)), while in polar organic solvents these tend to rearrange to give phosphorus in both ions followed by decomposition (equation (24)). In less polar organic

$$PCl_3 + (CN)_2 \rightleftharpoons [PCl_3(CN)_2] \xrightarrow{\text{rapid}} PCl_3(CN)^+CN^- + PCl_2(CN)_2{}^+Cl^- \quad \ldots (23)$$

$$PCl_5 + AgCN \xrightarrow[C_6H_5NO_2]{} [PCl_4(CN)] \xrightarrow{\text{rapid}} PCl_4{}^+PCl_4(CN)_2{}^- \xrightarrow{\text{slow}} PCl_3 + ClCN \quad \ldots (24)$$

solvents the molecular species decompose to give PCl_3 and ClCN with no intermediate ionic species being observed.

vi Attempts to prepare $PCl_{6-n}(CN)_n^-$ ($0 \leqslant n \leqslant 6$) compounds

a. By direct substitution into the hexachlorophosphate ion

The reaction of Pe_4NPCl_6 with AgCN, $Zn(CN)_2$ and LiCN gave rise to resonances upfield of PCl_6^- (δ 298.2 ppm) in the ^{31}P n.m.r. spectrum. With $Zn(CN)_2$ some reduction to PCl_3 was observed, presumably because the $ZnCl_2$ formed in the substitution reaction acts as a Lewis acid (equation (25)) to produce some PCl_5 which then reacts

$$2PCl_6^- + ZnCl_2 \rightleftharpoons 2PCl_5 + ZnCl_4^{2-} \quad \ldots (25)$$

with more $Zn(CN)_2$ to give PCl_3, as observed in the reactions of cyanides with PCl_5. LiCN reacted only very slowly, but with AgCN reaction occurred rapidly with no reduction of the phosphorus(V) species and this salt was used for subsequent experiments.

The course of the substitution reaction was followed by adding small quantities of AgCN to a strong solution of Pe_4NPCl_6 in CH_2Cl_2 and recording the ^{31}P n.m.r. spectrum after each addition. Figure 4.7 shows the course of the reaction and Table 4.3 the assignments of formulae based on this.

Table 4.3 Shifts for $PCl_{6-n}(CN)_n^-$ ions in CH_2Cl_2

n	0	1	2	3
δ	298.2	309.5	315.0 331.2*	340.0* 351.2

* denotes most abundant isomer

The anions were stable in solution and attempts were made to isolate them. The reaction of Pe_4NPCl_6 with AgCN in a 1:1 ratio in CH_2Cl_2 did not produce the desired $PCl_5(CN)^-$ ion in isolation, the ^{31}P n.m.r. spectrum showing some unreacted PCl_6^- and $PCl_4(CN)_2^-$ present in solution. Similarly the reaction of a 1:2 mole ratio of Pe_4NPCl_6 to AgCN produced both higher- and lower-substituted species than the isomers of $PCl_4(CN)_2^-$. When the reaction was carried out using 1:4 and 1:6 ratios the ^{31}P n.m.r. spectra of the resulting solutions were identical, showing two resonances at 340.0 and 351.2 ppm, assigned as the isomers of $PCl_3(CN)_3^-$. The product of the 1:6 ratio was isolated as a waxy solid which gave sharp resonances in the ^{31}P n.m.r. spectrum in good agreement with the solution values. Elemental analyses were poor and purification was difficult due to the high solubility of the salts and the Pe_4NCl (which was considered to be the likely impurity) in organic solvents.

As the tetra-n-pentylammonium salts were difficult to purify, attempts were made to find a less soluble hexachlorophosphate which might give more readily purified products. Although Et_4NPCl_6 is insoluble in CH_2Cl_2, on reacting a slurry with AgCN the resulting chlorocyanophosphates were found to be soluble. Thus reaction of Et_4NPCl_6 with excess AgCN in CH_2Cl_2 led to the isolation of $Et_4NPCl_3(CN)_3$. After recrystallisation from CH_2Cl_2 the solid was found to contain very little of the isomer giving a signal at 351.2 ppm . The corresponding filtrate was much enriched in this isomer. Isolation of the less abundant isomer by repeated recrystallisation was not possible due to insufficient material being available.

Addition of small quantities of AgCN to a slurry of Et_4NPCl_6 in CH_2Cl_2 gave no soluble materials which implies that $Et_4NPCl_5(CN)$ is insoluble in this solvent. Addition of slightly less than an equimolar quantity of AgCN to Et_4NPCl_6 would therefore be expected to give $Et_4NPCl_4(CN)_2$ as the only soluble product. To prepare $Et_4NPCl_4(CN)_2$, Et_4NPCl_6 and AgCN were reacted in a 1.1:1 mole ratio. This led to an isomeric mixture. Recrystallisation from CH_2Cl_2 increased the amount of the 332 ppm isomer, corresponding to an increase in the amount of the 315 ppm isomer in the filtrate (Experimental section viii). Complete separation could not be achieved, however. The solid containing relatively more of the 315 ppm isomer was obtained by adding 30 - 40° petroleum ether to the CH_2Cl_2 solution and filtering off the resulting solid. Elemental analyses of both solids obtained confirmed that $PCl_4(CN)_2^-$ ions are present.

As $Et_4NPCl_5(CN)$ is insoluble in CH_2Cl_2 it could not be prepared directly from the hexachlorophosphate. The method adopted was to treat a solution of Pe_4NPCl_6 with an equimolar amount of AgCN in

CH_2Cl_2. This yielded a solution containing predominantly $Pe_4NPCl_5(CN)$ with smaller quantities of PCl_6^- and $PCl_4(CN)_2^-$. The amount of hexachlorophosphate remaining in solution was estimated from the relative intensities of the peaks in the ^{31}P n.m.r. spectrum and the required amount of Et_4NCl added to the solution to precipitate the insoluble Et_4NPCl_6. This was filtered off and then more Et_4NCl added to precipitate $Et_4NPCl_5(CN)$ (after first checking the solution n.m.r. spectrum to ensure that no PCl_6^- remained).

Solid state n.m.r. spectra were recorded for each compound and gave broad peaks, agreeing well with the solution shifts. The infrared and Raman spectra were also recorded. The expected symmetry of the $PCl_5(CN)^-$ anion is C_{4v} which should theoretically give twelve Raman and nine infrared fundamental vibrations, with all the infrared bands giving corresponding bands in the Raman spectrum. The infrared spectrum shows eight bands in the 4000 - 250 cm^{-1} region not assignable to the Et_4N^+ group, while the Raman spectrum shows ten. Although some absorptions appear at the same frequency in both spectra, many bands observed in the infrared are absent in the Raman spectrum, possibly due to low intensity. The total number of different absorptions observed (in both infrared and Raman spectra) is more than the twelve expected, which could be due to the observation of overtone and combination bands. The spectra obtained for the $Et_4NPCl_4(CN)_2$ compounds are more difficult to interpret due to the presence of both isomers. The $PCl_3(CN)_3^-$ ion can have two possible configurations which in principle should be readily distinguishable by their vibrational spectra. The *fac*-isomer is expected to show fourteen fundamentals in both the infrared and Raman spectra, whereas the *mer*-isomer should give much more complex spectra with twenty two absorptions in the infrared and twenty four in the Raman spectrum. The infrared of the solid obtained shows eleven bands with only one 'CN stretch' (where two are expected). The Raman spectrum shows fourteen bands. Hence the number of lines observed indicates that the *fac*- as opposed to *mer*-isomer is formed. In principle ^{35}Cl n.q.r. spectroscopy should be able to distinguish between *fac*- and *mer*-isomers, but unfortunately no signals could be detected at 77K. (Vibrational spectra are shown in Appendix 1)

During the preparation of $Et_4NPCl_3(CN)_3$ a further upfield resonance at 356.2 ppm was observed. This is presumably caused by further substitution, giving $PCl_2(CN)_4^-$. Repeated recrystallisation enriched the solution but because of the relatively small amount present isolation of the pure material was not possible. Elemental analyses indicate a higher degree of substitution than in $PCl_3(CN)_3^-$ and the infrared spectrum is also different from that of $PCl_3(CN)_3^-$, although interpretation is difficult due to the presence of isomers of $Et_4NPCl_3(CN)_3$, as seen in the ^{31}P n.m.r. spectrum which is shown in Figure 4.8.

If the assignment of the predominant isomer of $Et_4NPCl_3(CN)_3$ as *fac* is correct it seems reasonable to assume that the most intense resonance observed for $PCl_4(CN)_2^-$ is from the *cis*-isomer. Thus for $PCl_4(CN)_2^-$ and $PCl_3(CN)_3^-$ the assignments to specific isomers can be made as shown in Table 4.4. During some preparations of $PCl_{6-n}(CN)_n^-$

Table 4.4 Assignments of the isomers of $PCl_4(CN)_2^-$ and $PCl_3(CN)_3^-$

ion	δ
cis $PCl_4(CN)_2^-$	331.2
trans $PCl_4(CN)_2^-$	315.0
fac $PCl_3(CN)_3^-$	340.0
mer $PCl_3(CN)_3^-$	351.2

species resonances were observed in the 0-50 ppm region of the spectrum. These are tentatively assigned as hydrolysis products. The anions $PCl_4(CN)_2^-$ and $PCl_3(CN)_3^-$ are remarkably stable towards hydrolysis. $Et_4NPCl_4(CN)_2$ was exposed to the atmosphere overnight and the resulting solid dissolved in CH_2Cl_2. The ^{31}P n.m.r. spectrum indicated that the bulk of the material was unchanged, and only small resonances were observed in the hydrolysis product region. These comprised four resonances at 0.0 ($POCl_3$), 14.5 ($POCl_2(CN)$), 29.1 ($POCl(CN)_2$) and 53.3 ppm ($PO(CN)_3$) and a possible doublet δ 33.1 ppm J_{PH} 355 Hz, (or two singlets), as shown in Figure 4.9, perhaps arising from further hydrolysis. The formation of P-H bonds in the hydrolysis of phosphorus(V) compounds does not normally occur and the assignment as two singlets may be more probable.

$Et_4NPCl_3(CN)_3$ is even more stable, showing no sign of hydrolysis even after prolonged exposure to the atmosphere. Indeed the $PCl_3(CN)_3^-$ ion seems most unwilling to react with reagents which fully substitute the PCl_6^- ion. Thus no reaction occurred with LiN_3 or NH_4NCS and attempts to introduce bromine into the ion with LiBr or NH_4Br met with no success. Attempts to substitute the $PCl_3(CN)_3^-$ ion further with cyanide by refluxing $Et_4NPCl_3(CN)_3$ with AgCN for 1 day in CH_3NO_2 led to the formation of a compound which was insoluble in all common organic solvents and gave a broad solid state resonance at 0.0 ppm . Due to its insolubility, separation from the silver salts was not possible. The compound is air- and moisture-stable and could possibly be $MeP(CN)_3^+$ obtained from reaction with the solvent. This assignment is only tentative since any other supporting evidence is lacking. $Et_4NPCl_4(CN)_2$ was slightly more reactive, giving some reaction with a small amount of LiN_3. No new resonances were seen in the six-coordinate region of the spectrum, only two peaks presumably due to decomposition products at 4.9 and 27.5 ppm, tentatively assigned as $\text{-(}NPCl_2\text{)-}$ and $\text{-(}NPCl(CN)\text{)-}$ units in polymeric phosphazenes.

b. <u>By oxidation of phosphorus(III) compounds in the presence of Lewis bases</u>

As will be seen in Chapter 8 many phosphorus(III) compounds form stable anionic adducts with halide and pseudohalide ions. Oxidation of these species might be expected to lead to anionic derivatives of phosphorus(V).

The oxidation of $Et_4NPCl(CN)_3$ by chlorine was carried out by reacting $P(CN)_3$, Et_4NCl and Cl_2 in a 1:1:1 molar ratio in CH_2Cl_2. The reaction produced mainly the 351.2 ppm isomer of $PCl_3(CN)_3^-$, tentatively assigned as the *mer*-isomer, with small quantities of the *fac*-isomer (δ 340.0 ppm) and some $PCl_2(CN)_2^-$ (δ 154.2 ppm). The compound was crystallised from CH_2Cl_2 to give $Et_4NPCl_3(CN)_3$ with a *fac*:*mer* isomer ratio of 1:3 (estimated by the relative intensity of the signals). The vibrational spectra tend to confirm assignment as the *mer*-isomer. The infrared spectrum shows fifteen bands where twenty two are expected. The Raman spectrum shows fourteen bands whereas twenty four would be expected. Again there are many frequencies in the infrared which give no corresponding bands in the Raman, presumably due to low intensity. Only one 'CN stretch' is observed where three are expected in both spectra. The total number of different bands observed in the spectra is twenty two which is certainly more than expected for the *fac*-isomer.

The use of the pairwise additivity method for this system might be expected to support the assignments. The three interactions terms were calculated by least squares fit of the experimental data. This gave Cl:Cl = 24.79. Cl:CN = 27.81 and CN:CN = 35.35 ppm. The recalculated shifts are shown in Table 4.5, the calculated values

Table 4.5 Calculated and observed shifts for $PCl_{6-n}(CN)_n^-$ ($0 \leq n \leq 3$) ions

ion	calc (1)	obs (1)	calc (2)	obs (2)
PCl_6^-	297.5	298.2	296.4	298.2
$PCl_5(CN)^-$	306.6	309.5	310.0	309.5
cis-$PCl_4(CN)_2^-$	326.2	331.2	326.4	315.0
trans-$PCl_4(CN)_2^-$	321.6	315.0	323.7	331.2
fac-$PCl_3(CN)_3^-$	347.3	340.0	345.5	351.2
mer-$PCl_3(CN)_3^-$	342.8	351.2	342.7	340.0

giving poor agreement with the observed values (calc (1) and obs (1)). This could indicate that the configurations of the isomers have been incorrectly assigned so the assignments of *cis*- and *trans*-$PCl_4(CN)_2^-$ and *fac*- and *mer*-$PCl_3(CN)_3^-$ were reversed and the pairwise interaction parameters recalculated giving values of Cl:Cl = 24.70, Cl:CN = 28.11 and CN:CN = 34.23 ppm. As can be seen the agreement between the calculated and observed values (calc (2) and obs (2)) is no better than before. Clearly this system does not obey the pairwise additivity rule. This could possibly be explained by large distortions from octahedral symmetry about the phosphorus atom. The pairwise additivity method assumes that the Cl:Cl interaction in PCl_6^- can be treated as being essentially the same as in $PCl_3(CN)_3^-$ say, that is successive replacements of chloride by cyanide have no effect on the Cl:Cl parameter. For chlorine - azide substitution this assumption is justified (witness the good agreement between calculated and observed values in the $PCl_{6-n}(N_3)_n^-$ series), but for cyanide substitution complicating factors may well occur. The cyanide group is a strongly π-bonding ligand and may well cause some P-Cl π-bonding. Indeed the fact that complete substitution of the PCl_6^- ion cannot be achieved, and the hydrolytic stability of $PCl_3(CN)_3^-$, suggest a considerable strengthening in the P-Cl bonds. This will be discussed further in Chapter 9.

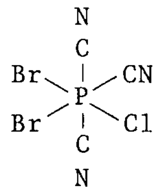
In view of the successful oxidation of $Et_4NPCl(CN)_3$ by chlorine, the corresponding reaction with bromine was carried out. When bromine was added to a solution of $Et_4NPCl(CN)_3$ in CH_2Cl_2 a violent exothermic reaction occurred. The ^{31}P n.m.r. spectrum showed mainly PBr_3 with a small quantity of PCl_3 to have formed, but four resonances were also seen in the six-coordinate region of the spectrum at 340.0 (*fac*-$PCl_3(CN)_3^-$), 399.0, 417.2 and 440.0 ppm . The resonances to higher field of that of $PCl_3(CN)_3^-$ are presumably due to bromine-containing anions. These signals rapidly decreased in intensity with a corresponding increase in the concentration of PBr_3. The rapid production of phosphorus(III) compounds indicates that exchange of the $PCl(CN)_3^-$ ion occurs with the bromine. This is not surprising as the $P(CN)_3 - Cl^-$ equilibrium is mobile and presumably the Br_2 reacts with the small amount of $P(CN)_3$ present to give PBr_3. The anions formed rapidly decompose indicating that the bromine-containing anions are unstable. In an attempt to suppress the initial dissociation, and any dissociation of the anions produced, the oxidation was carried out in the presence of excess Et_4NCl. Exothermic reaction again occurred on the addition of Br_2 to the solution. The ^{31}P n.m.r. spectrum of the solution showed no phosphorus(III) species, but a major resonance at 440.0 ppm , together with smaller signals readily assigned as the isomers of $PCl_4(CN)_2^-$ and $PCl_3(CN)_3^-$. After one day decomposition of the bromine-containing anion occurred, giving mainly *trans*-$PCl_4(CN)_2^-$ with smaller quantities of $PCl_2(CN)_2^-$ (δ 153.1 ppm, see Chapter 8) and PCl_3. After two days no resonance at 440.0 ppm was observable, decomposition to $PCl_2(CN)_2^-$ and *trans*-$PCl_4(CN)_2^-$ being complete. Other small signals were seen at 398.0 and 9.8 ppm during the decomposition. Isolation of the compound giving a resonance at 440.0 ppm was attempted by adding bromine dropwise to a solution of $Et_4NPCl(CN)_3$ containing excess Et_4NCl in CH_2Cl_2, until a slight colouration of the solution was produced, indicating that excess bromine was present. The solvent was removed under vacuum to give a red solid. The solid state n.m.r. spectrum showed sharp resonances due to $PCl_3(CN)_3^-$ (mostly the *mer*-isomer) with small amounts of $PCl_4(CN)_2^-$ (mainly the *trans*-isomer). These observations can be rationalised by equations (26) and (27) for the solution reactions,

$$PCl(CN)_3^- + Br_2 \longrightarrow PClBr_2(CN)_3^- \xrightarrow{Cl^-} PCl_2Br(CN)_3^- \xrightarrow{-BrCN} PCl_2(CN)_2^- \quad \ldots (26)$$

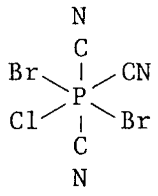
$$PClBr_2(CN)_3^- \xrightarrow{Br_2 \text{ or } BrCN} [P(CN)_2ClBr_3]^- \xrightarrow{Cl^-} PCl_4(CN)_2^- \quad \ldots (27)$$

$$PClBr_2(CN)_3^- \xrightarrow{Cl^-} PCl_3(CN)_3^- \quad \ldots (28)$$

while the attempted isolation of the bromine-containing anion (presumed to be $PClBr_2(CN)_3^-$) was carried out before the reactions to give $PCl_4(CN)_2^-$ had proceeded to any great extent. (The Br_2 required in equation (27) would not be present in large concentration.) The substitution reaction to give $PCl_3(CN)_3^-$ (equation (28)) may be more significant in the absence of competing reactions or may occur in the solid state. The production of *mer*-$PCl_3(CN)_3^-$ and *trans*-$PCl_4(CN)_2^-$ ions suggests a meridial arrangement of cyanide groups in $PClBr_2(CN)_3^-$ (as observed for the chlorine oxidation of $PCl(CN)_3^-$). Here two isomers are possible (I and II), although it is not possible to decide which



(I)



(II)

is produced.

A similar reaction was carried out using Pr_4NBr to suppress the dissociation of the $PCl(CN)_3^-$ ion. After the addition of bromine, the ^{31}P n.m.r. spectrum contained high field resonances at 398.0, 417.5 and 440.0 ppm, with the strongest signal at -225.7 ppm due to PBr_3.

The oxidation of $Pr_4NPBr(CN)_3$ with chlorine in the presence of Pr_4NBr led to the formation of approximately equal amounts of *fac*- and *mer*-$PCl_3(CN)_3^-$, with a stronger resonance at 440.0 ppm assigned as $PClBr_2(CN)_3^-$. Over a period of two days the signals for $PCl_3(CN)_3^-$ had increased in intensity and a small resonance became apparent at 399.7 ppm. No decomposition to phosphorus(III) compounds was observed. In this case decomposition occurred only very slowly, resonances at 440.0, and 398.0 ppm being still readily observable after one year, although very much reduced in intensity.

The resonance at 398.0 - 399.7 ppm is observed in many cases and is almost certainly due to one isomer of the $PCl_2Br(CN)_3^-$ anion, which would be expected to result from the substitution of $PClBr_2(CN)_3^-$ by chloride. The signal at 417.5 ppm is probably from another isomer of $PCl_2Br(CN)_3^-$ (or possibly of $PClBr_2(CN)_3^-$), but unambiguous assignment is not possible.

Attempts were made to prepare the $PCl_2Br_2(CN)_2^-$ anion by bromine oxidation of $PCl_2(CN)_2^-$ and chlorine oxidation of $PBr_2(CN)_2^-$. These salts were prepared in solution by addition of Et_4NCN to the appropriate trihalide dissolved in CH_2Cl_2. Reaction with halogen produced only $PCl_4(CN)_2^-$ and no evidence of bromine-containing anions could be obtained.

Cyanogen chloride did not oxidise $Et_4NPCl(CN)_3$, exchange only occurring to give $PCl_2(CN)_2^-$. Similarly attempts to introduce iodine by oxidation with ICl produced only $PCl_2(CN)_2^-$ with small amounts of $PCl_4(CN)_2^-$. An attempt to find an easier synthesis of $Et_4NPCl_5(CN)$ by oxidation of Et_4NPCl_4 with cyanogen chloride led only to the formation of PCl_3.

vii Attempts to identify phosphoryl and thiophosphoryl cyano-containing compounds

From the partial hydrolysis of $Et_4NPCl_4(CN)_2$ the series $POCl_{3-n}(CN)_n$ $(0 \leqslant n \leqslant 3)$ had been identified, indicating that these compounds exist even though there are no reports of their preparation.

AgCN did not react with $POCl_3$ in CH_2Cl_2. When $POCl_3$ was refluxed for one day with $Zn(CN)_2$ in CH_3CN a small resonance at 24.1 ppm was seen in addition to the main peak due to unreacted $POCl_3$. This new signal is close to that assigned to $POCl(CN)_2$. The reaction could be driven no further by prolonged refluxing. When $POCl_3$ was heated with AgCN at 413K for one day in CH_3CN in a sealed tube the resulting n.m.r. spectrum showed two small upfield resonances from $POCl_3$ at 8.9 and 25.1 ppm, readily assigned as $POCl_2(CN)$ and $POCl(CN)_2$ respectively. Once again the reaction could be driven no further.

The reaction of $POCl_3$ with Et_4NCN in CH_2Cl_2 was violently exothermic, giving a dark red solution. Cyano-substituted derivatives of $POCl_3$ and a higher field resonance at 333.3 ppm were seen in the ^{31}P n.m.r. spectrum. Further addition of Et_4NCN caused an increase in intensity of the resonance assigned to $POCl_2(CN)$, while $PCl_2(CN)_2^-$ and $PCl(CN)_3^-$ were also produced, together with another resonance to higher field at 327.1 ppm. With a greater than 1:4 ratio of $POCl_3$:Et_4NCN the spectrum showed mainly $POCl_2(CN)$ (δ 9.8 ppm), $POCl(CN)_2$ (δ 30.7 ppm), $PO(CN)_3$ (δ 50.0 ppm) and $PCl(CN)_3^-$ (δ 196.7 ppm), with unassigned resonances at 34.0, 36.4 and 38.0 ppm and a complex series of peaks between 320 and 340 ppm, not assignable as $PCl_{6-n}(CN)_n^-$ species (Figure 4.10). Although the main reaction here is substitution into $POCl_3$, other more complicated reactions seem to be occurring. The high field resonances could be due to species of the type $POCl_n(CN)_{4-n}^-$ ($0 \leqslant n \leqslant 3$), which would imply that the phosphoryl chloro-cyanides may have some acceptor properties. The compound $PO(CN)_3$.py has been proposed as the product from the reaction between $P(CN)_3$ and pyridine-N-oxide[84].

$POBr_3$ did not react with AgCN in CH_2Cl_2. The addition of a small quantity of $Eu(fod)_3$ catalyst caused the appearance of low intensity resonances downfield from that of $POBr_3$ at 83.1, 64.5, 38.7 and 34.4 ppm. The observation of more than three new resonances, and the fact that none of the observed shifts corresponds with that of $PO(CN)_3$, imply that a more complicated reaction is occurring. Thus assignment of resonances in the $POBr_{3-n}(CN)_n$ series is not possible. The reaction of $POBr_3$ with AgCN in CH_3CN was carried out in a sealed tube, the reaction mixture being heated to 413K for one day. Again little reaction was apparent but downfield resonances were observed at 62.9, 45.3 and 27.5 ppm, which are not readily assignable. The reaction of $POBr_3$ with Et_4NCN in CH_2Cl_2 was exothermic giving a dark red solution. The ^{31}P n.m.r. spectrum showed that the resonance due to $POBr_3$ had shifted downfield to 92.7 ppm (the normal shift observed in CH_2Cl_2 was 101 ppm), and other small peaks were seen at 45.6, 50.4 and 52.9 ppm.

$PSCl_3$ did not react with AgCN in CH_2Cl_2 or $C_6H_5NO_2$ at room temperature. When heated with AgCN at 408K for 5 days a CH_3CN solution of $PSCl_3$ showed a limited amount of reaction. Weak resonances were detected at -219.7 (PCl_3), and two upfield of $PSCl_3$ (δ -30.0 ppm) at -16.2 and 9.8 ppm, tentatively assigned as $PSCl_2(CN)$ and $PSCl(CN)_2$. The reaction with Et_4NCN was again exothermic, producing a dark red solution. New resonances were observed at -16.2 and 9.8 ppm ($PSCl_2(CN)$ and $PSCl(CN)_2$), with larger amounts of $PCl_2(CN)_2^-$ and $PCl(CN)_3^-$ also detectable. Small signals at lower field than the $PSCl_3$ resonance were observed at -80.7 and -51.6 ppm. The formation of derivatives containing no sulphur indicates that the reaction with Et_4NCN is complex, although some direct substitution is apparent. There was no evidence of resonances to higher field of 200 ppm.

It seems that phosphoryl and thiophosphoryl halides react with metal cyanides to a limited extent only under very forcing conditions. The small amounts of product are not always easy to identify, although in the case of the $POCl_{3-n}(CN)_n$ series confirmation of the assignments can be obtained from another system.

viii Experimental

<u>$P(CN)_3$ + $SbCl_5$ 1:2 in CH_2Cl_2</u> $P(CN)_3$ (0.043 g 0.039 mmole) was dissolved in CH_2Cl_2 in an n.m.r. sample tube. $SbCl_5$ (0.1 ml, 0.078 mmole) was added. Mole ratio 1:2.

<u>$P(CN)_3$ + PCl_5 1:2 in CH_2Cl_2</u> $P(CN)_3$ (0.040 g 0.036 mmole) was dissolved in CH_2Cl_2 in an n.m.r. sample tube, PCl_5 (0.134 g 0.064 mmole) was added. Mole ratio 1:1.8.

<u>$P(CN)_3$ + PCl_5 1:1 in CH_2Cl_2</u> $P(CN)_3$ (0.031 g 0.028 mmole) was dissolved in CH_2Cl_2 in an n.m.r. sample tube. PCl_5 (0.056 g 0.027 mmole) was added. Mole ratio 1:0.96.

<u>$P(CN)_3$ + PCl_5 3:2 in CH_2Cl_2</u> $P(CN)_3$ (0.073 g 0.067 mmole) was dissolved in CH_2Cl_2 in an n.m.r. sample tube. PCl_5 (0.081 g 0.039 mmole) was added. Mole ratio 3:1.8

<u>$P(CN)_3$ + Br_2 1:1 at 194K in CH_2Cl_2</u> $P(CN)_3$ (1.13 g 1.03 mmole) was dissolved in CH_2Cl_2. 0.5 mls Br_2 solution (1.35 mls in 10 mls CH_2Cl_2) was added to the stirred solution at 194K. Mole ratio 1:1.2. The solution was stirred at 194K for one hour and evaporated under vacuum to give an orange solid.

<u>$P(CN)_3$ + ICN 1:1 in CH_2Cl_2</u> $P(CN)_3$ (0.07 g 0.064 mmole) was dissolved in CH_2Cl_2 and ICN (0.09 g 0.058 mmole) was added directly to the n.m.r. sample tube. Mole ratio 1:0.9.

<u>PCl_3 + ClCN + BCl_3 1:1:1 in CH_2Cl_2</u> PCl_3 (1 ml 1.15 mmole) was dissolved in 10 mls CH_2Cl_2. The flask was frozen in liquid nitrogen and ClCN (0.5 mls 0.96 mmole) and BCl_3 (1 ml 1.16 mmole) were condensed into the vessel which was allowed to warm to room temperature. Mole ratio 1:0.8:1.

<u>PCl_3 + ClCN + $SbCl_5$ 1:1:1 in CH_2Cl_2</u> $SbCl_5$ (1 ml 0.8 mmole) was dissolved in CH_2Cl_2. The flask was frozen in liquid nitrogen and ClCN (0.43 mls 0.8 mmole) and PCl_3 (0.68 mls 0.8 mmole) were condensed into the vessel which was allowed to warm to room temperature. Mole ratio 1:1:1.

<u>PCl_3 + ClCN 1:1 in sealed tube</u> PCl_3 (0.5 mls 0.6 mmole) was placed in a tube inside the dry box. ClCN (0.4 mls 0.8 mmole) was condensed into the tube under vacuum. The tube was sealed and allowed to warm to room temperature. Mole ratio 1:1.3.

<u>PCl_5 + AgCN 1:1 in CH_2Cl_2</u> PCl_5 (1.52 g 7.3 mmole) was dissolved in 25 mls CH_2Cl_2 and AgCN (0.98 g 7.3 mmole) was added. Mole ratio 1:1.

<u>PCl_5 + AgCN 1:1 in $C_6H_5NO_2$</u> PCl_5 (0.040 g 0.2 mmole) was placed in an n.m.r. tube and dissolved in nitrobenzene. AgCN (0.021 g 0.16 mmole) was added. Mole ratio 1:0.8.

<u>$(C_5H_{11})_4NPCl_6$ + AgCN 1:1 in CH_2Cl_2</u> Pe_4NPCl_6 (1.46 g 2.7 mmole) was placed in an n.m.r. tube and dissolved in a small amount of CH_2Cl_2. AgCN (0.382 g 2.9 mmole) was added. Mole ratio 1:1.1.

<u>$(C_5H_{11})_4NPCl_6$ + AgCN 1:2 in CH_2Cl_2</u> Pe_4NPCl_6 (2.39 g 4.4 mmole) was dissolved in CH_2Cl_2 and AgCN (1.42 g 10.6 mmole) were added. Mole ratio 1:2.4.

<u>$(C_5H_{11})_4NPCl_6$ + AgCN 1:4 in CH_2Cl_2</u> Pe_4NPCl_6(0.2 g 0.37 mmole) was placed in an n.m.r. sample tube and a small amount of CH_2Cl_2 was added, followed by AgCN (0.22 g 1.68 mmole). Mole ratio 1:4.4.

<u>$(C_5H_{11})_4NPCl_6$ + AgCN 1:6 in CH_2Cl_2</u> Pe_4NPCl_6 (1.001 g 1.85 mmole) was dissolved in 10 mls CH_2Cl_2. AgCN (1.483 g 11.08 mmole) was added and the solution rapidly stirred. Mole ratio 1:5.99. After two weeks the solution was filtered and evaporated to give a low-melting waxy solid.

Analysis $(C_5H_{11})_4NPCl_3(CN)_3$ requires C 53.8% H 8.6% N 10.9% P 6.0% Cl 20.7%
found C 51.1% H 9.4% N 10.3% P 5.5% Cl 18.2%.

<u>Preparation of $(C_2H_5)_4NPCl_5(CN)$</u> Pe_4NPCl_6 (2.29 g 6.1 mmole) was dissolved in CH_2Cl_2 and AgCN (0.55 g 4.1 mmole) was added. The solution was stirred for 10 minutes and filtered. Et_4NCl was added in small portions (about 0.05 g) until the resulting ^{31}P n.m.r. spectrum showed that all the remaining hexachlorophosphate had reacted. Approximately 0.16 g Et_4NCl were required for this. The solution was filtered and Et_4NCl (0.32 g) was added. The small amount of precipitate formed was filtered off. Its i.r. spectrum and elemental analysis indicated the presence of $(C_5H_{11})_4N^+$ groups so the solid was rejected. The remaining solution was cooled to 253K for 2 hours. The crystals

were filtered off to give pure $Et_4NPCl_5(CN)$ (0.25 g). The volume of the solvent was reduced and the solution cooled to 253K to give a further 0.18 g .

Analysis $(C_2H_5)_4NPCl_5(CN)$ requires C 29.6% H 5.5% N 7.7% P 8.5% Cl 48.7%
found C 29.2% H 5.7% N 7.6% P 8.3% Cl 48.7%.

Preparation of $(C_2H_5)_4NPCl_4(CN)_2$ Et_4NPCl_6 (3.39 g 9.1 mmole) was powdered and made into a slurry with 20 mls CH_2Cl_2. AgCN (1.15 g 8.6 mmole) was added and the mixture stirred for 20 hours. The solution was filtered and the remaining solid washed several times with CH_2Cl_2. The filtrate and washings were combined and reduced in volume until crystallisation became apparent, the solution was then cooled to 253K. The long needle-like crystals were filtered and dried at the pump to give $Et_4NPCl_4(CN)_2$ (0.67 g). Treatment of the remaining solution with 30 - 40° petroleum ether precipitated a further 0.32 g .

Analysis $(C_2H_5)_4NPCl_4(CN)_2$ requires C 33.8% H 5.6% N 11.8% P 8.7% Cl 40.0%
found C 32.4% H 5.6% N 12.2% P 9.5% Cl 42.0%.

Preparation of $(C_2H_5)_4NPCl_3(CN)_3$ (*fac*-isomer) Et_4NPCl_6 (3.48 g 9.3 mmole) was powdered and made into a slurry with 20 mls CH_2Cl_2. AgCN (5.84 g 43.6 mmole) was added and the mixture stirred for 20 hours. The solution was filtered and the remaining solid extracted with CH_2Cl_2. The washings and filtrate were combined and reduced in volume until crystallisation started when the solution was cooled to 253K. The resulting crystals were filtered off to give 1.01 g $Et_4NPCl_3(CN)_3$ as an isomer mixture containing approximately a 10:1 ratio of *fac*:*mer* isomers as estimated by n.m.r. Further extraction of the solid silver residues with CH_2Cl_2 followed by treatment of the washings with 30 - 40° petroleum ether gave a further 0.48 g of product. To obtain the *fac*-isomer the solid was recrystallised twice from CH_2Cl_2 in which the *mer*-isomer is more soluble.

Analysis $(C_2H_5)_4NPCl_3(CN)_3$ requires C 38.2% H 5.8% N 16.2% P 9.0% Cl 30.8%

found C 39.0% H 6.3% N 15.9% P 9.2% Cl 30.7%.

The n.m.r. of the filtrate from the first crystallisation indicated the presence of another species, possibly $Et_4NPCl_2(CN)_4$. The filtrate was reduced in volume and cooled to 253K to precipitate as much of the remaining $Et_4NPCl_3(CN)_3$ as possible. The crystals were filtered off and the resulting filtrate retained and its n.m.r. spectrum run. This process was repeated twice. The solution was evaporated and the resulting solid analysed.

$(C_2H_5)_4NPCl_2(CN)_4$ requires C 42.9% H 6.0% N 20.8%

found C 41.2% H 7.4% N 18.9%

$(C_2H_5)_4NPCl_3(CN)_3$ requires C 38.2% H 5.8% N 16.2%.

There was insufficient material to obtain phosphorus and chlorine analyses.

Preparation of $(C_2H_5)_4NPCl_3(CN)_3$ (*mer*-isomer) $P(CN)_3$ (1.51 g 13.9 mmole) and Et_4NCl (2.51 g 15.2 mmole) were dissolved in CH_2Cl_2 and Cl_2 (0.6 mls at 194K) was condensed onto the solution frozen in liquid nitrogen under vacuum. The solution was warmed to 194K until the green colour of the solution disappeared. The solution was then evaporated and the resulting solid recrystallised from CH_2Cl_2 to give 0.8 g $Et_4NPCl_3(CN)_3$ with a *fac*:*mer* isomer ratio of 1:3 as estimated by n.m.r.

Analysis $(C_2H_5)_4NPCl_3(CN)_3$ requires C 38.2% H 5.8% N 16.2% P 9.0% Cl 30.8%

found C 38.6% H 5.8% N 15.8% P 8.1% Cl 32.5%.

Cyanogen was prepared by dry distillation at 423K of a mixture of P_2O_5 and oxamide. The gas phase infrared spectrum showed only small traces of HCN present as impurity. The gas was stored in a rotaflo vessel at 243K and handled on the vacuum line.

Cyanide Wastes Residues containing cyanide were treated with 'chloros' a commercially available solution of hypochlorite with permanganate indicator.

Chapter 5

Attempted Preparation of Simple Phosphorus(V) Species Containing the Thiocyanate Group

i Attempts to identify $PY_{4-n}(NCS)_n^+$ species (Y = Cl, Br; $0 \leqslant n \leqslant 4$)

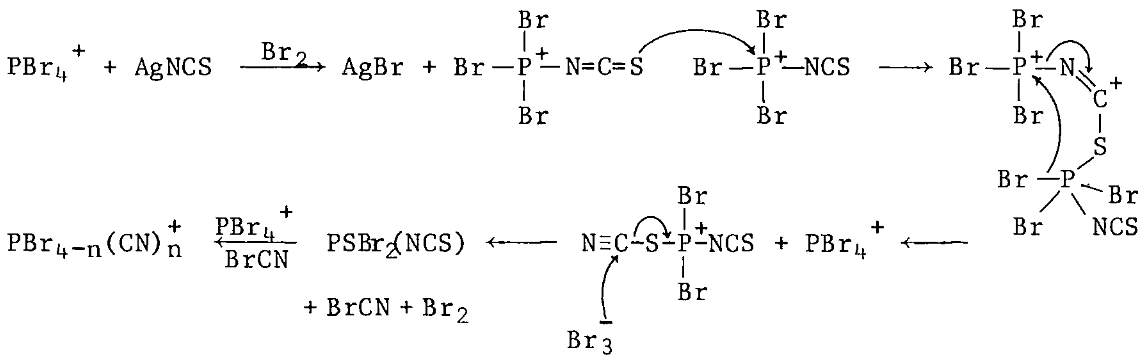
a. By direct substitution into tetrahalophosphonium ions

Addition of AgNCS to a $C_6H_5NO_2$ solution of PCl_4SbCl_6 led to no initial reaction. After five hours the production of small quantities of $PSCl_3$ (δ -34.0 ppm), $PSCl(NCS)_2$ (δ -4.9 ppm) and $PS(NCS)_3$ (δ 6.5 ppm) was apparent, together with two resonances at 40.4 and 53.3 ppm which are not readily assignable to the $PSCl_{3-n}(NCS)_n$ series or possible hydrolysis products. The corresponding reaction carried out in CH_3CN was much more rapid. The $PSCl_{3-n}(NCS)_n$ species were formed rapidly, together with the unassigned peak at 40.4 ppm. Similarly the reaction of LiNCS with PCl_4SbCl_6 in CH_3NO_2 produced only thiophosphorylchloro-thiocyanato-derivatives. When PCl_4BCl_4 was used reduction to PCl_3 occurred in addition to the production of $PSCl_3$. Thus it seems probable that any cationic derivatives formed decompose readily in normal organic solvents, possibly in a similar manner to the corresponding cyano-systems. To suppress dissociation into molecular forms which subsequently decompose, reactions were carried out in liquid halogens. PBr_5 reacted exothermically with AgNCS in Br_2. The resulting ^{31}P n.m.r. spectrum showed resonances readily assignable to the $PSBr_{3-n}(NCS)_n$ series ($1 \leqslant n \leqslant 3$) at 62.2, 26.7 and 8.9 ppm respectively[17]. Other resonances were seen which could be due to the $PBr_{4-n}(CN)_n^+$ series at 50.9, 38.4, 33.1 and 41.1 ppm respectively, with unassigned resonances at 15.8, 18.2 and 52.9 ppm, possibly due to $PBr_{4-n}(NCS)_n^+$

species. A possible mechanism for the formation of these species is shown in Scheme 5.1. The reaction of PCl_5 with AgNCS in Br_2 was again exothermic. The ^{31}P n.m.r. spectrum initially showed PCl_4^+ and several resonances upfield of it, some of which are readily assigned as PCl_3Br^+ (δ -47.6 ppm), $PCl_2Br_2^+$ (δ -9.8 ppm), $PS(NCS)_3$ (δ 8.2 ppm) and $PSCl(NCS)_2$ (δ -2.5 ppm). Two other intense resonances were observed at -52.4 and -24.2 ppm which are tentatively assigned as $PCl_3(NCS)^+$ and $PCl_2(NCS)_2^+$, as shown in Figure 5.1. Addition of more AgNCS to the solution caused an increase in intensity of the new resonances with a corresponding decrease in that of the PCl_4^+ signal. After two days other new peaks were visible at -44.0 ($PCl_3(CN)^+$), -34.0 ($PSCl_3$), -20.2, -5.8 and 20.5 ppm which are unassigned.

Scheme 5.1

A mechanism for the reaction between PBr_5 and AgNCS in Br_2



The use of the pairwise interaction method is possible for this system. It is possible however, that better values might be obtained if some parameters could be calculated from known tetrahedral systems containing chloride and thiocyanate ligands. The only such system is $POCl_{3-n}(NCS)_n$ ($0 \leqslant n \leqslant 3$) where O:Cl and O:NCS terms must also be evaluated. By assuming that terms such as Cl:Cl depend only on the geometry of the co-ordination polyhedron, the O:Cl term can be derived from the chemical shift of $POCl_3$. Thus O:Cl = 12.8 ppm . To test the validity of transferring pairwise interaction terms between different tetrahedral systems, the values of Br:Br, Br:Cl and Cl:Cl were used to calculate the shifts of $POCl_2Br$ and $POClBr_2$, the O:Cl and O:Br terms being derived from the chemical shifts of $POCl_3$ and $POBr_3$ respectively. The values obtained are $POCl_2Br$ δ 28.7 ppm , compared with the literature value of 29.6 ppm and $POClBr_2$ δ 63.1 ppm , comparing well with the literature value of 64.8 ppm . The calculation of the parameters necessary to evaluate the shifts of the ions $PCl_{4-n}(NCS)_n^+$ $(2 \leqslant n \leqslant 4)$ is outlined below.

Cl:Cl = −13.9 ppm
O:Cl = 12.8 ppm from PCl_4^+ and $POCl_3$

$PCl_3(NCS)^+$ = −52.4 ppm = 3Cl:Cl + 3Cl:NCS terms,
which gives Cl:NCS = −3.6 ppm .

$POCl_2(NCS)$ = 21.0 ppm [9] = 2 O:Cl + O:NCS + 2Cl:NCS + Cl:Cl
which gives O:NCS = 16.5 ppm.

$POCl(NCS)_2$ = 41.5 ppm [9] = O:Cl + 2 O:NCS + 2Cl:NCS + NCS:NCS
which gives NCS:NCS = 2.9 ppm.

To check that values obtained so far are reasonable, the chemical shift of $PO(NCS)_3$ was evaluated as $\delta(PO(NCS)_3)$ = 3 O:NCS + 3NCS:NCS = 58.2 ppm which compares very reasonably with the literature value of 61.9 ppm[9]. Thus the remaining shifts for the cationic species were calculated.

$\delta\ (PCl_2(NCS)_2^+)$ = Cl:Cl + 4Cl:NCS + NCS:NCS = -25.4 ppm

$\delta\ (PCl(NCS)_3^+)$ = 3Cl:NCS + 3NCS:NCS = - 2.1 ppm

$\delta\ (P(NCS)_4^+)$ = 6NCS:NCS = 17.4 ppm

Similarly the values of the shifts of the $PBr_{4-n}(NCS)_n^+$ $(0 \leqslant n \leqslant 4)$ and $PCl_xBr_y(NCS)_z^+$ (x+y+z = 4) series can be evaluated. δ $PSBr_3$ = 111.8 ppm, giving the S:Br term as 24.6 ppm, δ $PS(NCS)_3$ = 9.3 ppm, giving S:NCS = 0.2 ppm, and δ $PSBr_2(NCS)$ = 62.8 ppm so that Br:NCS equals 0.2 ppm. To check if this is reasonable the shift of $PSBr(NCS)_2$ was evaluated as 27.5 ppm, in very good agreement with the literature value of 28.4 ppm. The use of this parameter with others previously calculated give the shifts as δ $PBr_3(NCS)^+$ = 37.5 ppm, δ $PBr_2(NCS)_2^+$ = 14.8 ppm, δ $PBr(NCS)_3^+$ = 8.1 ppm, δ $PCl_2Br(NCS)^+$ = -24.9 ppm, δ $PClBr(NCS)_2^+$ = -6.5 ppm and δ $PClBr_2(NCS)^+$ = 5.1 ppm.

In the light of these calculations further possible assignments can be made. In the PBr_4^+-AgNCS-Br_2 system the unassigned resonances at 15.8 and 18.2 ppm may be assigned as $PBr_2(NCS)_2^+$ and $P(NCS)_4^+$ while the resonances at 38.4 and 8.9 ppm previously assigned as $PBr_2(CN)_2^+$ and $PS(NCS)_3$ could equally well be $PBr_3(NCS)^+$ and $PBr(NCS)_3^+$ respectively. In the PCl_5-AgNCS-Br_2 system the resonance at -20.2 ppm can now be assigned as $PCl_2Br(NCS)^+$, that at -5.8 ppm as $PClBr(NCS)_2^+$ and the signal at 20.5 as $P(NCS)_4^+$. It will also be noticed that the resonance at -3.6 ppm assigned as $PSCl(NCS)_2$ agrees well with the calculated value for $PCl(NCS)_3^+$. The observed shifts and assignments for these systems are shown in Table 5.1.

The reaction of PCl_4BCl_4 with AgNCS in liquid chlorine gave rise to a spectrum showing a broad resonance due to PCl_4^+ (δ -85.5 ppm), $PSCl_3$ (δ -34.7 ppm), $POCl_3$ (hydrolysis) or $PSCl(NCS)_2$ (δ -2.9 ppm) and an intense resonance at -40.4 ppm. This is somewhat higher than the expected value of -52 ppm for $PCl_3(NCS)^+$. Although differences in

Table 5.1

PBr_5-AgNCS-Br_2 system

Observed shift	Assignment	Calculated value for NCS-containing cations
76.2	PBr_4^+	-
62.2	$PSBr_2(NCS)$	-
52.9	-	-
50.9	$PBr_3(CN)^+$	-
41.1	$P(CN)_4^+$	-
38.4	$PBr_2(CN)_2^+$ or $PBr_3(NCS)^+$	37.5 (for $PBr_3(NCS)^+$)
33.1	$PBr(CN)_3^+$	-
26.7	$PSBr(NCS)_2$	-
18.2	$P(NCS)_4^+$	17.4
15.8	$PBr_2(NCS)_2^+$	14.8
8.9	$PS(NCS)_3$ or $PBr(NCS)_3^+$	8.1
	PCl_5-AgNCS-Br_2 system	
-83.2	PCl_4^+	-
-52.0	$PCl_3(NCS)^+$	-
-46.0	PCl_3Br^+	-
-44.0	$PCl_3(CN)^+$	-
-34.4	$PSCl_3$	-
-24.2	$PCl_2(NCS)_2^+$	-25.4
-20.2	$PCl_2Br(NCS)^+$	-24.9
-10.5	$PCl_2Br_2^+$	-
- 5.8	$PClBr(NCS)_2^+$	- 6.5
- 3.6	$PSCl(NCS)_2$ or $PCl(NCS)_3^+$	- 2.1
8.2	$PS(NCS)_3$	-
20.5	$P(NCS)_4^+$	17.4

counterion and solvent may account for such a shift, assignment as $PCl_3(CN)^+$ seems more reasonable in view of the formation of $PSCl_3$, presumably by an analogous mechanism to that indicated in Scheme 5.1.

b. <u>By oxidation of phosphorus(III) compounds</u>

The reaction of $P(NCS)_3$ with $SbCl_5$ in CH_2Cl_2 was exothermic; the ^{31}P n.m.r. spectrum of the resulting solution showed resonances at -87.1 ($P(NCS)_3$), -114.6 ($PCl(NCS)_2$) and -154.7 ppm ($PCl_2(NCS)$), with an unassigned resonance at 41.2 ppm . Addition of more $SbCl_5$ to this solution increased the intensity of the signal at 41.2 ppm and yielded intense resonances at 49.6 and 70.2 ppm , together with the series $PS(NCS)_{3-n}Cl_n$ ($0 \leqslant n \leqslant 3$) ($PS(NCS)_3$ being most intense whilst $PSCl_3$ had the lowest intensity), and $P(NCS)_{3-n}Cl_n$. There were smaller unassigned resonances at 18.5, 25.1 and 63.8 ppm . Clearly some oxidation is occurring in this reaction, although much ligand exchange to give $PCl_{3-n}(NCS)_n$ and later $PSCl_n(NCS)_{3-n}$ ($0 \leqslant n \leqslant 3$) is also apparent. Assignment of the remaining resonances is not simple. Obviously the desired cationic derivatives are not produced as the new resonances are at too high a field. Molecular species would not be expected to be stable in the presence of the strong Lewis acid $SbCl_5$. The most likely possibility is formation of thiophosphoryl derivatives since these seem to be produced quite readily in the decomposition of these systems. The simple isothiocyanato-derivatives are already observed, so the only other reasonable ligands would be S-bonded thiocyanate or cyanide. P-CN bonds do seem to be formed in the decomposition products of PY_4^+-NCS^- reactions (Y = Cl, Br) as noted before, although the results of direct substitution into $PSCl_3$ (Chapter 4 section vii) indicate that the compounds $PSCl_{3-n}(CN)_n$ ($0 \leqslant n \leqslant 3$) are not formed in the reaction between $P(NCS)_3$ and $SbCl_5$.

ii Attempted preparation of $PCl_{5-n}(NCS)_n$ species ($0 \leqslant n \leqslant 5$)

a. By direct substitution into PCl_5

PCl_5 reacted rapidly with AgNCS in CH_2Cl_2 to give an orange solution. The ^{31}P n.m.r. spectrum showed only PCl_3. After three days a new resonance at -34.0 ppm was seen, assigned to $PSCl_3$. After two months little PCl_3 remained in solution, the main peak being that due to $PSCl_3$. Similar reactions were observed between PCl_5 and NH_4NCS or LiNCS. The reaction could follow the course indicated below.

$$PCl_5 + AgNCS \xrightarrow{CH_2Cl_2} AgCl + [PCl_4NCS] \xrightarrow{fast} PCl_3 + ClSCN \xrightarrow{slow} PSCl_3 + ClCN \quad \ldots (1)$$

b. By oxidation of phosphorus(III) compounds

A solution of $P(NCS)_3$ was treated with a solution of thiocyanogen in CH_2Cl_2. The solution was a dark red colour, but no reaction could be detected by ^{31}P n.m.r. Treatment of PCl_3 with a solution of thiocyanogen in CH_2Cl_2 led to an exothermic reaction. The initial spectrum showed little sign of reaction; low intensity resonances were seen at 24.2 and 48.4 ppm in addition to peaks due to $PSCl_{3-n}(NCS)_n$. After one day the spectrum showed only the $PSCl_{3-n}(NCS)_n$ series and a small signal at -53.3 ppm, assigned as $PCl_3(NCS)^+$.

Little success was thus achieved in preparing molecular species containing the thiocyanate ligand. Certainly direct substitution into PCl_5 does not give any evidence to suggest their formation. The resonances observed at 24.2 and 48.4 ppm in the $PCl_3/(SCN)_2$ reaction could possibly be due to molecular species although definite assignments cannot be made.

iii Attempts to prepare $PCl_{6-n}(NCS)_n^-$ species ($0 \leq n \leq 6$)

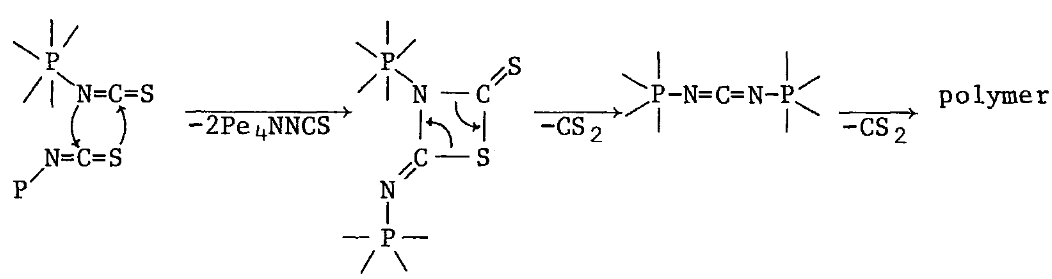
Reactions of Pe_4NPCl_6 with small amounts of AgNCS, NH_4NCS or LiNCS led to rapid reduction of the phosphorus, producing PCl_3 together with some new resonances to lower field of that due to PCl_6^-. Similarly when a solution containing PCl_6^- was treated with $P(NCS)_3$ or $PO(NCS)_3$, ligand exchange occurred to give $PCl_{3-n}(NCS)_n$ or $POCl_{3-n}(NCS)_n$ respectively ($0 \leq n \leq 3$), and species giving resonances downfield from the signal due to PCl_6^- at 286.9 and 276.1 ppm, assigned as $PCl_5(NCS)^-$ and an isomer of $PCl_4(NCS)_2^-$, together with unresolved signals in the 270 - 260 ppm range, presumably due to the $PCl_{6-n}(NCS)_n^-$ series. The peaks in the six-coordinate region rapidly diminished in intensity, with the formation of PCl_3 and $PSCl_3$.

If Pe_4NPCl_6 was treated with a large excess of thiocyanate one resonance only was observed in the ^{31}P n.m.r. spectrum, at 261.9 ppm. No signals due to PCl_3 or any other decomposition product were seen. As an excess of thiocyanate was used it seems reasonable to assume that $P(NCS)_6^-$ has been formed. This species seemed much more stable in solution than the mixed chlorothiocyanato-anions, and no decomposition was apparent in the spectrum after several hours. The compound was isolated by the reaction of Pe_4NPCl_6 in CH_2Cl_2 solution with an excess of NH_4NCS as an intractable orange oil. The ^{31}P n.m.r. spectrum of the liquid showed one sharp resonance at 261.1 ppm, confirming that it is the same species as observed in solution. Elemental analysis indicates that the compound is $Pe_4NP(NCS)_6$ (Experimental section). The infrared spectrum was obtained as a contact film, and shows strong broad bands at 2040 and 1900 cm^{-1} assigned as 'NCS antisymmetric stretches' by comparison with the bands at 2080 and 1920 cm^{-1}, similarly assigned, in $PO(NCS)_3$[85]. This indicates that the ligand is N- rather than

S-bonded. The liquid decomposes on standing at room temperature with evolution of CS_2, identified by a strong absorption at 1520 cm^{-1} in its gas phase infrared spectrum, but is considerably more stable at 243K. A sample of $Pe_4NP(NCS)_6$ was decomposed by heating to 373K under vacuum for five hours. The resulting solid was washed several times with CH_2Cl_2 to remove any tetrapentylammonium salts present. The solid state n.m.r. spectrum of the residue showed an extremely broad signal with no discernible maximum between -80 and +80 ppm . The route to decomposition presumably involves bi-molecular loss of CS_2 and a possible mechanism is shown in Scheme 5.2. The extremely

Scheme 5.2

A mechanism for the decomposition of the $P(NCS)_6^-$ ion



broad resonance of the final product of the decomposition indicates that many different types of phosphorus atom are present in the solid, possibly with four- or five-coordination around the phosphorus atoms. The simple straight chain polymer $\leftarrow P(NCS)_3\text{-}NCN \rightarrow_n$ could lose more CS_2, forming complex branched chain structures, which would contain many different types of phosphorus atom and explain the broadness of the solid state signal.

Confirmation that the resonance at 261.1 ppm was due to $P(NCS)_6^-$ indicated that the unresolved peaks in the 270 - 260 ppm region probably arise from other members of the $PCl_{6-n}(NCS)_n^-$ series. As $P(NCS)_6^-$ (δ 261.1 ppm) and $PCl_5(NCS)^-$ (δ 286.9 ppm) could be clearly observed and assigned the pairwise interaction parameters necessary to evaluate the shifts for the whole series could be calculated. This gave Cl:Cl = 24.9 (from PCl_6^-), Cl:NCS = 22.0 (from $PCl_5(NCS)^-$), and NCS:NCS = 21.8 ppm (from $P(NCS)_6^-$). The shifts of the remaining species were then calculated; the results are shown in column A of Table 5.2. These values suggest that the signals of the last members of the $PCl_{6-n}(NCS)_n^-$ series should indeed be very close together. Thus the addition of NH_4NCS to a strong solution of Pe_4NPCl_6 was repeated and the spectrum run over a narrow sweep width to resolve the signals. A typical spectrum is shown in Figure 5.2, and the chemical shifts and assignments of formulae are shown in column E of Table 5.2. In this case the best fit does not seem to follow a simple *cis* or *trans* pattern of substitution. The best agreement with the observed values indicates the preferential formation of *trans*-$PCl_4(NCS)_2^-$, *mer*-$PCl_3(NCS)_3^-$ and *cis*-$PCl_2(NCS)_4^-$. By using the least squares best fit method on the experimental data the three pairwise interaction terms were re-evaluated. The assumption of totally *cis*-substitution gave values of Cl:Cl = 24.91, Cl:NCS = 21.95 and NCS:NCS = 21.89, and the shifts recalculated on this basis are shown in column B of Table 5.2. Assumption of a *trans*-pattern of substitution gave values of Cl:Cl = 24.89, Cl:NCS = 22.27 and NCS:NCS = 21.82 ppm, the recalculated values being given in column C of Table 5.2. If the pattern of substitution indicated by the simple predictions (column A) is assumed to be correct then Cl:Cl = 24.83, Cl:NCS = 22.13 and NCS:NCS = 21.81 ppm, giving the recalculated shifts shown in column D of Table 5.2. The calculated data give best agreement if the pattern of substitution shown in Figure 5.3 is followed, corresponding to that deduced from column A.

Figure 5.3

The pattern of substitution in the $PCl_6^- - NCS^-$ reaction

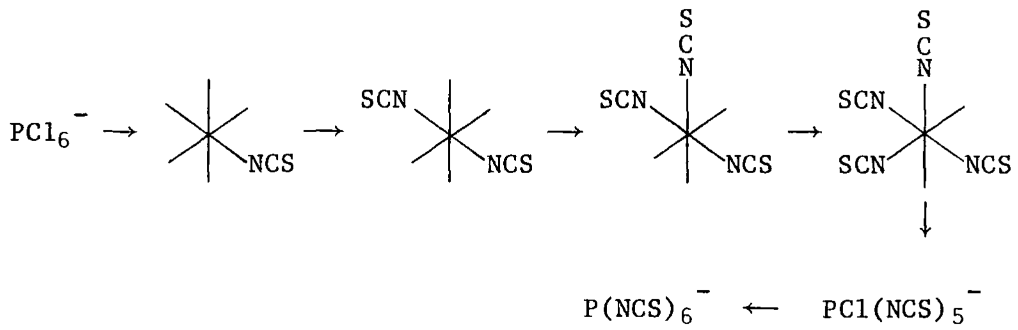


Table 5.2 Calculated and observed shifts for $PCl_{6-n}(NCS)_n^-$ in CH_2Cl_2 $(0 \leq n \leq 6)$

Ion	Calculated A	Calculated B	Calculated C	Calculated D	Observed δ E
PCl_6^-	-	298.9	298.7	298.0	298.2
PCl_5NCS^-	-	287.1	288.2	287.2	286.9
cis-$PCl_4(NCS)_2^-$	278.3	278.1	279.9	278.7	276.1
trans-$PCl_4(NCS)_2^-$	275.6	275.2	277.7	276.4	
fac-$PCl_3(NCS)_3^-$	272.2	272.1	273.8	272.7	270.5
mer-$PCl_3(NCS)_3^-$	269.6	269.2	271.6	270.3	
cis-$PCl_2(NCS)_4^-$	266.2	266.1	267.6	266.7	266.8
trans-$PCl_2(NCS)_4^-$	263.2	263.2	265.4	264.3	
$PCl(NCS)_5^-$	262.8	262.9	263.6	263.0	264.4
$P(NCS)_6^-$	-	262.7	261.8	261.7	261.9

iv Experimental

Anhydrous LiCNS was prepared by the method of Lee[86]. $LiOH.H_2O$ (8.4 g) and NH_4NCS (15.2 g) were mixed as solids with stirring and warming until the mixture dissolved in the water produced by the reaction. The mixture was then heated under vacuum at 373K for 3 hours to remove H_2O and NH_3. 12.5 g were obtained in this way.

$P(NCS)_3$ was prepared in CH_2Cl_2 solution by adding NH_4NCS to a solution of PBr_3. Vigorous reaction occurred on each addition until all the PBr_3 had reacted. The solution was then filtered, stored at 243K and used without further purification. Solutions stored at room temperature readily decomposed to insoluble red-brown polymeric materials.

Thiocyanogen was prepared in CH_2Cl_2 solution by adding AgNCS to a solution of Br_2 in CH_2Cl_2 until the liquid became decolourised[87]. This was then filtered and the solution used as such. Thiocyanogen is unstable and the solutions were freshly prepared for each experiment.

NH_4NCS was purified by recrystallisation from CH_3OH before use.

Preparation of $(C_5H_{11})_4NP(NCS)_6$

Pe_4NPCl_6 (3 g) was treated with a large excess of NH_4NCS in 50 mls CH_2Cl_2. The reaction was stirred for 10 mins and filtered. The resulting yellow solution was evaporated under vacuum, care being taken not to heat the flask too strongly to avoid decomposition of the $P(NCS)_6^-$ ion. This left an intractable orange oil.

Analysis	$(C_5H_{11})_4NP(NCS)_6$	requires	C 46.1%	H 6.5%	N 14.5%	P 4.6%	S 28.4%
		found	C 45.0%	H 7.9%	N 11.6%	P 4.6%	S 25.0%

Attempted recrystallisation at 194K failed and no further purification was possible due to the thermally unstable nature of the compound. One possible explanation for the relatively poor analysis could be rapid loss of CS_2 (see results and discussion). After heating for 5 hours at 373K under vacuum elemental analyses for the substance obtained were

	found	C 48.0%	H 6.9%	N 15.3%	S 25.0%
($2Pe_4NP(NCS)_6 - CS_2$)	requires	C 47.9%	H 7.6%	N 13.7%	S 25.0%.

Chapter 6

Cyanato-derivatives of Phosphorus(V) Compounds

i Attempts to prepare cyanato derivatives of the tetrahalophosphonium ions $PY_{4-n}(NCO)_n^+$ ($0 \leqslant n \leqslant 4$; Y = Br, Cl)

a. By direct substitution into PY_4^+ salts (Y = Br, Cl)

The reaction of PCl_4SbCl_6 with AgNCO in nitrobenzene proceeded slowly, yielding $POCl_3$(δ -4.9 ppm). After seven weeks only $POCl_3$ was seen in the ^{31}P n.m.r. spectrum. In CH_3CN the reaction was much more rapid, going to completion to give $POCl_3$ as the only product within a few minutes. PCl_4BCl_4 in CH_3NO_2 reacted exothermically with AgNCO, giving rise to a ^{31}P n.m.r. spectrum showing intense signals at -42.0. -21.1, -6.5 and 11.4 ppm. The last two may readily be assigned as $POCl_3$ and $POCl_2(NCO)$[17] respectively. The resonances at -42.0 and -21.1 ppm cannot be assigned as simple phosphoryl derivatives. The chemical shift of -42.0 ppm agrees well with that of $PCl_3(CN)^+$ and suggests that rearrangement to cyano-species may be occurring. No resonances were observed which could unambiguously be assigned to cyanato-containing cations. The reaction of PBr_5 and PCl_5 with AgNCO in liquid bromine led only to the formation of $POBr_3$ and $POCl_3$ respectively, and no indication of substitution into the cation could be observed.

b. By oxidation of $P(NCO)_3$

Upon addition of $SbCl_5$ to a CH_3NO_2 solution of $P(NCO)_3$ a violent exothermic reaction took place. The ^{31}P n.m.r. spectrum showed that ligand exchange had occurred, giving $PCl_{3-n}(NCO)_n$ ($0 \leqslant n \leqslant 3$) at δ -220.8, -167.7, - 128.9 and -98.4 ppm. Prominent resonances were also seen at -11.4 ($POCl_3$-$SbCl_5$ complex), 8.2 ($POCl_2(NCO)$), 25.8 ($POCl(NCO)_2$)

and 40.4 ppm ($PO(NCO)_3$), with other signals at -45.3, 17.8 and 35.5 ppm. The value of -45.3 ppm is in reasonable agreement with the shift assigned to $PCl_3(CN)^+BCl_4^-$ in the same solvent, thus assignment as $PCl_3(CN)^+SbCl_6^-$ seems reasonable here. The resonances at 17.8 and 35.5 ppm cannot be readily attributed to cationic species, but could be due to compounds from the series $POCl_{3-n}(OCN)_n$ ($0 \leqslant n \leqslant 3$). (Anderson believes $PO(OCN)_3$ to be formed during the preparation of $PO(NCO)_3$[12].) The reaction of $P(NCO)_3$ with Br_2 in CH_3CN gave rise to a ^{31}P n.m.r. spectrum which clearly showed the presence of $PBr_2(NCO)$ (δ -172.6 ppm), $PBr(NCO)_2$ (δ -130.2 ppm) and $P(NCO)_3$, with an intense resonance at 42.0 ppm readily assigned as $PO(NCO)_3$. Additional resonances were observed at 27.5, 34.7, 50.9 and 70.0 ppm which could be due to $PBr_{4-n}(NCO)_n^+$ ($0 \leqslant n \leqslant 4$), $POBr_{3-n}(NCO)_n$ ($0 \leqslant n \leqslant 3$) or cyano-containing cations but unambiguous assignment is not possible. Attempted chlorination of $P(NCO)_3$ in CCl_4 led only to the formation of $POCl_{3-n}(NCO)_n$ ($0 \leqslant n \leqslant 3$), consistent with previous work which indicated that oxidation had occurred, although the $PCl_2(NCO)_3$ postulated[23] is certainly not formed.

Cationic cyanato-derivatives of PCl_4^+ and PBr_4^+ thus do not seem to be observable in the experiments attempted and, if formed, rapidly rearrange to give phosphoryl compounds.

ii <u>Attempts to prepare cyanato-derivatives of PCl_5</u>

When equimolar amounts of AgNCO and PCl_5 in CH_2Cl_2 were reacted, the ^{31}P n.m.r. spectrum showed resonances at -22.7, -17.8, -4.9 ($POCl_3$), 11.4 ($POCl_2(NCO)$) and 80.5 ppm (unreacted PCl_5). With a 1:4 mole ratio of PCl_5:AgNCO a resonance at -16.2 ppm was seen together with signals readily assignable to $POCl_3$ and $POCl_2(NCO)$. After one day only $POCl_3$ and a small amount of $POCl_2(NCO)$ remained in solution.

KNCO reacted slowly with PCl_5 in CH_3NO_2 to give mainly $POCl_3$, with a small resonance at -38.7 ppm which could be due to $PCl_3(CN)^+$. On refluxing PCl_5 with KNCO in a 1:4 ratio for 5 hours $POCl_3$ was again the main product with smaller signals indicating the presence of $POCl_2(NCO)$ (δ 12.9 ppm), $POCl(NCO)_2$ (δ 29.1 ppm) and PCl_3 (δ -220.0 ppm). Addition of AgNCO to a nitromethane solution of PCl_5 caused an exothermic reaction. The ^{31}P n.m.r. spectrum of the solution showed $POCl_3$ and $POCl_2(NCO)$ together with a resonance at -23.5 ppm. After the reaction mixture had been stirred for 10 minutes the vessel was opened to the vacuum line and any volatile materials collected. The infrared spectrum of the gases evolved clearly indicated the presence of CO_2 with a strong absorption at 2320 cm^{-1} (together with absorptions due to CH_3NO_2 vapour), suggesting that an analogous decomposition route to that indicated for thiocyanates (where loss of CS_2 occurs) is followed. The resonance at -23.5 ppm could be due to the decomposition product associated with this loss of CO_2. The formation of $POCl_3$ and $POCl_2(NCO)$ might be rationalised by reactions (1) and (2), although cyanogen chloride was not detected in the gas phase infrared spectrum.

$$PCl_4(NCO) \longrightarrow POCl_3 + ClCN \quad \ldots (1)$$

$$PCl_3(NCO)_2 \longrightarrow POCl_2(NCO) + ClCN \quad \ldots (2)$$

The reaction of solid PCl_5 with HNCO yielded a colourless liquid, the ^{31}P n.m.r. of which showed a strong resonance at -17.8 ppm with less intense peaks at -32.4, -4.9 ($POCl_3$) and 11.4 ppm ($POCl_2(NCO)$). Distillation at atmospheric pressure gave only $POCl_3$ (boiling point 378K δ -1.6 ppm). The liquid, presumed to be some molecular species, solidified on standing but dissolved in CH_2Cl_2 without apparent change.

The addition of Pe_4NCl to this solution gave rise to the formation of PCl_6^- (δ 298.2 ppm), supporting assignment as a molecular species. Rapid substitution of NCO by Cl must occur here as no cyanato-containing anions could be observed.

The reaction of PCl_5 with LiNCO in CH_2Cl_2 led to the gradual formation (within 1 d.) of an intense resonance at -16.2 ppm together with smaller signals at -38.7, -3.3 ($POCl_3$) and 12.9 ppm ($POCl_2(NCO)$). The main peak has a similar shift to the major product of the PCl_5-HNCO reaction and may well be due to a molecular species. The reaction of a solution (which contained no unreacted PCl_5) with $SbCl_5$ was carried out in an attempt to produce cations. The ^{31}P n.m.r. spectrum showed resonances at -82.2 (PCl_4^+), -42.0 ($PCl_3(CN)^+$) and -27.5 ppm, indicating the production of cationic species, although once again no cyanato-containing species were observed.

In these reactions resonances between -16 and -17 ppm occur regularly and the available evidence suggests that this is due to some molecular species based on PCl_5. Assignment of a formula is not possible as no intermediate species were detected. In view of its ready decomposition to $POCl_3$ during distillation it must be assumed that at least three chlorines are present in the molecule, which might indicate a formula of $PCl_3(NCO)_2$, but this assignment can only be tentative. Other resonances to lower field observed in these systems may well be due to other molecular species, cationic derivatives or decomposition products. Again insufficient information is available to draw any firm conclusions.

iii Attempts to prepare cyanato-derivatives of the hexachlorophosphate ion

A relatively simple preparation of the $PCl_5(NCO)^-$ ion might be expected from the reaction of PCl_5 with Et_4NNCO in CH_2Cl_2. The reaction was violently exothermic and the ^{31}P n.m.r. spectrum showed unassigned resonances at 16.2, 19.4 and 22.7 ppm. These chemical shifts are certainly too low for six-coordinate species. Other reactions aimed at utilising the acceptor properties of molecular phosphorus(V) compounds were carried out by adding Pe_4NCl to the solutions of the proposed molecular species formed in section ii. Thus addition of Pe_4NCl to the reaction product of PCl_5-HNCO gave only PCl_6^-, as noted before. Corresponding addition to the PCl_5-LiNCO solution gave a ^{31}P n.m.r. spectrum showing resonances in the six-coordinate region at 274.0, 280.4, 290.0, 315.9, 340.0 and 388.4 ppm. The addition of more Pe_4NCl resulted in a simplification of the spectrum, giving just two resonances in the six-coordinate region at 280.4 and 298.2 ppm. After one day only the PCl_6^- signal (δ 298.2 ppm) remained in this area. The reaction was accompanied by a decrease in concentration of the molecular species, with corresponding increases in the concentrations of $POCl_3$ and $POCl_2(NCO)$ as shown in Figure 6.1. If substitution of NCO by Cl is occurring assignment of the resonance at 280.4 ppm as $PCl_5(NCO)^-$ seems reasonable since it is the last of the six-coordinate species (other than PCl_6^-) to be present. Assignment of the highest field resonance as $P(NCO)_6^-$ allows the calculation of the pairwise interaction parameters NCO:Cl and NCO:NCO as 20.4 and 32.4 ppm respectively. The assignments and calculated shifts are shown in Table 6.1.

Although perfect agreement between calculated and observed values is not obtained, the assignments as *cis*-$PCl_4(NCO)_2^-$, *fac*-$PCl_3(NCO)_3^-$ and *cis*-$PCl_2(NCO)_4^-$ seem reasonable. The formation of all the members of the $PCl_{6-n}(NCO)_n^-$ series is difficult to rationalise as the addition of chloride ion to a single molecular species would be expected to give a single anion. It is possible that some disproportionation may

Table 6.1 Calculated and observed shifts for the $PCl_{6-n}(NCO)_n^-$ anions in CH_2Cl_2

Structure	Calculated shift		Observed
	A	B*	
PCl_6^-	-	297.1	298.2
PCl_5NCO^-	-	279.2	280.4
cis-$PCl_4(NCO)_2^-$	279.0	278.0	274.0
trans-$PCl_4(NCO)_2^-$	262.6	261.2	
fac-$PCl_3(NCO)_3^-$	294.1	293.4	290.0
mer-$PCl_3(NCO)_3^-$	277.6	276.7	
cis-$PCl_2(NCO)_4^-$	309.1	308.8	315.9
trans-$PCl_2(NCO)_4^-$	292.7	292.1	
$PCl(NCO)_5^-$	340.6	340.9	340.0
$P(NCO)_6^-$	-	389.6	388.4

* From least squares fit of observed data.

occur, giving both higher and lower cyanato-substituted anions, or alternatively the anion initially produced could react with the LiNCO (present from the PCl_5-LiNCO reaction), substituting further before reaction with Pe_4NCl.

Direct substitution by AgNCO into Pe_4NPCl_6 in CH_2Cl_2 led only to the slow formation of $POCl_3$ and $POCl_2(NCO)$. When LiNCO was used the reaction was slower still, giving the same products. The reaction was repeated in the presence of excess Pe_4NCl to suppress any dissociation to molecular species which may provide a route to decomposition. When AgNCO was added to a solution of Pe_4NPCl_6-Pe_4NCl in CH_2Cl_2 a mildly exothermic reaction occurred. The ^{31}P n.m.r. spectrum showed resonances due to $POCl_3$, $POCl_2(NCO)$ and $POCl(NCO)_2$, together with small peaks downfield from that of PCl_6^- at 204.7 and 195.1 ppm, presumably due to anionic species.

As PCl_6^- undergoes ligand exchange with $P(NCS)_3$ (Chapter 5 section iii), a corresponding reaction with $P(NCO)_3$ was attempted. When $P(NCO)_3$ was added to a solution of Pe_4NPCl_6 in CH_3NO_2 rapid ligand exchange occurred, producing PCl_3 and $PCl_2(NCO)$ with small quantities of $POCl_3$. A weak resonance at 282.0 ppm, assigned as $PCl_5(NCO)^-$, was also observed. The addition of $P(NCO)_3$ caused an increase in the intensity of the signals due to $POCl_3$ and $POCl_2(NCO)$, and $PCl_5(NCO)^-$ was no longer present, but a resonance at 203.6 ppm was apparent. Similarly if the reaction was carried out in CH_3CN resonances assignable to $PCl_{3-n}(NCO)_n$ ($0 \leqslant n \leqslant 3$) and $POCl_{3-n}(NCO)_n$ ($0 \leqslant n \leqslant 2$) were readily observed, together with resonances in the six-coordinate region at 197.4 and 162.0 ppm. The signals to lower field of PCl_6^- are presumably due to anionic species, clearly different from those seen previously. Linkage isomerism involving O- or N-bonded cyanate ligands would make two sets of isomers possible. The low values of chemical shifts for these compounds suggest bonding through oxygen, by comparison with the shifts of catechyl-containing anions (e.g. $CatPCl_4^-$ $\delta = 159$ ppm [74]).

Although rapid ligand exchange occurred, insufficient $P(NCO)_3$ could be added to the solution to effect complete exchange, if the signals of the six-coordinate species were to remain readily detectable. This problem was overcome by reacting PCl_3 with NaNCO in CH_3CN solution in the presence of Pe_4NPCl_6. PCl_3 reacts with NaNCO to yield the compounds $PCl_{3-n}(NCO)_n$ ($0 \leqslant n \leqslant 3$), which then exchange with PCl_6^- giving $PCl_{6-n}(OCN)_n^-$ and PCl_3, which reacts further with more NaNCO as shown in equations (3) and (4). This

$$PCl_3 \xrightarrow[CH_3CN]{NaNCO} PCl_{3-n}(NCO)_n \qquad \ldots (3)$$

$$PCl_{3-n}(NCO)_n + PCl_6^- \longrightarrow PCl_3 + PCl_{6-n}(OCN)_n \qquad \ldots (4)$$

procedure gave rise to several resonances in the 220 - 150 ppm region of the spectrum at 214.4, 203.6, 197.4, 172.5, 162.0, 156.4 and 150.9 ppm. The strongest resonances were seen at 9.8 and 27.5 ppm, assigned as $POCl_2(NCO)$ and $POCl(NCO)_2$ respectively, while other smaller signals were seen at -98.4 ($P(NCO)_3$), -111.3, -79.1 and 32.4 ppm which cannot be readily assigned to isocyanatophosphorus(III) or (V) compounds, and may possibly be O-bonded derivatives. Assignment of the peaks in the six-coordinate region is not easy On the assumption that the lowest field resonances are due to $P(OCN)_6^-$ and $PCl(OCN)_5^-$, values of 12.8 and 13.5 ppm are obtained for the OCN:OCN and OCN:Cl pairwise interaction terms respectively. The calculated shifts are shown in Table 6.2. The agreement between calculated and observed values is reasonable, but the non-observation of $PCl_5(OCN)^-$, even when excess PCl_6^- is present, is difficult to rationalise. It is possible that $PCl_5(OCN)^-$ is particularly unstable with respect to rearrangement or disproportionation. It is also interesting to note that both *cis*- and *trans*-isomers are found in this system.

The anions are not stable in solution, decomposition to phosphoryl derivatives being rapid and complete within one day.

Table 6.2 Calculated and observed shifts for $PCl_{6-n}(OCN)_n^-$ in CH_3CN

Structure	Calculated		Observed
	A	B†	
PCl_6^-	-	296.5	298.2
$PCl_5(OCN)^-$	253.2	252.0	-
cis-$PCl_4(OCN)_2^-$	218.4	218.7	214.4
trans-$PCl_4(OCN)_2^-$	207.6	207.6	203.6, 204.7*
fac-$PCl_3(OCN)_3^-$	194.1	194.0	197.4, 195.1*
mer-$PCl_3(OCN)_3^-$	183.4	183.7	-
cis-$PCl_2(OCN)_4^-$	169.9	170.1	172.5
trans-$PCl_2(OCN)_4^-$	159.2	159.8	162.0
$PCl(OCN)_5^-$	-	156.4	156.4
$P(OCN)_6^-$	-	153.1	150.9

† From least squares fit of observed data.

* From the Pe_4NPCl_6-Pe_4NCl-AgNCO system in CH_2Cl_2

iv Experimental

PCl_5-AgNCO 1:1 in CH_2Cl_2 PCl_5(0.084 g 0.40 mmole) was placed in an n.m.r. sample tube and dissolved in CH_2Cl_2. AgNCO (0.065 g 0.43 mmole) was added. Mole ratio 1:1.1.

PCl_5-AgNCO 1:4 in CH_2Cl_2 PCl_5(0.096 g 0.46 mmole) was placed in an n.m.r. sample tube with CH_2Cl_2 and AgNCO (0.254 g 1.69 mmole) was added. Mole ratio 1:3.7.

PCl_5-KNCO 1:4 in CH_3NO_2 PCl_5(7.40 g 35.5 mmole) and KNCO (11.51 g 162 mmole) were placed in a flask and CH_3NO_2 was added. The mixture was stirred under reflux under dry nitrogen for 5 hrs. Mole ratio 1:4.5.

Preparation of LiNCO $Li_2SO_4.H_2O$ and KNCO were dissolved in the minimum quantity of water with stirring and heating. A large volume of ethanol was added and the resulting precipitate filtered. The solution was evaporated and the crude product dried at 303K. Elemental analysis showed no potassium to be present. The solid was digested for 5 minutes with ethanol and the solution filtered and evaporated to give a white solid, an aqueous solution of which did not give a precipitate with $BaCl_2$ solution.

Analysis LiNCO	requires	C 24.5%	H -	N 28.6%	Li 14.3%
	found	C 24.4%	H -	N 30.8%	Li 13.5%

Solutions of $P(NCO)_3$ For reactions involving $P(NCO)_3$ and requiring a polar organic solvent such as CH_3CN or CH_3NO_2, a solution of PCl_3 in that solvent was treated with excess NaNCO[88]. The reaction was exothermic and no refluxing was necessary. The solution was filtered and used as such. In less polar media NaNCO does not react with PCl_3. To obtain solutions of $P(NCO)_3$ in solvents of lower polarity PCl_3 and NaNCO were reacted in SO_2[89]. When the reaction had proceeded to completion the SO_2 was allowed to evaporate and the solid-liquid residue was extracted with the required solvent. Stock solutions of $P(NCO)_3$ were stored at 243K to reduce the formation of polymers.

Preparation of HNCO and its reaction with PCl_5 HNCO was prepared by the method of Goring and Holm[90]. Dry HCl was passed down a vertical column which was tightly packed with NaNCO. The lower end of the column led directly to the reaction vessel containing the PCl_5. Exothermic reaction occurred as the HCl passed down the column and the colourless liquid HNCO was collected in the reaction vessel at 194K. The reaction mixture was then allowed to warm to 273K.

Chapter 7

The Preparation of Six-coordinate Phosphorus(V) Anions Containing Fluorine and Pseudohalides

i Introduction

The species that will be discussed in this chapter are $PF_{6-n}X_n^-$ ($0 \leqslant n \leqslant 6$; X = N_3, CN, NCS, NCO) and $PF_aCl_bX_c^-$ (a+b+c = 6; X = N_3, CN, NCS, NCO), which may be considered as being derived from the hexafluorophosphate ion and the mixed fluoro-chlorophosphate ions $PF_aCl_{6-a}^-$ respectively.

Several methods of preparation are potentially available for the synthesis of these compounds. By analogy with the corresponding formation of $PCl_{6-n}X_n^-$ species, direct substitution into the hexafluorophosphate ion might be envisaged as shown in equation (1) where X is the pseudohalide.

$$PF_6^- + MX \longrightarrow PF_{6-n}X_n^- + MF \qquad \ldots (1)$$

Similarly as ligand exchange reactions were rapid with PCl_6^- similar reactions could be expected with PF_6^-; two such examples are outlined in equations (2) and (3). Reactions according to equation (2) would be

$$PF_6^- + PX_6^- \longrightarrow PF_{6-n}X_n^- + PX_{6-n}F_n^- \qquad \ldots (2)$$

$$PF_6^- + PX_3 \longrightarrow PF_{6-n}X_n^- + PX_{3-n}F_n \qquad \ldots (3)$$

especially useful in giving information on low- and highly-fluorinated anions simultaneously, although the experiments would obviously be limited to cases where PX_6^- is known and readily prepared. Preparations according to equation (3) might be expected to be more generally applicable since PX_3 is known for all the pseudohalides considered. Another potentially useful synthetic route to PF_5X^- salts is by reaction of PF_5 with the corresponding tetraalkylammonium salt (equation (4)).

$$PF_5 + R_4NX \longrightarrow R_4NPF_5X \qquad \ldots (4)$$

There are many analogous reactions to those above involving fluoro-chlorophosphates which would be expected to give $PF_aCl_bX_c^-$ salts (a+b+c = 6; X = pseudohalide). Thus direct substitution would be expected to follow equation (5), assuming chloride is substituted

$$PF_aCl_{6-a}^- + MX \longrightarrow PF_aCl_bX_c^- + MCl \qquad \ldots (5)$$

preferentially to fluoride. This method relies on the availability of suitable $PF_aCl_{6-a}^-$ salts. Similarly ligand exchange reactions are also feasible. Direct substitution by a metal fluoride into a preformed $PCl_{6-n}X_n^-$ salt is also possible in principle, although limited in practice to the case where X = CN because of the instability of other chloro-pseudohalophosphates.

ii <u>Anions containing fluoride and azide ligands</u>

a. <u>Ligand exchange between PF_6^- and $P(N_3)_6^-$</u>

A solution containing $Pe_4NP(N_3)_6$ was prepared as described in Chapter 3. To this solution Pr_4NPF_6 was added and the ^{31}P n.m.r. spectrum was monitored at intervals to observe any ligand exchange. After 4 d a new doublet δ 167.3 ppm, J_{PF} 884 Hz was apparent in the spectrum. Two weeks after the commencement of the reaction this doublet had increased in concentration and a lower intensity triplet δ 158.5 ppm, J_{PF} = 851 Hz was also visible, as shown in Figure 7.1. After one month the ligand exchange reaction had proceeded no further and the only new species identified from this experiment are $PF(N_3)_5^-$ (δ 167.3 ppm) and $PF_2(N_3)_4^-$ (δ 158.5 ppm). The reaction was accompanied by small amounts of decomposition, the products of which gave broad resonances at 4.9 and 13.8 ppm. No splitting of the signal was observed for the peaks in this region which indicated that the decomposition products contain no fluorine. The $PF_5(N_3)^-$ anion should also be produced (equation (6)) but was not observed. This could be due to low intensity of the peaks caused by the

$$P(N_3)_6^- + PF_6^- \rightleftharpoons PF(N_3)_5^- + PF_5(N_3)^- \quad \ldots (6)$$

high multiplicity of the signal, or rapid decomposition (c.f. $PCl_5(N_3)^-$), although the apparent lack of F-containing decomposition products would argue against the latter possibility.

The pairwise interaction method can be used to calculate the chemical shifts of $PF_{6-n}(N_3)_n^-$ species where $2 \leqslant n \leqslant 5$ if the assignment of $PF(N_3)_5^-$ is taken as correct. This gives the $F:N_3$ term as 11.8 ppm. The F:F and $N_3:N_3$ terms have been previously evaluated using the least squares best fit method as 12.5[72] and 15.1 ppm respectively. The calculated shifts are shown in Table 7.1 and as can be seen, there is excellent agreement between experimental and calculated values for *cis*-$PF_2(N_3)_4^-$ and *fac*-$PF_3(N_3)_3^-$. The values calculated for $PF_4(N_3)_2^-$ and $PF_5(N_3)^-$ are all very close to the observed shift of PF_6^- (δ 145.1 ppm), and it is thus possible that the signals from $PF_5(N_3)^-$ expected in the PF_6^--$P(N_3)_6^-$ reaction are obscured by strong PF_6^- bands.

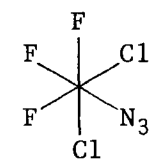
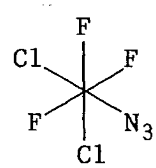
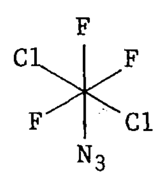
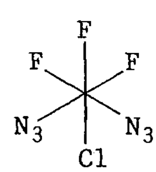
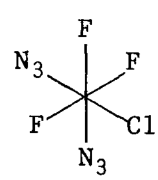
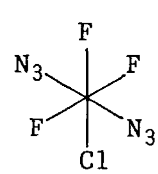
Table 7.1 Calculated shifts for $PF_{6-n}(N_3)_n^-$ series

ion	δ calculated	δ observed
cis-$PF_2(N_3)_4^-$	158.8	158.5
trans-$PF_2(N_3)_4^-$	154.8	
fac-$PF_3(N_3)_3^-$	152.1	151.2
mer-$PF_3(N_3)_3^-$	149.6	-
cis-$PF_4(N_3)_2^-$	146.6	-
trans-$PF_4(N_3)_2^-$	142.8	-
$PF_5(N_3)^-$	147.2	-

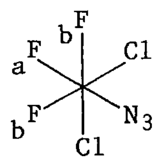
b. Direct substitution into the $PF_3Cl_3^-$ ions

The reaction of excess LiN_3 with a 3:1 mole ratio mixture of *fac*:*mer*-$PF_3Cl_3^-$ (see experimental section) gave rise to a 1:3:3:1 quartet δ 151.2 ppm, J_{PF} 822 Hz, readily assigned as *fac*-$PF_3(N_3)_3^-$. No doublet of triplets attributable to the *mer*-isomer could be detected. The addition of smaller amounts of azide to solutions of $Et_4NPF_3Cl_3$ or $Pe_4NPF_3Cl_3$ led to complex spectra. Resonances were observed which could be attributed to *fac*-PF_3Cl_3 (1:3:3:1 quartet δ 158.5 ppm, J_{PF} 960 Hz), *mer*-PF_3Cl_3 (doublet of triplets δ 142.7 ppm, J_{PF} 1081 and 970 Hz) with two additional doublets of triplets at δ 143.4 ppm J_{PF} 948, 855 Hz and δ 132.0 ppm J_{PF} 861 and 714 Hz. The use of the pairwise interaction method allows the calculation of all the anions $PF_xCl_y(N_3)_z^-$ (x+y+z = 6). For the case where x = 3 the results are shown in Table 7.2.

Table 7.2 Calculated shifts for $PF_3Cl_2(N_3)^-$ and $PF_3Cl(N_3)_2^-$

ion	structure	δ calculated	δ observed
		140.7	
$PF_3Cl_2(N_3)^-$		136.8	143.4
		119.8	
		138.6	
$PF_3Cl(N_3)_2^-$		134.7	132.0
		134.6	

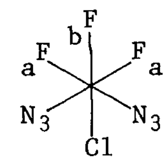
The calculated value for *fac*-$PF_3Cl_2(N_3)^-$ agrees moderately well with the observed value. The observation of this derivative of *fac*-$PF_3Cl_3^-$ is reasonable as this is the most abundant isomer present. Thus $PF_3Cl_2(N_3)^-$ is present as the isomer (I). The assignment to a particular isomer for $PF_3Cl(N_3)_2^-$ is less clear. Better agreement is obtained with the observed



J_{PF_a} 948 Hz

J_{PF_b} 855 Hz

(I)



J_{PF_a} 861 Hz

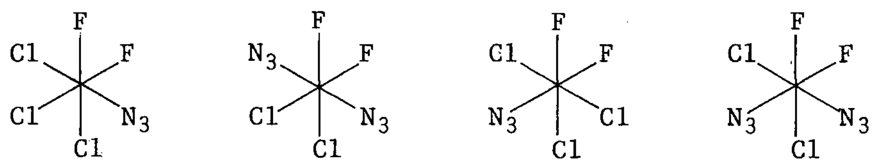
J_{PF_b} 714 Hz

(II)

value if assignment as an isomer derived from *mer*-$PF_3Cl_3^-$ is made. This, however, is difficult to rationalise on a chemical basis and assignment to (II) seems more likely. This mixed system was not stable; after one week an intense broad resonance due to decomposition products was present, centred at -0.9 ppm . P-F coupling would be expected if a route to decomposition analogous to that observed for chloro-azido systems, i.e. production of polymeric phosphazenes, were followed. No discernible splitting pattern occurred, and the resonance is not sufficiently broad to account for unresolved triplets. The normal coupling constant in cyclic phosphazenes is of the order of 900 Hz[66] which would necessitate a width of at least 80 ppm for the broad peak, whereas the absorption spans a range of only 40 ppm . Thus it must be concluded that polymeric phosphazenes of the type $(NPF_2)_n$ are not formed in the decomposition.

c. Direct substitution into the $PF_2Cl_4^-$ ion

The reaction between *cis*-$Et_4NPF_2Cl_4$ and LiN_3 was carried out in the presence of excess Pe_4NCl to suppress the dissociation of azido-containing anions into molecular forms. When excess LiN_3 was added to a solution of $Et_4NPF_2Cl_4$-Pe_4NCl in CH_2Cl_2, the ^{31}P n.m.r. spectrum showed a triplet δ 158.3, J_{PF} 853 Hz which is readily assigned to *cis*-$PF_2(N_3)_4^-$. When smaller quantities of the azide were used, two triplets downfield of that due to $PF_2Cl_4^-$ (δ 177.4, J_{PF} 1018 Hz) were observed at δ 161.7 ppm , J_{PF} 910 Hz and δ 149.3 ppm , J_{PF} 901 Hz. These can be reasonably assigned to $PF_2Cl_3(N_3)^-$ and $PF_2Cl_2(N_3)_2^-$. As the splitting pattern observed is a simple 1:2:1 triplet assignment to the specific isomers (III) and (IV) is unambiguous. Isomers of the type (V) and (VI) should give a doublet of

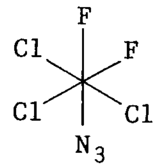
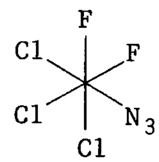
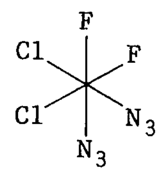
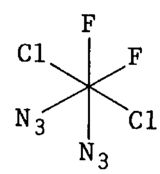
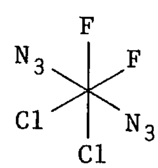
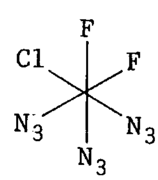
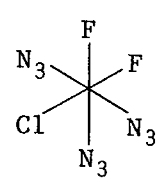


(III) (IV) (V) (VI)

doublets in the ^{31}P n.m.r. spectrum as the two fluorines are inequivalent. As noted previously, the chemical shifts for all possible isomers can be calculated by the use of pairwise interactions. The results for the $PF_2Cl_{4-n}(N_3)_n^-$ $(0 \leqslant n \leqslant 4)$ series are shown in Table 7.3. For $PF_2Cl_3(N_3)^-$ the best agreement with the observed value is for the isomer (III) as deduced from the P-F splitting pattern. The assignment of $PF_2Cl_2(N_3)_2^-$ as the isomer (IV) is ambiguous on the basis of pairwise interactions as the calculated shift for the isomer (VI) is closer to the observed shift. The P-F splitting, however, makes assignment certain. The possibility of the ions being fluxional (as is observed for some species) seems unlikely here as the $PF_3Cl_{3-n}(N_3)_n^-$ series are not, and results discussed later imply that fluxionality becomes more likely with an increase in the number of fluorine atoms. The non-observation of $PF_2Cl(N_3)_3^-$ could possibly be explained by its rapid reaction with further LiN_3 to give the fully-substituted $PF_2(N_3)_4^-$.

Decomposition, with evolution of N_2, occurred in this system. After two days strong resonances could be seen in the ^{31}P n.m.r. spectrum at -4.9, 12.2 and 34.0 ppm, and the peaks in the six-coordinate region of the spectrum were greatly reduced in intensity. The resonances at -4.9 and 34.0 ppm could be due to a doublet δ 14.6 ppm, J_{PF} 945 Hz possibly due to a (NPFCl) or (NPF(N_3)) unit in a polymeric phosphazene. No

Table 7.3 Calculated and observed shifts for $PF_2Cl_{4-n}(N_3)_n^-$ ions in CH_2Cl_2

ion	structure	δ calculated	δ observed
$PF_2Cl_3(N_3)^-$		148.3	161.7
		165.5	
$PF_2Cl_2(N_3)_2^-$		146.0	149.3
		128.7	
		145.8	
$PF_2Cl(N_3)_3^-$		143.7	-
		143.7	
$PF_2(N_3)_4^-$	one isomer	158.8	158.3

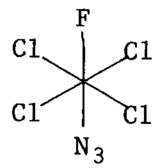
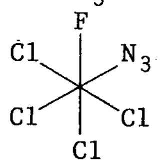
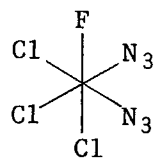
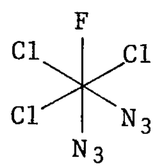
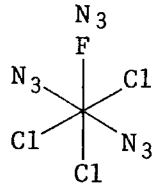
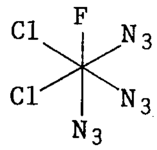
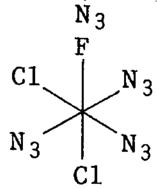
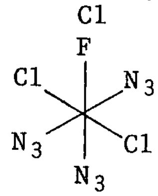
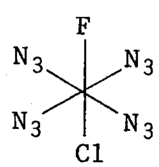
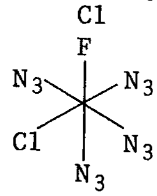
triplet structure due to an (NPF_2) unit could be observed.

d. Direct substitution into the $PFCl_5^-$ ion

Et_4NPFCl_5 is not particularly soluble in CH_2Cl_2 so CH_3NO_2 was used as the solvent for this compound. Treatment of an Et_4NPFCl_5-Pe_4NCl solution in CH_3NO_2 with LiN_3 led to the observation of several doublets downfield of that due to $PFCl_5^-$ (δ 233.2 ppm, J_{PF} 1054 Hz) at δ 193.9 ppm, J_{PF} 998 Hz, δ 169.5 ppm, J_{PF} 911 Hz, and δ 156.3 ppm, J_{PF} 882 Hz. Table 7.4 shows calculated and observed values for the isomers of the $PFCl_{5-n}(N_3)_n^-$ series. The addition of a large excess of LiN_3 to a solution of Et_4NPFCl_5-Pe_4NCl in CH_3NO_2 led to the observation of a doublet δ 168.3 ppm, J_{PF} 870 Hz which is readily assigned as $PF(N_3)_5^-$. As can be seen from Table 7.4 some definite assignments of structure can be made. In $PFCl_4(N_3)^-$ the calculated values clearly suggest that the azide ligand enters *cis*- to the fluorine. Similarly the second substitution places the azide ligand *cis*- to both fluorine and azide. In the case of $PFCl_2(N_3)_3^-$ it is not possible to say which of the isomers is formed. That with the *trans*-Cl configuration can be ruled out as its calculated chemical shift is too low, but the remaining two isomers have calculated shifts in good agreement with the observed value. Furthermore, both can be produced from the $PFCl_3(N_3)_2^-$ ion postulated above. $PFCl(N_3)_4^-$ is not observed. This may be due to rapid substitution to give $PF(N_3)_5^-$ or, since the calculated shifts are almost identical for both isomers and close to those of $PFCl_2(N_3)_3^-$, unambiguous identification of signals arising from this ion could be difficult.

Decomposition of these mixed species was again rapid. Within one day intense resonances were seen at -5.8, 13.8, 25.1 and 61.3 ppm, presumably due to phosphonitrilic derivatives. The higher field resonances of these decomposition products are presumably due to branches caused by

Table 7.4 Calculated and observed shifts for the $PFCl_{5-n}(N_3)_n^-$ series $(0 \leqslant n \leqslant 5)$

ion	structure	δ calculated	δ observed
$PFCl_4(N_3)^-$		176.8	193.9
		194.0	
$PFCl_3(N_3)_2^-$		174.5	169.5
		157.3	
		157.2	
$PFCl_2(N_3)_3^-$		155.1	156.3
		155.0	
		137.8	
$PFCl(N_3)_4^-$		152.8	-
		152.9	
$PF(N_3)_5^-$	one isomer		168.3

P-F splitting, the 25.1 and 61.3 ppm peaks could be due to a (NPFCl) or ($NPF(N_3)$) unit δ 43.2 ppm, J_{PF} 879 Hz although the chemical shift is possibly rather high[66].

iii Anions containing fluoride and cyanide ligands

a. Attempts to prepare $PF_{6-n}(CN)_n^-$ species ($0 \leqslant n \leqslant 6$)

1. Direct substitution into hexafluorophosphates

Pr_4NPF_6 did not react with AgCN or LiCN in any of the common solvents. This is presumably due to the strength of the P-F bond.

2. Ligand exchange reactions with the hexafluorophosphate ion

When $P(CN)_3$ was added to Pr_4NPF_6 in CH_2Cl_2 the solution gradually turned dark red. After 3 d the ^{31}P n.m.r. spectrum showed in addition to PF_6^- (δ 145.1 ppm, J_{PF} 718 Hz) a quartet δ -104.8 ppm, J_{PF} 1409 Hz (PF_3), a triplet δ -62.9 ppm, J_{PF} 1290 Hz, presumably $PF_2(CN)$, a doublet δ 66.9 ppm, J_{PF} 1370 Hz assigned as $PF(CN)_2$ and a resonance at 137.1 ppm due to $P(CN)_3$. No discrete resonances were seen which could be assigned to $PF_5(CN)^-$, but its presence was inferred by the intensities of the branches of the PF_6^- signal which did not show the expected intensity ratio. Presumably the bands due to $PF_5(CN)^-$ coincide with those of PF_6^- and are difficult to resolve. The shift of the resonance ascribed to $PF_2(CN)$ differs considerably from the literature value of -140.8 ppm, J_{PF} 1273 Hz [6], although better agreement is obtained with the coupling constant.

b. Attempts to prepare specific members of the $PF_{6-n}(CN)_n^-$ series ($0 \leqslant n \leqslant 6$)

1. $PF_5(CN)^-$

When PF_5 was passed directly into a solution of Et_4NCN in CH_2Cl_2 at 243K reaction occurred, giving a red solution. The compound was isolated as a dark red solid. The ^{31}P n.m.r. of a solution in CH_2Cl_2 showed a 1:5:10:10:5:1 sextet, δ 157.7 ppm, J_{PF} 744 Hz and not the doublet of quintets expected. This implies that the $PF_5(CN)^-$ ion is fluxional on the n.m.r. timescale, making both types of F atom equivalent.

2. $\underline{PF_4(CN)_2^-}$

The isomers of $PF_4(CN)_2^-$ were identified by reaction of the isomeric mixture of $PCl_4(CN)_2^-$ (Chapter 4) with AgF in CH_2Cl_2. The observation of the intermediate species was not possible owing to low intensity and rapid substitution to give the more fluorinated species. The ^{31}P n.m.r. spectrum of the solution showed PF_6^- (δ 145.1 ppm, J_{PF} 714 Hz), together with two 1:4:6:4:1 quintets δ 183.8 ppm, J_{PF} 753 Hz and δ 172.6 ppm, J_{PF} 741 Hz, assigned as *cis*-$PF_4(CN)_2^-$ and *trans*-$PF_4(CN)_2^-$ respectively on the basis of their intensity ratio compared with the *cis*:*trans* ratio in the starting material. In addition to the resonances in the six-coordinate region, an intense triplet δ 15.6 ppm, J_{PF} 961 Hz was observed and is presumably due to some molecular species formed by decomposition of the anions. The observation of a simple multiplet for *cis*-$PF_4(CN)_2^-$ indicates that this ion is fluxional; a triplet of triplets would be expected otherwise as observed for *cis*-$PF_4Cl_2^-$ [72].

Prediction of the chemical shifts of the $PF_{6-n}(CN)_n^-$ series is possible by pairwise interactions if the above assignments are taken as correct. The F:F term is derived as 12.1 ppm (from the shift of PF_6^-) and F:CN as 15.2 ppm (from $PF_5(CN)^-$), which then gives a calculated shift for *trans*-$PF_4(CN)_2^-$ as 170.0 ppm, in good agreement with the experimental result. From the shift of *cis*-$PF_4(CN)_2^-$ (δ 183.8 ppm) the CN:CN term is evaluated as 32.1 ppm. The values calculated on this basis for other members of the series are shown in column A of Table 7.5.

Table 7.5 Calculated and observed shifts for $PF_{6-n}(CN)_n^-$ ions ($0 \leq n \leq 6$)

ion	A	B	observed	J_{PF} Hz
PF_6^-	-	144.6	145.1	714
$PF_5(CN)^-$	-	158.4	157.7	744
cis-$PF_4(CN)_2^-$	-	184.3	183.8	753
trans-$PF_4(CN)_2^-$	170.0	172.1	172.6, 170.9*	741, 746*
fac-$PF_3(CN)_3^-$	223.8	222.4	225.5	744
mer-$PF_3(CN)_3^-$	210.0	210.2	210.5	780, 684
cis-$PF_2(CN)_4^-$	268.3	260.5	-	-
trans-$PF_2(CN)_4^-$	250.0	248.4	250.7	853
$PF(CN)_5^-$	317.6	310.8	-	-
$P(CN)_6^-$	385.2	373.3	-	-

* From the $PF_3Cl_3^-$-$P(CN)_3$ reaction

3. $PF_3(CN)_3^-$

The reaction of the isomeric mixture (ca. 3:1 *fac:mer*) of $Et_4NPF_3Cl_3$ with $P(CN)_3$ in CH_2Cl_2 led to rapid Cl-CN ligand exchange, giving PCl_3 (δ -217.7 ppm) and a complex spectrum in the six-coordinate region. The solution was evaporated under vacuum to remove the PCl_3, and the remaining dark red solid redissolved in CH_2Cl_2. (The presence of PCl_3 in solution would hamper the observation of the six-coordinate region over the narrow range required as its signal would be reflected back into the spectrum.) The spectrum was thus re-examined and showed a doublet of triplets δ 210.5 ppm, J_{PF} 780 Hz (triplet) and 684 Hz (doublet), two 1:4:6:4:1 quintets δ 170.9 ppm, J_{PF} 746 Hz (*trans*-$PF_4(CN)_2^-$) and δ 185.0 ppm, J_{PF} 724 Hz (*cis*-$PF_4(CN)_2^-$), a triplet δ 250.7 ppm, J_{PF} 853 Hz,

$P(CN)_3$, and other lower intensity resonances which are not readily assignable (Figure 7.2). The doublet of triplets is assigned as *mer*-$PF_3(CN)_3^-$, the observed shift giving excellent agreement with the calculated value. Similarly the triplet at δ 250.7 ppm is assigned as *trans*-$PF_2(CN)_4^-$. The presence of PF_4- and PF_2-containing anions can be rationalised by equation (7). This cannot, however, explain the relative

$$2PF_3(CN)_3^- \rightleftharpoons PF_4(CN)_2^- + PF_2(CN)_4^- \qquad \ldots (7)$$

intensities of these two ions, the $PF_4(CN)_2^-$ being much more intense. The possibility of some decomposition of $PF_2(CN)_4^-$, as shown in equations (8) and (9), could give rise to fluoride ion in solution which could

$$PF_2(CN)_4^- \longrightarrow P(CN)_3 + FCN + F^- \qquad \ldots (8)$$

$$PF_2(CN)_4^- \longrightarrow PF(CN)_2 + (CN)_2 + F^- \qquad \ldots (9)$$

react with the $PF_3(CN)_3^-$ to yield the observed product.

The ^{19}F n.m.r. spectrum of the solution showed an intense doublet at δ 31.6 ppm, J_{PF} 742 Hz assigned to *trans*-$PF_4(CN)_2^-$, a doublet of triplets δ 9.6 ppm, J_{PF} 781 Hz, J_{FF} 34 Hz and a doublet of doublets δ 40.8 ppm, J_{PF} 684 Hz, J_{FF} 34 Hz in a 1:2 intensity ratio which are entirely consistent with the proposed *mer*-$PF_3(CN)_3^-$, and a lower intensity doublet at δ 41.2 ppm, J_{PF} 742 Hz assigned as *cis*-$PF_4(CN)_2^-$. In addition to these other lower intensity signals were observed which could not be readily assigned.

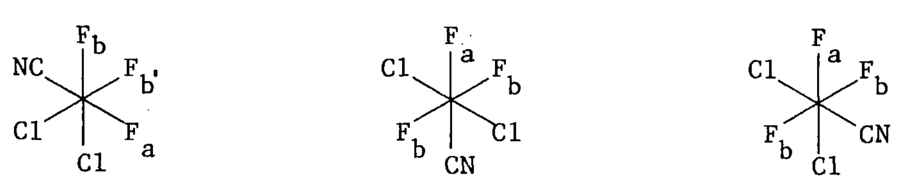
From these data better values for the pairwise interaction parameters were obtained by using the least squares method. This gave values of F:F = 12.05, F:CN = 15.49 and CN:CN = 31.11 ppm and the recalculated shifts for the entire series are shown in column B of Table 7.5.

The reaction of $Et_4NPF_3Cl_3$ with AgCN or LiCN did not give $PF_3(CN)_3^-$ ions (these reactions will be discussed in section iii part d). The reaction of $Pr_4NP(CN)_3Br$ with SF_4 in CH_2Cl_2 produced PF_6^- and *fac*-$PF_3(CN)_3^-$, however, the ^{31}P n.m.r. spectrum showing a 1:6:15:20:15:6:1 septet δ 145.1 J_{PF} 716 Hz readily assigned to PF_6^-, and a 1:3:3:1 quartet δ 225.5 ppm, J_{PF} 744 Hz which is attributed to *fac*-$PF_3(CN)_3^-$, the experimental value agreeing well with that calculated from pairwise interactions.

c. The preparation of $Et_4NPF_3Cl_2(CN)$

PF_3Cl_2 was condensed into a solution of Et_4NCN in CH_2Cl_2. The product was isolated as a dark red solid. The ^{31}P n.m.r. spectrum was complex, showing a doublet of triplets δ 180.0 ppm, J_{PF} 1017 Hz (doublet) and 814 Hz (triplet), a lower intensity doublet of triplets δ 167.2 ppm, J_{PF} 832 Hz (doublet) and 932 Hz (triplet), and a 1:3:3:1 quartet δ 168.5 ppm, J_{PF} 930 Hz, as shown in Figure 7.3.

The shifts of the possible isomers of $PF_3Cl_2(CN)^-$ may be evaluated if the Cl:CN term obtained from $PCl_5(CN)^-$ is used, other pairwise interaction parameters being transferred from the $PF_{6-n}Cl_n^-$ [72] and $PF_{6-n}(CN)_n^-$ series. Of the three possible isomers, (I) gives good agreement with the observed



(I) δ 180.4 ppm

(II) δ 164.0 ppm

(III) δ 159.5 ppm

chemical shift of 180.0 ppm. The remaining two shifts both agree reasonably with the calculated value for (II) and definite assignment is not possible.

The appearance of a quartet is difficult to rationalise for any of the above ions, and it must be assumed that one of them is fluxional, although it is impossible to say which. The ^{19}F n.m.r. showed a doublet of doublets δ 16.8 ppm, J_{PF} 810 Hz, J_{FF} 90 Hz and what appeared to be a doublet of triplets δ -14.0 ppm, J_{PF} 1015 Hz, J_{FF} 90 Hz. A closer inspection of the 'doublet of triplets' revealed that the centre band of each triplet comprised two closely spaced lines, thus each 'triplet' is really a doublet of doublets. The revised values for the F F couplings are J_{FF} 88 and 92 Hz. These data are consistent with the structure (I), where some distortion may occur making the F-atoms *trans* to Cl inequivalent. No corresponding splitting could be seen in the doublet of doublets although some unresolved fine structure was present. Other features present in the ^{19}F n.m.r. spectrum were a doublet δ -16.2 ppm, J_{PF} 940 Hz, corresponding to the quartet in the ^{31}P n.m.r. spectrum and confirming the presence of a fluxional ion, and a doublet of doublets δ -27.3 ppm, J_{PF} 925 Hz, J_{FF} 65 Hz with a doublet of triplets δ 6.8 ppm, J_{PF} 835 Hz, J_{FF} 65 Hz which corresponds to the doublet of triplets at δ 167.2 ppm in the ^{31}P n.m.r. spectrum.

The data can be summarised as

(I) δ ^{31}P 180.0 ppm, J_{PF_a} 1017 Hz, J_{PF_b} 814 Hz; δ ^{19}F -13.7 ppm (F_a), J_{PF_a} 1015 Hz, $J_{F_aF_b}$ 88Hz, $J_{F_aF_{b'}}$ 92 Hz; 16.8 ppm (F_b), J_{PF_b} 810 Hz, $J_{F_aF_b}$ 90 Hz.

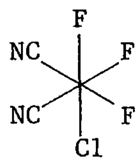
(II) or (III) δ ^{31}P 167.2 ppm, J_{PF_a} 837 Hz, J_{PF_b} 932 Hz; δ ^{19}F 6.8 ppm (F_a) J_{PF_a} 835 Hz, J_{FF} 65 Hz; -27.3 ppm (F_b) J_{PF_b} 925 Hz.

d. Direct substitution into $PF_3Cl_3^-$ ions

The reaction of $Et_4NPF_3Cl_3$ with AgCN in CH_2Cl_2 led to a complex ^{31}P n.m.r. spectrum, including a doublet of triplets at δ 190.5 ppm, J_{PF} 895 Hz (doublet) and 792 Hz (triplet) which is assigned as an isomer of $PF_3Cl(CN)_2^-$. Many other resonances were seen in the six-coordinate region of the spectrum which could not be assigned. When LiCN was used the reaction seemed much cleaner. The ^{31}P n.m.r. spectrum showed doublets of triplets at 180.0 ppm, J_{PF} 1017 Hz (doublet), 808 Hz (triplet), (assigned as $PF_3Cl_2(CN)^-$) and δ 190.5 ppm, J_{PF} 896 Hz (doublet) and 794 Hz (triplet). The use of excess LiCN gave rise to the doublet of triplets at 190.5 ppm. As this shift is considerably different from those observed for the $PF_3(CN)_3^-$ ions, assignment as $PF_3Cl(CN)_2^-$ seems reasonable. The crude material was isolated as a dark red-brown solid, elemental analysis of which indicates that the above formula is correct, although the compound is obviously not pure.

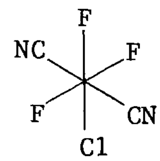
$Et_4NPF_3Cl(CN)_2$	requires	C 39.28%	H 6.55%	N 13.75%
	found	C 38.13%	H 7.54%	N 14.47%
$Et_4NPF_3(CN)_3$	requires	C 44.59%	H 6.76%	N 18.92%

Insufficient material was available for P and Cl analyses. The possible isomers for this ion are (IV), (V) and (VI), all of which would be expected to exhibit a doublet of triplets in the ^{31}P n.m.r. spectrum. As has been seen in the $PCl_{6-n}(CN)_n^-$ system, pairwise additivity appears to break down, presumably due to the presence of both Cl and CN groups (note the good agreement found for the $PF_{6-n}(CN)_n^-$ series). Thus the



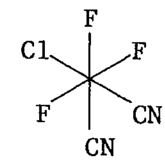
(IV)

δ calculated 201.5 ppm



(V)

δ calculated 189.1 ppm



(VI)

δ calculated 185.1 ppm

calculated chemical shifts cannot be expected to give reliable results for anions containing Cl and CN ligands. Although the calculated shifts for $PF_3Cl_2(CN)^-$ agree well with the observed values, the deviations from pairwise additivity may well increase with the number of cyanide groups present. On the basis of the best agreement with the calculated shift assignment as (V) would be reasonable, but since *fac*-$PF_3Cl_3^-$ is three times more abundant than the *mer*-isomer in the starting material (see experimental section) a facial arrangement of fluorine atoms would be expected in the product. Thus $PF_3Cl(CN)_2^-$ is assigned as (IV). One third of the $PF_3Cl_3^-$ was originally present as the *mer*-isomer and this still remains unaccounted for. Obviously *mer*-$PF_3Cl_3^-$ reacts with LiCN but no resonances were observed which could be assigned as its derivatives. This may be due to either insolubility or isomerisation to a facial arrangement of fluorine atoms. The observation of *fac*-$PF_3Cl_2(CN)^-$ at δ 180.0 ppm in this reaction indicates that the facial arrangement of fluorine atoms is maintained during the substitution reaction, thus the second substitution would not be expected to form a meridial isomer.

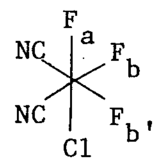
$Pe_4NPF_3Cl_3$ reacted in an identical manner with excess LiCN in CH_2Cl_2, giving a ^{31}P n.m.r. spectrum which showed a doublet of triplets at δ 190.4 ppm, J_{PF} 896 Hz (doublet) and 793 Hz (triplet). The ^{19}F n.m.r. of this compound showed evidence of similar distortions to those deduced for $PF_3Cl_2(CN)^-$. The pattern observed is consistent with all three fluorine atoms being inequivalent, although two are only slightly so. The splitting pattern expected for such a situation is shown in Figure 7.4 and this is observed in the ^{19}F n.m.r. spectrum, the data for which is

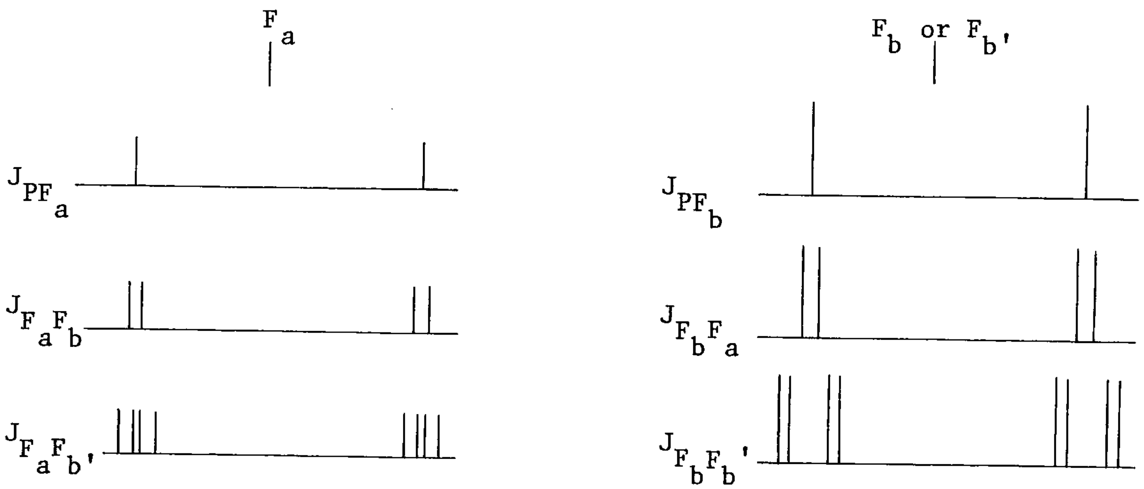
$\delta(F_a)$ -1.9 ppm, J_{PF_a} 900 Hz, $J_{F_aF_b}$ 66 Hz, $J_{F_aF_{b'}}$ 76 Hz. Overall intensity 1.

$\delta(F_{bb'})$ 8.7 ppm, J_{PF_b} 790 Hz, $J_{F_aF_b}$ 66 Hz, $J_{F_{b'}F_a}$ 75 Hz, $J_{F_bF_{b'}}$ 5 Hz. Overall intensity 2.

Figure 7.4

Splitting pattern for $PF_3Cl(CN)_2^-$ in the ^{19}F n.m.r. spectrum





Intensity 1

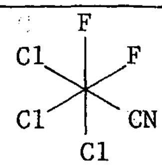
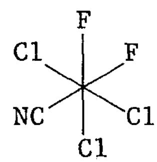
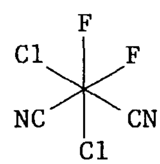
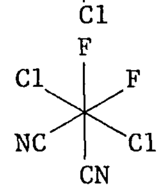
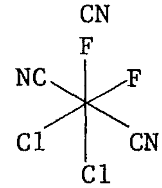
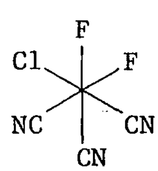
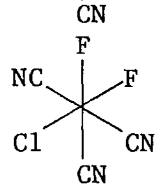
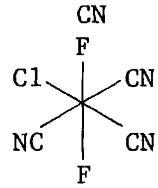
Intensity 2

e. Direct substitution into the *cis*-$PF_2Cl_4^-$ ion

The reaction of $Et_4NPF_2Cl_4$ with AgCN in CH_2Cl_2 showed initially the formation of a triplet and a doublet of doublets of approximately equal intensity in the ^{31}P n.m.r. spectrum, at δ 200.7 ppm, J_{PF} 989 Hz (triplet) and δ 201.3 ppm, J_{PF} 1009 and 752 Hz (doublet of doublets), in addition to unreacted starting material. These can be readily assigned as isomers VII and VIII of $PF_2Cl_3(CN)^-$, and the splitting pattern allows unambiguous assignment as shown in Table 7.6, which also shows the calculated chemical shifts. Further reaction of the solution with more AgCN caused the appearance of a new doublet of doublets δ 227.7 ppm, J_{PF} 761 and 978 Hz which can be assigned to the isomer (IX) of $PF_2Cl_2(CN)_2^-$. Also present in the spectrum were a lower intensity triplet δ 228.7 ppm, J_{PF} 726 Hz and a doublet of doublets δ 236.8 ppm, J_{PF} 707 and 867 Hz of lower intensity still. These two resonances increased in intensity with a corresponding decrease in the intensity of the signal from (IX) and are thus assigned as the isomers of $PF_2Cl(CN)_3^-$ (XII) and (XIII). The assignment of the doublet of doublets as (XIII) is unambiguous since in this system only three species giving such a splitting pattern are possible, two of which have been assigned earlier. In the presence of excess AgCN the spectrum showed an intense triplet δ 228.7 ppm, J_{PF} 726 Hz assigned as (XII) and a lower intensity triplet δ 234.4 ppm, J_{PF} 666 Hz. This spectrum showed no change over several weeks. The non-observation of the isomers (X) and (XI) of $PF_2Cl_2(CN)_2^-$, where both could be formed from (VIII) and (VII) respectively, implies a marked relative stability of the isomer (IX). The formation of (XI) would necessitate substitution of a Cl *trans* to CN which seems to be an unfavourable (although not impossible) route, c.f. the ratios of *cis*:*trans* $PCl_4(CN)_2^-$ in the PCl_6^--AgCN system.

The assignment of the triplet at δ 234.4 ppm is not easy. The observed chemical shift does not agree with the calculated value for *cis*-$PF_2(CN)_4^-$, which is expected to give good agreement with the experimental

Table 7.6 Calculated and observed shifts for $PF_2Cl_{4-n}(CN)_n^-$ ions in CH_2Cl_2 $(0 \leqslant n \leqslant 4)$

ion	structure		appearance of spectrum	δ calculated	δ observed	J_{PF} Hz
$PF_2Cl_3(CN)^-$		VII	triplet	205.6	200.7	989
		VIII	doublet of doublets	201.1	201.3	1009 752
$PF_2Cl_2(CN)_2^-$		IX	doublet of doublets	222.2	227.7	761 978
		X	triplet	217.8	-	
		XI	triplet	226.2	-	
$PF_2Cl(CN)_3^-$		XII	triplet	239.2	228.7	726
		XIII	doublet of doublets	243.3	236.8	707 867
		XIIIa	triplet	226.9	234.4	666
cis-$PF_2(CN)_4^-$	one isomer		triplet	260.7	-	-

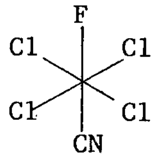
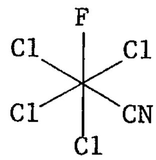
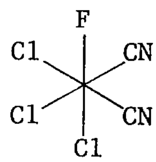
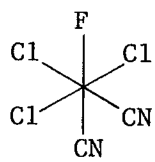
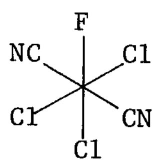
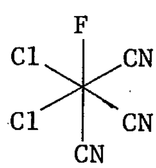
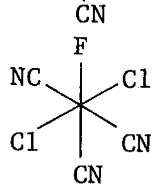
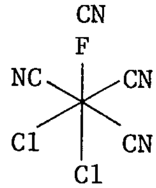
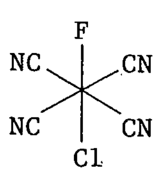
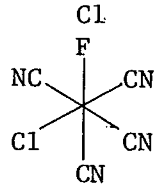
value since the shifts for the $PF_{6-n}(CN)_n^-$ series obey the pairwise rule well. The observation that the doublet of doublets due to (XIII) is not present in the final spectrum indicates that some may be removed either by further substitution (which seems unlikely) or by isomerisation to either (XII) or (XIIIa). Thus the triplet at 234.4 ppm could be due to the latter ion.

f. Direct substitution into the $PFCl_5^-$ ion

Although Et_4NPFCl_5 is not particularly soluble in CH_2Cl_2 the reaction of a slurry with AgCN produced compounds which are, in a similar manner to the Et_4NPCl_6-AgCN reaction. Thus the reaction of varying amounts of AgCN with Et_4NPFCl_5 in CH_2Cl_2 led to the observation of a number of doublets upfield from that of the $PFCl_5^-$ ion (δ 233.2 ppm, J_{PF} 1054 Hz) at δ 243.1 ppm, J_{PF} 1193 Hz, δ 244.4 ppm, J_{PF} 964 Hz, δ 258.7 ppm, J_{PF} 789 Hz, δ 268.7 ppm, J_{PF} 811 Hz, δ 269.3 ppm, J_{PF} 1035 Hz, δ 284.0 ppm, J_{PF} 704 Hz, and δ 291.6 ppm, J_{PF} 918 Hz. The calculated shifts and tentative assignments are shown in Table 7.7. The reaction of excess AgCN with Et_4NPFCl_5 gave rise to two doublets δ 284.0 ppm, J_{PF} 704 Hz and δ 291.6 ppm, J_{PF} 918 Hz, the latter having the lower intensity.

As can be seen from the table the assignment of structures, and even formulae in some cases, is not straightforward. It seems reasonable to suppose that the most intense resonances produced are due to the predominant isomers of different species. On this basis the doublets at δ 244.4 ppm, 268.7 ppm, and 284 ppm are assigned as $PFCl_4(CN)^-$, $PFCl_3(CN)_2^-$ and $PFCl_2(CN)_3^-$ respectively. On the assumption that pairwise additivity holds for anions containing one CN group, assignments of the isomers of $PFCl_4(CN)^-$ can be made as shown in Table 7.7, the predominant isomer having the *cis*-F-CN configuration. Further support for the assignment of (XV) rather than (XIV) as the predominant isomer for $PFCl_4(CN)^-$ is

Table 7.7 Calculated and observed shifts for $PFCl_{5-n}(CN)_n^-$ ions ($0 \leqslant n \leqslant 5$) in CH_2Cl_2

ion	structure	δ calculated	δ observed	J_{PF} Hz
$PFCl_4(CN)^-$	 XIV	242.7	243.1	1193
	 XV	247.1	244.4*	964
$PFCl_3(CN)_2^-$	 XVI	263.8	268.7*	811
	 XVII	259.3	258.7	789
	 XVIII	263.4	269.3	1035
$PFCl_2(CN)_3^-$	 XIX	276.4	284.0*	704
	 XX	276.2	-	
	 XXI	280.4	291.6	918
$PFCl(CN)_4^-$	 XXII	297.4	-	-
	 XXIII	293.4	-	-
$PF(CN)_5^-$	one isomer	310.8	-	-

* denotes most abundant isomer in solution

provided by the deduction that (XIV) should give only (XVII) on further substitution; the data in Table 7.7 indicate that (XVII) is not the predominant isomer for $PFCl_3(CN)_2^-$.

The predominant isomer of $PFCl_3(CN)_2^-$ would hence be expected to be derived from (XV), and all the possible isomers satisfy this criterion. From the previous discussion the isomer with a *cis* CN-CN arrangement is expected to be preferred, thus the predominant $PFCl_3(CN)_2^-$ isomer is assigned as (XVI). From the same reasoning (XIX) is expected to be the most abundant form of $PFCl_2(CN)_3^-$.

The shifts of 258.7 and 269.3 ppm are assigned as isomers of $PFCl_3(CN)_2^-$, as shown in Table 7.7. The structural assignments are tentative as they are based on the calculated values. The assignment of the doublet at 291.6 ppm as (XXI) seems reasonable by analogy with the corresponding PCl_6^--AgCN reaction where predominantly *fac*- with a small amount of *mer*-isomer was produced.

g. Reactions involving the $PCl_3(CN)_3^-$ ion

The ligand exchange reaction between Pr_4NPF_6 and $Et_4NPCl_3(CN)_3$ was very slow in CH_2Cl_2. After one month two additional low intensity doublets were seen in the six-coordinate region of the spectrum at δ 288.3 ppm, J_{PF} 901 Hz (stronger) and δ 283.9 ppm, J_{PF} 690 Hz (weaker). PF_6^- and $PCl_3(CN)_3^-$ were the major species present. The observed shifts and coupling constants agree fairly well with those observed in the $PFCl_5^-$-AgCN reaction where species giving δ 284.0 ppm, J_{PF} 704 Hz and δ 291.6 ppm, J_{PF} 918 Hz were observed. It is interesting to note that the predominant isomer of $PFCl_2(CN)_3^-$ from ligand exchange was not the most abundant isomer from the direct substitution reaction.

Attempted direct substitution of *fac*-$Et_4NPCl_3(CN)_3$ by AgF in CH_2Cl_2 led to a complex ^{31}P n.m.r. spectrum which showed the presence of a doublet δ 263.1 ppm, J_{PF} 840 Hz and a more intense triplet δ 250.6 ppm, J_{PF} 843 Hz, with many unassigned resonances to slightly lower field from more highly fluorinated species. The chemical shift and coupling constant of the intense triplet are in good agreement with those previously observed for *trans*-$PF_2(CN)_4^-$, which indicates that some ligand exchange may well be occurring. The doublet at δ 263.1 ppm cannot be readily assigned; although it must clearly belong to the $PFCl_{5-n}(CN)_n^-$ series it was not observed in the $PFCl_5^-$-AgCN reaction. The only isomer not observed in that reaction, (XX), has a meridial arrangement of CN ligands which might not be expected from *fac*-$PCl_3(CN)_3^-$. Since the reaction is obviously more complicated than a simple substitution process the formation of (XX) might be possible, particularly since the identified product is *trans*-$PF_2(CN)_4^-$.

iv <u>Anions containing fluorine and thiocyanate ligands</u>

a. <u>Ligand exchange between PF_6^- and $P(NCS)_6^-$</u>

The solution of $Pe_4NP(NCS)_6$ was prepared by the method of Chapter 5. To this solution Pr_4NPF_6 was added. The ^{31}P n.m.r. spectrum run immediately on mixing showed a new doublet downfield of the resonance due to $P(NCS)_6^-$ (δ 261.9 ppm) at δ 233.6 ppm, J_{PF} 735 Hz which is readily assigned as $PF(NCS)_5^-$. After 1 d several peaks were seen to lower field of the PF_6^- branches, presumably due to $PF_5(NCS)^-$, together with two branches of a triplet δ 209.5 ppm, J_{PF} 760 Hz assigned as $PF_2(NCS)_4^-$. Later spectra resolved the resonances to lower field of the PF_6^- peaks as a sextet δ 154.2 ppm, J_{PF} 735 Hz which can be assigned as $PF_5(NCS)^-$, assuming that the ion has the same fluxional nature as observed for $PF_5(CN)^-$. A typical spectrum from this reaction is shown in Figure 7.5.

From the shifts of PF_6^-, $P(NCS)_6^-$ and $PF_5(NCS)^-$ it is possible to calculate the shifts for the $PF_{6-n}(NCS)_n^-$ series. These results are shown in column A of Table 7.8, together with the observed values and coupling constants (obtained later) and the least squares best fit chemical shifts in column B.

Table 7.8 Calculated and observed shifts for $PF_{6-n}(NCS)_n^-$ $0 \leqslant n \leqslant 6$

ion	calculated A	calculated B	observed	J_{PF}
$P(NCS)_6^-$	-	261.2	261.9	-
$PF(NCS)_5^-$	-	232.9	233.6	741
cis-$PF_2(NCS)_4^-$	209.3	209.0	209.5	760
trans-$PF_2(NCS)_4^-$	204.8	204.5	-	-
fac-$PF_3(NCS)_3^-$	189.9	189.7	185.6	732
mer-$PF_3(NCS)_3^-$	185.4	185.2	-	-
cis-$PF_4(NCS)_2^-$	170.5	170.4	173.3	724
trans-$PF_4(NCS)_2^-$	166.0	165.9	-	-
$PF_5(NCS)^-$	155.6	155.6	154.2	735
PF_6^-	-	145.3	145.1	718

The reaction was maintained at 253K to prevent significant decomposition of the $P(NCS)_6^-$ ion, but some decomposition products were observed, giving resonances at 7.3, 42.7, 48.4 and 58.9 ppm, the latter possibly being caused by $PO(NCS)_3$ hydrolysis product.

b. Attempts to prepare specific members of the $PF_{6-n}(NCS)_n^-$ series ($0 < n < 6$

1. $PF_5(NCS)^-$

This was prepared by treating a solution of Et_4NNCS with PF_5. The resulting solution ^{31}P n.m.r. showed a 1:5:10:10:5:1 sextet δ 154.2 ppm, J_{PF} 735 Hz which confirms the presence of the $PF_5(NCS)^-$ ion in solution in the PF_6^--$P(NCS)_6^-$ reaction. The compound is unstable as a solid even at 243K. The infrared spectrum of a freshly prepared sample showed a strong absorption at 2100 cm^{-1}, whilst after two weeks of storage at 243K this band was totally absent. After standing in solution for one month the ^{31}P n.m.r. spectrum of the product clearly showed the presence of PF_6^- in addition to PF_5NCS^-.

2. $PF_4(NCS)_2^-$

This species was not readily observed in the PF_6^--$P(NCS)_6^-$ exchange reaction and as $PF_4Cl_2^-$ salts were not available an attempt to identify this species by ligand exchange reaction between PF_6^- and $PF_3(NCS)_3^-$ (see part 3) was attempted. The ^{31}P n.m.r. spectrum resulting from this mixture comprised a complex series of broad absorptions containing unresolved fine structure. On the basis of known shifts and intensity ratios of various branches of PF_6^-, $PF_5(NCS)^-$ and $PF_3(NCS)_3^-$ the presence of $PF_4(NCS)_2^-$ could be inferred and its chemical shift and coupling constant tentatively assigned values of δ 173.3 ppm, J_{PF} 724 Hz on the assumption that the ion exhibits a 1:4:6:4:1 quintet in the ^{31}P n.m.r. spectrum.

3. $PF_3(NCS)_3^-$

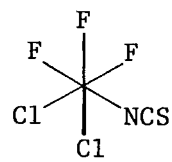
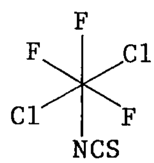
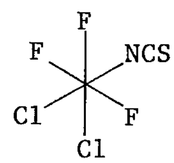
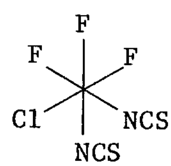
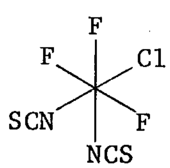
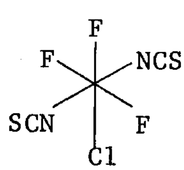
Addition of an excess of AgNCS or NH_4NCS to a solution of $Et_4NPF_3Cl_3$ in CH_2Cl_2 gave rise to a ^{31}P n.m.r. spectrum comprising a 1:3:3:1 quartet at δ 185.6 ppm, J_{PF} 732 Hz, assigned as *fac*-$PF_3(NCS)_3^-$. No doublet or triplets corresponding to *mer*-$PF_3(NCS)_3^-$ were observed. It is possible that if *mer*-$PF_3(NCS)_3^-$ were fluxional separate signals might not be resolved from those of the *fac*-isomer as the chemical shifts are calculated to be quite close together. The compound was isolated as a yellow solid by filtering the solution and evaporating the solvent. The elemental analyses, although not perfect, indicate that complete substitution of the $PF_3Cl_3^-$ ions has occurred (Experimental section).

c. Direct substitution into the $PF_3Cl_3^-$ ions

The addition of small quantities of AgNCS to a strong CH_2Cl_2 solution of $Pe_4NPF_3Cl_3$ gave rise to a complex ^{31}P n.m.r. spectrum, a typical example of which is shown in Figure 7.6. Although many of the branches overlap several assignments can be made. Doublets of triplets at δ 168.0 ppm, J_{PF} 836 Hz (triplet), 996 Hz (doublet) and δ 179.0 ppm, J_{PF} 869 Hz (triplet), 1039 Hz (doublet) were clearly observed in successive spectra and are assigned as *fac*-$PF_3Cl_2(NCS)^-$ and *fac*-$PF_3Cl(NCS)_2^-$. In addition, resonances readily assignable to members of the $PF_{6-n}(NCS)_n^-$ series were clearly observed. These were $PF_2(NCS)_4^-$ (triplet δ 209.6 ppm, J_{PF} 740 Hz), $PF_3(NCS)_3^-$ (quartet δ 185.5 ppm, J_{PF} 741 Hz), $PF_4(NCS)_2^-$ (quintet δ 174.2 ppm, J_{PF} 745 Hz) and $PF_5(NCS)^-$ (sextet δ 154.5 ppm, J_{PF} 738 Hz). The calculated shifts of the ions $PF_3Cl_{3-n}(NCS)_n^-$ and the experimental values, where observed, are shown in Table 7.9. In this system substitution of Cl by NCS is accompanied by ligand exchange to give lower and more highly fluorinated anions. This situation was not observed when $PF_3(NCS)_3^-$ was prepared as in section iv.b.3 and must arise from exchange between the starting material and substitution products. This implies that the substitution reaction is faster than ligand exchange, but in the system described above only a limited quantity of AgNCS was used to observe the stages of substitution and consequently ligand exchange became important.

Some decomposition of the anions occurred, and over a period of four days a new triplet at δ 31.2 ppm, J_{PF} 989 Hz was observed, presumably due to a molecular species. This resonance was only of low intensity, however, and the possible nature of the compound will be discussed in section v.

Table 7.9 Calculated and observed shifts for $PF_3Cl_{3-n}(NCS)_n^-$ $(0 \leqslant n \leqslant 3)$ in CH_2Cl_2

ion	structure	δ calculated	δ observed	J_{PF} Hz
$PF_3Cl_2(NCS)^-$		167.1	168.0	836 996
		146.4	-	-
		155.7	-	-
$PF_3Cl(NCS)_2^-$		177.0	179.0	869 1039
		165.9	-	-
		172.8	-	-
$PF_3(NCS)_3^-$	*fac*	189.9	185.5	746
	mer	185.4	-	-

d. Direct substitution into the *cis*-$PF_2Cl_4^-$ ion

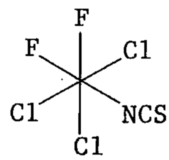
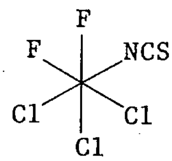
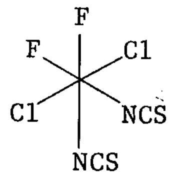
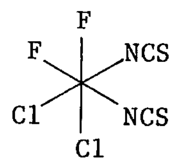
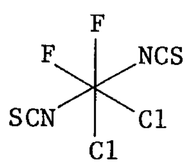
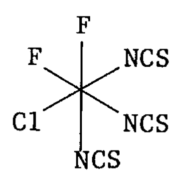
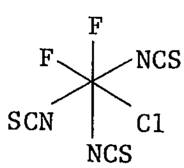
The addition of a small quantity of AgNCS to a CH_2Cl_2 solution of $Et_4NPF_2Cl_4$ led to a complex ^{31}P n.m.r. spectrum which showed two low field triplets δ 33.0 ppm, J_{PF} 1001 Hz and δ 15.6 ppm, J_{PF} 969 Hz, together with two doublets of doublets δ 194.0 ppm, J_{PF} 757 Hz, 1029 Hz and δ 204.5 ppm, J_{PF} 655 Hz, 887 Hz and a triplet δ 209.6 ppm, J_{PF} 746 Hz in the six-coordinate region. The assignments of the higher field resonances are shown in Table 7.10 with the calculated values. From the excellent agreement of the calculated and experimental values, and the observation of the splitting pattern, the assignments to definite structures are unambiguous.

v Anions containing fluoride and cyanate ligands

a. Ligand exchange between PF_6^- and $P(NCO)_3$

Pr_4NPF_6 was added to a CH_3NO_2 solution of $P(NCO)_3$. The reaction was monitored by ^{31}P n.m.r. spectroscopy and the solution was replenished with more $P(NCO)_3$ when its concentration became small due to either ligand exchange or thermal decomposition. After one week a 1:5:10:10:5:1 sextet was apparent in the spectrum at δ 148.4 ppm, J_{PF} 745 Hz. This is assigned as $PF_5(NCO)^-$, which must be fluxional from the simplicity of the splitting pattern. Over a period of two months this sextet became the dominant feature in the six-coordinate region of the spectrum. After this time three central branches of a 1:4:6:4:1 quintet were visible at δ 153.2 ppm, J_{PF} 768 Hz, tentatively assigned as $PF_4(NCO)_2^-$. The ligand exchange reaction was accompanied by much decomposition, the products of which gave resonances at δ 41.1 ppm ($PO(NCO)_3$), δ 27.5 ppm, J_{PF} 938 Hz (doublet) and δ 30.7 ppm, J_{PF} 998 Hz (triplet) which are tentatively assigned as $POF(NCO)_2$ and $POF_2(NCO)$ respectively. A typical spectrum showing all these features is shown in Figure 7.7. There was no evidence

Table 7.10 Calculated and observed shifts for $PF_2Cl_{4-n}(NCS)_n^-$ ($0 \leq n \leq 4$)

ion	structure	δ calculated	δ observed	J_{PF} Hz
$PF_2Cl_3(NCS)^-$		183.2	-	-
		192.5	-	-
$PF_2Cl_2(NCS)_2^-$		184.1	-	-
		193.2	194.0	757 1029
		200.3	-	-
$PF_2Cl(NCS)_3^-$		196.7	-	-
		203.6	204.5	655 887
$PF_2(NCS)_4^-$	*cis*-isomer	209.0	209.6	746

to suggest the formation of the $PF_{3-n}(NCO)_n$ species which might be expected. Presumably these are formed, but readily react further to give PF_3 (which may escape from the system) or decompose.

b. The reaction between PF_5 and Et_4NNCO in CH_2Cl_2

A CH_2Cl_2 solution of Et_4NNCO was saturated with PF_5. The ^{31}P n.m.r. spectrum of the resulting solid in CH_2Cl_2 showed that PF_6^- was the major product with smaller amounts of $PF_5(NCO)^-$ at δ 152.0 ppm, J_{PF} 732 Hz. The infrared spectrum of a solution in CH_2Cl_2 showed a strong absorption at 2270 cm^{-1} which clearly indicates the presence of a cyanate group[91]. The compound is not stable as a solid, the infrared spectrum showing no absorption in the 2270 cm^{-1} region after one month.

As the assignment of $PF_5(NCO)^-$ seems unambiguous, sufficient data are available to calculate the chemical shifts of the $PF_{6-n}(NCO)_n^-$ series. The F:NCO term is derived from the chemical shift of $PF_5(NCO)^-$ in CH_2Cl_2 rather than CH_3NO_2 since most of the other pairwise interaction parameters refer to CH_2Cl_2 solution. The calculated shifts are shown in Table 7.11 and support the previous assignment of the 153.2 ppm resonance in the PF_6^--$P(NCO)_3$ system as *trans*-$PF_4(NCO)_2^-$.

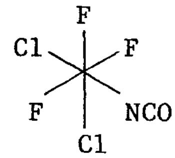
c. The reaction between $PF_3Cl_3^-$ and AgNCO

Addition of small quantities of AgNCO to a strong solution of $Pe_4NPF_3Cl_3$ in CH_2Cl_2 led to an exothermic reaction. The ^{31}P n.m.r. spectrum indicated that a reaction similar to that observed for the $PF_3Cl_3^-$-AgNCS system was occurring. A doublet of triplets was initially discernible at δ 158.8 ppm, J_{PF} 1004 Hz (triplet), 949 Hz (doublet) assigned as *fac*-$PF_3Cl_2(NCO)^-$. This reaction was followed by ligand exchange giving a readily observable sextet due to $PF_5(NCO)^-$ (δ 151.8 ppm, J_{PF} 709 Hz), a septet due to PF_6^- (δ 144.8 ppm, J_{PF} 709 Hz) and three branches of the

Table 7.11 Calculated and observed shifts for $PF_{6-n}(NCO)_n^-$ $(2 \leqslant n \leqslant 6)$

ion	δ calculated	δ observed
cis -$PF_4(NCO)_2^-$	173.0	-
trans-$PF_4(NCO)_2^-$	154.0	153.2
fac-$PF_3(NCO)_3^-$	213.0	-
mer-$PF_3(NCO)_3^-$	194.0	-
cis-$PF_2(NCO)_4^-$	253.0	-
trans-$PF_2(NCO)_4^-$	234.0	-
$PF(NCO)_5^-$	312.0	-

quintet due to $PF_4(NCO)_2^-$ (δ 152.0 ppm, J_{PF} 738 Hz). In addition other resonances were seen in the six-coordinate region which are not so readily assigned. These include a triplet δ 162.9 ppm, J_{PF} 748 Hz and a quartet δ 156.8 ppm, J_{PF} 738 Hz. As observed with the $PF_2Cl_4^-$-AgNCS system two lower field triplets were observed at δ 30.9 ppm, J_{PF} 991 Hz and δ 15.1 ppm, J_{PF} 989 Hz. The calculated shifts for the $PF_3Cl_{3-n}(NCO)_n^-$ anions are shown in Table 7.12. The addition of excess AgNCO to a solution of $Et_4NPF_3Cl_3$ gave rise to a quartet in the ^{31}P n.m.r. spectrum at δ 176.0 ppm, J_{PF} 738 Hz, tentatively assigned as *fac*-$PF_3Cl(NCO)_2^-$, which must be fluxional to account for the splitting pattern. The possible assignment as $PF_3(NCO)_3^-$ seems unlikely in view of the large discrepancy between calculated and observed shifts. The unassigned quartet in the $Pe_4NPF_3Cl_3$-AgNCO system could be due to a fluxional ion. The observed shift of 156.8 ppm falls between the values calculated for



and

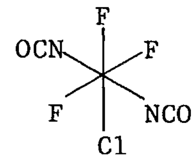
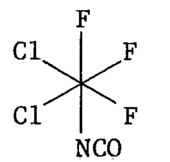
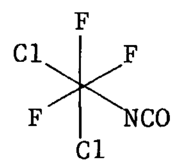
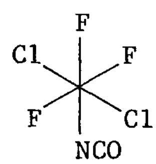
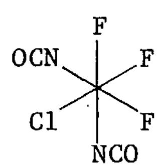
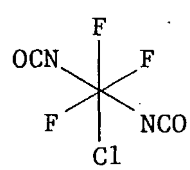
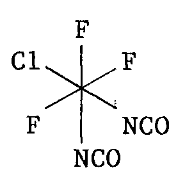
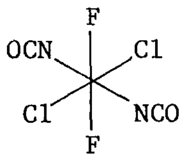


Table 7.12 Calculated and observed shifts for $PF_3Cl_{3-n}(NCO)_n^-$

ion	structure	δ calculated	δ observed	J_{PF} Hz
		162.9	158.8	1004 949
$PF_3Cl_2(NCO)^-$		151.6	-	-
		142.6	-	-
		179.6	176.0	738
$PF_3Cl(NCO)_2^-$		160.6	-	
		168.3	-	
$PF_3(NCO)_3^-$	*fac*	213.0	-	
	mer	194.0	-	

and a definite assignment cannot be made. The triplet at δ 162.9 ppm must arise from a PF_2-containing anion. The calculated value for



is 167.2 ppm which agrees reasonably well with that observed. Other members of the possible anions with two fluorine atoms present would be expected to have much higher shifts.

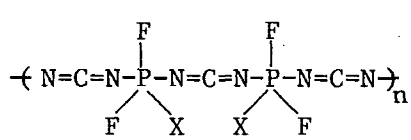
d. <u>The decomposition products of phosphorus(V) anions with fluorine and pseudohalogen ligands</u>

In the systems involving NCS and NCO ligands decomposition products giving triplets at about δ 32 ppm, J_{PF} 1000 Hz and δ 15 ppm, J_{PF} 970 Hz were observed. These arose from $PF_3Cl_3^-$ and $PF_2Cl_4^-$ reactions. In the reactions of AgF with $PCl_3(CN)_3^-$ and $PCl_4(CN)_2^-$ the 15 ppm triplet was prominent.

These data suggest that the same species is produced in each system. The values of chemical shift and coupling constant strongly support the contention that molecular species of some kind are formed. That the same species is formed regardless of the pseudohalide used suggests that no pseudohalogen group is incorporated (although the possibility of CN groups being formed by rearrangement of NCS or NCO ligands cannot be ruled out). The shift and coupling constant of the 32 ppm triplet agree well with the values quoted for PF_2Cl_3[92,93], but the formation of such a species by dissociation of an anion is rather hard to rationalise as PF_2Cl_3 readily accepts Cl^- to form $PF_2Cl_4^-$ which shows no sign of dissociation. Although the resonance tentatively assigned as PF_2Cl_3 is often intense it is never present in the spectra for any length of time, which is consistent with substitution-exchange to give an unstable pseudohalogen-containing molecular compound which would rapidly decompose.

The triplet at 15 ppm seems most unlikely to be due to a simple five-coordinate compound. As it is always present when most of the anions have decomposed, giving rise to free halide or pseudohalide ions in solution, it cannot possess any significant acceptor properties. If a five-coordinate species were to be proposed it would have to be of the form $PF_2Cl_aX_b$ (X = pseudohalide, a+b = 3). Work on the PF_3Cl_2-AgCN system, which produced PF_3 as the only phosphorus-containing species, strongly indicates that molecular species containing cyanide and fluoride ligands are unstable, and there is no reason to suspect that NCO or NCS ligands would stabilise such species to any extent.

One possible route to decomposition of NCO- and NCS-containing anions would be by loss of CO_2 or CS_2 respectively as noted for P(V) chloro-cyanato and chloro-thiocyanato species to give compounds of the form:-

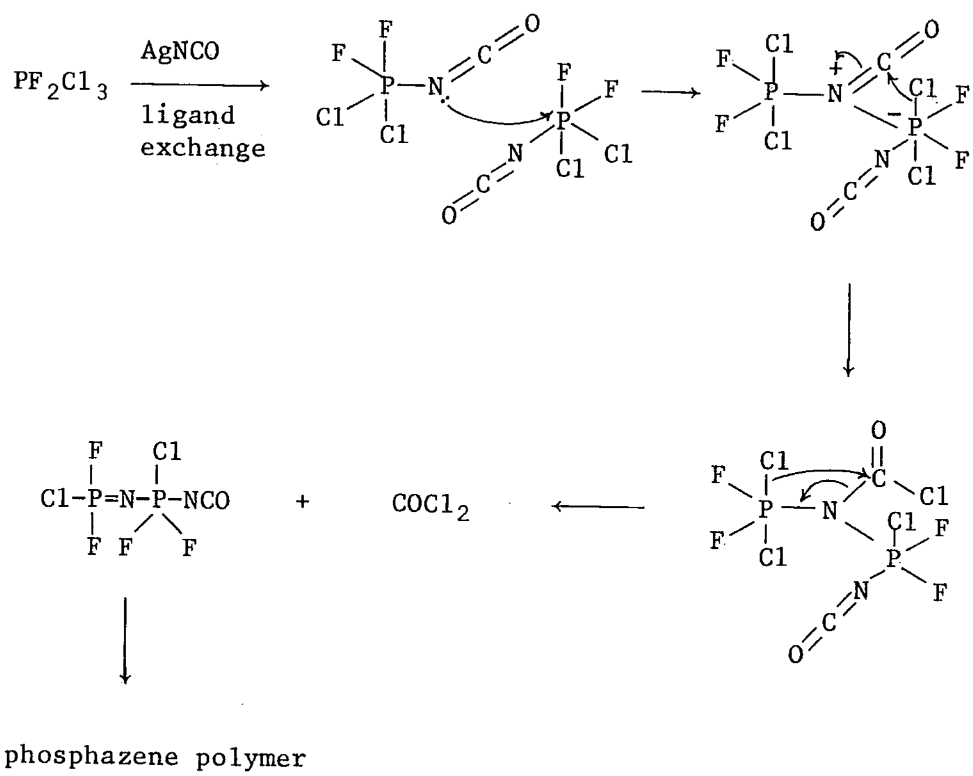


which could be cyclic or polymeric. The fact that only one triplet is seen would indicate that X is the same, regardless of the pseudohalide used, or has little effect on the chemical shift or coupling constant. It is also difficult to rationalise the absence of PF_3-groups since these might be expected to be preferentially retained during the decomposition of anions derived from $PF_3Cl_3^-$.

The chemical shift at 15 ppm agrees fairly well with that of $(NPF_2)_4$, and although the coupling constant is not in agreement with either of the two values quoted in the literature[94,66], it is well within the range quoted for fluorophosphazene derivatives[66]. Thus it is possible that difluoro-phosphazene derivatives are formed. This would explain the independence of the chemical shift from the pseudohalide used, and the triplet appearance of the spectrum. A mechanism for the formation of such species is illustrated in Scheme 7.1 for cyanate. For thiocyanato derivatives

Scheme 7.1

A mechanism for the formation of phosphazene derivatives from PF_2Cl_3



loss of $COCl_2$ would be replaced by loss of $CSCl_2$. This mechanism could not account for the formation of fluorophosphazenes form cyano-containing species.

vi Experimental

Preparation of $Et_4NPF_3Cl_3$

This was prepared by the action of PF_3 on a CH_2Cl_2 solution of Cl_2 and Et_4NCl at 243K. In a typical preparation Et_4NCl (2.9 g, 17.5 mmole) was dissolved in 30 ml CH_2Cl_2. Cl_2 (0.4 ml, at 191K) was condensed onto the solution at 77K under vacuum. PF_3 was passed into the solution at 243K until the green colour due to Cl_2 had been discharged. The solvent was removed under vacuum and the resulting solid recrystallised from CH_2Cl_2 to give pure $Et_4NPF_3Cl_3$ (1.45 g). The remaining solution was treated with one third its volume of CCl_4 and cooled to 253K and a further 1.37 g was obtained.

Analysis: $Et_4NPF_3Cl_3$	requires	C 29.58%	H 6.16%	N 4.31%	P 9.55%	Cl 32.89%
	found	C 29.69%	H 6.09%	N 4.59%	P 9.0 %	Cl 32.3 %

The ^{31}P n.m.r. spectrum showed a quartet due to the *fac*-isomer δ 156.8 ppm, J_{PF} 953 Hz (literature value δ 158.5 ppm, J_{PF} 940 Hz[72]), and a doublet of triplets due to the *mer*-isomer δ 142.7 ppm, J_{PF} 1081 Hz (triplet) and 970 (doublet) (literature value J_{PF} 1061 Hz and 950 Hz[72]), in a 3:1 ratio.

Preparation of *cis*-$Et_4NPF_2Cl_4$

This was prepared in an analogous way to $Et_4NPF_3Cl_3$ using PF_2Cl instead of PF_3. PF_2Cl was prepared by the method of Cavell[95].

$$3Me_2NH + PF_3 \rightarrow 2PF_2NMe_2 + Me_2NH_2HF_2$$

followed by

$$PF_2NMe_2 + 2HCl \rightarrow PF_2Cl + Me_2NH_2Cl$$

PF_3 (3 ml at 143K) and Me_2NH (4 ml at 273K) were condensed into the cold finger attachment of a 3 l bulb at 77K. The bulb was attached to the vacuum line by means of a rotaflo tap. The cold finger of the bulb was allowed to warm to 143K and was maintained at this temperature for 1 h after which it was allowed to warm to 193K. On opening the bulb to the vacuum line little increase in pressure was noted, indicating that the reaction had gone to completion. The contents of the bulb were slowly transferred under vacuum to a rotaflo vessel which contained the colourless liquid PF_2NMe_2. The PF_2NMe_2 was then condensed into a flask and small quantities of dry HCl were reacted with it at 143K followed by warming to 193K. This process was repeated until significant rises in pressure were noticed on warming to 193K, indicating that excess HCl was present. The PF_2Cl was condensed into a rotaflo and stored at 194K. A small quantity was sealed in a tube and its ^{31}P n.m.r. showed a triplet δ -175.7 ppm, J_{PF} 1369 Hz (literature value J_{PF} 1390 Hz[93]).

To prepare $Et_4NPF_2Cl_4$ equimolar amounts of Et_4NCl and Cl_2 were treated with an excess of the phosphine in CH_2Cl_2. The solid was purified by recrystallisation from CH_2Cl_2.

Analysis:	$Et_4NPF_2Cl_4$ requires	C 28.15%	H 5.87%	N 4.11%	P 9.09%	Cl 41.6%
	found	C 28.29%	H 6.00%	N 4.26%	P 8.98%	Cl 39.5%

The ^{31}P n.m.r. of a solution of $Et_4NPF_2Cl_4$ in CH_2Cl_2 showed one triplet δ 177.3 ppm, J_{PF} 1026 Hz (literature values for *cis*-$PF_2Cl_4^-$ δ 180 ppm, J_{PF} 1010 Hz[72]).

Preparation of Et_4NPFCl_5

This was prepared by the chlorination of $PFCl_2$ in the presence of Et_4NCl. $PFCl_2$ was prepared by the method of Holmes and Gallagher[93]. PCl_3 and SbF_3 were heated at 313K (12 cm Hg) with a catalytic amount of PCl_5. The gaseous products were passed through a fractionation column packed with glass helices to return PCl_3 to the reaction mixture. The crude $PFCl_2$ was condensed at 77K and then fractionated by passing through a trap at 188K and being retained at 175K. The ^{31}P n.m.r. spectrum showed a doublet δ -217.6 ppm, J_{PF} 1329 Hz (literature value J_{PF} 1320 Hz[93]). The phosphine was stored in a rotaflo at 193K. To prepare Et_4NPFCl_5 the phosphine was condensed onto a solution of Et_4NCl and Cl_2 in CH_2Cl_2. The white precipitate was filtered and washed with CH_2Cl_2 to give the salt.

Analysis Et_4NPFCl_5 requires C 26.86% H 5.59% N 3.92% P 8.67% Cl 49.62%

found C 27.86% H 6.19% N 3.21% P 8.3 % Cl 49.24%

The ^{31}P n.m.r. spectrum of the salt in CH_3NO_2 showed a doublet δ 223.2 ppm, J_{PF} 1054 Hz (literature values δ 224 ppm, J_{PF} 1050 Hz[72]).

Preparation of PF_3Cl_2 and reaction with Et_4NCN

PF_3Cl_2 was prepared by the low temperature chlorination of PF_3. Dry chlorine was condensed into a flask at 77K under vacuum and allowed to warm to 193K. The flask was connected to the vacuum line by a length of flexible tubing and a tap. With the tap closed PF_3 was admitted to the vacuum line from a cylinder. The tap to the flask was opened and the liquid chlorine agitated to promote reaction with the PF_3. The reaction was accompanied by a decrease in the pressure of the system. This procedure was repeated until the chlorine was completely decolourised. The PF_3Cl_2 was transferred to a rotaflo and stored at 193K.

For the reaction with Et_4NCN, PF_3Cl_2 was condensed into a solution of the cyanide in CH_2Cl_2. The solution turned a dark red colour. An excess of the phosphorane was added and the compound was isolated by removing the solvent under vacuum. The ^{31}P n.m.r. spectrum showed a mixture of isomers to be present, as discussed previously.

Analysis: $Et_4NPF_3Cl_2(CN)$ requires C 34.29% H 6.75% N 8.89% P 9.84% Cl 22.54%

found C 34.48% H 7.05% N 8.20% P 9.78% Cl 22.25%

Preparation of $Et_4NPF_5(X)$

X = CN An excess of PF_5 was passed through a solution of Et_4NCN cooled to 243K. The solution turned red during this process. The compound was isolated by removing the CH_2Cl_2 under vacuum. This left an orange solid which rapidly darkened.

Analysis: $Et_4NPF_5(CN)$ requires C 38.30% H 7.07% N 9.93%

found C 37.86% H 7.70% N 9.48%

Attempted recrystallisation of this solid gave only Et_4NPF_6.

X = NCS Et_4NNCS (1.59 g, 8.4 mmole) was treated with excess PF_5 in CH_2Cl_2 at 253K. The solvent was then removed under vacuum to give a yellow solid (2.5 g) which was recrystallised from CH_2Cl_2.

Analysis: $Et_4NPF_5(NCS)$ requires C 34.39% H 6.37% N 8.92% P 9.87%

found C 35.01% H 7.24% N 8.89% P 9.62%

X = NCO Et_4NNCO was treated with excess PF_5 in CH_2Cl_2 at 253K and the solvent removed under vacuum. The ^{31}P n.m.r. spectrum showed the presence of Et_4NPF_6 as well as $Et_4NPF_5(NCO)$. The impurity could not be separated by repeated recrystallisations.

Preparation of $Et_4NPF_3(NCS)_3$

A small quantity of $Et_4NPF_3Cl_3$ was treated with an excess of AgNCS in CH_2Cl_2. After the ^{31}P n.m.r. spectrum had been obtained the contents of the tube were filtered, the residue washed with CH_2Cl_2 and the resulting solution evaporated to give a yellow solid. There was insufficient material for P and S analyses.

Analysis: $Et_4NPF_3(NCS)_3$ requires C 33.67% H 5.10% N 14.29%

found C 35.27% H 6.17% N 14.47%

$Et_4NPF_3Cl(NCS)_2$ requires C 32.57% H 5.41% N 11.37%

Coupling constants were usually measured on the narrowest range possible to get the most accurate values. The likely error on a 200 ppm width is estimated as ±10 Hz and this is the error limit for most of the values quoted. From the 400 ppm range the error is ±20 Hz and this is the maximum expected for any of the coupling constants.

Infrared spectra were normally obtained as nujol mulls. Species which contained cyanide ligands did not mull well and only poor spectra could be obtained. The infrared spectra were recorded by dissolving a small quantity of the material in CH_2Cl_2 and allowing the solution to evaporate on the CsI plates. In this way a thin film of material covered the plate and the spectrum was obtained in the normal manner with much better results.

Chapter 8

The Acceptor Properties of Phosphorus(III) Halides and Pseudohalides

i The acceptor properties of PCl_3

a. The PCl_3-Cl^- system

The addition of a few drops of PCl_3 to a saturated solution of Et_4NCl in CH_2Cl_2 was carried out in an attempt to form the PCl_4^- ion. The ^{31}P n.m.r. spectrum showed mainly PCl_3 but a small resonance was seen at -209.5 ppm and is tentatively assigned as PCl_4^-. The equilibrium (1) for the formation of the ion lies well to the left. Et_4NCl was not

$$PCl_3 + Cl^- \rightleftharpoons PCl_4^- \qquad \ldots (1)$$

particularly soluble in CH_3CN, but on addition of PCl_3 a clear solution was formed. The ^{31}P n.m.r. spectrum showed a single resonance to higher field of the PCl_3 position, presumably due to a mobile equilibrium between PCl_3 and PCl_4^-, an average shift being seen. The addition of excess Et_4NCl gave a value of -191.8 ppm as the limiting shift of the PCl_4^- ion in this solvent. The difference in shift for the ion in CH_2Cl_2 and CH_3CN is rather large and may reflect specific solute - solvent interactions with CH_3CN.

The compound was isolated in a similar manner to the isolation of PBr_4^- [39]. A saturated solution of Et_4NCl and PCl_3 was cooled and the resulting colourless crystals filtered off. The crystals analysed as Et_4NPCl_4, and redissolved in CH_2Cl_2 to give PCl_3 and Et_4NCl. The PCl_4^- ion is readily oxidised by Br_2 to give PCl_4^+ (δ -82.2 ppm in liquid Br_2) confirming that four chlorine atoms are bonded to phosphorus.

The vibrational spectra, the Raman in particular, indicate that the structure is based on that of the trigonal bipyramid with the lone pair in an equatorial position. For this C_{2v} symmetry eight fundamental vibrations are expected in the infrared spectrum, while the Raman spectrum should show nine. Only two bands could be seen between 700-250 cm^{-1} in the infrared spectrum, but seven bands in the Raman spectrum for that region indicate that the ion has C_{2v} symmetry. The solid state n.m.r. showed a broad resonance with a sharp line at the centre at -201.5 ppm as shown in Figure 8.1. The agreement between solid state and solution shifts indicates that the same structure is retained. The crystal structure of the compound, determined recently by W.S. Sheldrick[97], shows that the ion has a structure based on a distorted trigonal bipyramid. The two axial P-Cl bonds are much longer than the equatorial ones as shown in Figure 8.2. The n.q.r. spectrum was obtained at 77K and showed two signals at 26.75 and 27.00 MHz due to the equatorial chlorines, but no signals could be detected for the axial chlorine atoms which would be expected to give resonances at a lower frequency.

b. The PCl_3-Br^- system

No apparent reaction occurred on addition of Pr_4NBr to a CH_2Cl_2 solution of PCl_3. The ^{31}P n.m.r. spectrum showed only PCl_3 with no small upfield resonances which might indicate the presence of PCl_3Br^-. Although a green solution was produced upon addition of Bu_4NBr to PCl_3 in CH_2Cl_2 no reaction could be detected in the ^{31}P n.m.r. spectrum. In the absence of solvent Bu_4NBr dissolved in PCl_3 to give a green solution. No additional resonances could be detected in the ^{31}P n.m.r. spectrum but the entire signal was shifted slightly upfield to -211.1 ppm. No precipitate was obtained on cooling the solution to 243K. Pr_4NBr is not very soluble in CH_3CN, but addition of PCl_3 caused the solid to dissolve giving a clear green-yellow solution. The ^{31}P n.m.r. spectrum again showed an upfield movement of the entire signal, the limiting shift observed being -211.1 ppm . Attempted isolation of the compound by cooling the solution of PCl_3 and Pr_4NBr in either CH_2Cl_2 or CH_3CN gave no product. The n.m.r. evidence suggests that the PCl_3Br^- ion is formed, but no structural data could be deduced.

c. The PCl_3-I^- system

A red solution was formed when Bu_4NI was added to PCl_3 in CH_2Cl_2 and the ^{31}P n.m.r. spectrum showed only PCl_3. Similarly Pr_4NI gave a brown solution with PCl_3 in CH_2Cl_2 but no evidence of reaction was obtained from the n.m.r. spectrum. In the absence of a solvent Bu_4NI dissolved to a limited extent in PCl_3, but again no resonances due to PCl_3I^- could be detected.

This evidence suggests that PCl_3I^- does not form under these conditions.

d. The PCl_3-CN^- system

The reaction between PCl_3 and Et_4NCN in CH_2Cl_2 was violently exothermic giving rise to a dark red solution. Resonances at -211.0, 9.8 and 156.4 ppm were observed in the ^{31}P n.m.r. spectrum. The addition of excess Et_4NCN gave a single resonance at 156.4 ppm . This is assigned to the $PCl_2(CN)_2^-$ ion since the analogous reaction of PBr_3 with cyanide ion is known to produce $PBr_2(CN)_2^-$ and PBr_4^- [96], and the shift is too low for $P(CN)_3Cl^-$ (section iii). Attempts to isolate the salt were made by reacting PCl_3 with Et_4NCN in a 1:2 mole ratio in CH_2Cl_2 and cooling the resulting solution. No crystals could be obtained in this manner, even after reducing the volume of solvent. Similarly the reaction in CH_3CN gave no isolable product. The n.m.r. of the solution showed two equally intense resonances at -204.0 and 156.4 ppm , indicating that the reaction follows the course of equation (2) and that no further reaction

$$2PCl_3 + 2Et_4NCN \longrightarrow Et_4NPCl_2(CN)_2 + Et_4NPCl_4 \quad \ldots (2)$$

of the PCl_4^- ion occurs with the excess Et_4NCN. A further attempt to isolate a salt containing $PCl_2(CN)_2^-$ by the reaction of $Me_2NP(CN)_2$ with HCl was made according to equation (3). The reaction carried out

$$Me_2NP(CN)_2 + 2HCl \longrightarrow Me_2NH_2^+PCl_2(CN)_2^- \quad \ldots (3)$$

in CH_3CN - diethyl ether solvent gave a white precipitate. The ^{31}P n.m.r. spectrum of the filtrate showed Me_2NPCl_2 (δ -166.0 ppm), $Me_2NPCl(CN)$ (δ -80.7 ppm) and PCl_3 (δ -220.8 ppm). The solid state n.m.r. of the precipitate showed a broad resonance centred at 160 ppm in good agreement with the solution value, indicating that the same structure is retained. The elemental analyses were poor, and the compound is probably contaminated with Me_2NH_2Cl. The white precipitate was insoluble in all common organic solvents and hence recrystallisation was not possible.

Thus it seems that CN^- addition to PCl_3 does not give the expected PCl_3CN^- species (although it is possible that the small resonance at 9.8 ppm could be due to this ion), the dicyanodichlorophosphite ion being preferred, as was found for the PBr_3-CN^- system[43,44].

e. The PCl_3-NCS^- system

The addition of Et_4NNCS to PCl_3 in CH_2Cl_2 gave a clear orange solution. The ^{31}P n.m.r. showed an upfield movement of the entire signal which depended on the amount of NCS^- ion in solution. The variation of chemical shift with the mole ratio PCl_3:NCS^- was recorded and the results are shown graphically in Figure 8.3. The break in the formation curve at the 1:1 ratio occurs at δ -158 ppm, in good agreement with the shift for PCl_2NCS. Similarly the limiting value of δ -122 ppm is close to the chemical shift of $PCl(NCS)_2$.

On cooling a solution of PCl_3 and Et_4NNCS in CH_2Cl_2 to 243K a mass of bright yellow crystals was obtained. These were thermally unstable giving a black solid within two days at room temperature; at 243K they were more stable, turning a yellow-orange colour after two months. Due to the thermal instability no solid state n.m.r. could be obtained; no ^{35}Cl n.q.r. signals could be detected at 77K. The solid, redissolved in CH_2Cl_2, gave a ^{31}P n.m.r. spectrum which showed a single resonance at -112.4 ppm in good agreement with the shift for $PCl(NCS)_2$. These data strongly suggest that the compound is $Et_4NPCl_2(NCS)_2$ which dissociates when redissolved in a similar manner to PCl_4^- according to equation (4).

$$PCl_2(NCS)_2^- \xrightarrow[CH_2Cl_2]{} PCl(NCS)_2 + Cl^- \quad \ldots (4)$$

As no n.q.r. data are available structural assignment from vibrational spectroscopy alone must be made. The compound decomposed in the laser, even at 77K, and thus no Raman spectrum could be obtained. The infrared spectrum, run as a nujol mull showed two intense absorptions at 2020 and 1930 cm^{-1}, assigned as NCS antisymmetric stretches in an N-bonded thiocyanate. If the structure were similar to that of PCl_4^-, i.e. C_{2v} symmetry, a total of eighteen fundamental modes would be expected to be active in the infrared spectrum. Only nine bands not assignable to nujol, Et_4N^+ or polythene discs were seen in the 2500 to 250 cm^{-1} region. It is possible that the other bands are to lower wavenumber and thus a definite assignment of structure is not possible, although the thiocyanate ligands do seem to be N-bonded.

As the 1:1 mole ratio of $PCl_3:NCS^-$ produced $PCl_2(NCS)$ (and Et_4NCl) a solution containing equimolar quantities of the reactants was cooled in an attempt to prepare $PCl_3(NCS)^-$. The yellow crystals formed were the $PCl_2(NCS)_2^-$ salt.

f. The PCl_3-NCO^- system

The addition of PCl_3 to a CH_2Cl_2 solution of Et_4NNCO caused violent exothermic reaction accompanied by boiling of the solvent. The ^{31}P n.m.r. spectrum showed intense resonances at δ -201.5, -165.7 and -143.5 ppm with lower intensity peaks at -182.2, -170.9, -154.7, -125.3, -112.4, -103.3 and 16.2 ppm . Unambiguous assignment of these resonances is not possible. The signals at δ -165.7 and -112.4 ppm are tentatively assigned to $PCl_2(NCO)$ and $PCl(NCO)_2$, but the intense resonances at -201.5 and -143.5 ppm do not correspond to any known three-coordinate species and could be $PCl_3(NCO)^-$ and $PCl_2(NCO)_2^-$, judging by the upfield shifts from PCl_3 and $PCl_2(NCO)$ respectively.

ii The acceptor properties of PBr_3

a. The PBr_3-Cl^- system

A saturated solution of Et_4NCl in CH_2Cl_2 turned a golden-yellow colour upon addition of a few drops of PBr_3. The ^{31}P n.m.r. spectrum showed the presence of unreacted PBr_3 with a small resonance at δ -219.3 ppm , possibly due to PCl_3. On cooling to 243K pale orange crystals were deposited. Redissolving in CH_2Cl_2 led to the formation of PBr_3 only, although PBr_2Cl would also be possible from the dissociation of the PBr_3Cl^- ion. The solid state n.m.r. showed a broad resonance at -230 ppm with a less intense sharp line superimposed at -227 ppm due to PBr_3, an identical type of spectrum to that observed for PCl_4^- salts. The elemental analyses indicate that the compound is Et_4NPBr_4 rather than the PBr_3Cl^- salt. The formation of PBr_4^- can be rationalised according to equations (5) and (6).

$$PBr_3 + Et_4NCl \longrightarrow PClBr_2 + Et_4NBr \quad \ldots (5)$$

$$PBr_3 + Et_4NBr \longrightarrow Et_4NPBr_4 \quad \ldots (6)$$

b. The PBr_3-Br^- system

The isolation of salts containing the PBr_4^- ion has been carried out previously by Dillon and Waddington who tentatively assigned a structure based on C_{2v} symmetry from the Raman spectrum[39]. Pr_4NPBr_4 was obtained by cooling a solution of Pr_4NBr and PBr_3 in CH_2Cl_2 to 243K to give yellow-green crystals. The structure of the PBr_4^- anion shows remarkable differences from that of PCl_4^- as shown in Figure 8.4[96]. At first sight the structure approximates to the expected trigonal bipyramidal structure observed for PCl_4^- with equivalent equatorial bonds and inequivalent axial P-Br bonds. The structure is dimeric with unsymmetric P-Br-P bridges. The solid state n.m.r. showed a broad absorption centred at -217 ppm with a sharp peak at -225.7 ppm, possibly due to slight decomposition to PBr_3. The considerable difference between solid state and solution shifts indicates that the unsymmetrical bridge breaks up in solution to give monomeric PBr_4^- (δ PBr_4^- in CH_2Cl_2 is -150 ppm [39]).

As observed previously the PBr_4^- ion is largely dissociated to PBr_3 and Br^- in all common organic solvents. In liquid bromine the ion was oxidised to PBr_4^+ as expected.

c. The PBr_3-I^- system

The addition of Bu_4NI to a PBr_3 solution in CH_2Cl_2 led to the formation of a dark brown solution. The ^{31}P n.m.r. spectrum showed an additional resonance at -150.0 ppm in addition to that of PBr_3. This peak decreased in intensity and was not present after one day. In the presence of Pr_4NI this new species was stable. Although the shift agrees well with that of PBr_4^- the high intensity and stability in solution rule out this assignment. Assignment as the simple adduct of PBr_3I^- is not unreasonable, but the formation of P_2Br_4 (Equation (7)) is also possible and the results of the reaction with AgCN make assignment as P_2Br_4 unambiguous (see

$$2PBr_3 + 2I^- \longrightarrow I_2 + P_2Br_4 + 2Br^- \qquad \ldots (7)$$

Appendix 3). The observed shift agrees well with that previously quoted for P_2Br_4 at -150.0 ppm[98].

d. The PBr_3-CN^- system

The reaction of Et_4NCN with PBr_3 in CH_2Cl_2 was exothermic. The ^{31}P n.m.r. spectrum showed a resonance at 164.4 ppm, assigned as $PBr_2(CN)_2^-$ in good agreement with the literature value[43], and a smaller resonance at 1.6 ppm is tentatively assigned as $PBr_3(CN)^-$ although supporting evidence is lacking.

e. The PBr_3-NCS^- system

Upfield shifts of the entire signal were noted when varying amounts of Et_4NNCS were added to a CH_2Cl_2 solution of PBr_3. The variation of chemical shift with mole ratio is plotted in Figure 8.5, but no break at the 1:1 or 1:2 ratio is apparent, unlike the PCl_3-NCS^- system. Indeed the limiting shift of the system approaches that of $P(NCS)_3$. At the 1:1 and 1:2 ratios of PBr_3:NCS^- the chemical shifts are -162 and -110 ppm respectively, in reasonable agreement with the shifts of $PBr_2(NCS)$ and $PBr(NCS)_2$ of -152.8 and -111.5 ppm[9]. On cooling a solution of Et_4NNCS and PBr_3 bright yellow crystals were deposited. The elemental analyses indicate that the compound is a $PBr_3(NCS)^-$ salt, although they are still rather poor for this. The infrared spectrum showed a strong broad absorption at 1970 cm^{-1} indicating the presence of a thiocyanate group. The corresponding band in Et_4NNCS appears at 2060 cm^{-1}, so compound formation has clearly occurred. On dissolving the solid in CH_2Cl_2 a single resonance at -222.2 ppm was observed, presumably due to rapid exchange between PBr_3 and NCS^-, although a much higher shift would have been expected if the dissociation occurred according to equation (8) since a 1:1 mole ratio of PBr_3:NCS^- would be present in solution. The yellow solid is thermally unstable and after two days no NCS stretch could be seen in the infrared spectrum.

$$PBr_3(NCS)^- \longrightarrow PBr_3 + NCS^- \qquad \ldots (8)$$

iii The acceptor properties of $P(CN)_3$

a. The $P(CN)_3$-Cl^- system

$P(CN)_3$ is not particularly soluble in CH_2Cl_2, but when chloride ion donors such as Et_4NCl, Pr_4NCl, Pe_4NCl or Et_3NHCl were added to a solution containing undissolved $P(CN)_3$ all the solid dissolved. The ^{31}P n.m.r. spectrum of the resulting solution showed upfield shifts from that of $P(CN)_3$, the limiting value observed in the presence of chloride ion being 191.8 ppm . The compound was isolated as its tetraethylammonium salt. The solid state n.m.r. spectrum did not show the expected single resonance but a broad peak at 192 ppm with a sharp peak at its centre, and other relatively sharp signals at 156.4 and 37.1 ppm as shown in Figure 8.6. The resonances at 192 and 156 ppm agree well with those observed for $P(CN)_3Cl^-$ and $PCl_2(CN)_2^-$. Possibly the compound exists as $Et_4NCN.Et_4NPCl_2(CN)_2$.

δ 156.4

$Et_4NP(CN)_2$. $Et_4NP(CN)_3Cl$. $P(CN)_4^+Cl^-$ in the solid state. Due to the

191.8 (sharp) 192 (broad) 37.1

complex nature of the solid state ^{31}P n.m.r. spectrum no attempt was made to interpret the infrared and Raman spectra. When the solid was redissolved in CH_2Cl_2 a single resonance was seen at 191.8 ppm indicating that the $P(CN)_3Cl^-$ ion is reformed in solution. Thus although the infrared spectrum of the solid would not be expected to yield structural information, the solution spectra should. In view of the limited range available using a KBr solution cell the analysis of the spectrum must be restricted to the observance of the "CN region" which is clearly visible. If the structure is analogous to those of $P(CN)_3Br^-$ and $P(CN)_3I^-$ where a bridged halogen dimer with appropriate C_{2h} symmetry is formed[44,96], then six infrared-active CN stretches should be seen. This situation is observed in the solution infrared spectrum of $Et_4NP(CN)_3Cl$ which showed absorptions at 2190 (s), 2170 (s), 2130 (w), 2070 (w), 2060 (w) and 2000 (w) cm^{-1}. Although weak bands at 2130 and 2060 cm^{-1} occur in the infrared spectrum of CH_2Cl_2 (the solvent used for these spectra) the bands assigned to $P(CN)_3Cl^-$ are more intense and there is no ambiguity in assignment. It thus seems reasonable to conclude that in solution the $P(CN)_3Cl^-$ ion has a dimeric structure with approximate C_{2h} symmetry as observed for $P(CN)_3Br^-$ [96] and $P(CN)_3I^-$ [44] where the crystal structures have been determined, but in the solid state rearrangement occurs.

b. <u>The $P(CN)_3$-Br^- system</u>

An analogous situation to the $P(CN)_3$-Cl^- system was found when Bu_4NBr was added to a solution of $P(CN)_3$ in CH_2Cl_2. A mobile equilibrium was observed, the chemical shift depending on the amount of Br^- added. The limiting shift for this system was δ 179.4 ppm in good agreement with the value of 182 ppm[43] for $P(CN)_3Br^-$ in T.H.F.

The ion was isolated as its Bu_4N and Pr_4N salts. $Bu_4NP(CN)_3Br$ is a low-melting solid, the ^{31}P n.m.r. of which consisted of a sharp line at 179 ppm. $Pr_4NP(CN)_3Br$ is a pale yellow solid; its ^{31}P n.m.r. spectrum showed a broad resonance at 180 ppm in good agreement with the solution value, which implies that the dimeric structure[96] is retained in both solid and solution. The infrared spectrum of $Bu_4NP(CN)_3Br$ in CH_2Cl_2 showed the expected six CN stretches, while the solid compound $Pr_4NP(CN)_3Br$ showed only the two most intense of these absorptions as a nujol mull.

c. The $P(CN)_3$-I^- system

The equilibrium between $P(CN)_3$ and I^- was mobile, the limiting shift observed for the $P(CN)_3I^-$ ion of 163.0 ppm being in good agreement with the literature value of 164 ppm[43]. A plot of the variation in chemical shift with the mole fraction of halide is shown in Figure 8.7 for the $P(CN)_3$-X^- systems, where X = Br and I.

The $P(CN)_3I^-$ ion was isolated as $Pr_4NP(CN)_3I$ and is a yellow solid, the ^{31}P n.m.r. spectrum of which consisted of a broad peak at 162 ppm, confirming that the same dimeric structure[44] persists in both solid and solution.

d. The $P(CN)_3$-CN^- system

The addition of a small quantity of Bu_4NCN to $P(CN)_3$ in CH_2Cl_2 caused a rapid darkening of the solution. The ^{31}P n.m.r. showed a single peak to higher field of that due to $P(CN)_3$. With a larger quantity of Bu_4NCN two resonances were observed at 193.5 and 238.6 ppm. The latter signal rapidly decreased in intensity. The resonance at 193.5 is in excellent agreement with the shift of the dicyanophosphide ion $P(CN)_2^-$ (δ 193 ppm[43]), whereas that at 238.6 ppm is assigned as $P(CN)_4^-$. The $P(CN)_4^-$ ion rapidly decomposes according to equation (9).

$$P(CN)_4^- \longrightarrow P(CN)_2^- + (CN)_2 \qquad \ldots (9)^{96}$$

The reaction of $P(CN)_3$ with Bu_4CN followed the same course in CH_3CN giving the $P(CN)_2^-$ salt. Removal of the solvent left a black oil, the ^{31}P n.m.r. spectrum of which showed three resonances at -264.4, 19.4 and 193.5 ppm indicating that the dicyanophosphide is unstable as the Bu_4N^+ salt. A similar procedure was carried out using the Et_4N^+ salt which showed no sign of decomposition, giving a single resonance at 193.5 ppm.

e. The $P(CN)_3$-NCS^- system

When a solution of $P(CN)_3$ in CH_2Cl_2 was treated with Et_4NNCS upfield shifts were seen in the ^{31}P n.m.r. spectrum; the limiting shift observed was δ 183.8 ppm for the $P(CN)_3(NCS)^-$ ion. The solution turned dark red during the reaction and small resonances at δ 48.4 and 53.3 ppm rapidly grew in intensity. After one day no signal attributable to $P(CN)_3(NCS)^-$ was detectable.

f. The $P(CN)_3$-NCO^- system

The addition of Et_4NNCO to a CH_2Cl_2 solution of $P(CN)_3$ caused a violent exothermic reaction. The solution rapidly darkened and the ^{31}P n.m.r. spectrum indicated the formation of $P(CN)_2^-$ (δ 195.1 ppm), together with a complex series of resonances between -45 and 32 ppm which cannot be readily assigned.

g. The acceptor properties of $P(CN)_3$ towards pyridine donors

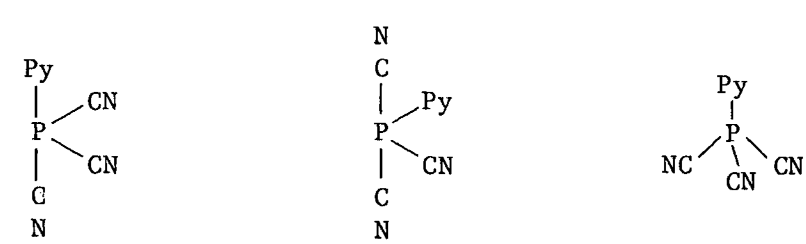
$P(CN)_3$ was found to form complexes with a variety of substituted pyridines. The limiting shifts for the adducts in CH_2Cl_2 are shown in Table 8.1. A general trend in the chemical shifts seems to be followed, the stronger bases giving larger upfield shifts, which may reflect the strength of the complex.

The 3-cyano, 4-cyano and 4-phenyl-pyridine adducts were isolated as solids. They did not analyse well however, possibly due to some reaction of the pyridine molecule with the acidic dry box atmosphere. The pyridine and 3-iodo-pyridine adducts were isolated as oils, the ^{31}P n.m.r. spectra of which gave gave good agreement with the solution values. Elemental analyses of these compounds were again poor.

Table 8.1

pyridine	$pk_a^{99,100}$	limiting shift in CH_2Cl_2
4-cyano-	1.9	145.1
3-cyano-	1.4	145.1
3-fluoro-	3.0	145.8
3-bromo-	2.8	149.1
3-chloro-	2.8	149.1
3-iodo-	3.3	151.5
4-phenyl-	5.2	156.4
pyridine	5.3	157.1
4-methyl-	6.0	162.0

As the nitrogen atom in the pyridine ring has only one electron pair the bridged dimer structure observed in the $P(CN)_3X^-$ (X = Cl, Br, I) compounds would not be expected. There are several other possible structures which in theory might be distinguished by the infrared spectrum. These are shown below with their respective point groups and the number of CN stretches expected in the infrared spectrum. Although



(I) C_s (3)

(II) C_s (3)

(III) C_{3v} (2)

bridged dimer structures might not be expected compounds such as the cyanopyridines have the option of bonding through either the pyridine or cyanide nitrogen atom and in these compounds a bridged structure may be possible, as shown in Figure 8.8. If a dimeric structure was

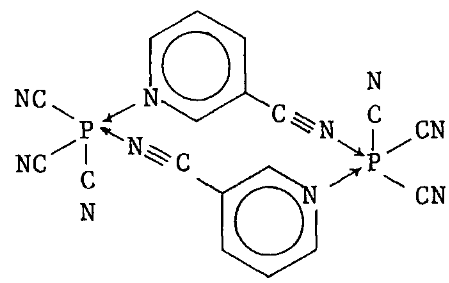


Figure 8.8 A possible structure for the $P(CN)_3$.3-cyanopyridine adduct

preferred an infrared spectrum similar to the simple halide adducts would be expected in the 'CN' region. The infrared spectra were recorded for the adducts with 3- and 4-cyano, 4-phenyl and 3-iodo-pyridine and with pyridine itself, and clearly indicate that the dimer structure is not formed in any case. The number of bands and frequencies in the CN region are listed in Table 8.2. In the case of the 4-cyano-pyridine adduct the observation of three CN stretches (apart from that due to the cyano-group on the pyridine) clearly indicates a structure based on (I) or (II). The assignment of a structure of the other adducts is more ambiguous as only two CN stretches were observed (the broad band in the 3-iodopyridine adduct is probably due to two close absorptions). It is possible that the third CN stretch was not observed due to low intensity.

The infrared spectra clearly show that the adducts are monomeric. The only reaction of $P(CN)_3$ with a bidentate pyridine attempted was with 2,2'-dipyridyl and although the chemical shift of 145.0 ppm indicated only weak complex formation there are interesting possibilities for the

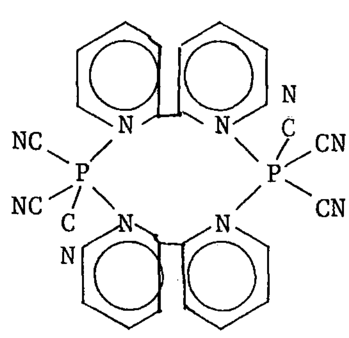
Table 8.2 Infrared data on $P(CN)_3$-pyridine adducts in the 2500-2000 cm^{-1} region

adduct	number of CN stretches	wavenumber (cm^{-1})
$P(CN)_3$.3-CN-py	3	2240*, 2200, 2190 nujol mull 2240*, 2195, 2190 in CH_2Cl_2
$P(CN)_3$.4-CN-py	4	2355, 2240†, 2195, 2185 in CH_2Cl_2
$P(CN)_3$.4-phenyl-py	2	2196, 2180 in CH_2Cl_2
$P(CN)_3$.3I-py	1	2195 (broad for CN stretch) contact film
$P(CN)_3$.py	2	2195, 2190 contact film

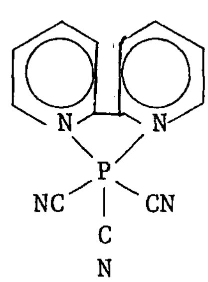
* Due to 3CN-pyridine, CN stretch at 2235 cm^{-1} in 3CN-pyridine

† Due to 4CN-pyridine, CN stretch at 2240 cm^{-1} in 4CN-pyridine

structure, which could have a bridged dimeric (IV) or monomeric (V) form.



(IV)



(V)

The solution infrared spectrum showed one broad absorption in the $2500-2000\ cm^{-1}$ region of the spectrum which probably contains two CN stretches. This implies that the monomer (V) is formed rather than the dimer (IV).

iv <u>The acceptor properties of $P(NCS)_3$</u>

a. <u>The $P(NCS)_3-Cl^-$ system</u>

The addition of Et_4NCl to $P(NCS)_3$ in CH_2Cl_2 caused the solution to turn deep red. The ^{31}P n.m.r. spectrum showed a downfield shift of the signal to -95.1 ppm with small resonances due to decomposition products at -17.8, 6.5 and 37.1 ppm. Attempts to crystallise any adduct by cooling the solution to 243K failed.

b. <u>The $P(NCS)_3-Br^-$ system</u>

A golden-yellow solution was formed initially when $P(NCS)_3$ and Bu_4NBr were mixed in CH_2Cl_2. The ^{31}P n.m.r. spectrum run immediately after mixing showed an upfield shift of the resonance to -74.4 ppm, indicating complex formation. The solution rapidly darkened and resonances due to decomposition products were observed, giving an intense signal at -191.8 with smaller peaks at -50.0, -17.8, and 8.2 ppm (possibly $PS(NCS)_3$). Although complex formation does seem to occur it is not certain that the limiting shift of the $P(NCS)_3Br^-$ ion was observed.

c. <u>The $P(NCS)_3-I^-$ system</u>

The reaction between $P(NCS)_3$ and Bu_4NI in CH_2Cl_2 produced a golden-yellow solution. The ^{31}P n.m.r. spectrum showed a small upfield shift to -83.8 ppm. The solution rapidly darkened and an intense resonance at -51.6, with smaller peaks at -64.5, -14.5, 1.6 and 8.2 ppm, ($PS(NCS)_3$) became apparent.

d. The $P(NCS)_3$-CN^- system

The reaction between $P(NCS)_3$ and Et_4NCN in CH_2Cl_2 was violently exothermic giving rise to a dark red solution. An intense resonance was seen at 172.6 ppm in the n.m.r. spectrum with smaller peaks at -80.7, -50.0, -27.5, -17.8 and 6.5 ppm. The resonance at 172.6 ppm seems too low for $P(CN)_3(NCS)^-$ which was observed at 183.8 ppm (section iii e) and by analogy with the reaction of Et_4NCN with PCl_3 and PBr_3 assignment as $P(NCS)_2(CN)_2^-$ seems reasonable.

e. The $P(NCS)_3$-NCS^- system

A dark red solution formed when $P(NCS)_3$ was treated with Et_4NNCS in CH_2Cl_2. An upfield shift of the signal to -82.2 ppm was observed. The solution rapidly darkened and after five days the ^{31}P n.m.r. spectrum showed a major resonance at -50.0 ppm with other small peaks at -16.2, -4.9 and 0.0 ppm due to other unassigned decomposition products.

v The acceptor properties of $P(NCO)_3$

The reaction of $P(NCO)_3$ with Et_4NCl was violently exothermic. Intense resonances were observed at -203.1, -143.5, -103.3, 11.4, 21.1, 27.5, and 32.4 ppm in the ^{31}P n.m.r. spectrum, none of which can be readily assigned.

Similarly the reaction of Et_4NNCO with $P(NCO)_3$ in CH_2Cl_2 was exothermic giving intense resonances in the ^{31}P n.m.r. spectrum at 14.7, 27.3 and 32.4 ppm with no evidence to suggest simple adduct formation. Presumably the main reaction is rearrangement to give phosphoryl derivatives, presumably containing cyano-groups.

vi The acceptor properties of PF_3

PF_3 showed no tendency to form adducts with Et_4NCl or Bu_4NBr in CH_2Cl_2. The ^{31}P n.m.r. spectrum showed only a quartet at δ -103.7 ppm, J_{PF} 1409 Hz.

With Et_4NCN in CH_2Cl_2 excess PF_3 gave a black solution, the ^{31}P n.m.r. spectrum of which showed a single line at -88.7 ppm which implies that rapid exchange is occurring, possibly according to equation (10).

$$PF_3 + CN^- \rightleftharpoons PF_3(CN)^- \quad \ldots (10)$$

After one day the main resonance had shifted downfield to -95.1 ppm and low intensity features were observed in the 100 - 200 ppm region.

vii Experimental

The preparation of Et_4NPCl_4

PCl_3 was added to a saturated solution of Et_4NCl in CH_2Cl_2 and the mixture cooled to 243K. After several days the large colourless crystals were filtered and washed with 30°-40° petroleum ether.

Analysis Et_4NPCl_4 requires	C 31.68%	H 6.60%	N 4.62%	P 10.32%	Cl 46.9%	
found	C 32.99%	H 7.46%	N 4.77%	P 9.5%	Cl 47.0%	

Due to the instability of the compound in solution no further purification was attempted.

The preparation of $Et_4NPCl_2(NCS)_2$

PCl_3 was added to a saturated solution of Et_4NNCS in CH_2Cl_2 which was then cooled to 243K. The yellow crystals were filtered off and stored at 243K.

Analysis $Et_4NPCl_2(NCS)_2$ requires	C 34.48%	H 5.75%	N 12.07%	P 8.91%	Cl 20.40%	S 18.39%
found	C 31.96%	H 5.76%	N 10.41%	P 8.17%	Cl 21.75%	S 18.1 %

Because of the solution and thermal instability of the compound no further purification was attempted.

The preparation of $Me_2NP(CN)_2$ and reaction with HCl

PCl_3 (5 ml) and Me_2NH (7.5 ml at 273K) were dissolved in 50 ml 30°-40° petroleum ether. The solution was filtered and the filtrate evaporated to leave a colourless liquid. This was dissolved in 50 ml Et_2O with 20 ml CH_3CN and refluxed with AgCN (16 g) for 12 h. The ^{31}P n.m.r. of the resulting solution showed one resonance at 6.5 ppm due to $Me_2NP(CN)_2$. The solution was filtered and an excess of HCl (2 ml at 178K) was condensed into the solution at 178K. The white precipitate was filtered and washed with CH_2Cl_2.

Analysis $Me_2NH_2PCl_2(CN)_2$	requires	C 24.00%	H 4.00%	N 21.00%
	found	C 29.63%	H 6.73%	N 24.39%

The PBr_3-Et_4NNCS reaction

PBr_3 was added to a strong solution of Et_4NNCS which was cooled to 243K. The yellow crystals were filtered off and dried at the pump.

Analysis $Et_4NPBr_3(NCS)$	requires	C 23.54%	H 4.36%	N 6.10%	P 6.8%	Br 52.2%
	found	C 23.25%	H 5.81%	N 4.23%	P 8.2%	Br 56.6%
$Et_4NPBr_2(NCS)_2$	requires	C 27.47%	H 4.57%	N 9.62%	P 7.1%	Br 36.6%

The preparation of $Et_4NP(CN)_3Cl$

$P(CN)_3$ (0.613 g, 5.6 mmole) and Et_4NCl (0.93 g, 5.6 mmole) were dissolved in 7 ml CH_2Cl_2. The volume of solvent was reduced to 3 ml, 1 ml CCl_4 was added and the solution cooled to 254K. The crystals were filtered off and dried at the pump to give 1.25g $Et_4NP(CN)_3Cl$.

Analysis $Et_4NP(CN)_3Cl$	requires	C 48.09%	H 7.29%	N 20.40%	P 11.29%	Cl 12.93%
	found	C 48.18%	H 7.70%	N 20.11%	P 11.65%	Cl 13.2 %

The preparation of $Pr_4NP(CN)_3Br$

$P(CN)_3$(0.569 g, 5.2 mmole) and Pr_4NBr (1.389 g, 5.2 mmole) were dissolved in 15 ml CH_2Cl_2. The solvent was removed in vacuo to leave $Pr_4NP(CN)_3Br$.

Analysis $Pr_4NP(CN)_3Br$ requires C 48.00% H 7.47% N 14.93% P 8.27% Br 21.33%

found C 47.31% H 9.74% N 12.92% P 8.04% Br 21.17%

The preparation of $Pr_4NP(CN)_3I$

$P(CN)_3$ (0.565 g, 5.2 mmole) and Pr_4NI (1.622 g, 5.2 mmole) were dissolved in 15 ml CH_2Cl_2. The solution was stirred for 10 mins and evaporated under vacuum.

Analysis $Pr_4NP(CN)_3I$ requires C 42.65% H 6.64% N 13.27% P 7.34% I 30.09%

found C 42.26% H 7.57% N 12.74% P 7.02% I 29.64%

The preparation of $P(CN)_3$-pyridine adducts

$P(CN)_3$.py $P(CN)_3$ (0.12 g, 1.7 mmole) and pyridine (0.14 ml, 1.7 mmole) were dissolved in 10 ml CH_2Cl_2. The solvent was removed under vacuum to leave a red oil which fumed in the dry box atmosphere.

$P(CN)_3$.3-iodopyridine $P(CN)_3$ (0.32 g, 3.0 mmole) and 3-iodopyridine (0.61g, 3.0 mmole) were dissolved in 20 ml CH_2Cl_2. The solution was evaporated to give a yellow oil.

Analysis $P(CN)_3$.3-iodopyridine requires C 30.57% H 1.27% N 17.83%

found C 28.49% H 1.60% N 13.67%

$P(CN)_3$.3-cyanopyridine $P(CN)_3$ (0.40 g, 3.7 mmole) and 3-cyanopyridine (0.38 g, 3.7 mmole) were dissolved in CH_2Cl_2. The solution was evaporated to give a pale yellow solid which was recrystallised from CH_2Cl_2.

Analysis $P(CN)_3$.3-cyanopyridine requires C 50.70% H 1.88% N 32.86%

found C 48.26% H 1.89% N 31.16%

$P(CN)_3$.4-cyanopyridine $P(CN)_3$ (0.43 g, 4.0 mmole) and 4-cyanopyridine (0.41 g, 4.0 mmole) were dissolved in 15 ml CH_2Cl_2. The solution was stirred for 15 mins to dissolve all the $P(CN)_3$. The green-yellow solution was evaporated under reduced pressure to leave a white solid which was recrystallised from CH_2Cl_2 as long needles.

Analysis $P(CN)_3$.4-cyanopyridine requires C 50.70% H 1.88% N 32.86%

found C 52.51% H 1.22% N 33.30%

$P(CN)_3$.4-phenylpyridine $P(CN)_3$ (0.28 g , 2.5 mmole) and 4-phenylpyridine (0.39 g , 2.5 mmole) were dissolved in 10 ml CH_2Cl_2. The green-yellow solution was evaporated and the yellow solid was recrystallised from CH_2Cl_2.

Analysis $P(CN)_3$.4-phenylpyridine requires C 63.64% H 3.41% N 21.21%

found C 57.55% H 3.46% N 18.23%

The possible reason for the poor analyses of the $P(CN)_3$-pyridine adducts has been discussed in section iii g.

Chapter 9

The Degree and Pattern of Substitution in Six-Coordinate Phosphorus(V) Species

i The degree of substitution

Starting from PCl_6^- it is possible to prepare PX_6^- either by direct substitution (X = F, N_3, NCS, and NCO) or by ligand exchange (X = NCS or OCN). Similarly from the $PFCl_5^-$, $PF_2Cl_4^-$ and $PF_3Cl_3^-$ ions the corresponding fully chloro-substituted derivatives can be obtained with N_3 and NCS. With cyanide the substitution reactions stop at the third stage for $PFCl_5^-$, $PF_2Cl_4^-$ and (usually) PCl_6^-, and at the second for the $PF_3Cl_3^-$ ion. This difference between cyanide and the other ligands can be explained in terms of simple molecular orbital theory.

The energy level diagram is adapted from the conventional diagram for octahedral transition metal complexes as derived from ligand field theory and is shown in Figure 9.1. The only difference between this and the conventional diagram is that the d orbitals have a higher energy than the s and p orbitals for phosphorus. The value Δ is the crystal field splitting energy, which depends only on the ligands for any particular central atom. The greater the value of Δ, the lower the energy of the t_{2g} orbitals (d_{xy}, d_{xz} and d_{yz}). The ability of ligands to split the e_g and t_{2g} levels is reflected in the spectrochemical series[102], part of which is shown below. The exact position of the azide ligand is subject

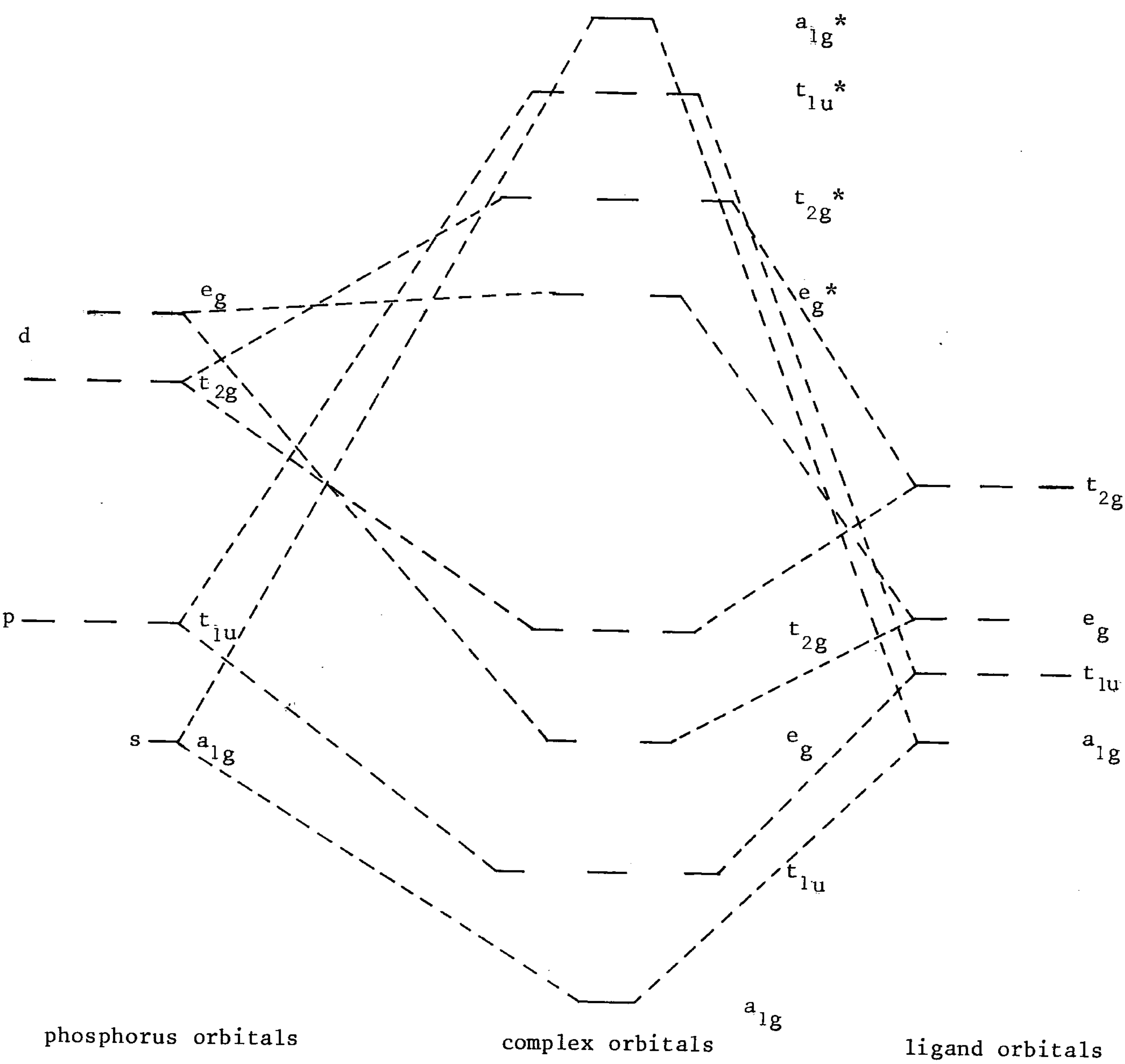
$Br^- < Cl^- < F^- \approx N_3^- < OH^- < SCN^- < NCS^- <$ pyridine < dipy << CN^-

low Δ ⟶ high Δ

to dispute but it appears to have a similar value to the fluoride ion[103,104],

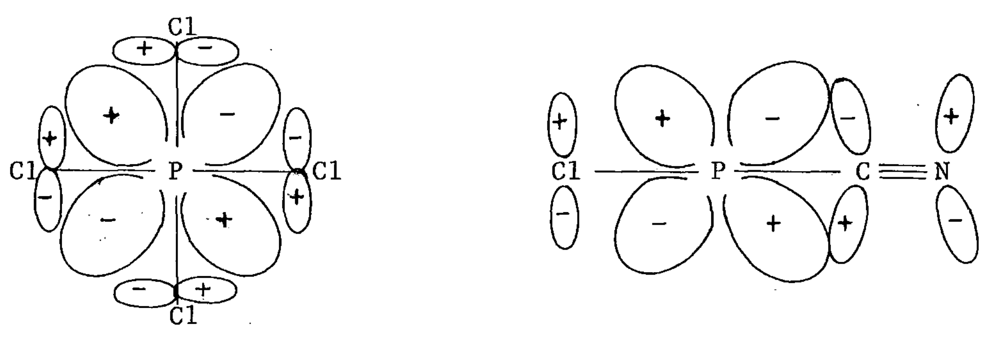
Figure 9.1

A qualitative representation of the orbital energy levels in six-coordinate phosphates where π-bonding is considered.



while OCN^- and NCO^- will probably be lower in the series than SCN^- and NCS^- respectively. From this it will be seen that cyanide ligands give the largest Δ value of all the common ligands, and thus lower the t_{2g} level to the greatest extent. The effect of this would be to increase the overlap between these orbitals and ligand orbitals of the same symmetry. Thus it is possible that some P-Cl π-bonding may occur as indicated in Figure 9.2a and that the P-Cl bond *trans* to a cyanide group might be preferentially strengthened (Figure 9.2b). This π-bonding would

Figure 9.2



P-Cl π-bonding in cyano-containing complexes

explain the predominance of *cis*- as opposed to *trans*-$PCl_4(CN)_2^-$ and *fac*- rather than *mer*-$PCl_3(CN)_3^-$, since the P-Cl bond *trans* to CN will be strengthened and thus rendered less liable to substitution. That the *fac*-isomer is the predominant product of the substitution does not indicate any particular instability for *mer*-$PCl_3(CN)_3^-$ since this isomer is the preferred product from the oxidation of $P(CN)_3Cl^-$. The occurrence of π-bonding could also explain the extreme difficulty of substituting into $P(CN)_3Cl_3^-$.

A similar rationalisation can be proposed to explain the observation that PCl_4dipy^+ does not react with LiN_3, even though the cations $PCl_{4-n}(N_3)_ndipy^+$ are stable and readily prepared by an alternative route.

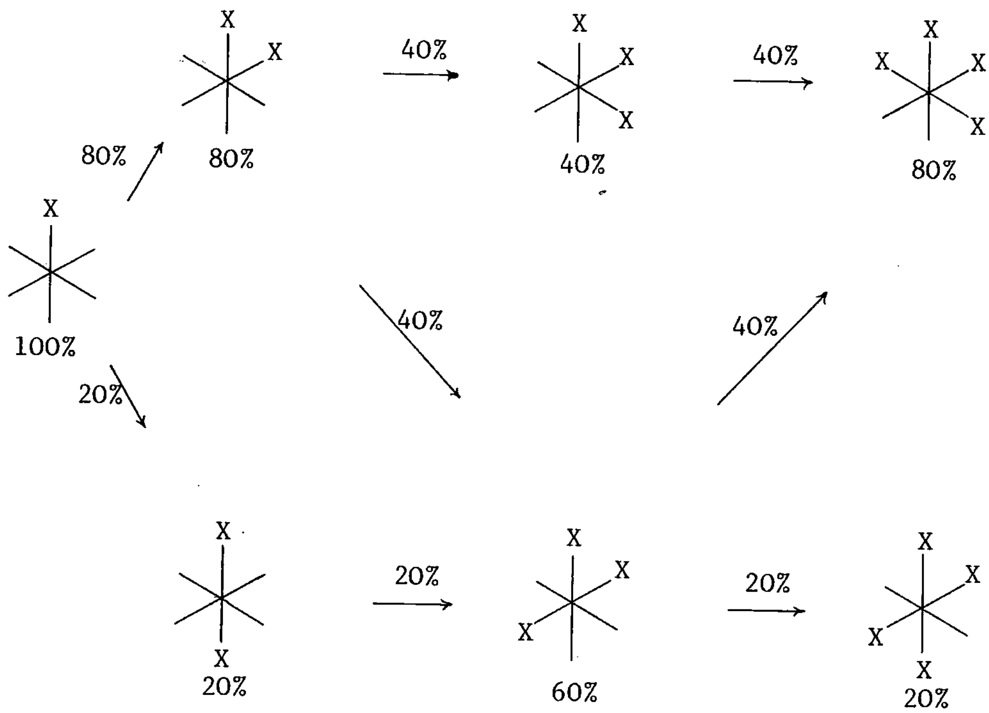
The bidentate dipyridyl ligand is relatively high in the spectrochemical series and may induce sufficient P-Cl π-bonding in the complex cation to reduce the susceptibility towards substitution. The d-orbitals would also be lower in energy because of the positive charge on the complex.

Thus the degree of substitution attainable in six-coordinate complexes seems to depend on the position of the ligands in the spectrochemical series. Ligands relatively low in the series can fully substitute the hexachlorophosphate ion, whereas the presence of ligands with high Δ values, e.g. in PCl_4dipy^+ and $PCl_3(CN)_3^-$, renders the P-Cl bonds relatively inert towards further substitution. The PCl_5.py complex does undergo substitution (with N_3^- at least) and thus it would seem that no significant π-bonding is occurring here. Obviously more work could be done on substitution into the PCl_4dipy^+ and PCl_5.py systems since so far they have only been studied with respect to azide substitution.

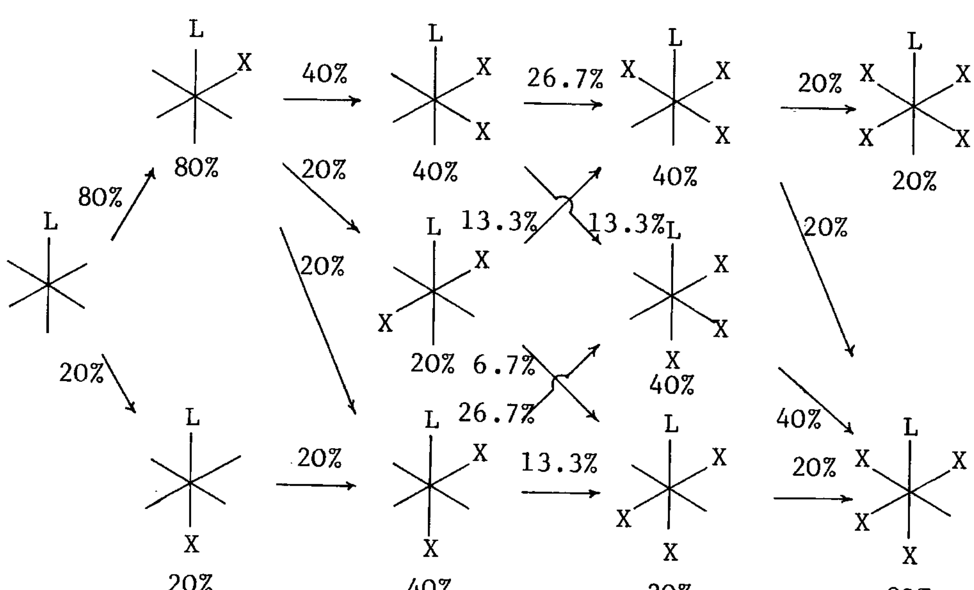
ii Pattern of substitution

If, in a PY_5X^- complex, the ligand X has no directive effect on further substitution of the complex by X, the relative intensities of *cis*:*trans* $PY_4X_2^-$ should be 4:1 since there are four P-Y bonds *cis* to X and only one *trans*. Similarly the *fac*:*mer* $PY_3X_3^-$ ratio would be 2:3 and *cis*:*trans* $PY_2X_4^-$ would be 4:1 as shown in Scheme 9.1. The analogous situation for PCl_5L^{n-}, which could apply to the $PFCl_5^-$ ion and the PCl_5.pyridine adduct, where L is not considered liable to substitution and is different from the incoming ligand, is shown in Scheme 9.2. Similarly the case of $PY_4X_2^{n-}$, applicable to the *cis*-$PF_2Cl_4^-$ and PCl_4dipy^+ complexes is shown in Scheme 9.3.

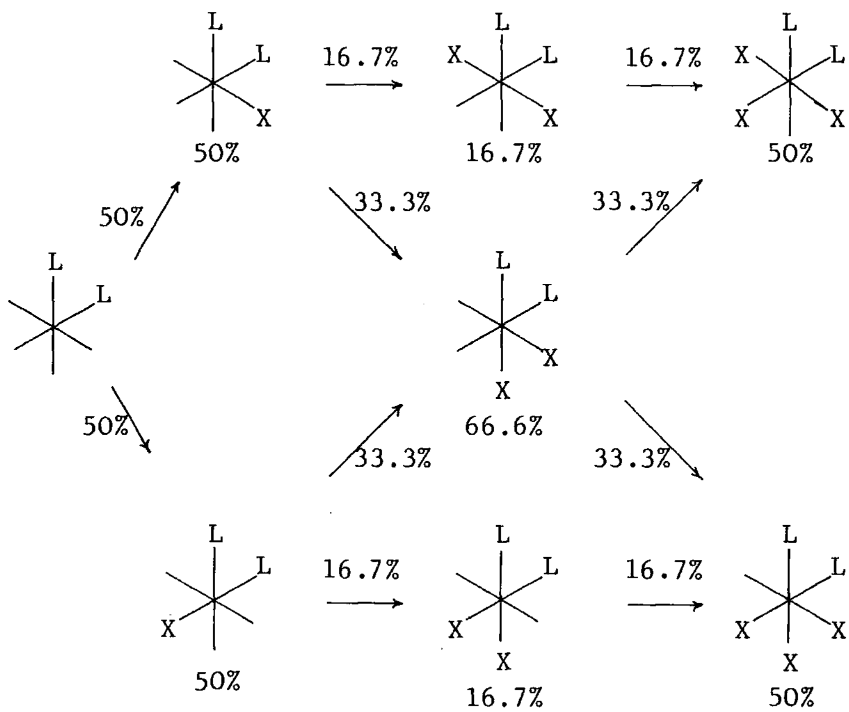
Scheme 9.1



Scheme 9.2



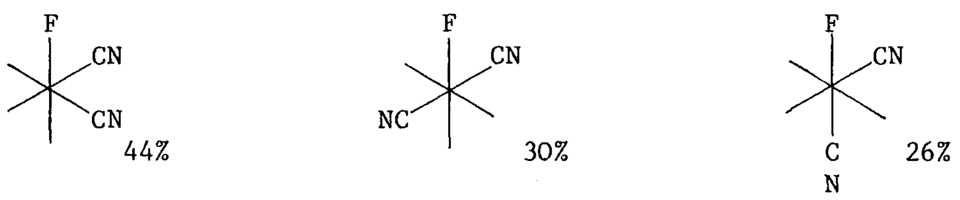
Scheme 9.3



If the direct substitution reactions into PCl_6^- with N_3^-, NCS^- and NCO^- are considered, (the pattern of substitution with CN^- having already been adequately accounted for), it can be seen that the presence of one pseudohalogeno-group does influence the position adopted by the next, since only one isomer is observed in each case. Where isomers were observed for the same ions, in the $PCl_{6-n}(OCN)_n^-$ series produced by ligand exchange, the ratio of *cis*:*trans* $PCl_4(OCN)_2^-$ was approximately 5:8, *mer*-$PCl_3(OCN)_3^-$ was not observed and the *cis*:*trans* ratio in $PCl_2(OCN)_4^-$ was roughly 2:3, which again indicates directive effects. The ligand exchange reaction between $P(NCS)_3$ and PCl_6^- gave an identical pattern of substitution to the PCl_6^- -NH_4NCS system. Thus it is apparent that strong directive effects are operating in substitution reactions into the PCl_6^- anion.

The only instances where isomers were observed in the $PCl_5.L$ and

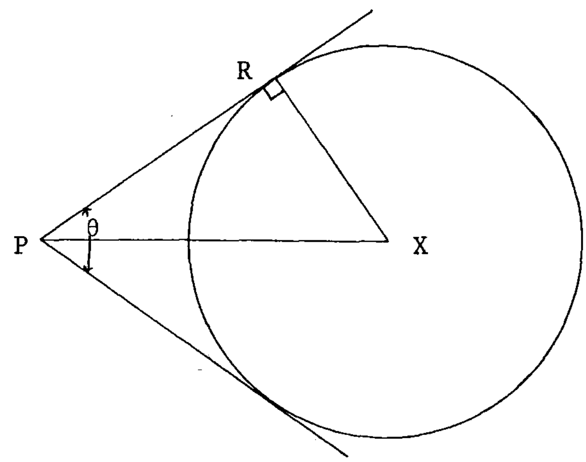
PCl_4L_2 systems were from the reactions of $PFCl_5^-$ and $PF_2Cl_4^-$ with CN^-. The first substituted species gave a ratio of isomers *cis*(CN to F):*trans* (CN to F) of approximately 70:30, which is reasonably close to the 80:20 ratio expected if the F atom was exerting no directive influence. Thereafter the intensity ratios deviated from those expected for no directive effect. The ratios for the $PFCl_3(CN)_2^-$ ions are shown below and indicate that the effect of the cyanide group predominates. Similarly with $PF_2Cl_4^-$ approximately



equal amounts of both isomers of $PF_2Cl_3(CN)^-$ were formed, indicating that the fluorine is having no marked effect on the cyanide substitution, but further reaction with more cyanide gave only one isomer for $PF_2Cl_2(CN)_2^-$, showing that the strong directive effect of the CN-group then dominates.

With ligands other than cyanide only one isomer is formed in each case, which implies that some directive effect is operating. One possible factor is a steric effect. A model for this has been devised by Zahrobsky[105]. This assigns to each ligand a steric angle which is estimated from the P-X bond length and the van der Waals radius of X as shown in Figure 9.3. If the P-X bond length is not known (as will be the case in most of the complexes) it can be estimated from the sum of the covalent radii of the elements concerned. The distance RX is the van der Waals radius of X. Thus the calculation of steric angles is relatively simple. The prediction of which isomer is preferred is carried out by summing the steric angles in the three mutually perpendicular planes of the octahedral complex. The isomer giving the largest sum of steric angles is considered to possess the greatest

Figure 9.3



Construction of the steric angle θ

non-bonding repulsive interaction and hence will not be preferred. As Zahrobsky points out this treatment invariably leads to the prediction of *cis*-MX_4Y_2 and *fac*-MX_3Y_3 regardless of the relative size of X and Y (where X and Y are monatomic ligands). This prediction has been confirmed by results on the $SnF_{6-n}Cl_n^{2-}$ series where a *cis*, *fac*, *cis* pattern was seen for n = 2,3 and 4 respectively[106]. Similarly the complexes $SnX_4Y_2^{2-}$ (X = Cl, Br, I; Y = Cl, Br, I; X ≠ Y) were all found to have the *cis* arrangement[107,108], although the other isomers have recently been observed for X = Cl, Y = Br[109], whilst in $NbCl_{6-n}Br_n^-$ and $SbCl_{6-n}Br_n^-$ systems similar arrangements for n = 2,3 and 4 were observed[70,71]. To test this method further the steric angles were calculated for the $PF_{6-n}Cl_n^-$ series $2 \leqslant n \leqslant 4$ where the *cis*, *fac*, *cis* pattern is well-established.

By using covalent radii[110] of phosphorus as 1.10 Å, fluorine 0.64 Å and chlorine 0.99 Å, and van der Waals radii for fluorine of 1.35 Å and chlorine of 1.8 Å, the steric angles are calculated as F = 101.8° and Cl = 118.8°. The results of the summation of steric angles are shown below in Table 9.1. For *cis* and *trans*-$PF_2Cl_4^-$ the sum of steric

Table 9.1

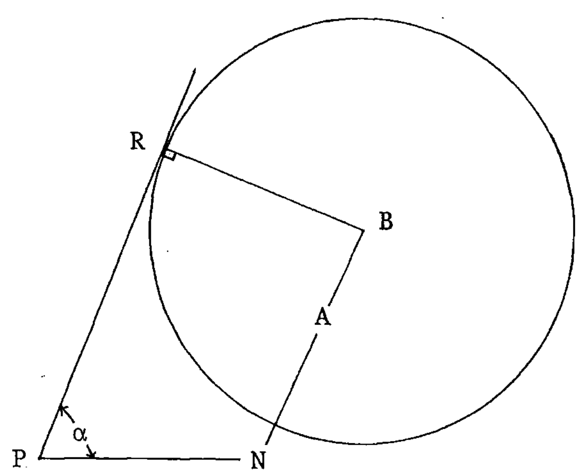
ion	sum of steric angles			preferred isomer	observed isomer
cis-$PF_2Cl_4^-$	441.2°	456.7°	456.7°	*cis*	*cis*
trans-$PF_2Cl_4^-$	441.2°	441.2°	473.2°		
fac-$PF_3Cl_3^-$	441.2°	441.2°	441.2°	*fac*	*fac*
mer-$PF_3Cl_3^-$	424.2°	456.7°	441.2°		
cis-$PF_4Cl_2^-$	441.2°	424.2°	424.2°	*cis*	*cis*
trans-$PF_4Cl_2^-$	407.2°	441.2°	441.2°		

angles of 473.2° is clearly the highest and hence the *cis* isomer is predicted to be more stable on this basis, as is observed. Similarly the results for $PF_3Cl_3^-$ and $PF_4Cl_2^-$ agree with the experimental observations.

With polyatomic ligands there is the possibility of repulsive interactions occurring outside the coordination sphere, and as Zahrobsky points out, in some $SnCl_4.2L$ complexes a *trans* arrangement of ligands is found. Thus the complexes of $SnCl_4$ with pyridine, Et_3N, Et_2O and Et_2S all have *trans* ligand configurations[111,112,113]. This Zahrobsky attributes to repulsive ligand-ligand interactions between atoms other than the donor atoms in the *cis* configuration. A *trans* arrangement of the sterically hindered ligands totally removes these interactions and hence the *trans* complex is more stable. The non-bonded interactions between chloride and ligand can then be considered to be represented by the steric angles of Cl and the donor atom. The ligand-ligand interaction will only become important if the atoms, other than the donor atom, of the ligand lie outside the steric angle of the donor atom.

For ligands such as NCS, NCO and N_3 it may well be necessary to calculate the steric angle taking into account the non-donor atoms. For this the values of covalent and van der Waals radii from reference 110 were used, and it was assumed that the PNX bond angle was 120° (X = CS, CO or N_2) on the basis of sp^2 hybridised nitrogen. The bond lengths in the NCS ion were taken as NC 1.17 Å and CS 1.61 Å [114], in the NCO ion as NC 1.21 Å and CO 1.17 Å [115], and the N N distances in N_3^- as 1.16 Å [116]. The OCN length was taken to be approximately the same as in the NCO compounds, the P-O-C angle being assumed to be tetrahedral, on the basis of sp^3 hybridisation of the oxygen. The steric angles were constructed as shown in Figure 9.4 and are taken as $\theta = 2\alpha$, while BR is the van der Waals radius of the terminal ligand atom. The full set

Figure 9.4



Construction of steric angle for bulky ligands

of steric angles calculated is shown in Table 9.2.

The summation of steric angles for complexes with bulky ligands is slightly more involved than in the case of monatomic ligands. With

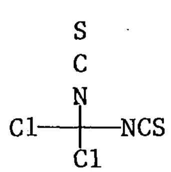
NCS groups (say) in a *cis* arrangement relative to each other the steric angle will be represented by the repulsions between the atoms

<u>Table 9.2</u>

Steric angles for octahedral P(V) complexes

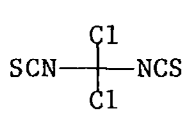
ligand	steric angle	comments
F	101.8°	
Cl	118.8°	
N	113.0°	For all N-containing ligands when *cis* to Cl or F
O	105.4°	
N_3	121°	}
NCO	115°	} Angles used to represent interactions of bulky ligands when in a *cis* configuration
OCN	125°	}
NCS	130°	}

outside the coordination sphere i.e. 130°, but for NCS *trans* to Cl the repulsive interactions will be considered as arising from contact between the Cl and the N atoms, as indicated below:-



sum of steric angles = 2Cl + NCS + N

237.6°+ 130° + 113° = 480°



sum of steric angles = 2Cl + 2N

237.6°+ 226° = 463°

The results of the calculations for the $PCl_{6-n}X_n^-$ ions where X = N_3, NCO, OCN and NCS are shown in Table 9.3. Generally the isomer observed experimentally is the preferred species on the basis of the steric model. The observation of the *trans-mer-cis* pattern in the $PCl_{6-n}(NCS)_n^-$ series gives some confidence in this treatment as a predictive method. The observation of *cis*-$PCl_2(NCO)_4^-$ where the *trans*-isomer is expected is not surprising in view of the prediction, and observation, of *fac*-$PCl_3(NCO)_3^-$. Rearrangement of the molecule would then be required to generate *cis*-$PCl_2(NCO)_4^-$.

The largest discrepancy is in the $PCl_{6-n}(OCN)_n^-$ series, where the most abundant isomers are those which are predicted to be thermodynamically less stable. A possible explanation would be the formation of a kinetically preferred product initially, followed by decomposition and rearrangement of the anions. The decomposition is rapid in these systems and thus the anions may not have been observed in their thermodynamically most stable configuration, which would be predicted by the steric model. Since these ions could not be obtained by direct substitution into PCl_6^-, there was no independent data for comparison.

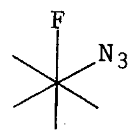
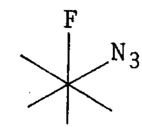
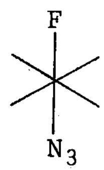
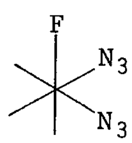
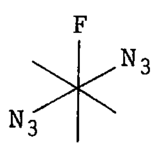
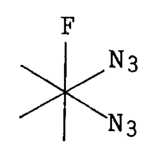
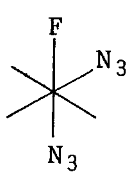
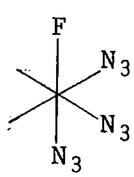
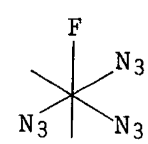
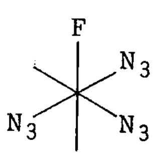
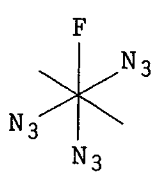
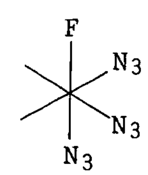
Similar calculations can be performed for the $PFCl_{5-n}(N_3)_n^-$ and $PF_2Cl_{4-n}X_n^-$ series (X = N_3, NCS). The results for the $PFCl_{5-n}(N_3)_n^-$ ions (where observed) are shown in Table 9.4. It can be seen that the agreement between the predicted and experimentally observed isomers is good. The only ambiguity arises in the case of $PFCl_2(N_3)_3^-$ where the ion could not be unambiguously assigned to one isomer. In view of the very good agreement between experimental results and those obtained by this method so far, assignment may be made on the basis of steric angles in this instance and it is concluded that $PFCl_2(N_3)_3^-$ has structure A (Table 9.4).

Table 9.3 Sums of steric angles for some octahedral complexes

ion \ X	N_3			NCO			NCS			OCN		
cis-$PCl_4X_2^-$	471.6	469.4	469.4*	465.6	469.4	469.4*	497.6	469.4	469.4	468.0	448.4	448.4*
trans-$PCl_4X_2^-$	463.6	463.6	475.2	475.2	469.4	469.4	475.2	469.4	469.4*	475.2	448.4	448.4
fac-$PCl_3X_3^-$	471.6	471.6	471.6*	465.6	465.6	465.6*	497.6	497.6	497.6	468.0	468.0	468.0*
mer-$PCl_3X_3^-$	473.8	469.4	463.6	461.8	469.4	463.6	491.8	469.4	463.6*	474.2	448.4	448.4
cis-$PCl_2X_4^-$	473.8	479.4	473.8*	461.8	461.8	465.6	491.8	480.6	491.8*	474.2	474.2	468.0*
trans-$PCl_2X_4^-$	484.0	463.6	463.6	460.0	463.6	463.6*	520.0	463.6	463.6	500.0	448.4	448.4

* indicates the preferred isomer

Table 9.4 Sums of steric angles for the observed $PFCl_{5-n}(N_3)_n^-$ ions

isomer	sum of steric angles	observed isomer
	452.4 458.2 469.4*	
	475.2 452.4 452.4	
	452.4 452.4 454.6*	
	446.6 463.6 458.2	
	452.4 454.6 469.4	
	454.6 454.6 471.6	A 
	473.8 452.4 446.6	or
	463.6 456.8 452.4*	B 

* indicates predicted isomer

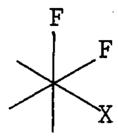
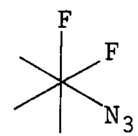
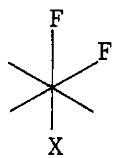
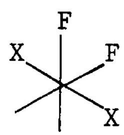
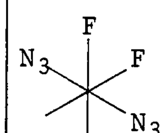
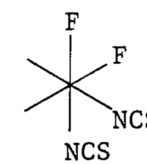
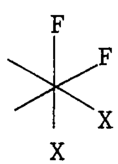
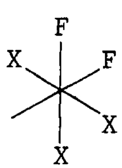
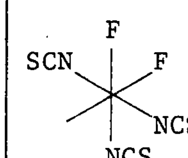
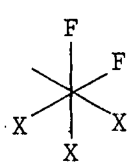
The values for the various isomers in the $PF_2Cl_{4-n}X_n^-$ series ($X = N_3$, NCS) are shown in Table 9.5. The agreement with the observed species is good for the azides, but the thiocyanates do not form the predicted isomers. This indicates that factors other than simple steric effects may be operating in this case.

In conclusion, it seems that the geometries of most of the mixed complexes can be explained in terms of the steric requirements of the ligands. In the case of cyano-complexes π-bonding would seem to be the most important factor. In the relatively few instances where octahedral complexes have been prepared by oxidation interesting ratios of isomers are formed. The oxidation of $P(CN)_3$ by Cl_2 in the presence of Cl^- gives a 1:3 ratio of *fac:mer* $PCl_3(CN)_3^-$ whereas the corresponding reaction with PF_3 gives a 3:1 ratio of *fac:mer* $PF_3Cl_3^-$. This difference probably arises from the fact that in the formation of $PCl_3(CN)_3^-$ the $P(CN)_3Cl^-$ complex is undergoing oxidation whereas PF_3 is presumably first oxidised to PF_3Cl_2 which then accepts Cl^- to give the anion. In view of this it is rather surprising that the oxidation of PF_2Cl yields only *cis*-$PF_2Cl_4^-$.

iii Future Work

Some aspects of the work in this thesis may prove profitable for further investigation. The reactions of the PCl_4dipy^+ and $PCl_5.py$ complexes have only been studied with respect to azide substitution and there is no reason to assume that other pseudohalogeno-derivatives cannot be formed. Aspects of the studies on six-coordinate systems could readily be carried out for other elements with suitable n.m.r. active nuclei, e.g. Sn, Pb, Tl, Se, Te and Pt, where a wider variety of complexes could be studied. The degree and patterns of substitutions in these mixed systems would provide an interesting comparison with

Table 9.5 Sums of steric angles for $PF_2Cl_{4-n}X_n^-$ ions (X = N_3, NCS)

ion	X	steric angles	observed isomer	X	steric angles	observed isomer
	N_3	441.2 452.4 452.4*		NCS	441.2 452.4 452.4*	-
		441.2 458.2 435.4			441.2 458.2 435.4	
	N_3	446.6 446.6 441.2*		NCS	446.6 446.6 441.2*	
		454.6 452.4 435.4			435.4 463.6 452.4	
	N_3	435.4 456.8 446.6	-	NCS	435.4 474.8 446.6	
		437.6 454.6 454.6*			446.6 463.6 463.6*	

* denotes preferred isomer

the results of the present work. The application of the pairwise additivity method could be applied to a wider range of systems where the effect of varying charge e.g. SnX_6^{2-}, PbX_6^{2-}, TlX_6^{3-}, and the presence of stereochemically inactive lone pairs e.g. SeX_6^{2-} and TeX_6^{2-}, could be studied. Also of interest with respect to the pairwise additivity method would be the pseudo-octahedral systems, e.g. SeX_5^- and TeX_5^- where X:lone pair interactions may have to be considered.

All the four-coordinate pseudohalogeno species were prepared in mixtures and it would clearly be advantageous to isolate and purify individual species. The only possible method to achieve this would be chromatography. This would be tedious in the extreme, however, requiring the use of large amounts of bromine as solvent.

The range of adducts formed by phosphorus trihalides seems rather limited; attempts to prepare mixed halogeno species failed and further work in this area would probably not be profitable. The introduction of more electronegative groups into the phosphine e.g. CF_3PCl_2 may enhance the Lewis acidity, and thus favour adduct formation.

Appendix 1

Infrared and Raman Spectra

Key to spectra

c = contact film

n = nujol mull

p = polythene discs

On the spectra

N = peaks due to nujol

S = peaks due to solvent

R = peaks due to tetraalkylammonium groups

P = peaks due to polythene

Index to Spectra

1. $(NP(N_3)_2)_x$ c, p, KBr
2. Decomposition products of PCl_2N_3 in CH_2Cl_2 0.1 mm NaCl
3. $Et_4NPCl_5(CN)$ m, CsI
4. $Et_4NPCl_4(CN)_2$ isomer mixture m, CsI
5. $Et_4NPCl_3(CN)_3$ *fac* isomer m, CsI
6. $Et_4NPCl_3(CN)_3$ 3:1 *mer*:*fac* ratio m, CsI
7. $Pe_4NP(NCS)_6$ c, p, CsI
8. $Et_4NPF_5(CN)$ thin layer from CH_2Cl_2 on CsI
9. $Et_4NPF_3Cl_2(CN)$ isomer mixture, thin layer from CH_2Cl_2 on CsI
10. $Et_4NPF_3Cl(CN)_2$ thin layer from CH_2Cl_2 on CsI
11. $Et_4NPF_5(NCS)$ m, CsI
12. $Et_4NPF_5(NCO)/PF_6$ in CH_2Cl_2 0.05 mm KBr
13. Et_4NPCl_4 m, CsI

14. $Et_4NPCl_2(NCS)_2$ m, CsI

15. $Et_4NPBr_3(NCS)$ m, CsI

16. $Et_4NP(CN)_3Cl$ m, KBr

17. $Et_4NP(CN)_3Cl$ in CH_2Cl_2 0.1 mm KBr

18. $Bu_4NP(CN)_3Br$ c, CsI

19. $Bu_4NP(CN)_3Br$ in CH_2Cl_2 0.1 mm KBr

20. $Pr_4NP(CN)_3Br$ m, CsI

21. $Bu_4NP(CN)_3I$ in CH_2Cl_2 0.1 mm KBr

22. $Pr_4NP(CN)_3I$ m, CsI

23. $P(CN)_3$.pyridine c, CsI

24. $P(CN)_3$,3I-pyridine c, CsI

25. $P(CN)_3$.3CN-pyridine m, CsI

26. $P(CN)_3$.3CN-pyridine in CH_2Cl_2 0.05 mm KBr

27. $P(CN)_3$.4CN-pyridine in CH_2Cl_2 0.05 mm KBr

28. $P(CN)_3$.4phenylpyridine in CH_2Cl_2 0.05 mm KBr

29. $P(CN)_3$.dipyridyl in CH_2Cl_2 0.05 mm KBr

Raman Spectra

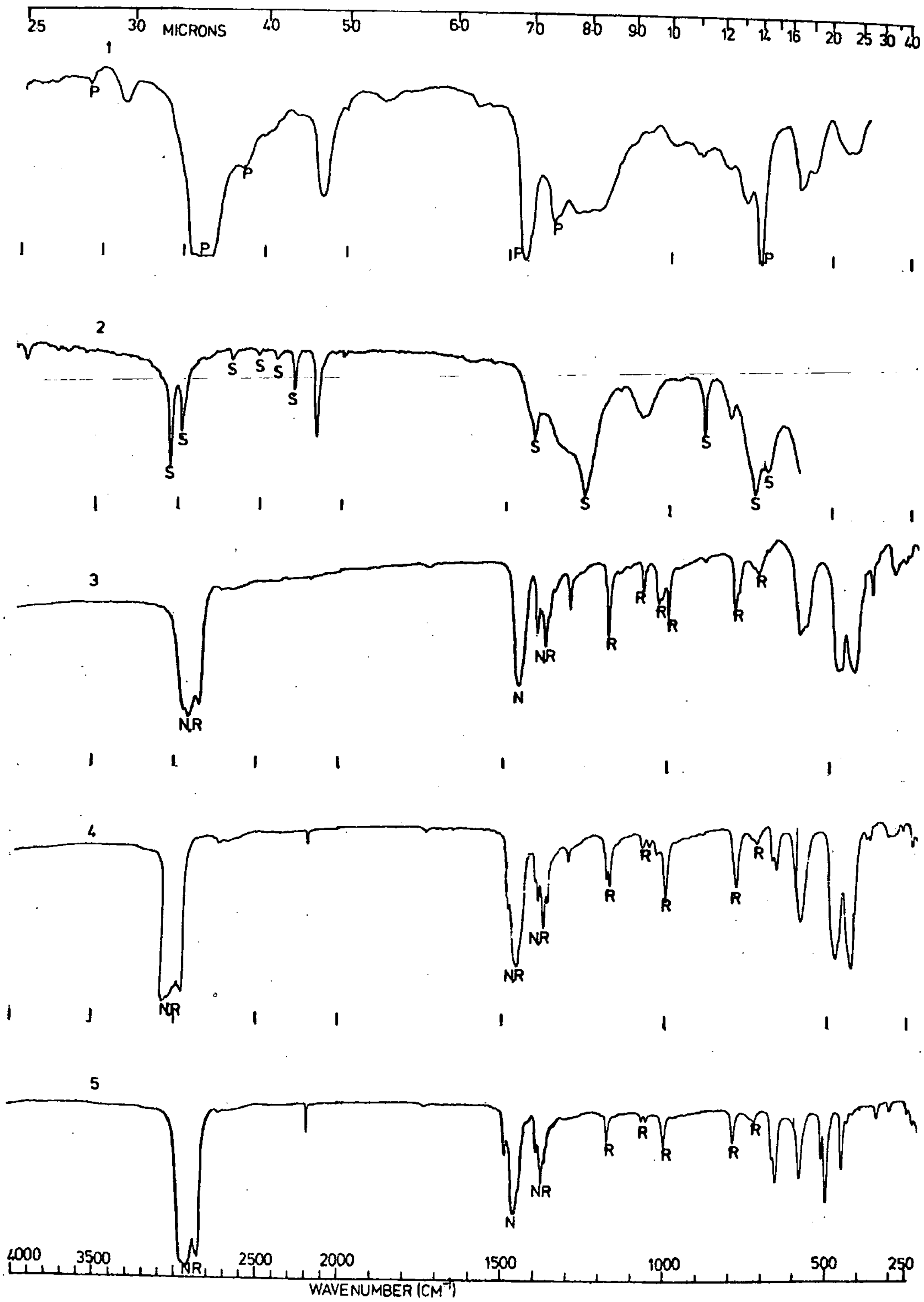
30. $Et_4NPCl_5(CN)$

31. $Et_4NPCl_4(CN)_2$ isomer mixture

32. $Et_4NPCl_3(CN)_3$ *fac* isomer

33. $Et_4NPCl_3(CN)_3$ 3:1 *mer*:*fac* ratio

34. Et_4NPCl_4


25 30 MICRONS 40 50 60 70 80 90 10 12 14 16 20 25 30 40
1
P P P P P P
2
S S S S S S S S S S S S
3
NR N NR R R R R R R
4
NR NR NR R R R R R
5
N NR R R R R R NR
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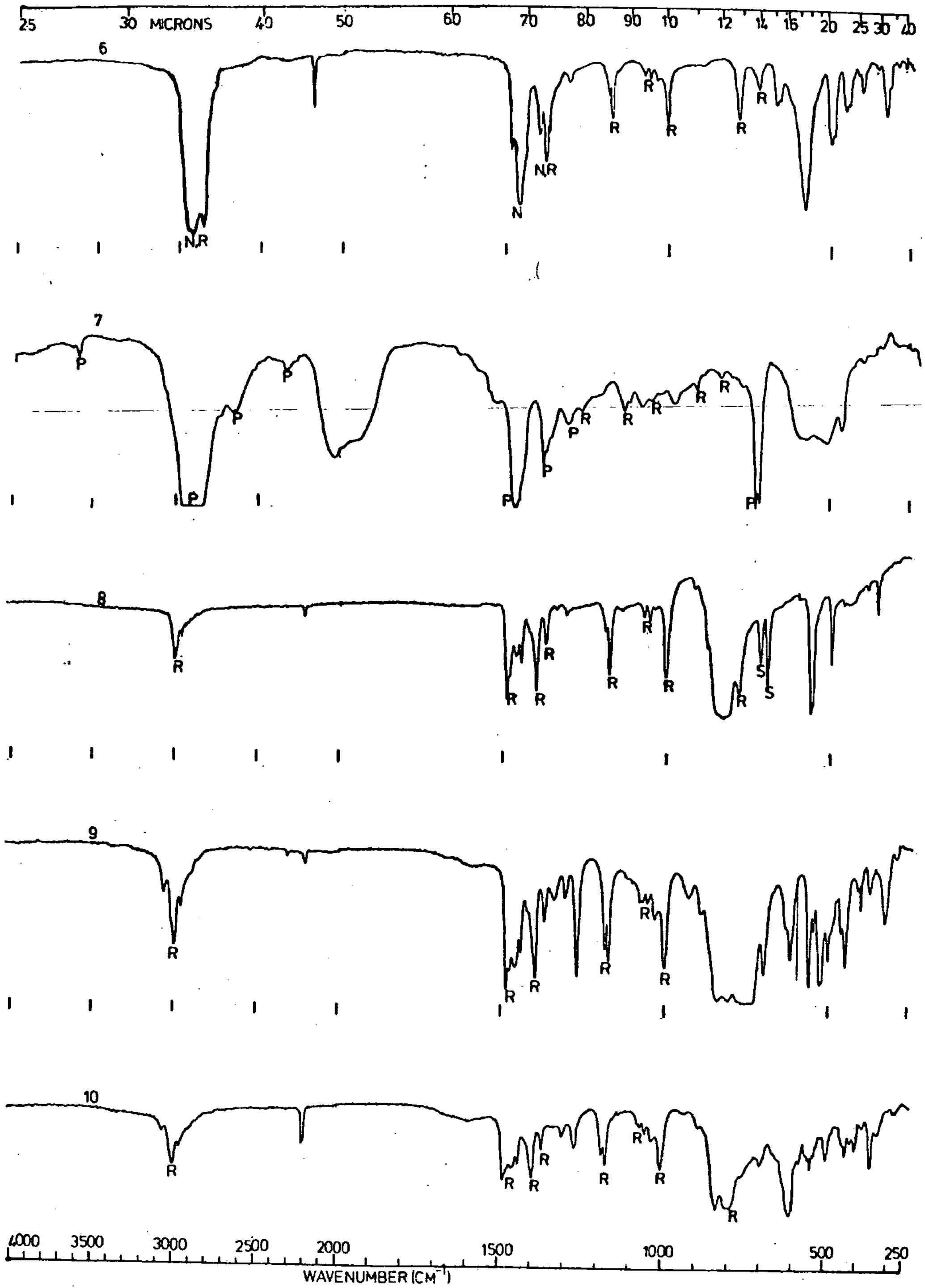
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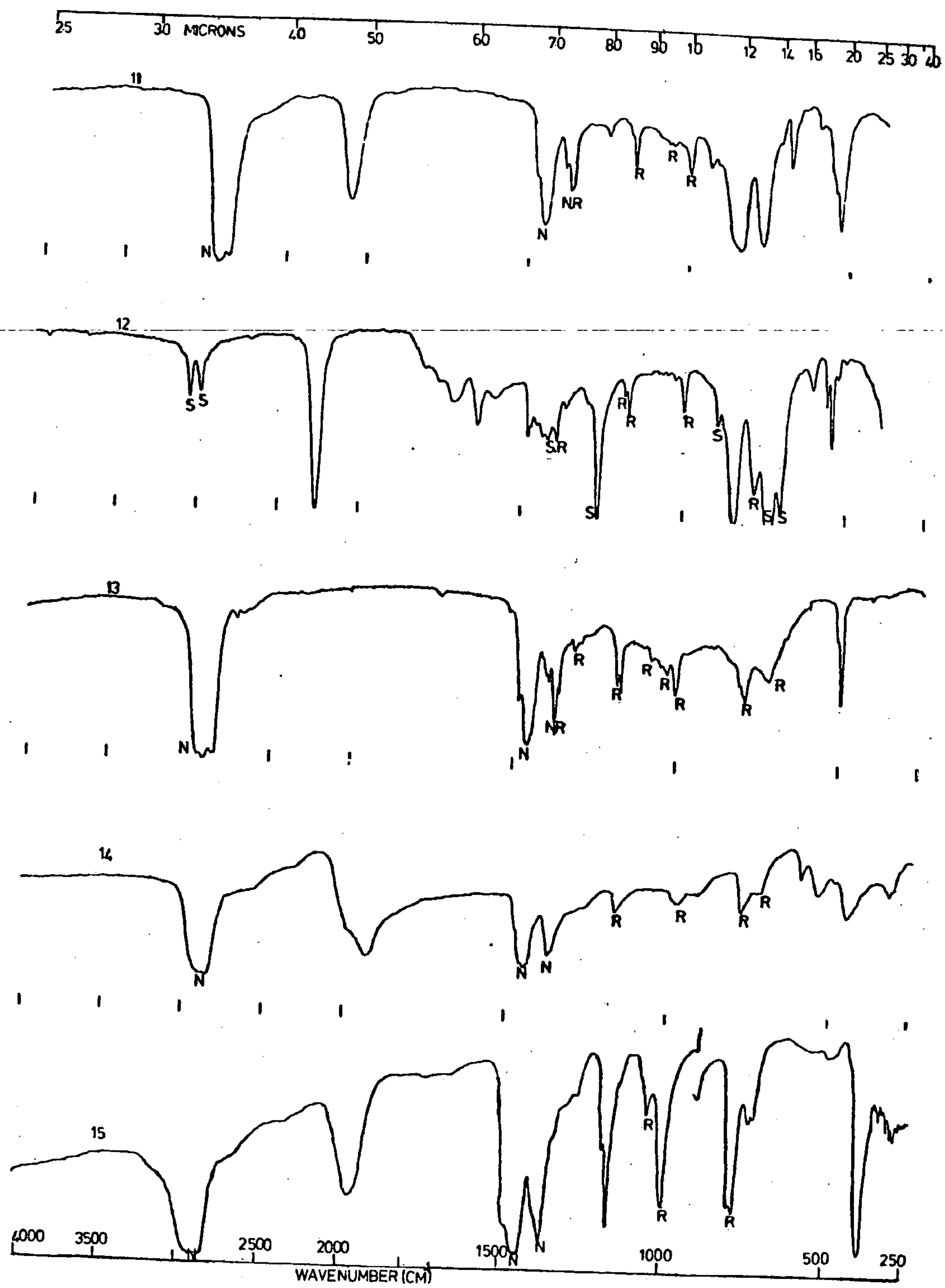
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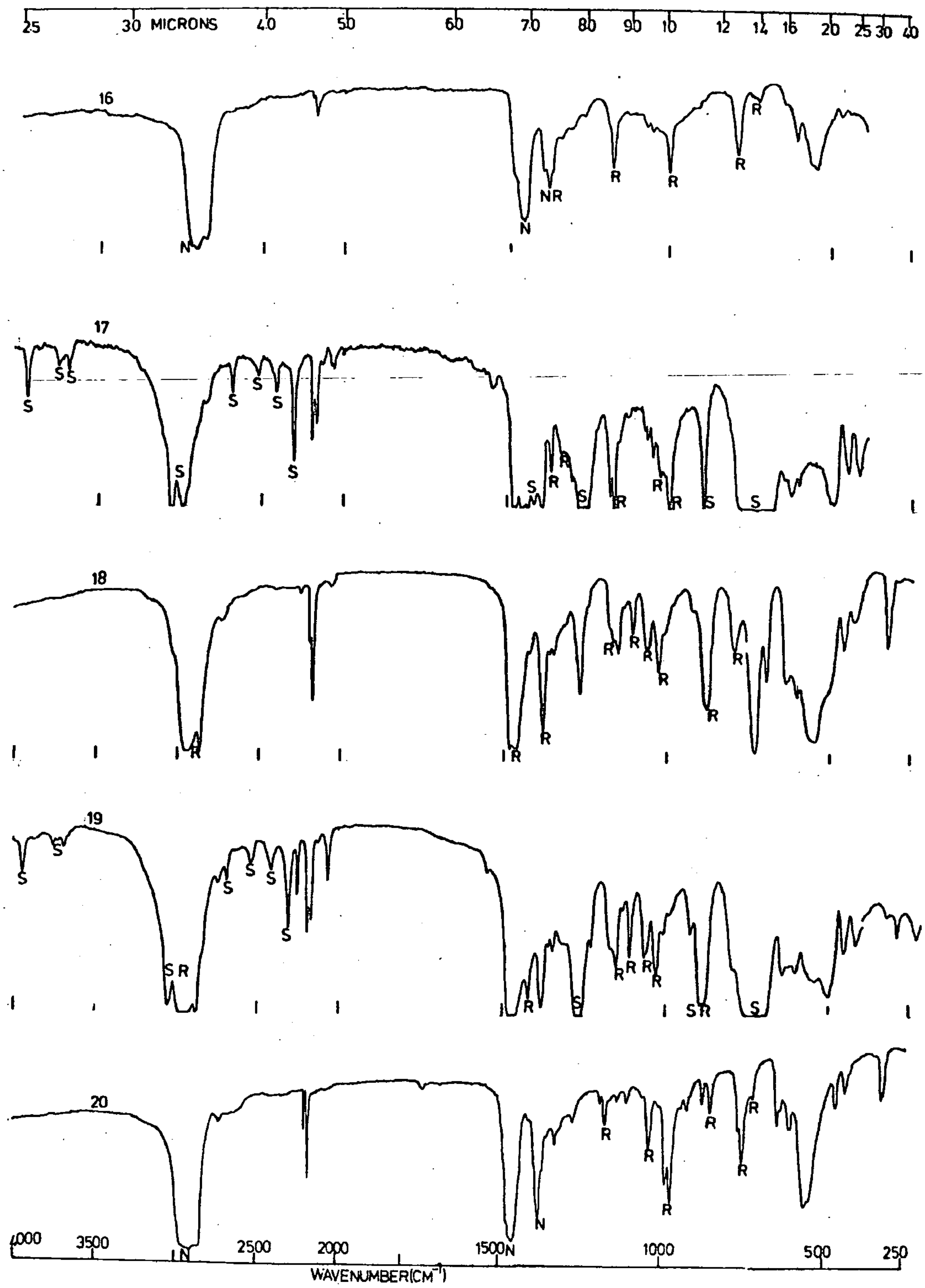

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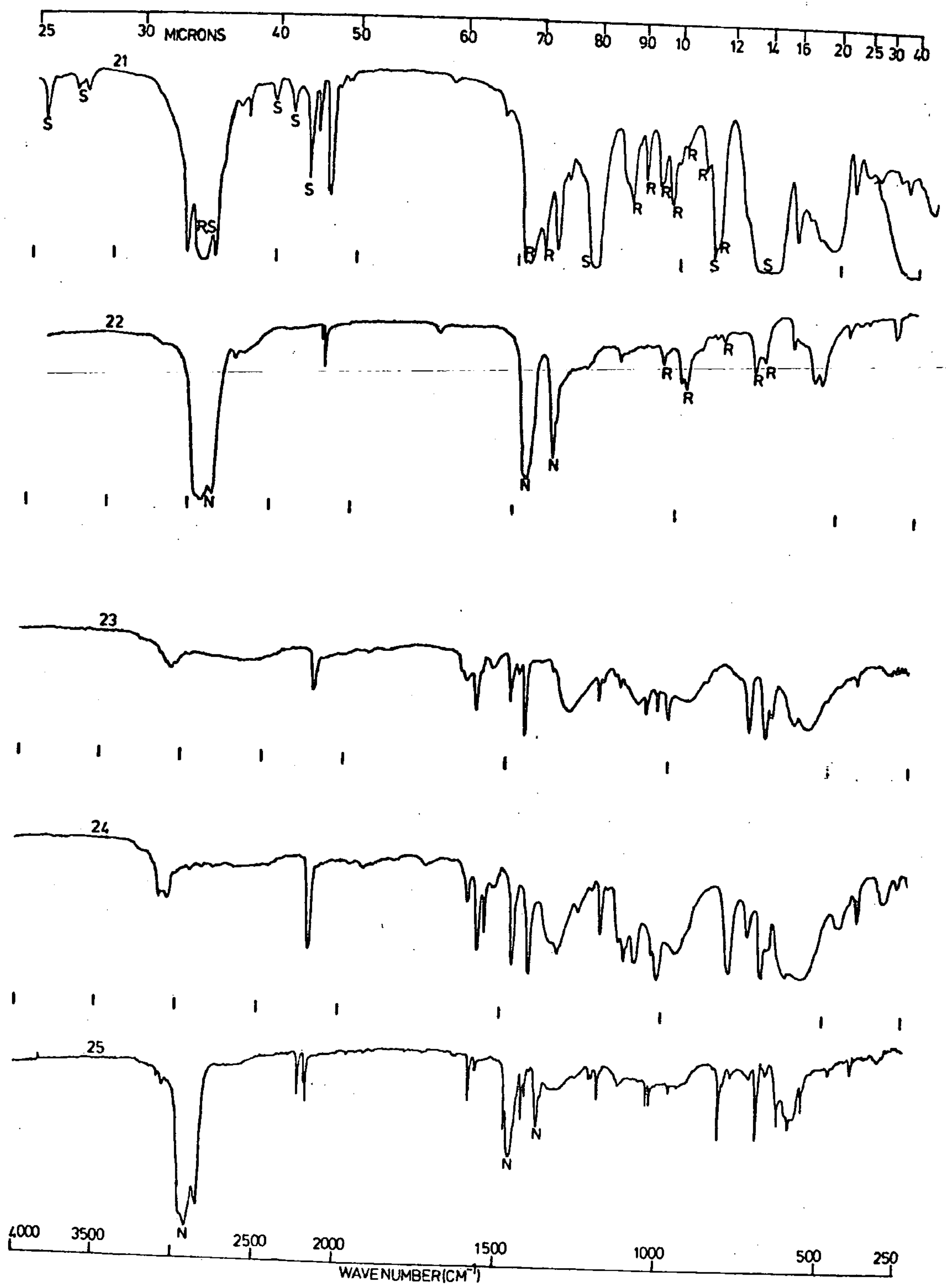
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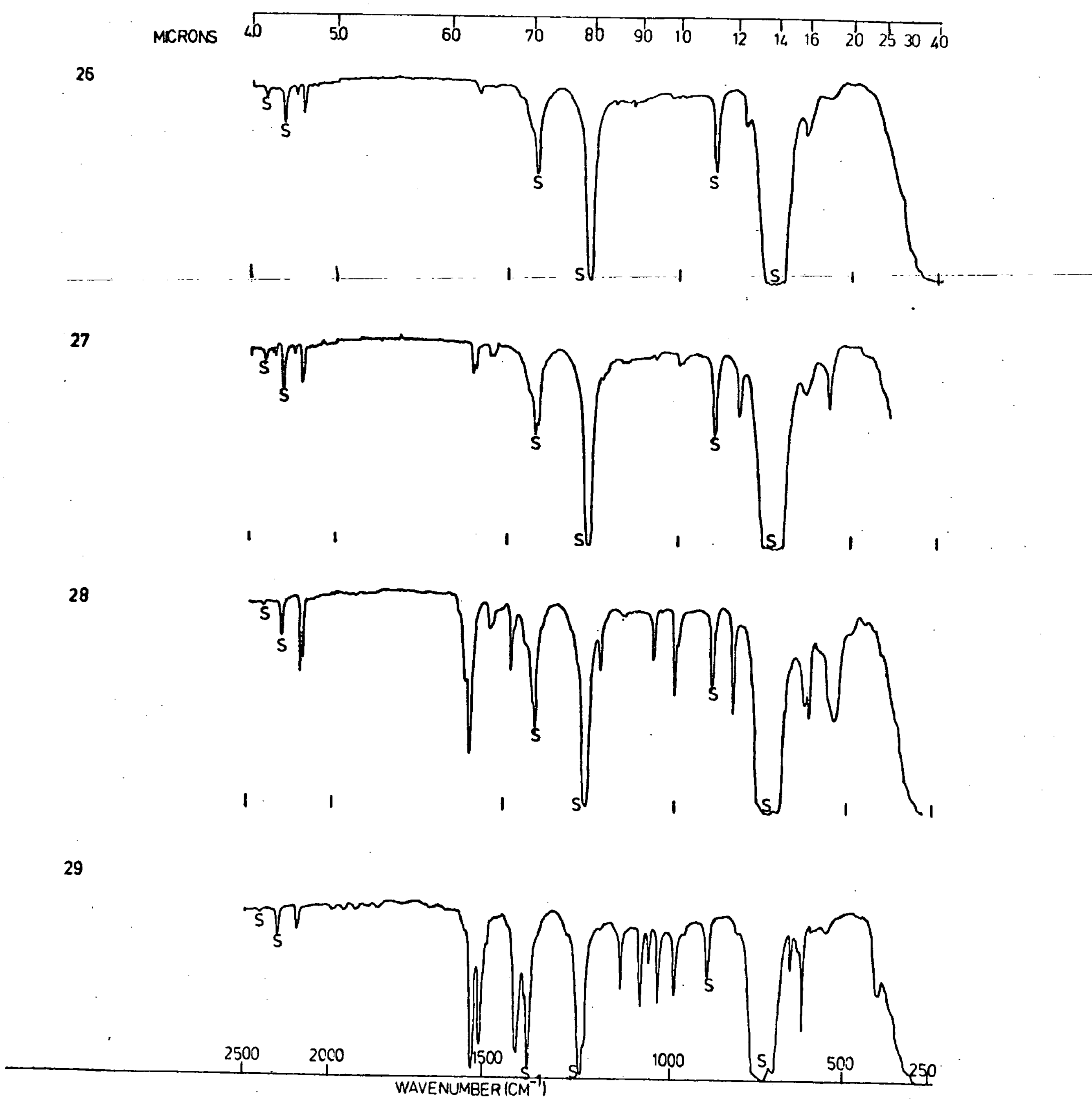
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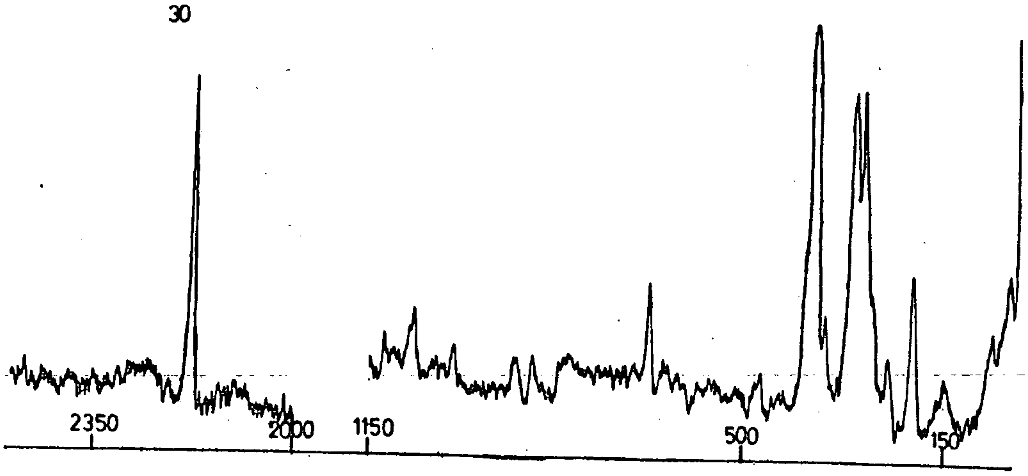
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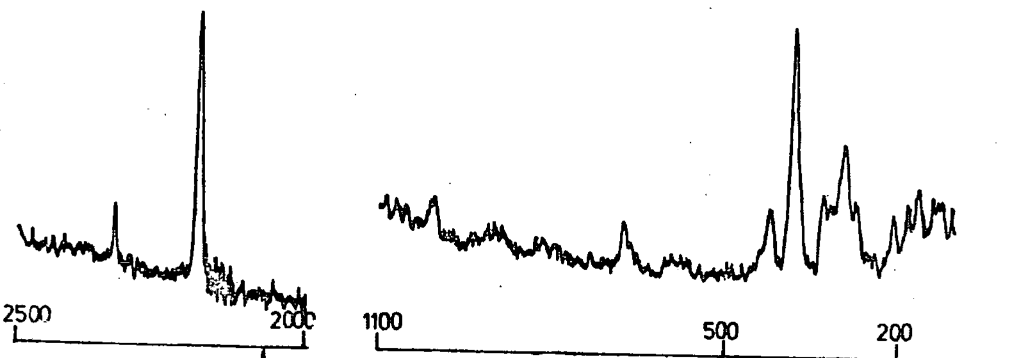
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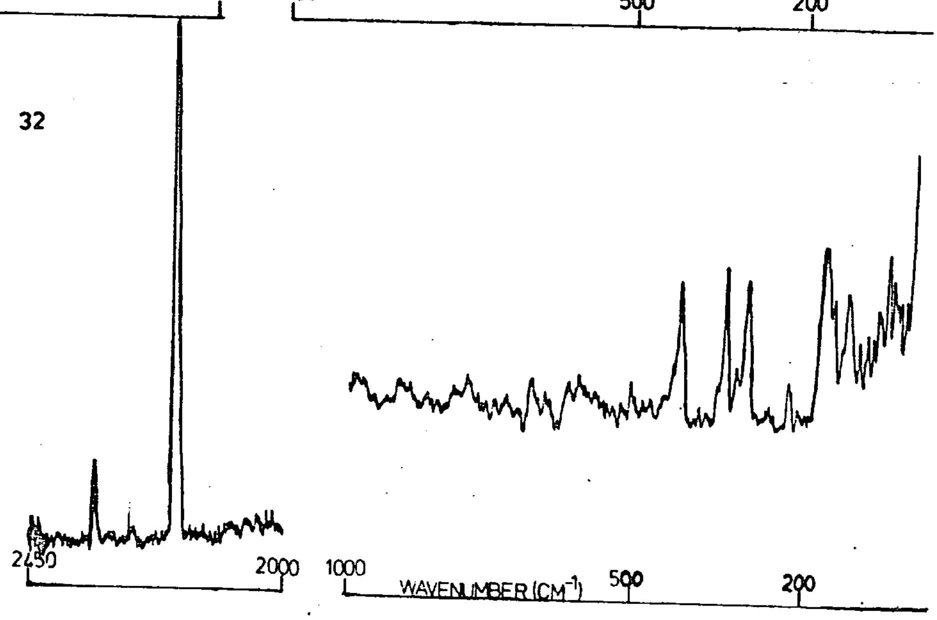
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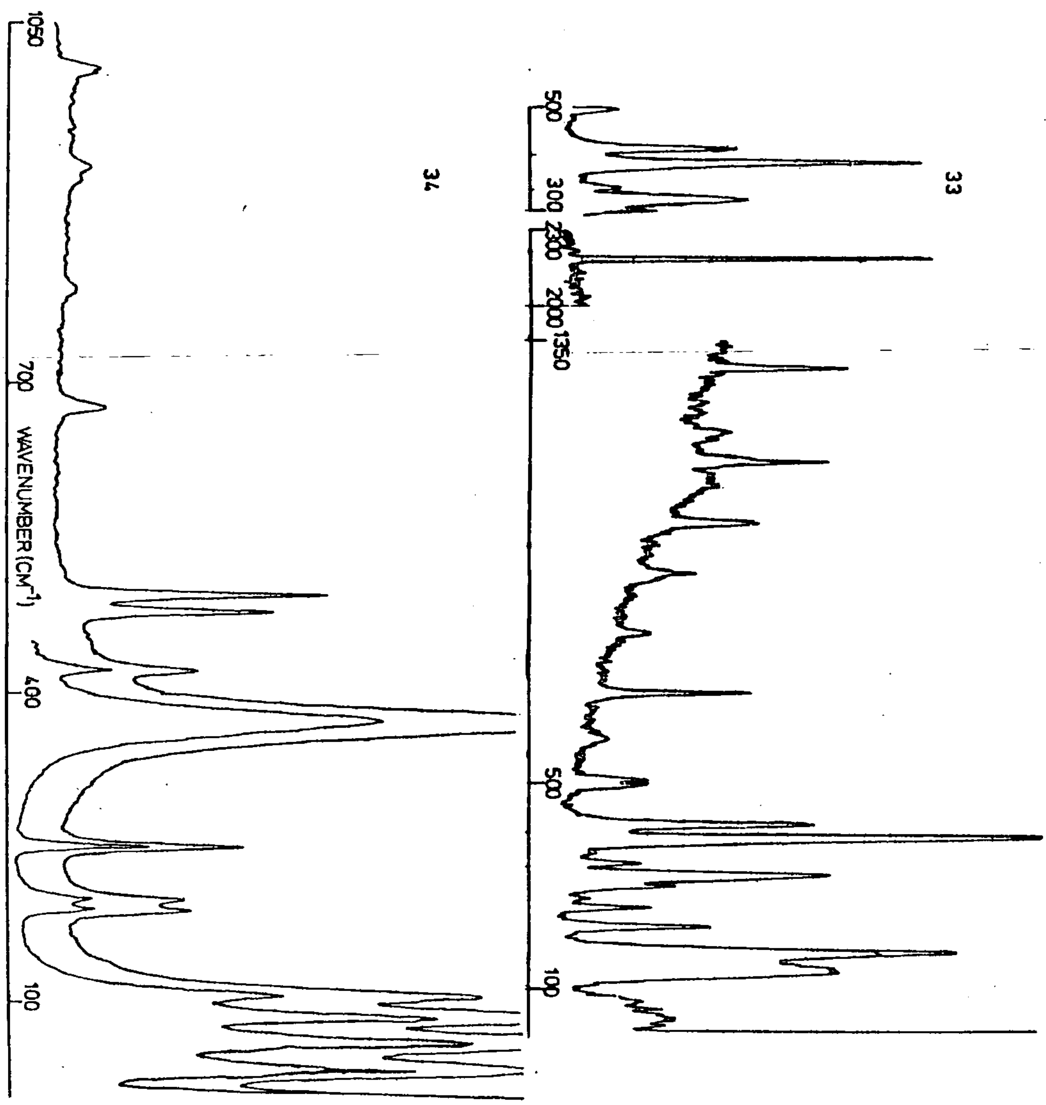
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Appendix 2

The Reactions of Phosphorus(III) Halides with Hydrogen Cyanide

i PCl_3

PCl_3 and HCN were reacted together in a sealed silica tube. Initially two immiscible layers were formed. Gradually a white solid was produced and the ^{31}P n.m.r. spectrum showed strong resonances at -30.7 and -4.9 ppm in addition to unreacted PCl_3 (δ -219.3 ppm). After the tube had been shaken at 303K for 16 h the contents had solidified to a yellow-brown substance. The ^{31}P n.m.r. spectrum showed two intense resonances at -3.3 and -30.7 ppm, with a smaller peak at -62.9 ppm.

The tube was opened inside the dry box, the solid which initially seemed moist rapidly dried, presumably losing excess HCN. The elemental analyses indicate a 2:1 reaction of HCN:PCl_3.

Analysis	$PCl_3.2HCN$ requires	C 12.53%	H 1.50%	N 14.62%
	found	C 14.64%	H 1.04%	N 15.39%.

From the chemical shifts of the product it is clear that simple solvolysis to produce $PCl_{3-n}(CN)_n$ ($0 \leqslant n \leqslant 3$) is not occurring. The product is probably polymeric, but no definite assignment of structure is possible.

ii PBr_3

PBr_3 and HCN formed immiscible layers which with continual agitation formed a yellow solid. On standing overnight at 300K the contents of the tube solidified. The ^{31}P n.m.r. spectrum showed resonances at 59.6 ppm ($PBr(CN)_2$) and either a doublet δ 109.5 ppm, J_{PH} 203 Hz or two singlets of equal intensity at 105.5 and 113.6 ppm. The tube was opened inside the dry box and the excess HCN allowed to evaporate. The elemental analyses indicate an approximate 1:1 reaction.

Analysis $PBr_3.HCN$ requires C 4.50% H 0.37% N 5.25%

found C 5.21% H 0.62% N 5.91%.

In this reaction some solvolysis was observed, although the peak due to $PBr(CN)_2$ was low in intensity. If oxidative addition to give $PBr_3H^+CN^-$ were occurring a doublet would be expected in the ^{31}P n.m.r. spectrum, but the value of 203 Hz is rather low for P-H coupling and so assignment as two singlets seems more probable.

iii PI_3

PI_3 and HCN reacted slowly over a period of 12 h to produce $PI_2(CN)$ (δ 12.9 ppm) and $PI(CN)_2$ (δ 112.9 ppm), with smaller unassigned resonances at -190.2, -93.5 and 45.3 ppm. The main reaction seen here is solvolysis to give the $PI_{3-n}(CN)_n$ series.

Appendix 3

Solution N.M.R. Investigations into the $P_2Y_{4-n}X_n$ Systems Y = I, Br; X = CN,Cl,Br

i The P_2I_4-AgCN system

The preparation of $P_2(CN)_4$ has been reported by the reaction of P_2I_4 with AgCN in dichloroethane[117], but no ^{31}P n.m.r. data were reported for this compound or any of the possible intermediates of the reaction. AgCN was added in small quantities to a suspension of P_2I_4 in 1-iodopropane (a solvent in which P_2I_4 is moderately soluble). The main products of the reaction were the $PI_{3-n}(CN)_n$ species, but several other resonances were seen which are readily assigned to the $PI_{4-n}(CN)_n$ series as shown in Table A.1.

Table A.1 ^{31}P n.m.r. data for $P_2I_{4-n}(CN)_n$ ($0 \leqslant n \leqslant 4$) in 1-iodopropane

Compound	Appearance of spectrum	Chemical shift	J_{PP} Hz
$PI_2PI(CN)$ (α β)	two doublets	α −94.8 β 39.9	177
$PI_2P(CN)_2$ (α β)	two doublets	α −77.0 β 81.2	170
PI(CN)PI(CN)	singlet	51.3	-
$PI(CN)P(CN)_2$ (α β)	two doublets	α 57.9 β 87.2	183
$P_2(CN)_4$	singlet	65.5	-

ii The P_2Br_4-AgCN system

The solution containing P_2Br_4 was prepared by the action of Pr_4NI on PBr_3 in CH_2Cl_2 (Chapter 8, section iic). AgCN reacted with this system to produce a marked decrease in intensity of the signal due to P_2Br_4. Two doublets assigned as PBr_2PBrCN were clearly observed at δ −165.2 ppm

(PBr_2–) and δ 34.3 ppm (PBr(CN)–), J_{PP} 225 Hz, together with a singlet at δ 45.3 ppm due to PBr(CN)PBr(CN). These features were all of low intensity; the main product of the reaction seemed to be $P(CN)_3I^-$ (δ 164.4 ppm). The final stages of the substitution reaction into P_2Br_4 could not be observed, presumably due to decomposition to $PBr_{3-n}(CN)_n$ which rapidly react with the excess AgCN and Pr_4NI to give $P(CN)_3I^-$.

iii The P_2I_4-PCl_3 system

The identification of $P_2I_{4-n}Cl_n$ ($0 \leqslant n \leqslant 4$) species was attempted by ligand exchange between P_2I_4 and PCl_3 in CS_2. The ^{31}P n.m.r. spectrum indicated that exchange had occurred giving the $PCl_{3-n}I_n$ species ($0 \leqslant n \leqslant 3$). In addition a resonance was seen due to P_2I_4, together with new peaks at -100.6 and -147.8 ppm of equal intensity and a single more intense signal at -139.3 ppm. These are tentatively assigned as PI_2PICl and PIClPICl. No coupling was observed in the PI_2PICl molecule.

The addition of more PCl_3 caused the disappearance of all the new signals, which indicates that more highly chlorinated members of the series might be unstable.

iv The P_2I_4-PBr_3 system

The reaction between PBr_3 and P_2I_4 in CS_2 caused ligand exchange, giving the $PBr_{3-n}I_n$ series, with many low intensity resonances in the ^{31}P n.m.r. spectrum which can be assigned to $P_2I_{4-n}Br_n$ species. Again no PP coupling was observed, and the assignments are shown in Table A.2.

Table A.2 ^{31}P n.m.r. data for $P_2I_{4-n}Br_n$ ($0 \leqslant n \leqslant 4$) in CS_2

Compound	Appearance of spectrum	Chemical shift
P_2I_4	singlet	-106.7
PI_2PIBr (α β)	two singlets	α -98.6 β-137.5
PIBrPIBr	singlet	-129.1
PI_2PBr_2 (α β)	two singlets	α-101.9 β-154.7
P_2Br_4	singlet	-145.8

Appendix 4

Departmental Colloquia and First-Year Induction Course for Post-Graduates

The Board of Studies in Chemistry requires that each post-graduate research thesis contains an appendix listing

(a) all research colloquia, research seminars and lectures arranged by the Department of Chemistry during the period of the writer's residence as a post-graduate student;

(b) all research conferences attended and papers read out by the writer of the thesis, during the period when the research for the thesis was carried out; and

(c) details of the first-year induction course.

Events in (a) which were attended are marked *.

Research Colloquia, Seminars and Lectures

1. University of Durham Chemistry Colloquia

Academic Year 1977-1978

19 Oct. Dr. B. Heyn (U.of Jena, D.D.R.), "Sigma-organo molybdenum complexes as alkene polymerisation catalysts".

* 27 Oct. Professor R.A. Filler (Illinois Institute of Technology, U.S.A.), "Reactions of organic compounds with xenon fluorides".

* 2 Nov. Dr. N. Boden (U. of Leeds), "N.m.r. spin-echo experiments for studying structure and dynamical properties of materials containing interacting spin-Y_2 pairs".

9 Nov. Dr. A.R. Butler (U. of St. Andrews), "Why I lost faith in linear free energy relationships".

7 Dec. Dr. P.A. Madden (U. of Cambridge), "Raman studies of molecular motions in liquids".

* 14 Dec. Dr. R.O. Gould (U. of Edinburgh), "Crystallography to the rescue in ruthenium chemistry".

25 Jan. Dr. G. Richards (U. of Oxford), "Quantum pharmacology".

1 Feb. Professor K.J. Ivin (Queens U., Belfast), "The olefin metathesis reaction, mechanism of ring opening polymerisation of cycloalkenes".

* 3 Feb. Dr. A. Hartog (Free U., Amsterdam), "Surprising recent studies in organo-magnesium chemistry".

* 22 Feb. Professor J.D. Birchall (Mond Division, I.C.I.), "Silicon in the biosphere".

1 Mar. Dr. A. Williams (U. of Kent), "Acyl group transfer reactions".

* 3 Mar. Dr. G. van Koten (U. of Amsterdam), "Structure and reactivity of aryl-copper cluster compounds".

15 Mar. Professor G. Scott (U. of Aston), "Fashioning plastics to match the environment".

* 22 Mar. Professor H. Vahrenkamp (U. of Freiburg, Germany), "Metal-metal bonds in organometallic complexes".

19 Apr. Dr. M. Barber (UMIST), "Secondary ion mass spectra of surfaces and adsorbed species".

16 May Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface plasma waves and adsorbed species on metals".

18 May Professor M. Gordon (U. of Essex), "Three critical points in polymer chemistry".

22 May Professor D. Tuck (U. of Windsor, Ontario), "Electrochemical synthesis of inorganic and organometallic compounds".

24 & 25 May Professor P. von Schleyer (U. of Erlangen, Nürnberg),

* I "Planar tetra-coordinate methanes, perpendicular ethenes and planar allenes".

II "Aromaticity in three dimensions".

III "Non-classical carbo-cations".

21 June Dr. S.K. Tyrlik (Acad. of Sci., Warsaw), "Dimethylglyoxime-cobalt complexes - catalytic black boxes".

23 June Professor G. Mteescu (Case Western Reserve U., Ohio), "A concerted spectroscopy approach to the characterisation of ion and ion-pairs: facts, plans and dreams".

8 Sept. Dr. A. Diaz (I.B.M., San Jose, California), "Chemical behaviour of electrode surface bonded molecules".

15 Sept. Professor W. Siebert (Marburg, W. Germany), "Boron heterocycles".

* 22 Sept. Professor T. Fehlner (Notre Dame, U.S.A.), "Ferraboranes: synthesis and photochemistry".

Academic Year 1978-1979

12 Dec. Professor C.J.M. Stirling (U. of Bangor), "Parting is such sweet sorrow - the leaving group in organic chemistry".

31 Jan. Professor P.D.B. de la Mare (U. of Auckland, New Zealand), "Some pathways leading to electrophilic substitution".

* 14 Feb. Professor B. Dunnel (U. of British Columbia), "The application of n.m.r. to the study of motions of molecules in solids".

14 Mar. Dr. J.C. Walton (U. of St. Andrews), "Pentadienyl radicals".

28 Mar. Dr. A. Reiser (Kodak Ltd.), "Polymer photography and the mechanism of cross-link formation in solid polymer matrices".

* 25 Apr. Dr. C.R. Patrick (U. of Birmingham), "Chlorofluorocarbons and stratospheric ozone: an appraisal of the environmental problem".

1 May Dr. G. Wyman (European Research Office, U.S. Army), "Excited state chemistry of indigoid dyes".

2 May Dr. J.D. Hobson (U. of Birmimgham), "Nitrogen-centred reactive intermediates".

8 May Professor A. Schmidpeter (Inst. of Inorg. Chem., Munich U.), "Five-membered phosphorus heterocycles containing dicoordinate phosphorus".

* 9 May Professor G. Maier (Lahn Giessen U.),"Tetra-tert-butyltetrahedrane".

9 May Dr. A.J. Kirkby (U. of Cambridge), "Structure and reactivity in intramolecular and enzymic catalysis".

* 16 May Dr. J.F. Nixon (U. of Sussex), "Some recent developments in platinum-metal phosphine complexes".

23 May Dr. B. Wakefield (U. of Salford), "Electron transfer in reaction of metals and organometallic compounds with polychloropyridine derivatives".

13 June Professor I. Ugi (U. of Munich), "Synthetic uses of super nucleophiles".

25 Sept. Professor R. Soulen (Southwestern U., Texas), "Applications of HSAB theory to vinylic halogen substitution reactions and a few copper coupling reactions".

Academic Year 1979-1980

* 21 Nov. Dr. J. Müller (U. of Bergen) "Photochemical reactions of ammonia".

28 Nov. Dr. B. Cox (U. of Stirling), "Macrobicyclic cryptate complexes: dynamics and selectivity".

5 Dec. Dr. G.C. Eastmand (U. of Liverpool), "Synthesis and properties of some multicomponent polymers".

12 Dec. Dr. C.I. Ratcliffe, "Rotor motions in solids".

* 18 Dec. Dr. K.E. Newman (U. of Lausanne), "High pressure multinuclear n.m.r. in the elucidation of mechanism of fast simple inorganic reactions".

* 30 Jan. Dr. M. Barrow (U. of Edinburgh), "The structures of some simple inorganic compounds of silicon and germanium - pointers to structural trends in group IV".

6 Feb. Dr. J.M.E. Quirke (U. of Durham), "Degradation of chlorophyll-a in sediments".

23 Apr. B. Grievson B.Sc. (U. of Durham), "Halogen radio-pharmaceuticals"

14 May Dr. R. Hutton (Waters Associates), "Recent developments in multi-milligram and multi-gram scale preparative high performance liquid chromatography".

21 May Dr. T.W. Bentley (U. of Swansea), "Medium and structural effects on solvolytic reactions".

10 July Professor D. Des Marteau (U. of Heidelberg), "New developments in organonitrogen fluorine chemistry".

2. Durham University Chemical Society

Academic Year 1977-1978

13 Oct. Dr. J.C. Young and Mr. A.J.S. Williams (U. of Aberystwyth), "Experiments and considerations touching colour".

* 20 Oct. Dr. R.L. Williams (Metropolitan Police Forensic Science Dept.), "Science and Crime".

3 Nov. Dr. G.W. Gray (U. of Hull), "Liquid crystals - their origins and applications".

24 Nov. Mr. G. Russell (Alcan), "Designing for social acceptability".

* 1 Dec. Dr. B.F.G. Johnson (U. of Cambridge), "Chemistry of binary metal carbonyls".

2 Feb. Professor R.A. Raphael (U. of Cambridge), " Bizarre reactions of acetylenic compounds".

16 Feb. Professor G.W.A. Foules (U. of Reading), "Home winemaking".

2 Mar. Professor M.W. Roberts (U. of Bradford), "The discovery of molecular events at solid surfaces".

9 Mar. Professor H. Suschitzky (U. of Salford), " Fruitful fissions of benzofuroxans".

* 4 May Professor J. Chatt (U. of Sussex), "Reactions of coordinated dinitrogen".

9 May Professor G.A. Olah (Case Western Reserve U., Ohio), "Electrophilic reactions of hydrocarbons".

Academic Year 1978-1979

10 Oct. Professor H.C. Brown (Purdue U.), "The tool of increasing electron demand in the study of cationic processes".

* 19 Oct. Mr. F.C. Shenton (Public Analyst, Co. Durham), "There is death in the pot".

26 Oct. Professor W.J. Albery (Imperial College, London), "Photogalvanic cells for solar energy conversion".

9 Nov. Professor A.R. Katritsky (U. of East Anglia), "Some adventures in heterocyclics".

16 Nov. Dr. H.C. Fielding (Mond Division, I.C.I.), "Fluorochemical surfactants and textile finishes".

* 23 Nov. Dr. C. White (Sheffield U.), "The magic of chemistry".

18 Jan. Professor J.C. Robb (Birmingham U.), "The plastics revolution".

* 8 Feb. Mr. C.G. Dennis (Vaux Ltd.), "The art and science of brewing".

* 1 Mar. Professor R. Mason (Govt. Scientific Advisor), "The Scientist in defence policy".

10 May Professor G. Allen (Chairman SRC), "Neutron scattering for polymer structures".

Academic Year 1979-1980

18 Oct. Dr. G. Cameron (U. of Aberdeen), "Synthetic polymers - twentieth century polymers".

25 Oct. Professor P. Gray (U. of Leeds), "Oscillatory combustion reactions".

1 Nov. Dr. J. Ashby (I.C.I. Toxicological Laboratory), "Does chemically-induced cancer make chemical sense?".

8 Nov. Professor J.H. Turnbull (R.M.C. Shrivenham), "Luminescence of drugs".

* 15 Nov. Professor E.A.V. Ebsworth (U. of Edinburgh), "Stay still, you brute: the shape of simple silyl complexes".

24 Jan. Professor R.J.P. Williams (U. of Oxford), "On first looking into biology's chemistry".

14 Feb. Professor G. Gamlen (U. of Salford), "A yarn with a new twist -fibres and their uses".

21 Feb. Dr. M.L.H. Green (U. of Oxford), "Synthesis of highly reactive organic compounds using metal vapours".

* 28 Feb. Professor S.F.A. Kettle (U. of East Anglia), "Molecular shape, structure and chemical blindness".

6 Mar. Professor W.D. Ollis (U. of Sheffield), "Novel molecular rearrangements".

Research Conference Attended

3rd Annual Congress of the Chemical Society, Durham, 9-11 April, 1980.

First Year Induction Course

In each part of the course, the use and limitations of the various services available are explained by the people responsible for them.

Departmental organisation	Dr. E.J.F. Ross
Safety Matters	Dr. M.R. Crampton
Electrical appliances and infrared spectroscopy	Mr. R.N. Brown
Chromatography and microanalysis	Mr. T.F. Holmes
Library facilities	Mr. W.B. Woodward (Keeper of science books)
Atomic absorptiometry and inorganic analysis	Mr. R. Coult
Mass spectrometry	Dr. M. Jones
N.m.r. spectroscopy	Dr. R.S. Matthews
Glassblowing techniques	Mr. W.H. Fettis and Mr. R. Hart

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