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SPECTROSCOPIC AND STRUCTURAL STUDIES OF SOME NEW ORGANOPHOSPHORUS COMPOUNDS

by

R.M.K. DENG, B.Sc. (KHARTOUM)

A Thesis submitted for the degree of Doctor of Philosophy in
the University of Durham

October 1981

To Mamerdit, Tiirdit and Almg.

"The search for truth is one way difficult and one way easy, for it is certain that one can neither find it completely nor miss it wholly".

Aristotle

DECLARATION

The work described in this thesis was carried out in the University of Durham between October 1978 and September 1981. It has not been submitted, either wholly 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.

ACKNOWLEDGEMENTS

My sincere thanks are due to Dr. K.B. Dillon for his excellent supervision, and to the late Professor T.C. Waddington for the enthusiasm he showed for this work. I dare not try to list all the many others to whom I am indebted, lest I do some an injustice by inadvertently omitting their names, but I must mention Dr. A. Royston for writing the F.T. n.m.r. programme, R. Coult for the numerous analyses he performed, Mrs. Cocks for the C, H, and N micro-analyses, and J. Lincoln and A.W.G. Platt for their great assistance in the initial stages of this work.

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ABSTRACT

The acceptor properties of the alkyl-substituted phosphoranes $MePCl_4$ and $EtPCl_4$ towards chloride and pyridine ligands have been studied by ^{31}P n.m.r. spectroscopy. In $PhNO_2$ they react with $R_4'NCl$ to produce six-coordinate anions, which equilibrate with the parent compound.

$$RPCl_4 + Cl^- \rightleftharpoons RPCl_5^- \quad (R = Me \text{ or } Et)$$

With pyridine, $MePCl_4$ forms a five-coordinate cation ($MePCl_3py^+Cl^-$) in solution, whereas $EtPCl_4$ gives a white precipitate which analysed as a 1:1 adduct. Cationic species $RPCl_3L'^+Cl^-$ are formed with bidentate ligands L' (L' = bipy or phen). $RPCl_3^+SbCl_6^-$ salts also react with the bidentate pyridines to form six-coordinate complexes, which exist in two isomeric forms. Introduction of more than one alkyl group into the compound $R_nPCl_{4-n}^+Cl^-$ reduces the acceptor properties, however, and no adduct formation has been detected.

$CatPBr_3$ decomposes on addition of bromide ion to give catPBr and Br_3^-, while cat_2PBr is inert to this ion. Pyridine gives a 1:1 molecular adduct with cat_2PBr and a cationic species with $catPBr_3$, whereas bidentate pyridines form six-coordinate cationic derivatives $cat_2PL'^+$ and $catPBr_2L'^+$ respectively. $PhPBr_4$ like $catPBr_3$, decomposes in the presence of a bromide ion to give $PhPBr_2$ and Br_3^-, and shows no acceptor properties towards mono- or bidentate pyridines, but the adduct $PhPBr_3^+BBr_4^-$ forms six-coordinate complexes with bipy or phen. Several new compounds have been isolated and further characterised by ^{31}P n.m.r., vibrational spectroscopy and elemental analysis.

The organophosphorus dicyanides $RP(CN)_2$ (R = Me, Et, Ph) add on halide (Cl^-, Br^-, I^-) or thiocyanate ions to form four-coordinate anionic derivatives. The addition of CN^- to these cyanides, however, yields organocyanophosphide (I) ions, and cyanogen. Unlike the cyanides the organophosphorus halides $RPCl_2$ (R = Me, t-Bu, Ph) show no tendency to coordinate, although they react with

the cyanide ion to give $RP(CN)^-$. Most of the cyanide adducts have been isolated and characterised as above.

The solution chemistry of some mixed organohalogeno-phosphorus (V) compounds in 25 oleum and 100% H_2SO_4 has also been studied by ^{31}P n.m.r. spectroscopy. The 'compounds' $MePCl_2Br_2$ and Me_2PClBr_2 contain a series of mixed cations $MePCl_{3-n}Br_n^+$ and $Me_2PCl_{2-n}Br_n^+$ respectively. Direct halogen exchange between $Me_2PCl_2^+$ and $Me_2PBr_2^+$ in 25 oleum to form Me_2PClBr^+ has been established for the first time.

Azido- derivatives of the cationic species $RPCl_3^+$ (R = Et or Ph) and $R_2PCl_2^+$ (R = Me or Et) have been detected in solution. The organophosphate ions $RPCl_5^-$ (R = Me, Et or Ph) yield decomposition products with the azides, while cyanide give the fully-substituted ion $MeP(CN)_5^-$ from $MePCl_5^-$, as well as the intermediate species. Substitution of $PhPCl_5^-$ by CN^- seems to stop at $PhPCl_2(CN)_3^-$, however. The compounds $Et_4NMeP(CN)_5$ and $Et_4NPhPCl_2(CN)_3$ have been isolated and characterised. Isomeric configurations have been suggested for the species observed on the basis of pairwise additivity and statistical considerations.

ABBREVIATIONS USED

Et = ethyl

Me = methyl

pr = n-propyl, n-C_3H_7

Bu = n-butyl, n-C_4H_9

Pe = n-pentyl, n-C_5H_{11}

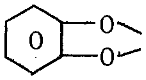
X = halogen or pseudo-halogen

py = pyridine

bipy = 2,2'-bipyridine

phen = 1,10-phenanthroline

cat = catechyl



R = any alkyl group

Miscellaneous

n.m.r. = nuclear magnetic resonance

n.q.r. = nuclear quadrupole resonance

b.p. = boiling point

m.p. = melting point

cm^{-1} = wave number

MHz = megahertz = 1×10^{-6} sec^{-1}

p.p.m. = parts per million

T = Tesla

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CHAPTER ONE

Introduction.

1. The acceptor properties of pentavalent compounds of group V.

The elements Phosphorus, Arsenic, Antimony and Bismuth form pentahalides with one or more of the halogens[1]. Lewis acid-Lewis base adducts formed between these pentahalides and other donor molecules or ions are known, e.g. $PF_5.Me_2O$[2], $SbCl_5$.pyridine[3], $SbCl_5Br^-$[4-6], $AsCl_6^-$[7] and PCl_5.pyridine[8]. Most of the complexes are six-coordinate with octahedral structures. Six-coordinate cationic species are also known in which a bidentate ligand is coordinated to MCl_4^+, e.g. PCl_4phen^+[9,10], $SbCl_4phen^+$[10] (phen = 1,10-phenanthroline), whereas two monodentate ligands coordinate to form species such as $PCl_4py_2^+$[11] (py = pyridine) or $SbCl_4(MeCN)_2^+$[12].

The work of Beattie et al[13] on the addition compounds of PCl_4^+ using $PCl_4^+SbCl_6^-$ as the source of the cation has been extended by Dillon and Reeve[11] and their results and conclusions are in good agreement. The bidentate pyridines bipy or phen (L') give stable complexes $PCl_4L'^+SbCl_6^-$ in solution, whereas $PCl_4^+SbCl_6^-$ reacts with pyridine in nitrobenzene to give the following equilibrium[11]:-

$$PCl_4py_2^+SbCl_6^- \rightleftharpoons PCl_5py + SbCl_5py \qquad (1)$$

The effect on the acceptor properties of the introduction of an aromatic organo-group has been investigated for $PhPCl_4$, $PhPCl_3^+SbCl_6^-$, $PhPCl_3^+PCl_6^-$, $catPCl_3$ (cat = $C_6H_4O_2$), $catPCl_2^+SbCl_6$, $cat_2PCl_2^-$, and $cat_2P^+SbCl_6^-$[14,15]. $PhPCl_3^+SbCl_6^-$ and $PhPCl_3^+PCl_6^-$ react rapidly with pyridine, apparently to give adducts of the molecular species $PhPCl_4py$ and MCl_5py (M = P or Sb), while bidentate ligands L' yield 1:1 complexes $PhPCl_3L'^+MCl_6^-$. These are stable in solution if soluble, and the cations exist in two isomeric forms. $CatPCl_2^+SbCl_6^-$ reacts with pyridine to give the cationic species $catPCl_2py_2^+SbCl_6^-$

while bidentate ligands L' form cations of the type $catPCl_2L'^+$. Similarly, equimolar mixtures of $cat_2P^+SbCl_6^-$ with bidentate pyridines yield cationic complexes $cat_2PL'^+$ (L' = bipy or phen).

Systematic studies by Dillon and Reeve[14,15] have shown that phenyltetrachlorophosphorane $PhPCl_4$, catechylphosphorustrichloride $catPCl_3$, and biscatechylphosphoruschloride cat_2PCl, form six-coordinate anions with the chloride ion which are partially dissociated in solution, whereas molecular 1:1 adducts of pyridine are formed with relative ease, only $PhPCl_4.py$ dissociating in solution. In excess pyridine, however, a labile equilibrium is established between the adduct $catPCl_2py_2^+Cl^-$ or $cat_2Ppy_2^+Cl^-$ and the 1:1 adducts. Schmidpeter et al[16] have similarly described the formation of both neutral 1:1 and cationic 1:2 complexes of cat_2PCl and pyridine or 4-methylpyridine, formulated as cat_2PClpy and $cat_2PPy_2^+Cl^-$ respectively. These phosphoranes have also been found to form cationic species with bidentate ligands L' (L' = bipy or phen), formulated as $PhPCl_3L'^+Cl^-$ [14], $catPCl_2L'^+catPCl_4^-$ or $cat_2Pbipy^+Cl^-$ [15].

In general the introduction of an organo-group into a halogenophosphorane reduces the acceptor properties of the five-coordinate species quite markedly. $PhPCl_4$, for example, reacts with phosphorus (V) chloride to form $PhPCl_3^+PCl_6^-$ [15], showing that PCl_5 is a better chloride acceptor than $PhPCl_4$. The introduction of a second organo-group continues this trend, and no acceptor properties were apparent in Ph_2PCl_3[17].

2. The acceptor properties of phosphorus (III) compounds.

The acceptor properties of some phosphorus (III) pseudohalides and trihalides have been investigated recently[18-21]. Thus tetrahalogenophosphites (III) PX_4^- (X = Cl[21] or Br[19]) and cyanohalogenophosphites (III) $P(CN)_{4-n}X_n^-$ (n = 1 or 2, X = Cl, Br or I[18,20]) have been prepared, whereas addition of CN^- to $P(CN)_3$ results in a reductive elimination to give $P(CN)_2^-$ and cyanogen[22]. Two groups of workers have reported the formation of thermally unstable adducts of phosphorus trihalides with trimethylamine $PX_3.NMe_3$ (X = F, Cl or Br)[23,24]. Adducts of PCl_3 and PBr_3 with pyridines and amides have also been reported, but no structural information is available[25-9]. Adducts of PCl_3[29] and PI_3[30] with pyridine have been identified by ^{31}P n.m.r. measurements, and a four-coordinate anion obtained from deprotonating a hydrido-spiro-phosphorane[31], has been described. $PCl_3.3Et_3N$ has been reported from vapour pressure measurements on the PCl_3 triethylamine system[32]. The acceptor properties of PX_3 (X = Cl, Br, CN or SCN) towards the halides or pseudohalides X (X = Cl, Br, I, CN, SCN or OCN) have been investigated[21], and several anionic derivatives obtained. $P(NCS)_3$ forms a well-defined 1:1 adduct with aniline which is precipitated from benzene solution[33]. The acceptor properties of phosphorus (III) compounds with an organo-group attached to phosphorus have been little investigated, however. $PhP(CN)_2$ forms an adduct with chlorine[34], but the compound is probably a phosphorane $PhPCl_2(CN)_2$. Kirk and Smith have shown by ^1H n.m.r. that $PhP(CN)_2$ form 1:4 and 1:6 complexes with $HCON(Me)_2$[35].

3. ^{31}P nuclear magnetic resonance spectroscopy.

The ^{31}P isotope has a nuclear spin of $\frac{1}{2}$ and a large magnetic moment. It is present in 100% natural abundance, thus making it suitable for high resolution n.m.r. spectroscopy. Its sensitivity is low, being 6.63×10^{-2} as sensitive as ^1H n.m.r. for equal numbers of nuclei at a constant magnetic field.

The application of ^{31}P n.m.r. spectroscopy to structure determinations and for analytical purposes is of immense importance to chemists. This technique provides direct information about the phosphorus nucleus itself. ^{31}P chemical shifts cover a range greater than 700 p.p.m.[36]. Usually changes in ^{31}P shifts on change of coordination are large and a structural assignment can often be made on this basis. In spite of the fact that triply-connected phosphorus compounds cover the entire known range of shifts, species with higher coordination numbers usually give values within specific ranges, which depend in general, on the ligands attached to phosphorus. The greater the coordination number of the phosphorus the greater is the nuclear shielding and so the higher is the chemical shift. The shielding also increases with increasing negative charge on the phosphorus. This assertion can be illustrated by the data below[36].

PCl_3	PCl_4^-	$POCl_3$	PCl_5	PCl_6^-
-219	-86	-2.5	83	296 p.p.m.

The value of ^{31}P n.m.r. spectroscopy in studying the acceptor properties of phosphorus compounds is apparent from much of the work described in the previous sections. In the present work the Fourier Transform n.m.r. spectrometer described in the next chapter was used. Although expensive, it is fast and gives ca. 100 times the sensitivity of a standard instrument with a signal averager (C.A.T.)[37].

4. The present work.

The aims of the present work were to study the Lewis acid properties of some organophosphorus (III) halides and pseudohalides towards halides and pseudohalide ions, and the acceptor properties of some organophosphorus (V) compounds towards suitable Lewis bases (Cl^-, pyridine and bidentate pyridines), using ^{31}P n.m.r. spectroscopy as the main technique. Other methods used included elemental analysis (in the case of isolable compounds), vibrational spectroscopy and to a lesser extent ^{35}Cl n.q.r. spectroscopy.

The behaviour of some mixed halo-organophosphorus (V) compounds has also been investigated in 25 oleum and 100% H_2SO_4 by means of ^{31}P n.m.r., and interesting results have been obtained.

CHAPTER TWO

Experimental.

1. The dry box.

All manipulations were carried out under an atmosphere of dry nitrogen (dried by passing through a column packed with P_2O_5), because of the great susceptibility of most of the compounds studied to moisture. All products containing phosphorus were stored under nitrogen in closed containers.

The glove box had two entry ports, a large port and a small quick entry port. The large port was purged for a period of about 30 minutes before opening to the box. The quick entry port was flushed with nitrogen by means of excess internal pressure. A large dish of P_2O_5 was kept exposed in the box to remove any traces of moisture. An external water pump was attached to a filter apparatus inside the box via a liquid nitrogen-cooled trap as a precaution against any water vapour diffusing into the box. A short vacuum line was sometimes used for drying processes, as well as for removing excesses of volatile reagents.

2. ^{31}P nuclear magnetic resonance spectroscopy.

The Fourier transform nuclear magnetic resonance spectrometer used in this work was constructed and programmed by Dr. A. Royston, and has been described elsewhere[38]. The spectrometer utilises a permanent magnet of field 1.4T from a Perkin-Elmer R10 spectrometer and is controlled by a Varian 620/L mini-computer. The ^{31}P resonance frequency is 24.29 MHz. The system stores and accumulates the free induction decay n.m.r. signal induced by a powerful R.F. pulse applied to a sample containing phosphorus. After the completion of the required number of pulses, the computer processes the accumulated F.I.D.'s to give the spectrum, which is displayed on the oscilloscope. The sweep width could be varied from 40 to ca. 800 p.p.m., and the origin could be altered so that ^{31}P resonance was observable in the range - 400 to 1100 p.p.m.

On this instrument 85% H_3PO_4 was employed as an external shift reference, with the upfield direction taken as positive. The spectrometer operates at a temperature of 307.2 K. Samples were contained in 8.4 mm outside diameter non-spinning tubes, closed with neoprene bungs covered with parafilm tape.

3. ^{11}B nuclear magnetic resonance spectroscopy.

^{11}B n.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer operating at 19.25 MHz, with a Digiac signal averaging accessory. Chemical shifts were measured relative to external trimethyl borate and results have been expressed relative to this standard. Literature data relative to $BF_3.Et_2O$ as external reference have been converted to this scale using the experimental relationship.

$$\delta\ ^{11}B\ (B(OMe)_3) = \delta\ ^{11}B\ (BF_3.Et_2O) + 18.75\ \text{p.p.m.}^{39}$$

4. Other spectroscopic techniques.

Raman spectra were recorded by Mrs. J. Slegrova on a Cary 82 spectrometer with an Argon Laser, model 164, using the 5145 Å line for excitation.

Infrared spectra of solids were recorded on a Perkin-Elmer 577 instrument as Nujol mulls between CsI plates. Phosphorus chloro- and bromo- compounds were run in KBr plates to give spectra from 4000 - 650 cm^{-1} and then in CsI plates protected with polythene discs to give spectra between 650 and 250 cm^{-1}.

N.Q.R. spectra were recorded on a mid-range Decca spectrometer operating from 5 to 55 MHz., with 13 mm outside diameter glass containers being used. Zeeman modulation was used throughout. Spectra were recorded at 77 K (liquid nitrogen), sometimes at 195 K (acetone/cardice), and at room temperature, where observable.

5. Analysis.

C, H and N were determined by microcombustion with a Perkin-Elmer 240 instrument. The reliability of this instrument was variable.

The phosphorus and halogen analyses were carried out by R. Coult. In the case of phosphorus and chlorine, a sample weighed in a gelatin capsule was decomposed by fusing with sodium peroxide in a nickel Parr bomb. The residue was washed into a flask, 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 420mμ 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 schöniger oxygen flask combustion of the compound.

6. Solvents.

Solvents of the best available commercial grade were used without further purification. Chlorocarbons were stored and dried over 4 A mesh molecular sieve under nitrogen, while hydrocarbon solvents were first dried over sodium wire and then stored over molecular sieve under a nitrogen atmosphere.

A.R. grade nitrobenzene was distilled from P_2O_5 and stored over activated molecular sieve under nitrogen.

Pyridine was distilled from KOH pellets into a flask containing more KOH pellets, and stored under dry nitrogen.

100% H_2SO_4 and 25 oleum were used without purification.

7. Starting materials.

(a) Tetra-ethylammonium cyanide was prepared according to the procedure of Norris[40].

25 mls of a 25% aqueous solution of Et_4NOH were dissolved in 40 mls CH_3OH. 1.8 mls of HCN was condensed onto the solution frozen under vacuum at 77 K. The solution was allowed to warm to room temperature and the solvent removed in vacuo. 20 mls of dry benzene were added to the solid and stirred for 10

minutes. Benzene was then removed in vacuo to isolate a white solid, which was then heated at 373 K under vacuum for 4 hours to ensure complete dryness.

Analysis

Et_4NCN requires	C = 69.23	H = 12.82	N = 17.95
Found	C = 69.48	H = 12.89	N = 17.76

(b) Tetra-n-pentylammonium chloride $(n\text{-}C_5\text{-}H_{11})_4NCl$, was dried by heating to 373 K for 3 hours under vacuum. Tetra-ethylammonium and tetra-propylammonium chlorides were similarly dried by heating to 433 K for 6 hours in vacuo.

(c) Methyldichlorodibromophosphorane.

$MePCl_2Br_2$ was prepared according to the procedure of Meisenheimer[41].

Bromine (2.5 mls, 45.8 mmoles) dissolved in methylene chloride was added slowly to a solution of $MePCl_2$ (4 mls, 45.8 mmoles) dissolved in the same solvent with stirring. A vigorous reaction commenced and after a few minutes a white precipitate had formed. The solution was left to stir for 5 minutes, filtered and washed with $^{30}/40$ Pet. ether to isolate a white product.

Analysis

Found	C = 3.89	H = 0.89	P = 11.40	Cl = 25.84	Br = 56.04
Calculated	C = 4.34	H = 1.08	P = 11.20	Cl = 25.65	Br = 57.73

(d) Dimethylchlorodibromophosphorane.

Me_2PCl (2.6 mls, 31.2 mmoles) and bromine (1.7 mls, 31.1 mmoles) were each separately dissolved in methylene chloride. The bromine solution was added to the Me_2PCl solution with stirring. The white precipitate which formed was filtered off, and washed with methylene chloride and $^{30}/40$ Pet. ether to isolate a white solid. Analysis was not carried out as the starting material Me_2PCl, contained some $MePCl_2$ which was also brominated to give $MePCl_2Br_2$.

(e) Trimethyldibromophosphorane.

Excess bromine (1.4 mls, 26.0 mmoles) was added to a solution of Me_3P (2 mls, 25.2 mmoles) in methylene chloride. A yellow precipitate was instantly formed. The solution was then filtered, and washed with ^{30}/40 Pet. ether to isolate an orange solid.

Analysis

Found C = 15.30 H = 3.40 P = 12.80 Br = 67.50

Calculated C = 15.27 H = 3.82 P = 13.14 Br = 67.77

(f) Tetrabromomethylphosphorane.

$MePBr_2$ (4 mls, 31.5 mmoles) was treated with a slight excess of bromine (1.7 mls, 32.0 mmoles) in methylene chloride. A yellow precipitate was immediately formed. The product was filtered off and washed with ^{30}/40 Pet. ether to isolate a yellow solid.

Analysis

Found C = 3.17 H = 0.83 P = 8.40 Br = 87.30

Calculated C = 3.28 H = 0.82 P = 8.47 Br = 87.43

(g) Tetrabromophenylphosphorane.

A solution of bromine (1.2 mls, 22.0 mmoles) in methylene chloride was added to $PhPBr_2$ (6.5 mls, 22.0 mmoles) in the same solvent. An orange precipitate was immediately formed, which was filtered off and washed with ^{30}/40 Pet. ether to isolate a yellow solid.

Analysis

Found C = 16.86 H = 1.01 P = 6.92 Br = 74.42

Calculated C = 16.83 H = 1.18 P = 7.23 Br = 74.76

(h) Catechylphosphorusmonobromide was prepared according to the procedure of Gross et al[42].

PBr_3 (11 mls, 0.1 mmole) was added to a solution of catechol (11 gm, 0.1 mmole) in dry ether (40 mls) containing 0.1 ml of water. The mixture was heated to reflux for two hours. A yellow-orange solid formed. The solution mixture was transferred to a vacuum line. CatPBr was distilled in vacuo (at 357 K) and collected in a flask cooled in liquid nitrogen. A white crystalline solid which melts at room temperature was isolated. Its ^{31}P n.m.r. spectrum gave a single peak at -195.1 p.p.m.

(i) Biscatechylphosphorusmonochloride.

(2-chloro-2,2'-spiro bi(1,3,2-benzodioxaphosphole))

This compound was prepared according to the procedure of Ramirez and coworkers[43].

Catechol (30 g, 0.28mmoles) was added to a solution of Phosphoruspentachloride (30 g, 0.14mmoles) in dry benzene at 298 K over a period of 45 minutes. The mixture was kept at 333 - 353 K for 1 hour, and the solvent removed in vacuo to isolate a white solid. Its ^{31}P n.m.r. spectrum showed a single peak at +27.5 p.p.m. in methylene chloride.

(j) Dimethyltribromophosphorane.

This compound was prepared by following the method of Kuchen et al[44] employed for the preparation of Et_2PBr_5.

$Me_2PSSPMe_2$ (8.97 g, 48.2 mmoles) was dissolved in CCl_4 (40 mls). The solution was treated dropwise with a solution of bromine (12 mls, 48.2 mmoles) in CCl_4 (30 mls) with constant stirring in a stream of dry nitrogen, while the solution mixture was cooled in an ice bath. The solution turned yellow and then orange-red. Finally a yellow-reddish precipitate was deposited at the bottom of the flask with a red layer of liquid at the top. The solution was filtered and washed with CCl_4 to isolate an orange solid. Analysis showed that the product was Me_2PBr_5.

Analysis of Me_2PBr_5 requires

C = 5.21 H = 1.30 P = 6.72 Br = 86.77

Found C = 5.11 H = 1.64 P = 6.43 Br = 86.40

Me_2PBr_3 requires

C = 7.97 H = 2.00 P = 10.30 Br = 79.73

(k) The preparation of methyltribromophosphonium tetrabromoborate, $MePBr_3^+BBr_4^-$.

BBr_3 (0.5 mls, 5.46 mmoles) was added slowly with stirring to a suspension of $MePBr_4$ (2g, 5.46 mmoles) in methylene chloride. A white precipitate formed. The solution was left to stir for a few minutes then filtered to isolate a white solid.

Analysis

Found C = 2.04 H = 0.54 P = 5.10 Br = 89.93

Calculated C = 1.94 H = 0.49 P = 5.02 Br = 90.76

(l) The preparation of dimethyldibromophosphonium tetrabromoborate, $Me_2PBr_2^+BBr_4^-$.

Me_2PBr_5 (3.51 g, 7.6 mmoles) was suspended in methylene chloride. BBr_3 (0.8 ml, 7.6 mmoles) was then added with stirring. A white precipitate was formed. This was then filtered off and washed with $^{30}/40$ Pet. ether to isolate a white product.

Analysis

Found C = 3.70 H = 1.40 P = 5.78 Br = 85.60

Calculated C = 4.35 H = 1.09 P = 5.62 Br = 86.96

(m) Trimethylbromophosphonium tetrabromoborate.

Me_3PBr_2 (1.3953 g, 5.9 mmoles) was suspended in methylene chloride. BBr_3 (0.6 ml, 5.9 mmoles) was added cautiously with stirring. The solution was then left to stir for 20 minutes, filtered and washed with $^{30}/40$ Pet. ether yielding a white solid.

Analysis

Found C = 6.04 H = 2.08 P = red Br = 79.05

Calculated C = 7.39 H = 1.85 P = 6.37 Br = 82.14

(n) Sodiumdiethylphosphite $NaOP(OEt)_2$, was prepared by the method of Pudovik and Arbuzov[45].

A suspension of sodium metal (3 g, 0.13 mmoles) in Et_2O (200 mls) was treated with $(EtO)_2POH$ (16.8 mls, 0.13 moles) in an ice bath. A white precipitate was formed, filtered off and washed with $^{30}/40$ Pet. ether to yield a white solid.

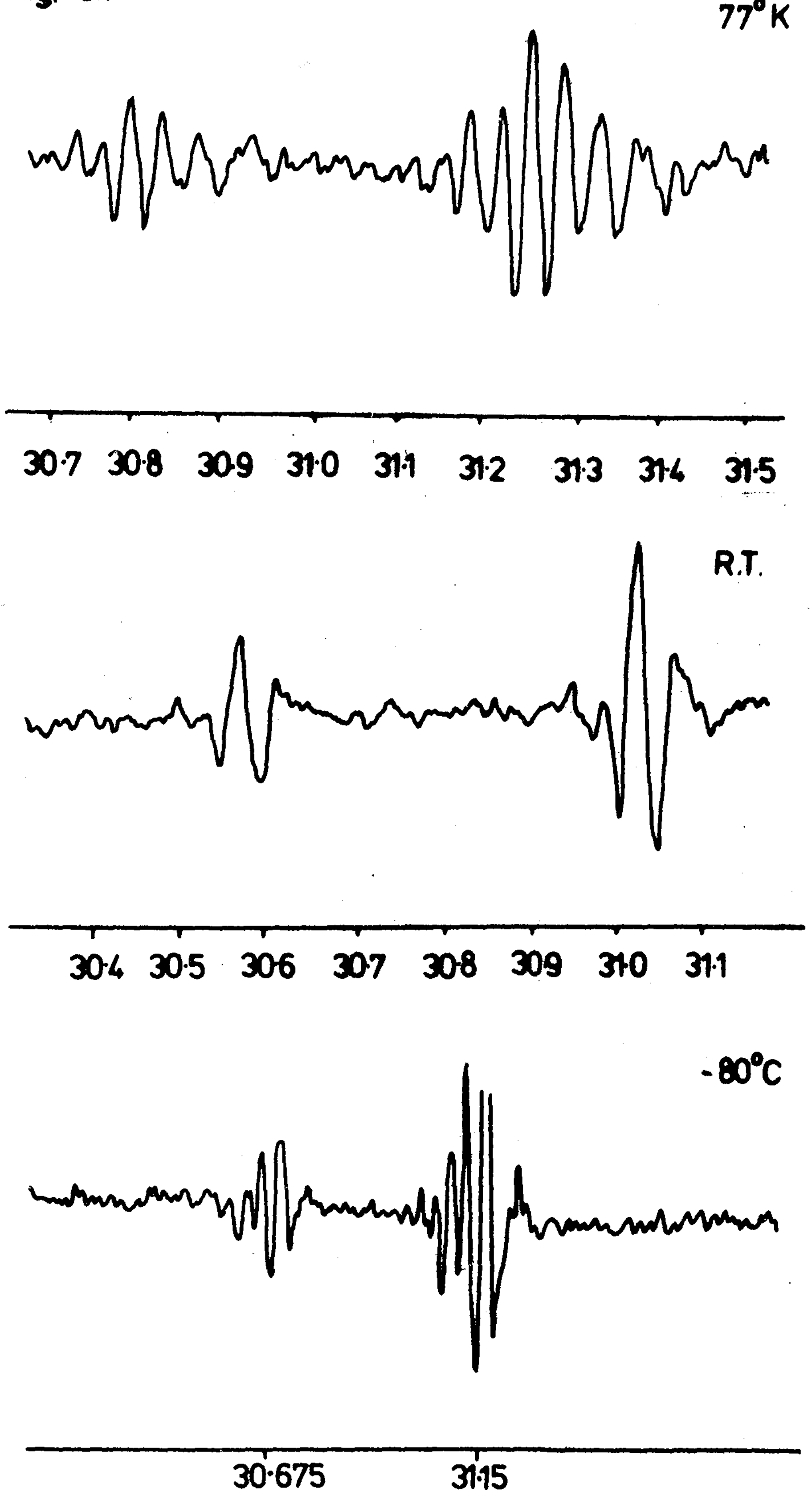
Analysis

Found C = 27.90 H = 7.00 Na = 13.30

Calculated C = 30.00 H = 6.25 Na = 14.38

$MePCl_3^+Cl^-$ ^{35}Cl n.q.r. spectra

Fig. 3.1



CHAPTER THREE

The acceptor properties of $MePCl_4$ and related compounds.

(a) Introduction.

Methyltetrachlorophosphorane $MePCl_4$ is the first member of the series Me_nPCl_{5-n} ($1 \leqslant n \leqslant 4$). It was first prepared by Reinhardt and co-workers[46] and later by Komkov et al[47]. This compound has been intensively studied, particularly with regard to its structure[48-50]. Its acceptor properties towards suitable bases were briefly investigated by Reeve[17], but no substantial results were recorded due to an insufficient amount of the compound being available.

I.R. and Raman studies indicate C_{2v} symmetry in non-ionising solvents[48], whereas the solid has the ionic structure $MePCl_3^+Cl^-$ [48,49]. Dillon et al[50] have recorded the ^{31}P n.m.r. and ^{35}Cl n.q.r. spectra of a number of methylchlorophosphoranes and their ionic 1:1 adducts with Lewis acids X. The results confirmed that the compound $MePCl_4$ has a phosphonium salt structure $MePCl_3^+Cl^-$ in the solid state while the structure $[MePCl_3]^+[XCl]^-$ was deduced for the adducts.

The present work confirms the ionic nature of the solid compound. Its ^{35}Cl n.q.r. spectrum at 77 K showed two signals at 30.80 and 31.225 MHz. With an intensity ratio of 1:2. It also showed signals at 293 K (30.575 and 31.03 MHz) and 193 K (30.675 and 31.15 MHz) with the same intensity ratio of 1:2 respectively, Fig. 3.1, compatible with the $MePCl_3^+$ cation.

Its ^{31}P n.m.r. solid state spectrum showed a single peak at -120.0 p.p.m., which is within the four-coordinate region for phosphorus chloro- compounds. This shift is in good agreement with the values found for its salts $MePCl_3^+AuCl_4^-$ (-119.6 p.p.m.) and $MePCl_3^+ICl_4^-$ (-116.0 p.p.m.), as well as the result reported by Dillon et al[50].

The ionic nature of $MePCl_4$ is also supported by i.r. The spectra of $MePCl_4$

and derivatives with Lewis acids are very similar, except for a few additional bands below 500 cm^{-1} for the salts. These bands can readily be assigned to the different counter-ions associated with the $MePCl_3^+$ cation, Table 3.1.

Table 3.1

I.R. spectra of $MePCl_4$ and its salts, 800 - 250 cm^{-1}

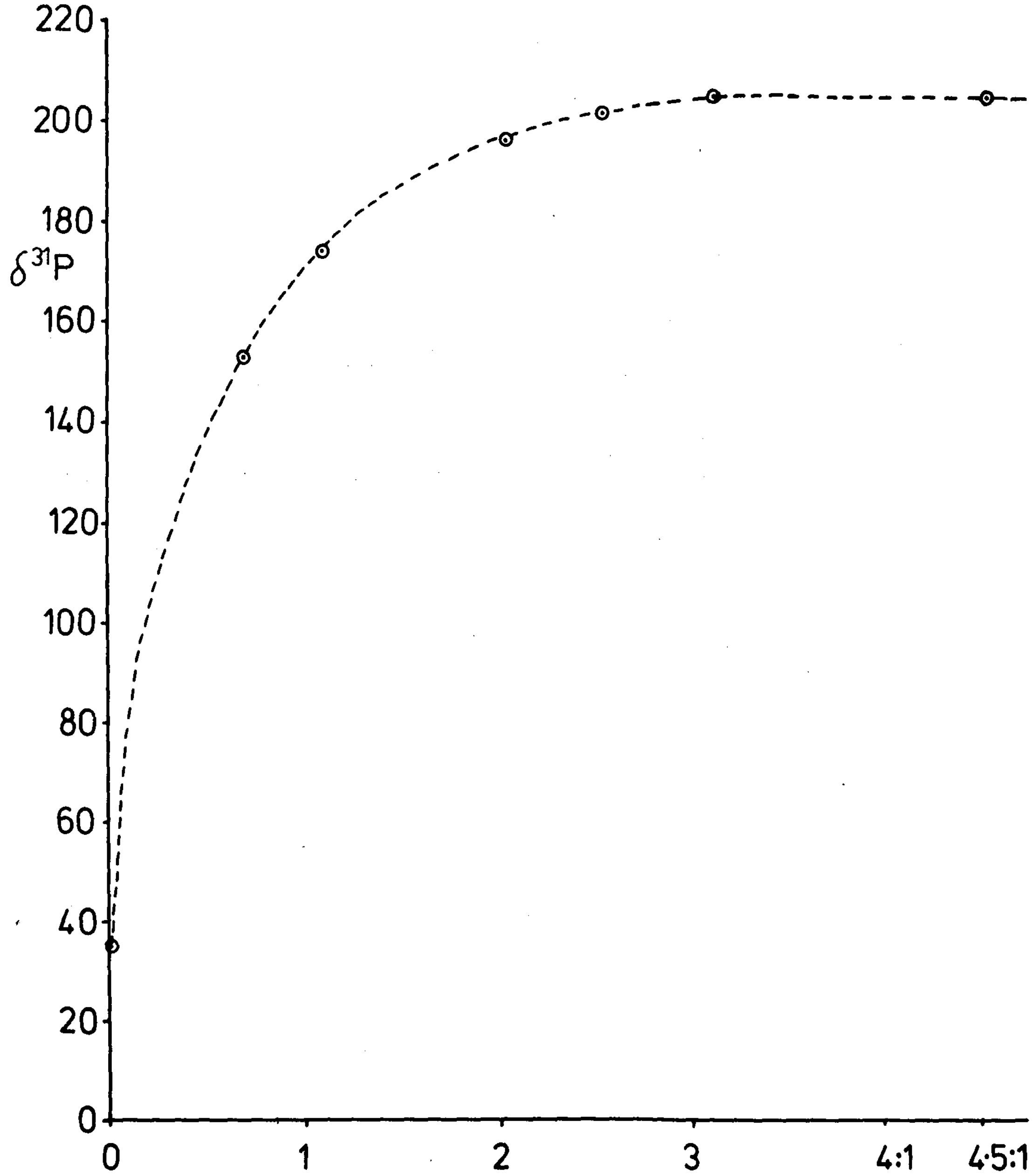
$MePCl_4$	$AuCl_4^-$	$SbCl_6^-$	ICl_4^-
790s	790s	790s	790s
730s	730s	730s	730s
720s	718s	720s	720s
		630s	
606s	620s	618s	620s
	576w		
546s	546s	540s	550s
	520w		
498w			
480s	490s	490s	490s
440s	430Br	420s	430Br
394w			
	358*Br	346*Br	
330w	320w	310w	330w
284s	294w	286w	285s
270s	270s	265s	270s
			260*Br

* = counter-ion

No ^{35}Cl n.q.r. signals were observed for the salts prepared, although satisfactory ^{31}P n.m.r. spectra were recorded in each case. This may be due to disorder phenomena in the solids, possibly because of random orientations of the alkyl and chloro-groups in the pseudo-spherical cations[50].

Its ^{31}P n.m.r. spectra in a variety of solvents were recorded and showed different chemical shifts as indicated in Table 3.2. The values obtained all suggest a predominantly molecular species in solution, although slight ionisation is possible in $EtNO_2$, on the assumption that rapid exchange takes

Fig. 3.2 ^{31}P CHEMICAL SHIFT OF $(C_5H_4)_4N^+Cl^-/MePCl_4$ SOLUTIONS IN $PhNO_2$



place between $MePCl_3^+$ and $MePCl_4$, as it does for the $MePCl_4$-$MePCl_5$ system.

Table 3.2

δ ^{31}P (p.p.m.) of $MePCl_4$ in various solvents

Solvent	δ ^{31} (p.p.m.)	Reference
$EtNO_2$	21.1	present work
CCl_4	43.6	present work
C_6H_6	41.0	present work
CH_2Cl_2	38.7	17
$PhNO_2$	35.5	present work

(b) Acceptor properties of $MePCl_4$ towards the chloride ion.

Solutions containing approximately 0.5:1, 1:1, 2:1, 3:1 and 5:1 molar ratios of tetra-n-pentylammonium chloride to methyltetrachlorophosphorane were prepared in nitrobenzene. As more chloride was added to the $MePCl_4$ solution, the chemical shift of the single peak moved upfield, Table 3.3. The highest shift attained was 204.7 p.p.m., but a limiting shift of 205.0 p.p.m. (Fig. 3.2) was found on extrapolation. This value can be ascribed to the methylpentachlorophosphate ion, $MePCl_5^-$, as it lies in the six-coordinate region of the spectrum for organochloro- compounds of phosphorus.

It is thus apparent that with stoichiometric quantities of $MePCl_4$ and chloride present $MePCl_5^-$ is not completely formed, and equilibrates rapidly with free $MePCl_4$.

$$MePCl_4 + (C_5H_{11})_4N^+Cl^- \rightleftharpoons (C_5H_{11})_4N^+MePCl_5^- \qquad (1)$$

Table 3.3

Shifts found for $(C_5H_{11})_4N^+Cl^-/MePCl_4$ systems in nitrobenzene

Molar Ratio $(C_5H_{11})_4N^+Cl^-/MePCl_4$	δ ^{31}P (p.p.m.)	% Association of $MePCl_5$[a]
0.70:1	153.0	69.3
1.09:1	175.6	82.7
2.07:1	196.0	94.7
2.53:1	201.3	97.8
3.10:1	204.7	99.8
4.51:1	204.7	99.8

[a] Assuming δ ^{31}P $MePCl_4$ 35.5 p.p.m.; $MePCl_5^-$ 205.0 p.p.m.

n-$(C_5H_{11})_4N^+MePCl_5^-$ was prepared from stoichiometric amounts of n-$(C_5H_{11})_4N^+Cl^-$ and $MePCl_4$ dissolved in the minimum quantity of methylene chloride. A sticky white solid was isolated. Its ^{31}P n.m.r. solid state spectrum showed a sharp peak at 208.0 p.p.m. This peak looked more like a solution peak than a normal solid resonance, probably due to the viscous nature of the complex. On exposure to air it hydrolysed, resulting in the appearance of a peak at -45.3 p.p.m., readily assigned to $MePOCl_2$[36]. Its I.R. spectrum showed new bands below 600 cm^{-1} (Table 3.4) compared with $MePCl_4$, but the region from 1200 - 600 cm^{-1} was obscured by a broad band, probably due to the cation.

$Et_4N^+MePCl_5^-$ was isolated by mixing equimolar amounts of the reactants Et_4NCl and $MePCl_4$, separately dissolved in a minimum amount of methylene chloride. Its ^{31}P n.m.r. solid state spectrum showed a broad signal at +206.5 ± 1.5 p.p.m., thus confirming the limiting solution shift of 205.0 p.p.m. Its I.R. showed a lowering of intensity of the bands in the region 600 - 400 cm^{-1} compared with the starting material, and the appearance of a broad band at 375 cm^{-1}, Table 3.4. The lowering of I.R. frequency on formation of six-coordinate neutral or anionic species from five- coordinate phosphorus chloro-compounds is generally observed[14,51,52], and is ascribed to a reduction in the P-Cl bond strength. New bands were also discerned in the region 1200 - 1000 cm^{-1} which can be assigned to the ethyl groups of the cation.

Both solids are moisture-sensitive but are stable under an inert atmosphere of dry nitrogen. No ^{35}Cl n.q.r. signals were observed for the two compounds isolated.

Table 3.4

I.R. spectra of the chloride derivatives of $MePCl_4$, 800 - 250 cm^{-1}

$(C_5H_{11})_4N^+MePCl_5^-$	600Br, 544s, 494s, 470w, 450m, 384Br, 360m, 348m, 330w, 320w, 286w.
$(C_2H_5)_4N^+MePCl_5^-$	790m, 700w, 690w, 600Br, 544m, 520w, 510m, 470m, 414m, 375Br, 330w, 296s, 280m.

The I.R. spectra of $MePCl_5^-$ salts differ clearly from that of $MePCl_4$ in the region 800 - 250 cm^{-1}.

(c) <u>The reaction of methyltetrachlorophosphorane with phenyltetrachlorophosphorane</u>.

Methyltetrachlorophosphorane and phenyltetrachlorophosphorane are capable of forming complexes with other metal halides which are themselves potential Lewis acids, e.g. $MePCl_3^-AuCl_4^-$ and $PhPCl_3^+SbCl_6^-$, but they are good chloride ion acceptors in the absence of competing reactions, forming chlorophosphate ions. An investigation to determine which of the two compounds is the stronger chloride ion acceptor was carried out by mixing solutions of these compounds in either methylene chloride or nitrobenzene in an n.m.r. tube, and recording the ^{31}P n.m.r. spectrum of the mixture. No change in the ^{31}P n.m.r. peak positions ascribed to the individual compounds was observed (δ ^{31}P found 45.3, 38.7 p.p.m.) as compared with the shifts recorded for these compounds separately in $PhNO_2$ (δ ^{31}P $PhPCl_4$ 45.4, $MePCl_4$ 38.7 p.p.m.). From a consideration of inductive effects, methyltetrachlorophosphorane is expected to be a weaker acceptor than phenyltetrachlorophosphorane, whereas the bulk of the phenyl group could impose a steric effect and as such reduce the acceptor ability of $PhPCl_4$ towards the chloride ion. From the above ^{31}P n.m.r. solution data it appears that these effects (electronic as opposed to steric) influence the acceptor abilities in the same direction and as a result, $MePCl_4$ and $PhPCl_4$ are virtually of the same acceptor ability towards the chloride ion.

(d) <u>The acceptor properties of $MePCl_4$ towards pyridine</u>.

A solution of $MePCl_4$ in methylene chloride showed a single peak at 38.7 p.p.m. When pyridine was added, a white precipitate was immediately formed and the ^{31}P n.m.r. spectrum of the resulting solution showed a broad peak at -48.3 p.p.m.

In neat pyridine a very exothermic reaction occurred followed by the precipitation of a pale yellow solid. The ^{31}P n.m.r. spectrum of the mixture showed a broad solution peak at -48.5 p.p.m. From the value of the chemical shift the product formed appears to be five-coordinate, which is compatible with an ionic product, formulated as $MePCl_3py^+Cl^-$.

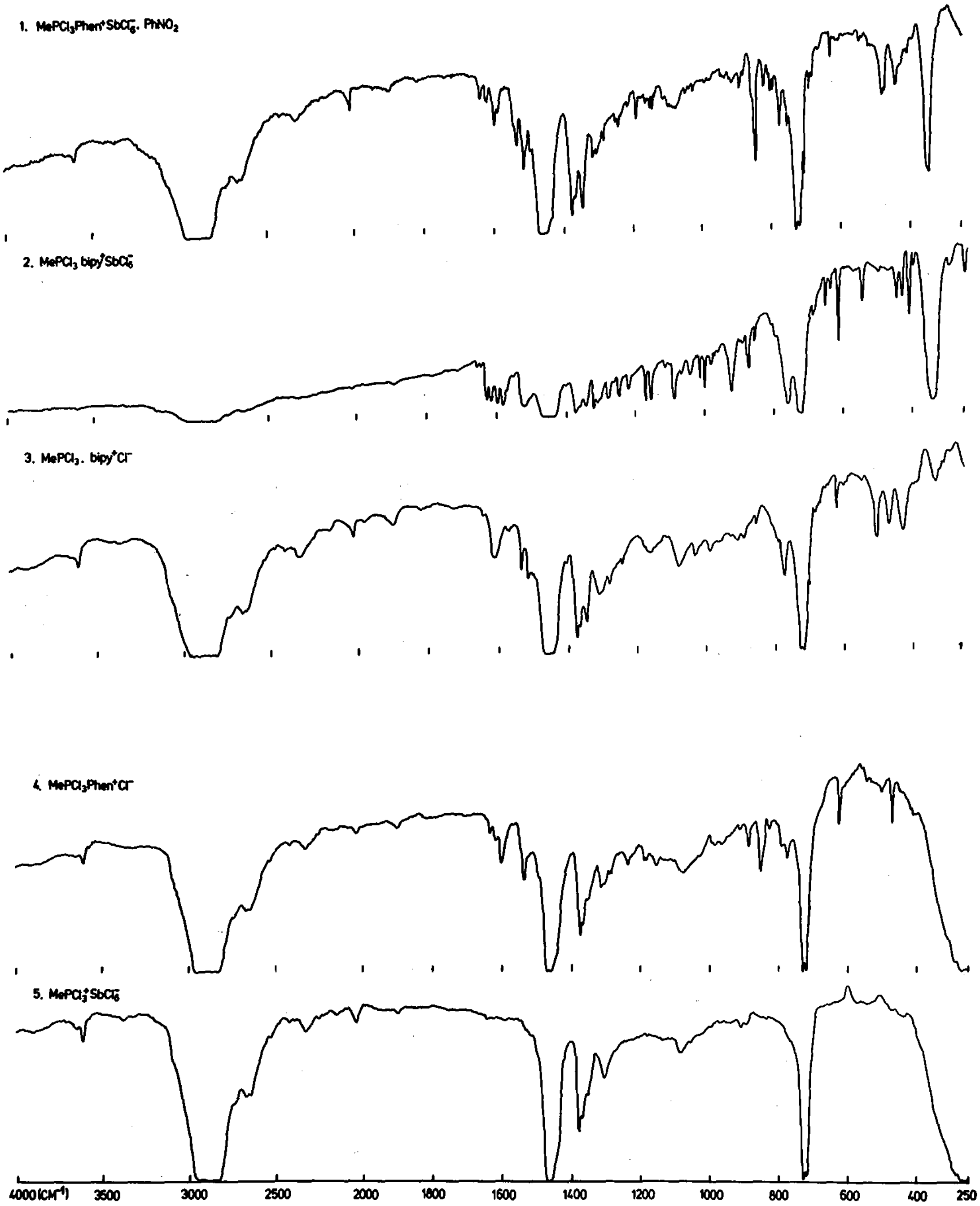
Attempts were then made to isolate the product. On many occasions a white solid was isolated which analysed as pyridinium chloride, formation of which was confirmed by the presence of broad N-H absorptions in its I.R. spectrum at 2842 and 2745 cm^{-1} [53]. This was probably due to hydrogen chloride present in the box atmosphere, which tends to build up as a result of hydrolysis of phosphorus-chlorine compounds by residual traces of water. The hydrogen chloride would then react with the pyridine to form the contaminant pyridinium chloride. In consequence the reaction was carried out in the fume cupboard under an atmosphere of dry nitrogen. Under these conditions a pale brown solid was isolated from methylene chloride. Analysis indicated that two moles of pyridine were present in the adduct, with one mole present possibly as a solvate (experimental section). The solid state spectrum gave a broad peak at -29.0 p.p.m., which tends to support the five-coordinate formulation of the product, tentatively assigned as $MePCl_3py^+Cl^-$. Although this shift is somewhat different from the solution values above, differences in shift between the solid state and solution are by no means uncommon in phosphorus compounds[54]. Unfortunately no ^{35}Cl n.q.r. signals were observable which could have given valuable information on the stereochemistry of this complex in the solid state. Its i.r. spectrum showed a number of new bands, not present in the spectrum of the parent compound.

(e) The reaction of $MePCl_4$ with bidentate pyridines.

When a solution of either 2,2'-bipyridine or 1,10-phenanthroline was added to a solution of $MePCl_4$ in methylene chloride or nitrobenzene, an immediate precipitate was formed, so no solution n.m.r. data could be obtained.

Elemental analysis and i.r. revealed that $MePCl_3bipy^+Cl^-$ and $MePCl_3phen^+Cl^-$

Fig. 33



1. $MePCl_3Phen^+SbCl_6^-$. $PhNO_2$

2. $MePCl_3$ $bipy^+SbCl_6^-$

3. $MePCl_3$. $bipy^+Cl^-$

4. $MePCl_3Phen^+Cl^-$

5. $MePCl_3^+SbCl_6^-$

are formed with relative ease. No solid state ^{31}P n.m.r. spectrum was observed in the case of the 1,10-phenanthroline complex, but spectrum accumulation showed a broad peak with maxima at 145.1 and 148.4 p.p.m. for the solid 2,2'-bipyridine complex. No ^{35}Cl n.q.r. signals could be discerned from either complex. The i.r. spectra of the 2,2'-bipyridine and 1,10-phenanthroline complexes revealed new bands in the regions 1250 - 800 and 600 - 250 cm^{-1} compared with $MePCl_4$, which can be partially attributed to the ligands, Fig. 3.3. The isolated complexes were insoluble in most of the common solvents available, hence no solution shifts could be recorded.

(f) <u>The acceptor properties of methyltrichlorophosphonium salts.</u>

Reaction with pyridine.

The methyltrichlorophosphonium cation can be prepared by the addition of an appropriate chloride ion acceptor to methyltetrachlorophosphorane. The hexachloroantimonate salt was prepared to study its acceptor properties as compared with those of the parent compound. It may be prepared either by the reaction between stoichiometric amounts of the phosphorane and antimony (V) chloride, or by direct reaction of two moles of antimony (V) chloride with one mole of the corresponding phosphine following the procedure of Ruff[55].

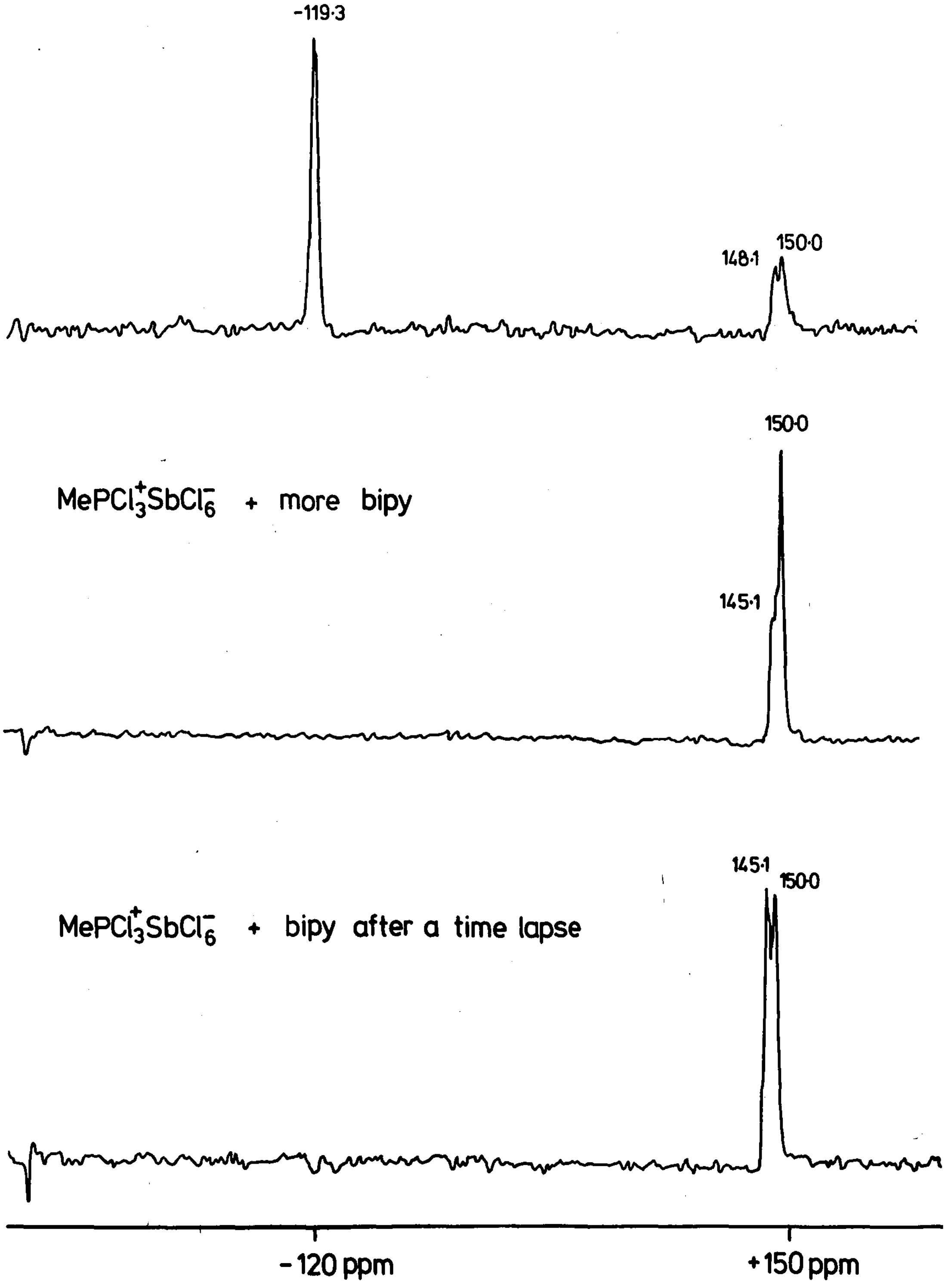
$$MePCl_4 + SbCl_5 \longrightarrow MePCl_3^{+}SbCl_6^{-} \qquad (2)$$

or $$MePCl_2 + 2SbCl_5 \longrightarrow MePCl_3^{+}SbCl_6^{-} + SbCl_3 \qquad (3)$$

The method employed was the one in which stoichiometric amounts of $MePCl_4$ and the chloride were used. A white solid soluble in most solvents was isolated. The ionic nature of this adduct was revealed by its solid state ^{31}P n.m.r. shift of -120.9 p.p.m. The shift recorded in nitrobenzene was -120.9 p.p.m., whereas a shift of -120.4 p.p.m. was observed in methylene chloride. No ^{35}Cl n.q.r. signals were found.

When excess pyridine was added to a nitrobenzene solution of the $MePCl_3^{+}SbCl_6^{-}$ a white precipitate was immediately formed, with the ^{31}P n.m.r.

Fig. 3.4.



$MePCl_3^+SbCl_6^-$ + bipy

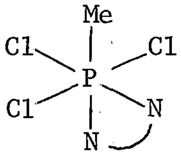
$MePCl_3^+SbCl_6^-$ + more bipy

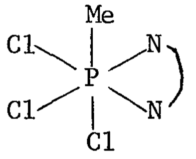
$MePCl_3^+SbCl_6^-$ + bipy after a time lapse spectrum showing a broad resonance at -48.3 p.p.m. This value lies in the five-coordinate region for phosphorus-chloro compounds and is tentatively assigned to $\overset{+}{MePCl_3py}\overset{-}{Cl}$. The following mechanism was assumed to operate, by analogy with the reaction of py with $Me_2PCl_2SbCl_6$ (section 3(j)).

$$\overset{+}{MePCl_3}\overset{-}{SbCl_6} + 2py \longrightarrow \overset{+}{MePCl_3py_2}\overset{-}{SbCl_6} \xrightarrow{rapid} \overset{+}{MePCl_3py}\overset{-}{Cl} + SbCl_5.py \quad (4)$$

(g) <u>The reaction of $\overset{+}{MePCl_3}\overset{-}{SbCl_6}$ with 2,2'-bipyridine</u>

In a trial experiment 2,2'-bipyridine was added to a solution of $\overset{+}{MePCl_3}\overset{-}{SbCl_6}$ in nitrobenzene. The ^{31}P n.m.r. spectrum showed two peaks at 145.1 and 150.0 p.p.m. These peaks are well within the six-coordinate region of the spectrum for phosphorus-chlorine compounds. Because of the geometry of 2,2'-bipyridine, unidentate or bridging behaviour of this ligand is unlikely, and these peaks can thus be assigned to the isomeric forms (I and II) of the $MePCl_3bipy^+$ cation.


I


II

$\overset{\frown}{N\ N}$ = bidentate ligand

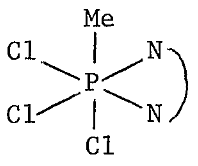
When a small amount of 2,2'-bipyridine was added to a nitrobenzene solution of $\overset{+}{MePCl_3}\overset{-}{SbCl_6}$, three peaks were observed at -119.3, 145.1 and 150.0 p.p.m. With addition of more 2,2'-bipyridine, only two peaks were observed in the ^{31}P n.m.r. spectrum at 145.1 and 150.0 p.p.m. with the peak at higher field predominating. When the same sample was monitored after two hours, the spectrum showed again two peaks at 145.1 and 150.0 p.p.m. but this time of equal intensity, Fig. 3.4. No change in the intensities of the two peaks was observed when the same sample was run again after a further two hours. The increase in the intensity of the lower field peak suggests that a rearrangement of one isomer to the other takes place, but that both forms are of comparable stability. Isomeric configurations can sometimes be deduced for six-coordinate phosphorus compounds by the method of Pairwise interactions[56-63], but that is not possible in this instance because there are too many unknown terms, such as the N-N 'internal' term for the bidentate ligand. Assignment of peaks to specific configurations was therefore not attempted.

$MePCl_3bipy^+SbCl_6^-$ was prepared by adding cautiously a solution of $SbCl_5$ in methylene chloride with stirring to a mixture of equimolar amounts of $MePCl_4$ and 2,2'-bipyridine, each dissolved in methylene chloride. The mixture was allowed to stand for a few minutes. The precipitate which formed was filtered off, and washed with methylene chloride and low boiling petroleum ether, to yield a brown solid.

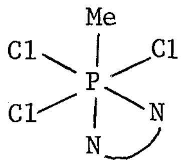
The solid state ^{31}P n.m.r. spectrum showed a broad peak at 145.1 p.p.m., but no ^{35}Cl n.q.r. signals were obtained. Elemental analysis and i.r. data for $MePCl_3bipy^+SbCl_6^-$ are given in the experimental section and Table 3.5 respectively.

(h) <u>The reaction of $MePCl_3^+SbCl_6^-$ with 1,10-phenanthroline</u>

When 1,10-phenanthroline was added to a solution of $MePCl_3^+SbCl_6^-$ in nitrobenzene or nitroethane, two peaks were observed in the ^{31}P n.m.r. spectrum at 143.5 and 148.4 p.p.m. respectively. An additional peak at -45.3 p.p.m. was observed in the nitroethane spectrum and ascribed to $MePOCl_2$, which is a partial hydrolysis product. The observed ^{31}P n.m.r. spectrum is consistent with the formation of an octahedral complex since the peaks are in the six-coordinate region of the spectrum for phosphorus-chlorine compounds. The magnitude of the difference between the shifts observed (5.0 p.p.m.) is too large to be attributed to 'H-C-^{31}P coupling and the peaks can be undoubtedly assigned to the two isomeric forms (I and II) of the complex.



I



II

$\overset{\frown}{N\;\;N}$ = phen

Isomerism in six-coordinate phosphorus compounds has been reported in the literature with fluoride as one of the ligands[64,65], and has also been observed by Platt[21] in many six-coordinate anionic phosphorus (V) complexes. Reeve[17] detected two peaks in the ^{31}P n.m.r. spectrum of a nitrobenzene solution of equimolar amounts of $PhPCl_4$ and 1,10-phenanthroline at 135.4 and 150.6 p.p.m. and assigned them to the isomeric forms of the cation $PhPCl_3phen^+$. N.m.r. evidence for the existence of isomeric species has been reported for ^{59}Co and ^{195}Pt nuclei[66,67], and also in mixed octahedral fluorochloride anions of niobium (V) and tantalum (V)[68,69]. The two chemically shifted signals are of equal intensity here, suggesting that the isomers are present in equimolar proportions and are of comparable stability. Isomeric assignment of peaks was not attempted.

Analysis of the ^1H n.m.r. spectrum of the 1,10-phenanthroline complex cannot be utilised for assignment of the observed shifts to specific isomers, since ^1H n.m.r. is only useful where the isomers can be prepared separately and not when they form a mixture[70,71].

The ^{31}P n.m.r. solid state spectrum of $MePCl_3phen^+SbCl_6^-$ prepared from $EtNO_2$ showed two solid peaks at 145.1 and 150.0 p.p.m. and a sharp peak at -45.3 p.p.m. (presumably $MePOCl_2$). The complex was not analysed as it contained the impurity $MePOCl_2$.

The solid isolated from $PhNO_2$ did not give a ^{31}P n.m.r. solid state spectrum, nor did the solid from $MeNO_2$. The solid prepared from $PhNO_2$ analysed as having one mole of $PhNO_2$ present, which was confirmed by the sharp absorption bands at 1350 and 840 cm^{-1}, and a weak band at 400 cm^{-1} in its i.r. spectrum[72,73]. Reeve[17] isolated analogous compounds containing $PhNO_2$ of solvation.

The i.r. spectrum of the complex $MePCl_3phen^+SbCl_6^-$ (from $PhNO_2$) was found to resemble that of the complex $MePCl_3phen^+Cl^-$, except for the strong band at 344 cm^{-1} which can be attributed to $SbCl_6^-$ and the $PhNO_2$ bands mentioned above.

The similarity of the i.r. spectra indicates the same mode of coordination in the 1,10-phenanthroline adducts. No ^{35}Cl n.q.r. signals were detected for the isolated complex.

Table 3.5

I.R. bands for complexes of $MePCl_3^+$ with bidentate pyridines as Nujol Mulls in the region 650 - 250 cm^{-1}

$MePCl_3phen^+Cl^-$	650m, 616s, 600w, 542s, 520m, 510s, 462w, 432w, 420s, 380s, 340s, 308w, 280w.
$MePCl_3phen^+SbCl_6^-PhNO_2$	620s, 600w, 556w, 536s, 530w, 520w, 470s, 446s, 420w, 400s, 384s, 344Br, 280s.
$MePCl_3bipy^+Cl^-$	650w, 646w, 620s, 540w, 500s, 470s, 430s, 400w, 388w, 340Br, 320w, 310w, 284w.
$MePCl_3bipySbCl_6^-$	644s, 630s, 610s, 540s, 490m, 440s, 424s, 404s, 390m, 344Br, 284s.

The acceptor properties of Me_2PCl_3.

(i) Introduction

The second member in the series Me_xPCl_{5-x} ($1 \leqslant x \leqslant 5$), Me_2PCl_3, is ionic in the solid state. Its ^{35}Cl n.q.r. spectrum showed one signal at 29.80 MHz at 77 K, which is in excellent agreement with the work of Dillon et al[50]. ^{35}Cl n.q.r. frequencies of 29.30 and 29.63 MHz were also observed at 293 K and 195 K respectively. The solid state ^{31}P n.m.r. spectrum showed a broad resonance at -127.5 ± 3 p.p.m. which is in the four-coordinate region of the spectrum for phosphorus-chlorine compounds. This shift is in good agreement with the value reported by Dillon et al[50]. It had been deduced previously from vibrational spectroscopic measurements that Me_2PCl_3 has an ionic structure in the solid state[49].

Its i.r. spectrum shows a remarkable similarity to the spectra of its derivatives, except in the region below 450 cm^{-1} in which minor differences in frequency can be discerned, attributable to the counter-ions, Table 3.6.

A band at 336 cm^{-1} in the spectrum of $Me_2PCl_2^+SbCl_6^-$ can be assigned to $SbCl_6^-$. Similarly a broad band at 430 cm^{-1} in the spectrum of $Me_2PCl_2^+PCl_6^-$ may be assigned to PCl_6^- [12,74]. This band is usually found at rather higher frequency (∿ 450 cm^{-1}). The assignment of the bands at 265 cm^{-1} and 358 cm^{-1} to ICl_4^- and $AuCl_4^-$ respectively is in agreement with earlier work[75-77], and is also in accordance with the assignments of Page[78].

No ^{35}Cl n.q.r. signals were observed for any of the derivatives isolated. Similarly no resonances were found previously for the ionic derivatives $Me_2PCl_2^+SbCl_6^-$ and $Me_2PCl_2^+BCl_4^-$ although signals were detected for $Me_2PCl_2^+ICl_2^-$ [50].

Table 3.6

I.R. spectrum of Me_2PCl_3 and its derivatives 1000 - 250 cm^{-1}

Me_2PCl_3	970w, 938Br, 900s, 870w, 846w, 580s, 500s, 374w, 288s.
$Me_2PCl_2^+SbCl_6^-$	952s, 919s, 878s, 770w, 600s, 510s, 336*Br, 275s.
$Me_2PCl_2^+PCl_6^-$	954s, 920s, 878s, 770vw, 600s, 510s, 430*Br, 285m.
$Me_2PCl_2^+ICl_4^-$	952s, 940w, 920s, 880s, 770vw, 600s, 514s, 355Br, 284w, 272w, 265*Br.
$Me_2PCl_2^+AuCl_4^-$	950s, 914s, 876s, 770vw, 600s, 516s, 358*s.

* = counter-ion

The ^{31}P n.m.r. spectra of the $Me_2PCl_2^+$ cation in the salts are very similar to the spectrum of Me_2PCl_3 (Table 3.7), and to previous data for this ion. This similarity in shift is compatible with an ionic structure for Me_2PCl_3.

Table 3.7

^{31}P n.m.r. shifts in solution and in the solid state for Me_2PCl_3 and derivatives

Compound	δ ^{31}P (p.p.m.) for:- solid state	PhNO$_2$ solution
Me_2PCl_3	-127.5 ± 3	
$Me_2PCl_2^+SbCl_6^-$	-119.3	-124.2
$Me_2PCl_2^+PCl_6^-$	-122.6;301.1[a]	-124.2;298[a]
$Me_2PCl_2^+ICl_4^-$	-120.9	
$Me_2PCl_2^+AuCl_4^-$	-117.7	

[a] PCl_6^- ion[51]

(j) Acceptor properties towards chloride, mono- and bidentate pyridines.

The acceptor properties of the compound could not be investigated successfully, mainly because Me_2PCl_3 was found to be insoluble in all the common solvents available.

Attempts to force it into solution were made by adding a solution of a tetra-n-alkylammonium chloride or 1,10-phenanthroline to the solid, but to no avail. An intimate mixture of Me_2PCl_3 and tetra-n-pentylammonium chloride (1:1) was melted in a sealed tube and the ^{31}P n.m.r. spectrum of the cooled mixture recorded. No peak which could be attributed to a six-coordinate anion was observed, although several peaks were apparent at -206.4 (m), -195.2 (m), -88.7 (s) and -51.5 (s) p.p.m., some of them probably P(III) compounds. These peaks were tentatively assigned to PCl_4^- (206.4), $MePCl_2$ (-195.2) and Me_3PCl^+ (-88.7) while the peak at -51.5 p.p.m. was difficult to assign. This suggests that Me_2PCl_3 may undergo scrambling to give mono- and trimethyl compounds although the presence of P(III) species would also imply loss of chlorine, possibly as the Cl_3^- ion. As Me_2PCl_3 was found not to possess any acceptor properties towards unidentate or bidentate ligands, attempts were then made to study its acceptor properties towards the bidentate pyridines by using

$Me_2PCl_2^+SbCl_6^-$ (prepared by treating the slurry of Me_2PCl_3 in methylene chloride with antimony (V) chloride). Addition of either 2,2'-dipyridine or 1,10-phenanthroline to the solution of $Me_2PCl_2^+SbCl_6^-$ in either methylene chloride or nitrobenzene did not reveal any new peak, or alteration in the $Me_2PCl_2^+$ peak position, indicating that no coordination occurred between the adduct and the ligands.

A solution of either $Me_2PCl_2^+SbCl_6^-$ or $Me_2PCl_2^+PCl_6^-$ in neat pyridine resulted in the formation of a precipitate and the absence of a signal due to $Me_2PCl_2^+$, but in the case of $Me_2PCl_2^+PCl_6^-$ the spectrum showed a signal at 230.6 p.p.m. This shift is readily assigned to the PCl_5.py complex which has a chemical shift of about +233 p.p.m.[29,79], while the precipitate is probably Me_2PCl_3, reaction 5.

$$Me_2PCl_2^+PCl_6^- + py \longrightarrow PCl_5.py + Me_2PCl_3 \qquad (5)$$

By analogy $Me_2PCl_2^+SbCl_6^-$ probably reacts with pyridine in a similar manner to that shown by $Me_2PCl_2^+PCl_6^-$, thus accounting for the absence of a ^{31}P n.m.r. resonance in its spectrum.

$$Me_2PCl_2^+SbCl_6^- + py \longrightarrow SbCl_5.py + Me_2PCl_3 \qquad (6)$$

(k) Raman spectra of some $MePCl_3^+$ and $Me_2PCl_2^+$ complexes.

The Raman spectra of some solid complexes of $MePCl_3^+$ or $Me_2PCl_2^+$ with square planar or octahedral counter-ions have been investigated and found to be consistent with the expected D_{4h} and O_h symmetries of the species. Partial assignment of the frequencies has been carried out where possible.

Table 3.8

Raman frequencies (550 - 140 cm^{-1}) of some complexes with square planar anions in the solid state and their assignments

$MePCl_3^+ICl_4^-$	$Me_2PCl_2^+ICl_4^-$	$MePCl_3AuCl_4^-$	$Me_2PCl_2^+AuCl_4^-$	Assignment	Type
489	515	490	514	cation	
284	283	352	352	ν_1	A_{1g}
260	262	325	326	ν_5	B_{2g}
201	-	-	-	?	
190	-	-	-	?	
148	145	172	175	ν_3	B_{1g}

In the Raman spectra of the compounds $Me_2PCl_2^+AuCl_4^-$ and $MePCl_3^+AuCl_4^-$, three bands were observed for the anion, as expected for D_{4h} symmetry[78,80-82], Table 3.8. The A_{1g} - mode (ν_1) corresponds to symmetric stretching while the B_{2g} - mode (ν_5) corresponds to an out-of-phase stretching motion of the two pairs of opposite chlorine atoms, and its frequency is expected to be very close to that of the A_{1g} - mode. Finally, the lowest of the observed Raman bands has to be ascribed to the planar bending mode ν_3 (B_{1g}). The rest of the observed frequencies can be attributed to the cations, as they are in quite good agreement with the frequencies observed for the free cations, Table 3.9.

The spectra of the ICl_4^- complexes contained a number of Raman bands. $Me_2PCl_2^+ICl_4^-$ showed the three modes expected for D_{4h} symmetry and a centrosymmetric ion. A fourth band observed at 515 cm^{-1}, results from the $Me_2PCl_2^+$ cation, Table 3.9. The A_{1g} and B_{2g} modes correspond to I-Cl stretching vibrations with frequencies 283 and 262 cm^{-1}, respectively. The lower frequency band at 145 cm^{-1} must be assigned to the bending mode B_{1g}. ν_1 and ν_5 agree well with values given by Page[78] for analogous systems, while ν_3 is at a higher frequency than his value, but is in good agreement with the results of Stammreich et al[82].

Similarly in the spectrum of $MePCl_3^+ICl_4^-$, the frequencies at 284 and 260 cm^{-1} can be assigned to the A_{1g} and B_{2g} modes respectively, while the other frequency at 148 cm^{-1} is a bending mode B_{1g}. The frequencies at 190 and 201 cm^{-1} can be assigned to ICl_2^- [83], which is a possible impurity in the sample. These bands were not observed in the spectrum of the freshly prepared complex, supporting the hypothesis that they are due to an impurity. The band at 487 cm^{-1} is due to the cation, Table 3.9.

The three bands at 332 (3) A_{1g}, 290 (0) E_g and 172 F_{2g}, Table 3.10, represent Raman-active modes of the $SbCl_6^-$ octahedron. These assignments are in good agreement with those reported by Beattie et al[84], Gerding[85] and Shamir[86].

The frequencies marked (?) are difficult to assign as they do not correspond to any of the frequencies recorded for the cations or $SbCl_6^-$.

Table 3.9

Raman spectra of some starting materials from 650 - 200 cm^{-1}

$MePCl_4$	Me_2PCl_3
480	515
-	284
272	272
248	-
220	-
208	216

Table 3.10

Raman frequencies from 650 - 150 cm^{-1} of some complexes with octahedral anions and their partial assignments

$MePCl_3^+SbCl_6^-$	$MePCl_2^+SbCl_6^-$	$Me_2PCl_2^+PCl_6^-$	Assignment	Type
491*	510*	520*		
333	332	360	ν_1	A'_{1g}
290	290	282	ν_2	E_g
272*	272*	-		
262(?)	-	243		
-	230(?)	223		
207*	208*	205*		
-	-	170		
171	172	155	ν_5	F_{2g}

* = cation bands

The three frequencies (155, 282 and 360 cm^{-1}) in the Raman spectrum of $Me_2PCl_2^+PCl_6^-$, are presumably the Raman-active fundamentals of PCl_6^-. 360 cm^{-1} is assigned as ν_1 (A_{1g}) P-Cl stretch, 282 as ν_2 (E_g) P-Cl stretch and 155 cm^{-1} as ν_5 (F_{2g}) which is the P-Cl deformation. These frequencies and assignments are in good agreement with those reported by Carlson[74].

(1) Experimental.

The preparation of $(C_5H_{11})_4\overset{+}{N}MePCl_5^-$.

$MePCl_4$ (0.207 g, 1.1 mmoles) and $(C_5H_{11})_4NCl$ (0.367 g, 1.1 mmoles) were separately dissolved in the minimum amount of methylene chloride. The chloride solution was added to the methyltetrachlorophosphorane solution with stirring. A yellow solution was then formed. This was placed in a refrigerator in the hope of obtaining crystals, but no crystals formed. The solvent was therefore removed in vacuo to yield a white sticky solid.

Analysis

Found C = 46.69 H = 9.37 N = 2.71 P = 6.10 Cl = 34.00

Calculated C = 48.35 H = 9.51 N = 2.68 P = 5.94 Cl = 34.04

The preparation of $Et_4\overset{+}{N}MePCl_5^-$.

$MePCl_4$ (1.037 g, 5.5 mmoles) and a stoichiometric amount of Et_4NCl (0.916 g, 5.5 mmoles) were separately dissolved in a small amount of methylene chloride. The chloride solution was added to the methyltetrachlorophosphorane solution with constant stirring. After complete addition of the chloride, the solution was left to stir for 10 minutes. The solvent was then removed in vacuo, leaving behind in the flask a fine white solid.

Analysis

Found C = 30.51 H = 6.90 N = 3.92 P = 8.30 Cl = 49.70

Calculated C = 30.55 H = 6.51 N = 3.96 P = 8.77 Cl = 50.21

The preparation of $MePCl_3^+AuCl_4^-$.

$MePCl_4$ (0.634 g, 3.4 mmoles) was dissolved in a small amount of methylene chloride. This solution was then treated with an equimolar amount of $AuCl_3$ (1.024 g, 3.4 mmoles). The mixture was stirred to complete the reaction, then filtered, and the yellow product was washed with $^{30}/40$ Pet. ether. This was then dried in vacuo to remove any traces of the solvent.

Analysis

Found C = 2.70 H = 0.87 P = 6.39 Cl = 50.10 Au = 39.98

Calculated C = 2.44 H = 0.61 P = 6.31 Cl = 50.56 Au = 40.08

The preparation of $MePCl_3^+ICl_4^-$.

$MePCl_4$ (1.1 g, 5.9 mmoles) and ICl_3 (1.4 g, 5.9 mmoles) were separately dissolved in the minimum amount of methylene chloride. The ICl_3 solution was added slowly to the $MePCl_4$ solution with stirring and a yellow precipitate was immediately formed in a brick-red solution. The precipitate was filtered off, washed with $^{30}/40$ Pet. ether and dried in vacuo, yielding a fine yellow solid.

Analysis

Found C = 2.87 H = 1.24 P = 7.50 Cl = 57.91 I = 30.30

Calculated C = 2.85 H = 0.71 P = 7.35 Cl = 58.96 I = 30.13

The preparation of $MePCl_3^+SbCl_6^-$.

$MePCl_4$ (1.087 g, 5.8 mmoles) and antimony (V) chloride (0.7 mls, 5.5 mmoles) were dissolved separately in a small amount of methylene chloride. The antimony (V) chloride solution was added to the $MePCl_4$ solution with stirring. After complete addition, the mixture was allowed to stand for a few minutes. A pale brown precipitate separated out. This was then filtered off and washed with methylene chloride to yield a white solid, which was dried in vacuo.

Analysis

Found C = 2.42 H = 0.69 P = 6.32 Cl = 65.37 Sb = 25.00

Calculated C = 2.46 H = 0.62 P = 6.36 Cl = 65.54 Sb = 25.02

The preparation of $MePCl_4$ pyridine.

An excess of pyridine was added to a solution of $MePCl_4$ in methylene chloride, with stirring. A yellow precipitate was immediately formed. The excess pyridine and methylene chloride were removed in vacuo to produce a pale brown solid. Analysis indicated that two moles of pyridine were present in the adduct.

Analysis as $MePCl_3py_2^+Cl^-$

Found C = 36.75 H = 4.23 N = 7.55 P = 9.25 Cl = 39.50

Calculated C = 38.15 H = 3.76 N = 8.09 P = 8.96 Cl = 41.04

The preparation of $\mathrm{MePCl_3bipy^+Cl^-}$.

$\mathrm{MePCl_4}$ (0.614 g, 3.3 mmoles) was dissolved in a small quantity of methylene chloride. Similarly 2,2'-bipyridyl (0.51 g, 3.3 mmoles) was dissolved in the minimum amount of the same solvent. The bipy solution was added to the $\mathrm{MePCl_4}$ solution with stirring, leading to the immediate formation of a white precipitate. The solution was filtered and the product washed with methylene chloride and $^{30}/40$ Pet. ether, yielding a white solid.

Analysis

Found C = 39.42 H = 3.37 N = 9.14 P = 9.33 Cl = 42.60

Calculated C = 38.37 H = 3.20 N = 8.14 P = 9.01 Cl = 42.28

The preparation of $\mathrm{MePCl_3phen^+Cl^-}$.

$\mathrm{MePCl_4}$ (0.71 g, 3.8 mmoles) and o-phenanthroline (0.68 g, 3.8 mmoles) were dissolved separately in the minimum amount of nitrobenzene. The phen solution was added to the $\mathrm{MePCl_4}$ solution with stirring. A white precipitate was instantly formed. The mixture was then filtered and the product washed with $^{30}/40$ Pet. ether, yielding a white solid.

Analysis

Found C = 42.51 H = 2.87 N = 8.45 P = 8.96 Cl = 39.37

Calculated C = 42.39 H = 2.99 N = 7.61 P = 8.42 Cl = 38.59

The preparation of $\mathrm{MePCl_3phen^+SbCl_6^-}$.

(i) in $\mathrm{PhNO_2}$

$\mathrm{MePCl_3^+SbCl_6^-}$ (1.90 g, 3.9 mmoles) and phen (0.7 g, 3.9 mmoles) were separately dissolved in the minimum amount of nitrobenzene. The phen solution was added slowly with stirring to the $\mathrm{MePCl_3^+SbCl_6^-}$, forming a yellow solution. After a few minutes a thick yellow precipitate was formed. The solid was then separated and washed with $^{30}/40$ Pet. ether to give a yellow product. Analysis revealed that it contained one mole of nitrobenzene.

Analysis for $\mathrm{MePCl_3phen^+SbCl_6^-PhNO_2}$

Found C = 29.05 H = 2.14 N = 5.72 P = 3.25 Cl = 38.10 Sb = 19.20

Calculated C = 28.84 H = 2.02 N = 5.31 P = 3.92 Cl = 40.42 Sb = 15.43

(ii) in CH_3NO_2

A solution of stoichiometric amounts of $MePCl_4$ and phen in CH_3NO_2 was made up in an n.m.r. tube. $SbCl_5$ was added dropwise to the above solution. A sandy coloured solid was precipitated. It was then filtered off and washed with $^{30}/40$ Pet. ether to isolate it as a light brown material.

Analysis

Found C = 23.36 H = 2.00 N = 4.99 P = – Cl = 41.43 Sb = 24.38

Calculated C = 23.37 H = 1.65 N = 4.19 P = 4.64 Cl = 47.87 Sb = 18.28

The preparation of $MePCl_3bipy^+SbCl_6^-$.

$MePCl_4$ (0.74 g, 3.9 mmoles) and bipy (0.62 g, 3.9 mmoles) were separately dissolved in methylene chloride. Antimony (V) chloride (0.5 ml) was then dripped into the solution mixture of $MePCl_4$ and bipy with stirring. A brown solution was formed. After a few minutes a light brown precipitate was deposited at the bottom of the flask. The solution was then filtered and the product washed with $^{30}/40$ Pet. ether to yield a brown solid.

Analysis

Found C = 18.89 H = 1.65 N = 4.66 P = red Cl = 48.70

Calculated C = 20.51 H = 1.71 N = 4.35 P = 4.82 Cl = 49.65

The preparation of Me_2PCl_3.

A solution of 0.05 mmole tetra-methyldiphosphinedisulphide ($Me_2P(S)P(S)Me_2$) in 150 ml carbon tetrachloride was treated with a slow stream of dry chlorine (passed through phosphorous pentoxide) with stirring, until saturated. The mixture was then boiled in the dark for 6 hours until the solution went red. The white precipitate which had formed was then filtered off, washed with carbon tetrachloride and $^{30}/40$ Pet. ether and dried in vacuo to produce a fine white solid.

Analysis

Found C = 14.36 H = 3.37 P = 18.90 Cl = 63.54

Calculated C = 14.32 H = 3.58 P = 18.50 Cl = 63.58

The preparation of $Me_2PCl_2^+AuCl_4^-$.

Me_2PCl_3 (0.45 g, 2.7 mmoles) was suspended in a small amount of methylene chloride. A stoichiometric amount of $AuCl_3$ (0.83 g, 2.7 mmoles) was dissolved separately in the same solvent. The Me_2PCl_3 suspension was added to the $AuCl_3$ solution with stirring. A yellow precipitate was immediately formed. The solution was filtered and the product washed with $^{30}/40$ Pet. ether, yielding a yellow solid.

Analysis

Found	C = 3.57	H = 1.42	P = 6.47	Cl = 45.18
Calculated	C = 5.10	H = 1.27	P = 6.58	Cl = 45.22

The preparation of $Me_2PCl_2^+ICl_4^-$.

To a slurry of Me_2PCl_3 (1.19 g, 7.1 mmoles) in methylene chloride was added a stoichiometric amount of ICl_3 (1.66 g, 7.1 mmoles) dissolved in the same solvent. The solution mixture was left to stir for a few minutes. A yellow precipitate separated out. This was then filtered off, and washed with methylene chloride and $^{30}/40$ Pet. ether to yield a fine yellow solid.

Analysis

Found	C = 7.69	H = 2.33	P = 7.48	Cl = 51.02	I = 30.96
Calculated	C = 6.91	H = 1.48	P = 7.65	Cl = 52.60	I = 31.36

The preparation of $Me_2PCl_2^+SbCl_6^-$.

A slurry of Me_2PCl_3 (2.1 g, 12.5 mmoles) in methylene chloride was treated cautiously with an equimolar quantity of antimony (V) chloride (1.6 ml, 12.4 mmoles). The mixture was stirred to ensure a complete reaction. The solution was then filtered, and the product washed with methylene chloride and $^{30}/40$ Pet. ether to yield a white solid.

Analysis

Found	C = 5.05	H = 1.50	P = 6.60	Cl = 60.90	Sb = 26.20
Calculated	C = 5.14	H = 1.29	P = 6.64	Cl = 60.81	Sb = 26.12

The preparation of $Me_2PCl_2^+PCl_6^-$.

PCl_5 (0.88 g, 4.2 mmoles) was dissolved in methylene chloride and added to a slurry of Me_2PCl_3 (0.71 g, 4.2 mmoles) in the same solvent. An off-white precipitate was formed. The solution was left to stir for 10 minutes to ensure complete reaction, the solid filtered off and washed with $^{30}/40$ Pet. ether to yield an off-white product.

Analysis

Found C = 6.05 H = 1.59 P = 16.28 Cl = 74.60

Calculated C = 6.38 H = 1.60 P = 16.48 Cl = 75.33

CHAPTER FOUR

The acceptor properties of $EtPCl_4$ and related compounds.

1. The acceptor properties of $EtPCl_4$.

(a) Introduction.

Ethyltetrachlorophosphorane can be synthesised by reducing the complex $EtPCl_3^+AlCl_4^-$ according to the procedure of Komkov et al[87], followed by chlorination of the $EtPCl_2$ thus produced, or by the reaction of the complex with dry Et_4NCl to give $EtPCl_4$[88], equation (1).

$$EtPCl_3^+AlCl_4^- + Et_4NCl \xrightarrow{CCl_4} EtPCl_4 + Et_4N^+AlCl_4^- \qquad (1)$$

The complex was prepared by the method of Parshall[89].

The ^{31}P n.m.r. solid state spectrum showed a broad peak at -127.5 ± 2 p.p.m., indicative of the ionic nature of the compound. Dillon et al[50] have recorded the ^{31}P n.m.r. and ^{35}Cl n.q.r. spectra of some ethylchlorophosphoranes and their 1:1 ionic adducts with Lewis acids (X) and have suggested that the parent compouds are ionic $Et_nPCl_{4-n}^+Cl^-$, and the adducts have the structure $Et_nPCl_{4-n}^+XCl^-$. The ^{31}P n.m.r. solid state spectra of the salts $EtPCl_3^+AlCl_4^-$ (-125.8 p.p.m.), $EtPCl_3^+SbCl_6^-$ (-127.5 p.p.m.) and $EtPCl_3^+ICl_4^-$ (-128.4 p.p.m.) have been recorded in the present work and agree well with the values published by Dillon et al[50] for similar compounds.

The ^{35}Cl n.q.r. at 77 K consisted of three signals at 31.025, 31.200 and 31.375 MHz, with an intensity ratio of 1:1:1, suggesting that the compound is ionic in the solid state. Signals were also recorded at 195 K (30.800, 31.025 and 31.175 MHz) and 293 K (30.575, 30.725 and 30.950 MHz) with the same intensity ratio. The ^{35}Cl n.q.r. spectrum has been recorded by Dillon et al[50] for the compound $EtPCl_3^+AlCl_4^-$ at 77 K and the pattern was very similar to that of the parent compound, with three signals in a 1:1:1 intensity ratio. No ^{35}Cl n.q.r. signals were observed for the other Lewis acid derivatives mentioned above.

The i.r. spectra of $EtPCl_4$ and its salts showed remarkable similarities, except for broad bands below 400 cm^{-1} which are not found in the $EtPCl_4$ spectrum. These bands were readily assigned to the different counter-ions attached to the cation $EtPCl_3^+$. This similarity of the spectra tends to support the ionic nature deduced for the parent compound, Table 4.1.

Table 4.1

I.R. spectra of $EtPCl_4$ and its salts (700 - 250 cm^{-1})

$EtPCl_4$	640s, 612s, 588s, 550w, 500s, 480s, 456w, 420s, 380s, 350w, 334w, 284w, 264m.
$EtPCl_3^+ICl_4^-$	644s, 618s, 568s, 540s, 504m, 484s, 384w, 340w, 290w, 260*Br.
$EtPCl_3^+SbCl_6^-$	650Br, 624s, 588m, 564s, 490s, 470s, 450m, 346*Br, 280w, 254s.

* = counter-ion

$EtPCl_4$ was found to be very soluble in most common organic solvents, and its ^{31}P n.m.r. chemical shifts are given in Table 4.2.

Table 4.2

Chemical shifts of $EtPCl_4$ in various solvents

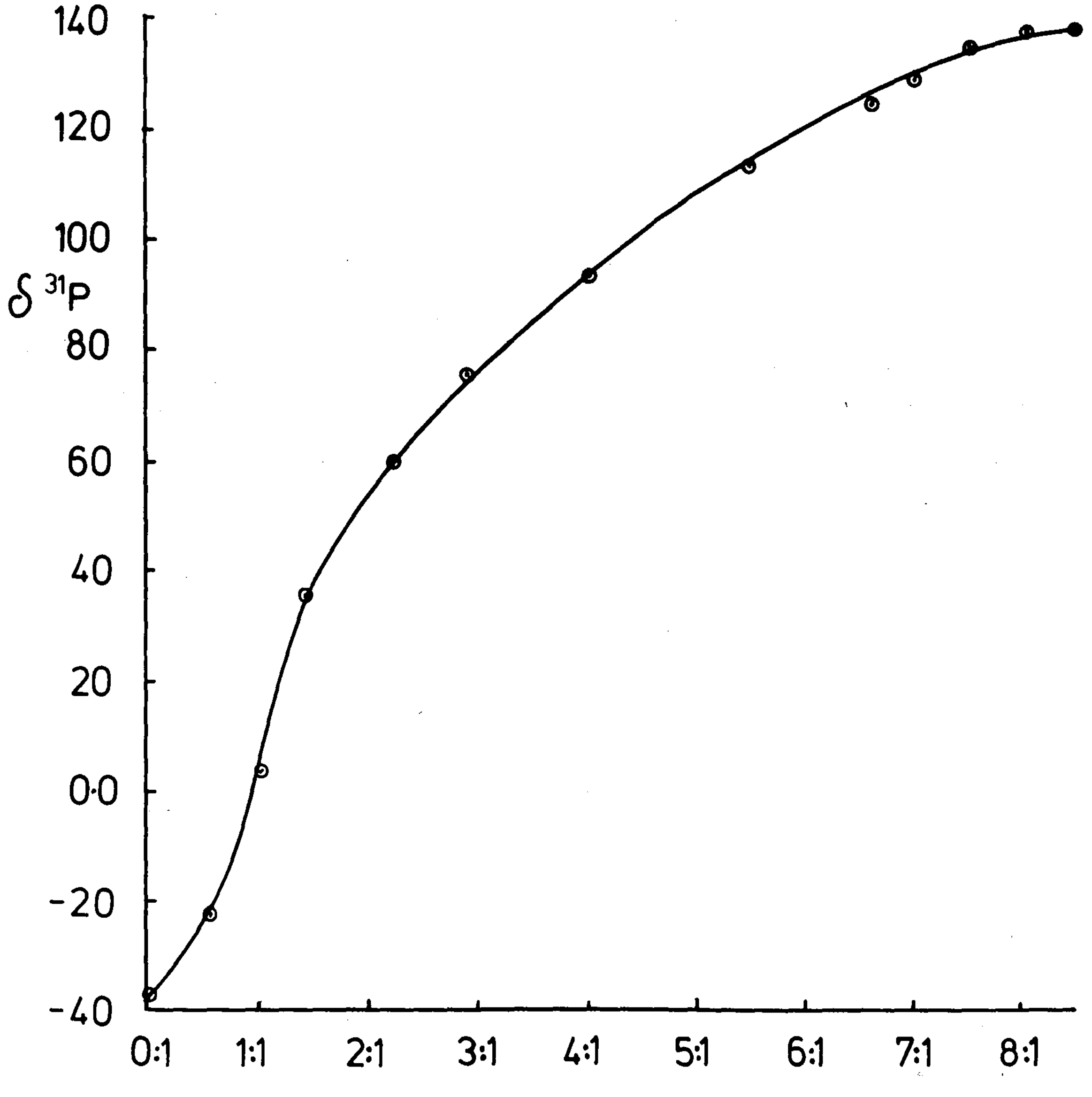
Solvent	Shift (p.p.m.)	Reported shift[90]
$PhNO_2$	-35.5	-
$MeNO_2$	-21.1	-24.7
MeCN	-12.9	-24.4
CS_2	27.5	-
C_6H_6	24.2	25.7
CH_2Cl_2	24.2	-

From the above table, it is apparent that the chemical shift of $EtPCl_4$ shows a remarkable solvent dependence, with the compound showing a degree of ionicity in the first three solvents (i.e. the equilibrium $EtPCl_3^+Cl^- \rightleftharpoons EtPCl_4$ with rapid exchange on the n.m.r. time scale between $EtPCl_3^+$ and $EtPCl_4$). The very similar chemical shifts in the last three solvents suggest the presence of a single molecular species. This is in line with known effects in chemical

Fig. 4.1

^{31}P CHEMICAL SHIFT OF $(C_5H_{11})_4N^+Cl^-/EtPCl_4$

Solutions in $PhNO_2$



equilibria of phosphorus (V) species, where solvents with high dielectric constant shift the position of equilibrium towards the ionic form[91,92].

(b) Acceptor properties towards the chloride ion.

Solutions with approximately 0.5:1, 1:1, 1.5:1, 4 .0:1 and 7:1 molar ratios of tetra-n-pentylammonium chloride to ethyltetrachlorophosphorane were made up in nitrobenzene. Addition of chloride to the phosphorane solution resulted in an upfield shift of the single peak, Table 4.3. The limiting shift attained was 137.1 p.p.m., although extrapolation gave a value of 138.0 p.p.m., Fig. 4.1. The limiting shift is ascribed to the ethylpentachlorophosphate ion, as it lies in the six-coordinate region of the spectrum for this kind of compound. Thus with stoichiometric amounts of $EtPCl_4$ and the chloride, there is a labile equilibrium between $EtPCl_5^-$ and free $EtPCl_4$.

$$EtPCl_4 + (C_5H_{11})_4NCl \rightleftharpoons (C_5H_{11})_4N^+EtPCl_5^-$$

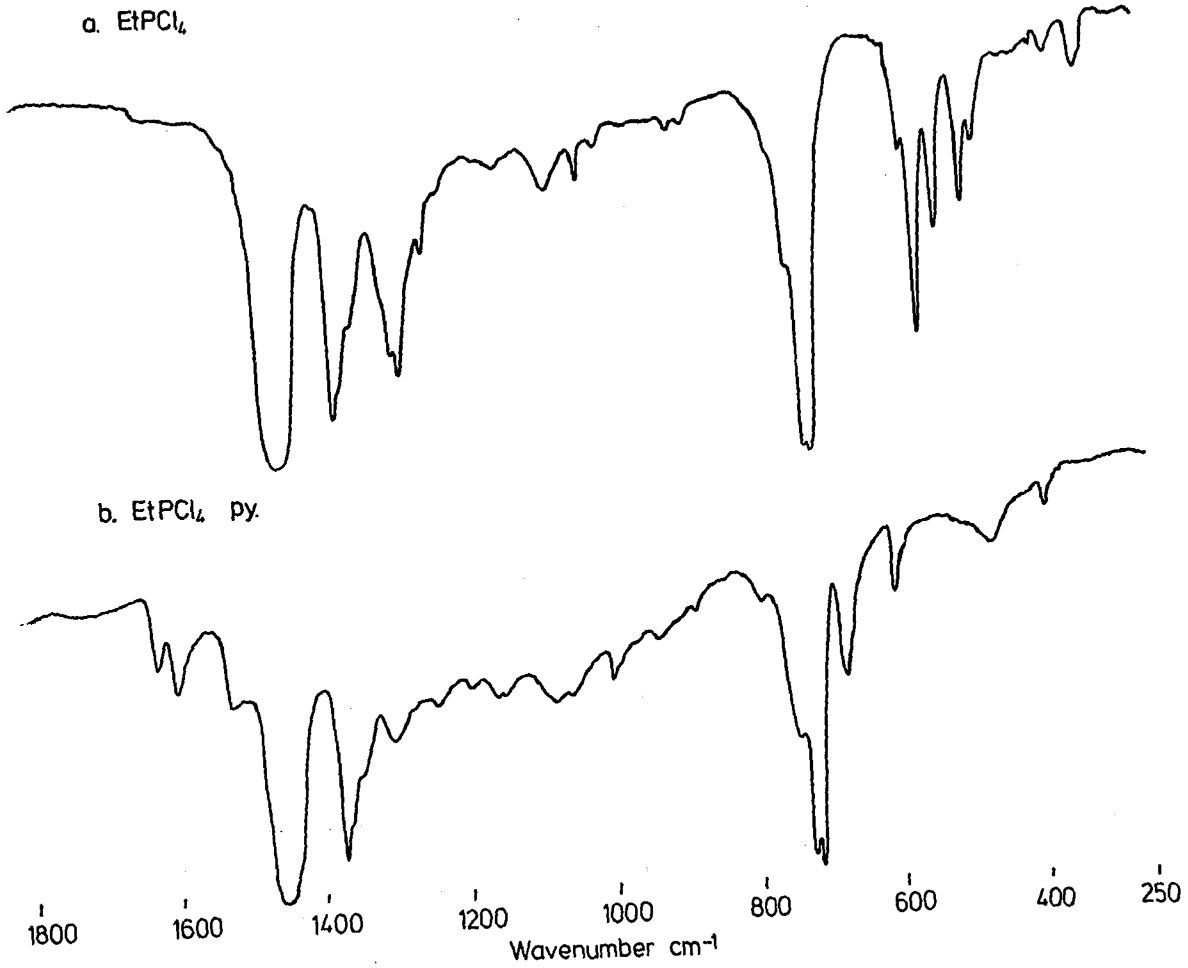
Table 4.3

Shifts recorded for $Cl^-/EtPCl_4$ system in $PhNO_2$

Molar ratio $(C_5H_{11})_4N^+Cl^-/EtPCl_4$	$\delta\ ^{31}P$ (p.p.m.)
0.56:1	-22.7
1.04:1	3.3
1.46:1	35.5
2.25:1	60.0
2.90:1	75.0
4.00:1	93.2
5.50:1	113.0
6.60:1	124.0
7.00:1	128.1
7.50:1	137.1
8.00:1	137.1

Percent associations have not been calculated for this system because of the difficulty in assigning a shift value to the molecular species[90].

Fig. 4.2 Infrared spectra of



Isolation of the compounds was then carried out. A sticky yellow solid was isolated from a 1:1 reaction of $EtPCl_4$ and tetra-n-pentylammonium chloride. Its i.r. spectrum was found to be different from that of the parent compound, with bands at 648s, 620s, 592s, 576w, 512s, 490m, 460w, 448s, 390s, 352w, 320m and 260w cm^{-1} in the range 700 - 250 cm^{-1}. No ^{35}Cl n.q.r. spectrum was recorded for this solid due to an insufficient amount of the compound being available. The ^{31}P n.m.r. solid state spectrum consisted of a sharp peak at 63.8 p.p.m., indicating an equilibrium between $EtPCl_4$ and $EtPCl_5^-$ and showing that the compound is partially dissociated at the spectrometer operating temperature. Et_4NCl was found not to coordinate with $EtPCl_4$ in either methylene chloride or acetonitrile and no adduct could be isolated.

(c) Acceptor properties towards pyridine.

When pyridine was added to a solution of ethyltetrachlorophosphorane in methylene chloride, a white precipitate was immediately formed and no solution spectrum could be detected. Similarly dissolution of $EtPCl_4$ in neat pyridine was accompanied by evolution of heat and the formation of a white solid in a slightly yellow solution, the ^{31}P n.m.r. spectrum showing no solution peak. The white solid isolated from a 1:1 molar ratio reaction gave an i.r. spectrum different from that of either $EtPCl_4$ or pyridine, with bands derived mainly from py or $EtPCl_4$ apparent in the spectrum, although with reduced intensities and slightly shifted, relative to the starting materials, Fig. 4.2. The analysis confirmed the formation of a 1:1 adduct. No ^{31}P n.m.r. spectrum could be detected. Similarly the ^{35}Cl n.q.r. spectrum showed no signals. Attempts to redissolve the isolated compound in order to observe its solution shift were unsuccessful, since it was found not to dissolve in neat pyridine or nitrobenzene.

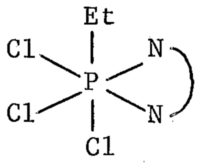
(d) Reaction of $EtPCl_4$ with bidentate pyridines.

(i) 2,2'-bipyridine.

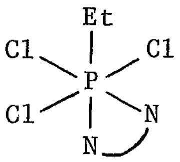
When a small amount of bipy was added to a solution of $EtPCl_4$ in methylene chloride, four peaks were observed in the ^{31}P n.m.r. spectrum at -53.3(w) ($EtPOCl_2$, hydrolysis), 24.2(m) ($EtPCl_4$), 127.5(s) and 135.5(s) p.p.m. The last two peaks are well within the six-coordinate region for phosphorus chloro-compounds and can be readily assigned to the two isomers of the cation from the $EtPCl_3bipy^+Cl^-$ complex which is the most probable product. Further addition of bipy resulted in the formation of a thick white precipitate, with the solution spectrum giving a single peak at -53.3 p.p.m (partial hydrolysis). A similar reaction in nitrobenzene was found to give two peaks at 127.5 and 137.1 p.p.m. in the ^{31}P n.m.r. spectrum, ascribed to the two isomers, with the signal at 127.5 being the more intense. Other minor peaks were observed at -98.4 and -53.3 p.p.m. The resonance at -98.4 p.p.m. if genuine is difficult to account for, as it does not correspond to the shift of any likely product under these conditions. When the same solution was reinvestigated after two hours, the intensities of the two peaks at 127.5 and 137.1 p.p.m. had diminished and a white precipitate had formed. After five hours the peaks had completely disappeared with an increased level of the precipitate in the n.m.r. tube. The solid was isolated, but its ^{31}P n.m.r. spectrum gave no detectable signal, and no ^{35}Cl n.q.r. signals were apparent either. The i.r. spectrum showed a number of new bands absent in the spectrum of the starting material (Table 4.4). Analysis showed that the $EtPCl_3bipy^+Cl^-$ complex had indeed been formed with relative ease.

(ii) <u>1,10-phenanthroline</u>.

1,10-phenanthroline was added to a solution of $EtPCl_4$ in methylene chloride. The ^{31}P n.m.r. spectrum showed three peaks at 24.2 ($EtPCl_4$), 127.5 and 130.6 p.p.m. The two equally intense upfield signals were assigned to the two possible isomers of the $EtPCl_3phen^+Cl^-$ complex (I and II) as they lie in the six-coordinate region of the spectrum for phosphorus chloro- compounds. This is consistent with the molecule having an octahedral structure.



I



II

$\overset{\frown}{N\ N}$ = phen

When more phen was added, no signal was observed in the ^{31}P n.m.r. spectrum but instead a white precipitate formed. When this reaction was carried out in nitrobenzene, a white precipitate was immediately formed and only one signal was observed at -53.3 p.p.m., probably due to the hydrolysis product $EtPOCl_2$.

The solid state spectrum of the isolated compound showed a broad resonance at 138.2 ± 5 p.p.m., in good agreement with the solution peak. Its i.r. spectrum was quite different between 650 - 400 cm^{-1} from the spectrum of the parent compound, Table 4.4, as expected for complex formation. The region 1000 - 750 cm^{-1} was characterised by a number of new bands not observed in the spectrum of $EtPCl_4$. These bands are probably due to 1,10-phenanthroline. Analysis confirmed that the compound was the 1:1 complex $EtPCl_3phen^+Cl^-$.

Table 4.4

I.R. bands of some $EtPCl_4$ complexes between 700 - 250 cm^{-1}

$EtPCl_3bipy^+Cl^-$	674s, 656s, 644w, 630w, 620s, 600m, 572s, 548w, 510s, 504w, 476s, 460w, 446s, 430m, 406s, 382w, 340Br
$EtPCl_3phen^+Cl^-$	652s, 620s, 600m, 570m, 554w, 532m, 510s, 500w, 480w, 466s, 454w, 440Br, 410m, 360w, 334m, 320m, 260m

(e) Reaction of $EtPCl_3^+SbCl_6^-$ with bidentate pyridines.

When bipy was added to a solution of $EtPCl_3^+SbCl_6^-$ in methylene chloride, the ^{31}P n.m.r. spectrum showed two signals at 130.0 and 132.2 p.p.m. with the peak at 132.2 p.p.m. being more intense. These peaks were assigned to the two possible isomers of the cation from $EtPCl_3bipy^+SbCl_6^-$. When the same solution was monitored after two hours, no signal was discerned in the ^{31}P n.m.r. spectrum, but a white precipitate had formed. Since the relative intensities were reversed in the $EtPCl_3bipy^+Cl^-$ spectrum, it thus appears that the two isomers are of comparable stability, and that the nature of the starting material affects the isomeric proportions.

In the case of phen, a white precipitate was instantly formed and no solution peak was observed. The ^{31}P n.m.r. solid state spectrum showed a broad resonance at 130.1 ± 6 p.p.m. for the phen complex, while the bipy compound showed no detectable signal. No ^{35}Cl n.q.r. signals could be obtained for either of the complexes. The i.r. spectra of the complexes showed a number of new bands compared with $EtPCl_3^+SbCl_6^-$ (Tables 4.1 and 4.5).

Table 4.5

I.r.s of new compounds 700 - 250 cm^{-1}

$EtPCl_3bipy^+SbCl_6^-$	646s, 632m, 610s, 540s, 520w, 508w, 490m, 442m, 424m, 406s, 890w, 340*Br, 302w, 285m.
$EtPCl_3phen^+SbCl_6^-$	620s, 590s, 562w, 540s, 532w, 520m, 508vw, 500w, 484s, 462s, 432w, 416s, 394s, 340*Br, 304w, 280m.

* = counter-ion

2. The acceptor properties of Et_2PCl_3.

(a) Introduction.

This compound is the second member of the series Et_nPCl_{5-n} $(1 \leq n \leq 4)$. It can be prepared by the reaction of $Et_2PSPSEt_2$ with dry chlorine in CCl_4 [44,49]. The product Et_2PCl_3 is ionic, both in the solid and in solution[49,50]. Its solid state ^{31}P n.m.r. spectrum showed a broad resonance at -141.8 ± 2 p.p.m. in good agreement with the value recorded by Dillon et al[50]. Its ^{31}P n.m.r. spectra in methylene chloride and nitrobenzene consisted of single peaks at -127.3 and -125.8 p.p.m. respectively, indicating that it exists predominantly in the ionic form in these solvents. I.r. and Raman studies of this compound indicated that it exists as a phosphonium salt[49]. Further evidence of its ionic nature is provided by the ^{35}Cl n.q.r. frequencies reported by Dillon et al[50]. Its i.r. spectrum showed a marked resemblance to the spectrum recorded for $Et_2PCl_2^+SbCl_6^-$, thus further supporting the ionic structure. $Et_2PCl_2^+ICl_4^-$ was also isolated as a dark brown solid (experimental section). Its i.r. was not recorded as it would not mull properly, but its ^{31}P n.m.r. spectrum in CH_2Cl_2 consisted of a single peak at -138.7 p.p.m.

(b) Acceptor properties towards the chloride ion.

When a source of chloride ion (Et_4NCl or Pe_4NCl) was added to a solution of Et_2PCl_3 in either methylene chloride or nitrobenzene, no change in the position of the single peak ascribed to Et_2PCl_3 was discerned, indicating no complex formation under the experimental conditions.

(c) Reaction with mono- and bidentate pyridines.

Addition of pyridine, 2,2'-bipyridine or 1,10-phenanthroline to a solution of Et_2PCl_3 in either methylene chloride or nitrobenzene did not show a new peak or shift in the Et_2PCl_3 position. Similarly, the salt $Et_2PCl_2^+SbCl_6^-$ showed no acceptor properties towards the mono- or bidentate pyridines. No alteration in the shift of the ^{31}P n.m.r. signal attributed to $Et_2PCl_2^+SbCl_6^-$ was detected on the addition of these bases to a solution of $Et_2PCl_2^+SbCl_6^-$ in either methylene chloride (-137.1 p.p.m.) or nitrobenzene (-137.1 p.p.m.)

3. The acceptor properties of Et_3PCl_2.

(a) Introduction.

This compound has been known to inhibit tumour growth in mice bearing ascites with the simultaneous prolongation of their survival[93-95]. It has been used by Guenter[96] for the preparation of $(R_3PNHNHPR_3)Cl_2$ where R = Ph, P-MeC_6H_4, P-$MeOC_6H_4$, Bu and cyclohexyl.

Dillon et al[50] have reported its solid state ^{31}P n.m.r. spectrum, which is in agreement with an ionic structure $Et_3PCl^+Cl^-$. Its structural study by radiospectroscopic methods[97] indicated that it is ionic or partly ionic in the crystal state but exists in the molecular form in benzene solution.

It was prepared by the chlorination of Et_3P with dry gaseous chlorine in methylene chloride. After the removal of excess solvent in vacuo, the solid was filtered off in an inert atmosphere box, and washed with low boiling petroleum ether, isolating a white solid. Its ^{31}P n.m.r. solid state spectrum gave a chemical shift of -106.4 ± 1 p.p.m. which is in good agreement with the value recorded by Dillon and co-workers[50].

The present work on this compound was an attempt to investigate its acceptor properties toward suitable bases. No change in the ^{31}P n.m.r. shift attributed to Et_3PCl_2 was observed, however, on adding the chloride ion, pyridine, bipy or phen to its solution in methylene chloride or nitrobenzene, and it was deduced to exhibit no acceptor properties towards these bases under the experimental conditions.

The adduct $Et_3PCl^+SbCl_6^-$ was prepared from stoichiometric amounts of Et_3PCl_2 and antimony (V) chloride in methylene chloride. No ^{35}Cl n.q.r. signals were obtained for the parent compound, possibly due to disorder phenomena in the solid, caused by random orientations of the ethyl and chloro-groups in the pseudo-spherical cations[50]. ^{35}Cl n.q.r. frequencies of 28.88 and 28.93 MHz at 77 K were obtained for the adduct $Et_3PCl^+SbCl_6^-$, indicating that there must be two independent cations in the asymmetric unit of the unit cell. These values were in excellent agreement with the corresponding values recorded by Dillon et al[50].

Addition of pyridine, 2,2'-bipyridine or 1,10-phenanthroline to a solution of $Et_3PCl^+SbCl_6^-$ in methylene chloride or nitrobenzene did not reveal any new peak, or shift in the $Et_3PCl^+SbCl_6^-$ position, hence no coordination occurred between the adduct and the bases.

Its solid state ^{31}P n.m.r. spectrum showed a broad resonance at -111.3

p.p.m. The i.r. spectrum showed a marked resemblance to that of the parent compound except for a broad band at 340 cm^{-1} which can be easily assigned to $SbCl_6^-$ [12], confirming that Et_3PCl_2 is ionic in the solid state. $Et_3PCl^+ICl_4^-$ was also prepared as a yellow liquid. Its chemical shift was found to be -111.3 p.p.m. Its infrared spectrum was recorded and found to be similar to that of the parent compound, apart from a broad band at 270 cm^{-1} which was assigned to ICl_4^- [98].

Table 4.6

The infrared spectra of Et_3PCl_2 and its derivatives (650 - 250 cm^{-1})

Et_3PCl_2	650s, 630w, 552m, 532s, 510s, 478w, 440m, 412s, 368s, 320s.
$Et_3PCl^+ICl_4^-$	649s, 530s, 515m, 485w, 435m, 410s, 270*Br.
$Et_3PCl^+SbCl_6^-$	644s, 580Br, 540s, 520s, 410s, 340*Br, 288w.

* = counter-ion

The introduction of more than one alkyl group into the compounds $Et_nPCl_{4-n}^+Cl^-$ thus clearly reduces the acceptor properties to such an extent that no detectable complex formation occurs. This is in accordance with the trend observed previously in the methyl (this work) and phenyl[17] compounds, and is presumably due mainly to the inductive effects of the organo-groups.

4. Experimental.

The preparation of $EtPCl_4$.

$EtPCl_3^+AlCl_4^-$ (11.9 gm, 35.5 mmoles) was dissolved in CCl_4. Et_4NCl (5.9 gm, 35.6 mmoles) was added to the above solution with stirring. The mixture was filtered and the solvent removed in vacuo to isolate an off-white solid.

Analysis

	C	H	P	Cl
Found	C = 12.02	H = 2.50	P = 15.26	Cl = 70.42
Calculated	C = 11.88	H = 2.48	P = 15.34	Cl = 70.30

Subsequent batches were prepared by the chlorination of $EtPCl_2$ in methylene chloride.

The preparation of $Pe_4N^+EtPCl_5^-$.

$EtPCl_4$ (0.6753 g, 3.0 mmoles) and tetra-n-pentylammonium chloride (1.0492 g, 3.0 mmoles) were each separately dissolved in a small amount of methylene chloride. The chloride solution was added to the phosphorane solution with stirring, and a yellow solution was formed. The solvent was removed in vacuo to isolate a yellow sticky solid.

Analysis

Found	C = 50.24	H = 10.47	N = 3.53	P = 5.35	Cl = 32.50
Calculated	C = 49.30	H = 9.15	N = 2.61	P = 5.79	Cl = 33.15

The attempted preparation of $Et_4N^+EtPCl_5^-$.

A 1:1 reaction of $EtPCl_4$ and Et_4NCl in CH_2Cl_2 gave a white product, which was found to be a mixture of the starting materials as its ^{31}P n.m.r. spectrum showed a broad resonance at -127.5 ± 3 p.p.m., ascribed to $EtPCl_4$.

The preparation of $EtPCl_4py$.

Pyridine (1 ml, 12.3 mmoles) was added dropwise to a solution of $EtPCl_4$ (2.5 g, 12.4 mmoles) in methylene chloride with constant stirring. A white precipitate was immediately formed. It was then filtered off and washed with $^{30}/40$ Pet. ether to isolate a white solid.

Analysis

Found	C = 30.97	H = 3.84	N = 6.61	P = 10.84	Cl = 49.40
Calculated	C = 29.87	H = 3.56	N = 4.98	P = 11.03	Cl = 50.53

The preparation of $EtPCl_3^+ICl_4^-$.

$EtPCl_4$ (0.8734 g, 4.0 mmoles) was dissolved in a small amount of methylene chloride. ICl_3 (1.013 g, 4.0 mmoles) separately dissolved in the same solvent was added with stirring, and a yellow precipitate was immediately formed. The solution was filtered, washed with $^{30}/40$ Pet. ether and dried at the pump to yield a yellow solid.

Analysis

Found C = 6.07 H = 1.52 P = 7.06 I = 30.80 Cl = 55.70

Calculated C = 5.51 H = 1.15 P = 7.12 I = 29.16 Cl = 57.06

The preparation of $\mathrm{EtPCl_3^+SbCl_6^-}$.

Antimony (V) chloride (0.85 mls, 7.0 mmoles) was dripped into a solution of $\mathrm{EtPCl_4}$ (1.3278 g, 7.0 mmoles) in methylene chloride. A white precipitate was immediately formed. The precipitate was filtered off, washed with methylene chloride and low boiling petroleum ether to isolate a white solid.

Analysis

Found C = 4.31 H = 0.64 P = 6.10 Cl = 61.54 Sb = 24.00

Calculated C = 4.78 H = 1.00 P = 6.18 Cl = 63.71 Sb = 24.33

The preparation of $\mathrm{EtPCl_3bipy^+Cl^-}$.

$\mathrm{EtPCl_4}$ (0.8387 g, 4.0 mmoles) and bipy (0.6495 g, 4.0 mmoles) were each separately dissolved in the minimum amount of methylene chloride. The bipy solution was added to the $\mathrm{EtPCl_4}$ solution with stirring. The yellow solution which formed was placed in a fridge. A white precipitate formed. The solution was then filtered and the product washed with $^{30}/40$ Pet. ether to yield an off-white solid.

Analysis

Found C = 39.69 H = 3.60 N = 7.12 P = 8.26 Cl = 38.40

Calculated C = 40.22 H = 3.63 N = 7.82 P = 8.66 Cl = 39.66

The preparation of $\mathrm{EtPCl_3phen^+Cl^-}$

1,10-phenanthroline (1.2416 g, 7.0 mmoles) was added to a solution of $\mathrm{EtPCl_4}$ (1.432 g, 7.0 mmoles) in methylene chloride with stirring. A white precipitate was formed after a few minutes. The solution was left to stir for 15 minutes then filtered and the product washed with $^{30}/40$ Pet. ether to isolate a white solid.

Analysis

Found C = 45.28 H = 3.78 N = 9.10 P = 8.42 Cl = 36.84

Calculated C = 43.98 H = 3.40 N = 7.33 P = 8.11 Cl = 37.17

The preparation of $EtPCl_3bipy^+SbCl_6^-$.

$EtPCl_3^+SbCl_6^-$ (1.90 g, 4.0 mmoles) was dissolved in methylene chloride (20 mls). Bipy (0.5924 g, 4.0 mmoles) was then added with stirring. A yellow solution was observed, followed by the formation of a white precipitate. The solution was left to stir for 10 minutes thenfiltered and washed with low boiling petroleum ether to isolate a white solid.

Analysis

Found C = 21.04 H = 1.24 N = 5.30 P = 4.60 Cl = 47.30

Calculated C = 21.90 H = 1.98 N = 4.26 P = 4.71 Cl = 48.59

The preparation of $EtPCl_3phen^+SbCl_6^-$

$EtPCl_3^+SbCl_6^-$ (0.7705 g, 1.0 mmoles) was dissolved in methylene chloride (10 mls). 1,10-phenanthroline (0.2813 g, 1.0 mmoles) was added to the above solution with stirring. A white precipitate was immediately formed. The solution was stirred for 20 minutes, filtered, and washed with methylene chloride and $^{30}/40$ Pet. ether to isolate a white solid.

Analysis

Found C = 23.73 H = 2.09 N = 3.16 P = red Cl = 45.83

Calculated C = 24.65 H = 1.91 N = 4.11 P = 4.55 Cl = 46.88

The preparation of Et_2PCl_3.

$(Et_2PS)_2$ (5 gm, 20.7 mmoles) was dissolved in 300 mls of CCl_4. This was refluxed for 1 hour, while introducing dry chlorine. The reflux was continued for another 3 hours until a precipitate formed. This was filtered off and washed with $^{30}/40$ Pet. ether to isolate a pale brown solid.

Analysis

Found C = 24.83 H = 5.24 P = 15.74 Cl = 54.06

Calculated C = 24.55 H = 5.11 P = 15.86 Cl = 54.48

The preparation of $Et_2PCl_2^+ICl_4^-$.

Et_2PCl_3 (2.433 g, 12.4 mmoles) was dissolved in a small amount of methylene chloride. ICl_3 (2.9047 g, 12.4 mmoles) was added to the Et_2PCl_3 solution with stirring. A brown solution was formed. The solvent was then removed in vacuo to isolate a dark brown solid.

Analysis

Found C = 11.48 H = 3.27 P = 6.90 Cl = 48.23 I = 32.30

Calculated C = 11.19 H = 2.33 P = 7.23 Cl = 49.65 I = 29.60

The preparation of $Et_2PCl_2^+SbCl_6^-$.

Et_2PCl_3 (2.0275 g, 10.3 mmoles) was dissolved in the minimum amount of methylene chloride. Antimony (V) chloride (1.3 mls, 10.3 mmoles) was dripped into the above solution with constant stirring. A brown precipitate was immediately formed. The solution was filtered and the product washed with $^{30}/40$ Pet. ether to yield a dark brown solid.

Analysis

Found C = 9.45 H = 2.40 P = 6.38 Cl = 58.00 Sb = 25.20

Calculated C = 9.70 H = 2.02 P = 6.26 Cl = 57.37 Sb = 24.65

The preparation of Et_3PCl_2.

A solution of Et_3P in methylene chloride was saturated with dry gaseous chlorine. After the removal of excess solvent in vacuo, the solid was filtered off in an inert atmosphere box, and washed with $^{30}/40$ Pet. ether to isolate a white solid.

Analysis

Found C = 38.63 H = 8.10 P = 16.34 Cl = 37.80

Calculated C = 38.10 H = 9.94 P = 16.40 Cl = 37.56

The preparation of $Et_3PCl^+ICl_4^-$.

Et_3PCl_2 (0.8794 g, 4.6 mmoles) was dissolved in 10 mls of methylene chloride. ICl_3 (1.0803 g, 4.6 mmoles) was added to the above solution with stirring. A yellow solution formed, the solvent was removed in vacuo leaving a yellow liquid. Its ^{31}P n.m.r. spectrum showed a single peak at -111.3 p.p.m. No analysis was performed on this liquid. The quantity of liquid was insufficient for n.q.r. studies at 77 K.

The preparation of $Et_3PCl^+SbCl_6^-$.

Et_3PCl_2 (1.54 g, 8.0 mmoles) was dissolved in methylene chloride (15 mls), An equivalent amount of antimony (V) chloride (1 ml, 8.0 mmoles) was added dropwise with stirring. A white precipitate was immediately formed. This was filtered off and washed with $^{30}/40$ Pet. ether to isolate a white solid.

Analysis

Found C = 14.70 H = 3.94 P = 6.58 Cl = 51.40 Sb = 25.08

Calculated C = 14.74 H = 3.07 P = 6.35 Cl = 50.87 Sb = 24.97

CHAPTER FIVE

The acceptor properties of catPBr$_3$, cat$_2$PBr and PhPBr$_4$.

1. CatPBr$_3$.

(a) Introduction.

This compound was first prepared by Gross, Gloede and co-workers[99,100]. It has been widely used in the preparation of acidic bromides[101]. Its acceptor properties had not been investigated previously, and this was undertaken in the present work. The compound can be considered as an example of bi-substituted PBr$_5$, and the results could then be compared with those for its chloro-analogue catPCl$_3$ [15]. It was found to be soluble in most of the common solvents, thus allowing the determination of its ^{31}P n.m.r. chemical shifts. The ^{31}P n.m.r. results indicated a molecular structure in chloroform (189.0 p.p.m.) and CS$_2$ (188.6 p.p.m.) as well as methylene chloride (186.9 p.p.m.). Its solid state spectrum gave a broad signal at 190.1 ± 1 p.p.m., in excellent agreement with the chemical shift in CHCl$_3$ solution recorded by Fluck[102] and with the solution chemical shifts mentioned above.

(b) Acceptor properties towards the bromide ion.

When a small amount of tetra-n-butylammonium bromide was added to a solution of catPBr$_3$ in methylene chloride, the ^{31}P n.m.r. spectrum showed two peaks at -196.7 and 195.1 p.p.m. Addition of more bromide resulted in the appearance of a single peak at -196.7 p.p.m. This peak can easily be assigned to catPBr [102], suggesting that catPBr$_3$ decomposes in the presence of a bromide ion to catPBr with the release of bromine and formation of the tribromide ion, equation 1. This behaviour is analogous to that shown by PhPBr$_4$ (this work) and PBr$_5$ towards the bromide ion.

$$\text{catPBr}_3 + \text{Br}^- \longrightarrow \text{catPBr} + \text{Br}_3^- \qquad (1)$$

(c) Acceptor properties towards pyridine.

When a 1:1:2 molar ratio of catechylphosphorus bromide, bromine and pyridine was mixed in methylene chloride, a bright orange precipitate was immediately formed and no solution peak could be discerned. The solid state spectrum showed no signal, but when a small amount of the solid was dissolved in nitrobenzene, a single sharp peak was observed at 217.6 p.p.m. Although two isomeric forms are possible for the cation $[\text{catPBr}_2\text{py}_2]^+$, the observation of one resonance only suggests that either a single isomer is formed preferentially, or that there is a rapid exchange between the possible species. Its Raman spectrum showed a frequency at 168 cm^{-1} which could readily be assigned to the Br_3^- ion[98]. Analysis indicated that the compound should be formulated as $[\text{catPBr}_2\text{py}_2]_2^+\ \text{Br}^-,\ \text{Br}_3^-$.

(d) Acceptor properties towards 2,2'-bipyridine.

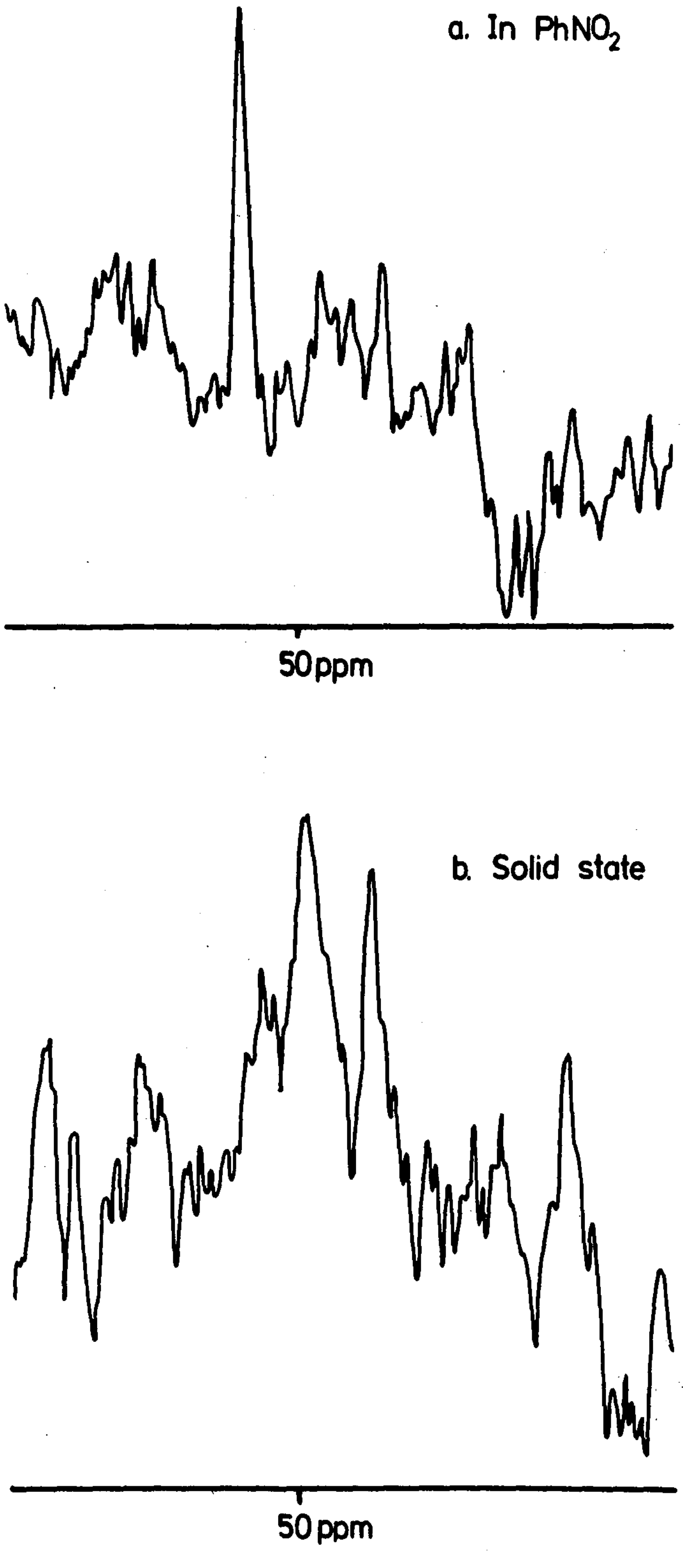
A solution in methylene chloride containing a 1:1:1 molar ratio of bipyridine, bromine and catechylphosphorus bromide produced an orange precipitate in addition to a single peak at 198.2 p.p.m., assigned to the complex cation $[\text{catPBr}_2\text{bipy}]^+$. When the same solution was monitored after 1 hour, no ^{31}P resonances could be detected, indicating that complete precipitation had occurred.

The solid state spectrum of the product $[\text{catPBr}_2\text{bipy}^+]_2\text{Br}^-\text{Br}_3^-$ (as indicated by analysis) consisted of a broad peak at 198.2 ± 3 p.p.m. which agreed well with the solution shift mentioned above. The formation of Br^-, Br_3^- in the two above reactions implies the presence also of a phosphorus (III) compound, which presumably remains in solution, equation 2.

$$\left.\begin{array}{lr} 2\ \text{catPBr} + 3\text{Br}_2 + 4\text{py} \longrightarrow & \text{catPBr}_2\text{py}_2 \\ 2\ \text{catPBr} + 3\text{Br}_2 + 2\text{bipy} \longrightarrow & \text{bipy} \end{array}\right]_2^+ \text{Br}^-,\ \text{Br}_3^- \tag{2}$$

The reason for the non-observation of a signal from catPBr in solution is not clear, however. The Raman spectrum of the solid below 650 cm^{-1} showed three frequencies at 114, 173 (ν_1) and 224 cm^{-1}, with the frequency at 173 (ν_1) cm^{-1} being assigned to Br_3^- [98].

Fig. 5.1 ^{11}B nmr spectra of CatPBr$_2$ bipy$^+$ BBr$_4^-$



$\mathrm{CatPBr_2bipy^+BBr_4^-}$ was prepared and its ^{31}P n.m.r. solid state spectrum consisted of a broad peak at 193.5 ± 4 p.p.m. Its i.r. spectrum (650 - 250 $\mathrm{cm^{-1}}$) was very similar to the i.r. recorded for $\mathrm{[catPBr_2bipy^+]_2Br^-, Br_3^-}$, except for a broad band at 590 $\mathrm{cm^{-1}}$ which was easily assigned to the $\mathrm{BBr_4^-}$ ion, and is in good agreement with the published i.r. data[115,116]. Its ^{31}P n.m.r. spectrum in nitrobenzene showed a single resonance at 195.1 ± 2 p.p.m.

The ^{11}B solid state and solution spectra of $\mathrm{catPBr_2bipy^+BBr_4^-}$ are shown in Fig. 5.1. The chemical shift of 44.5 p.p.m. in nitrobenzene solution is in good agreement with literature values of 42.4 [104] and 42.6 p.p.m.[105], while the solid peak at 53.5 p.p.m. also agrees well with the value of 52.5 p.p.m. recorded for $\mathrm{(C_2H_5)_4N^+BBr_4^-}$ by Dillon et al[106].

Its Raman spectrum showed four frequencies at 169, 187, 216, and 244 $\mathrm{cm^{-1}}$ (ν_1). The frequency at 244 $\mathrm{cm^{-1}}$ is in good agreement with the value of 243 $\mathrm{cm^{-1}}$ reported by Claassen for $\mathrm{BBr_4^-}$ [103].

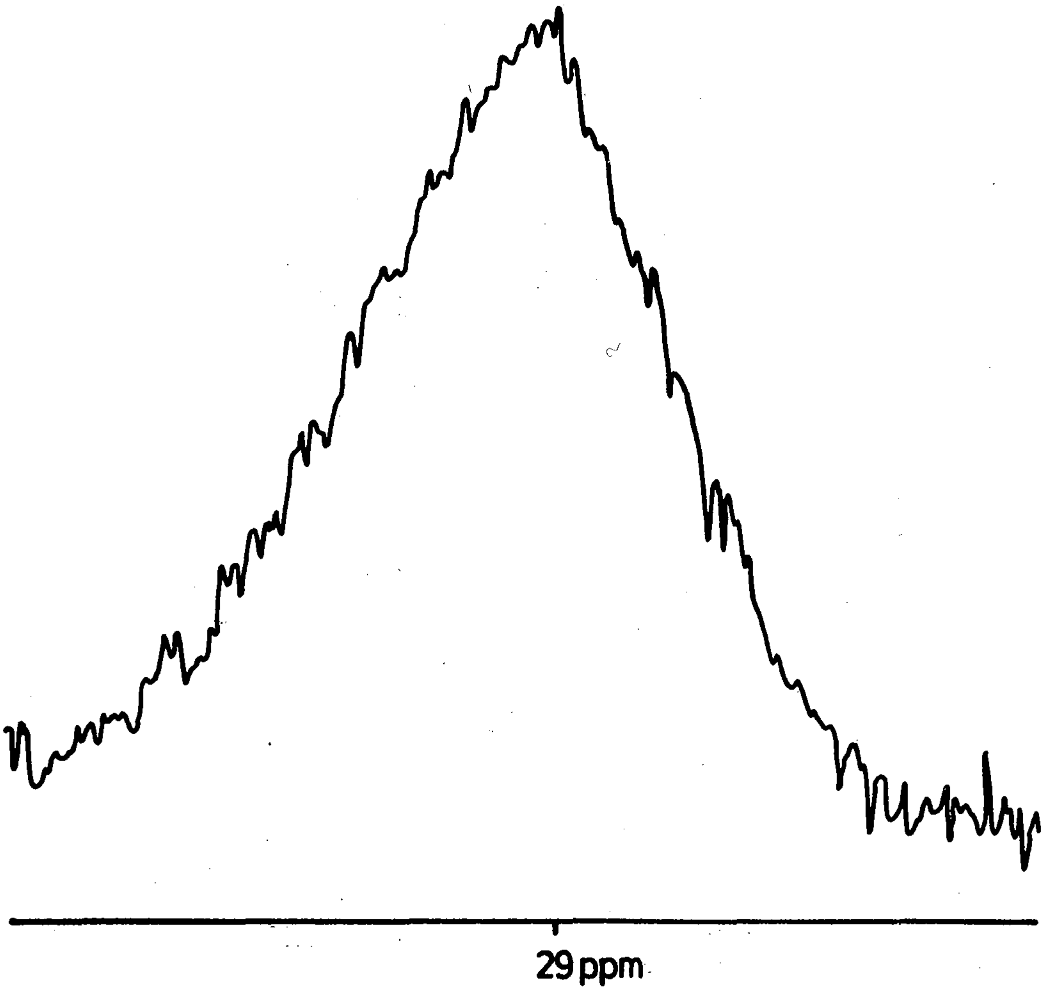
(e) Acceptor properties towards 1,10-phenanthroline.

When an equimolar amount of phenanthroline was added to a solution of $\mathrm{catPBr_3}$ in methylene chloride, a yellow precipitate was immediately formed and no solution spectrum could be observed.

The solid state n.m.r. spectrum of the product showed no signal, but its Raman spectrum revealed four bands below 650 $\mathrm{cm^{-1}}$ at 168, 256, 286 and 490 $\mathrm{cm^{-1}}$. The band at 168 $\mathrm{cm^{-1}}$ agrees well with previous Raman data for symmetrical tribromide ions[98], although different frequencies have been reported for unsymmetrical tribromide ions[107]. The band at 490 $\mathrm{cm^{-1}}$ is ascribed to a P-Br frequency[108-110].

The i.r. spectrum showed a number of bands in the region 650 - 250 $\mathrm{cm^{-1}}$, the band at 412 $\mathrm{cm^{-1}}$ being assigned to a P-Br stretching vibration. Analysis has shown that the product formed is $\mathrm{catPBr_2phen^+Br_3^-}$. This behaviour has been encountered before in compounds such as $\mathrm{PBr_7}$ which is known to have the

Fig. 5.2 Solid state spectrum of cat_2 PBr



structure $PBr_4^+Br_3^-$ [111]. The formation of $catPBr_2phen^+Br_3^-$ is rather surprising, since this implies the formation of catPBr which should have been detected in solution, equation 3.

$$2catPBr_3 + phen \longrightarrow catPBr_2phen^+Br_3^- + catPBr \qquad (3)$$

A possible explanation could be that the solid was occupying most of the coil region of the probe, so that no solution spectrum could be obtained.

2. Cat_2PBr.

(a) Introduction.

Biscatechylphosphorus monobromide has not been reported in the literature. It was prepared in this work by the reaction of liquid bromine with cat_2PCl in an inert solvent. This compound was found to be very readily soluble in most of the common solvents and solution shifts of 27.5 p.p.m. in methylene chloride and 29.1 p.p.m. in nitrobenzene have been determined.

Its solid state spectrum showed a broad resonance at 29.1 p.p.m. (Fig. 5.2) which agrees well with the solution data. Its i.r. spectrum showed a sharp band at 420 cm^{-1} which may be assigned to the P-Br stretching vibration[79]. This data supports the assertion that cat_2PBr is probably molecular in the solid state, like cat_2PCl [102].

(b) Acceptor properties towards the bromide ion.

A solution of cat_2PBr in methylene chloride gave a single peak at 27.5 p.p.m., but when tetra-n-butylammonium bromide was added, a slight upfield shift to 29.1 p.p.m. was observed. This shift is close to that of the starting material, and a much higher shift would be expected for the $cat_2PBr_2^-$ anion which is the most probable product if reaction occurs. Although anionic species of the type $cat_2PCl_2^-$ [15] and $cat_2PR_1R_2^-$ are known (where R_1 = organic group, R_2 = organic group or H)[112], it is thus unlikely that $cat_2PBr_2^-$ is formed under these conditions.

(c) Acceptor properties towards the chloride ion.

Addition of tetra-n-pentylammonium chloride to a solution of cat_2PBr in nitrobenzene caused the single peak to move upfield in the ^{31}P n.m.r. spectrum. A limiting shift was established at 69.5 p.p.m., ascribed to the anion cat_2PBrCl^-. A white solid isolated from equimolar amounts of tetra-n-pentylammonium chloride and biscatechyl phosphorus monobromide analysed as $(C_5H_{11})_4N^+cat_2PBrCl^-$. Its solid state spectrum showed no detectable signal but its i.r. spectrum revealed a number of new bands absent in the spectrum of the parent compound. The intensities of some absorption bands present in the cat_2PBr i.r. spectrum were also considerably reduced, Table 5.1.

Table 5.1

Infrared frequencies (650 - 400 cm^{-1}) of cat_2PBr and related compounds

cat_2PBr	636s, 590w, 578s, 552Br, 538w, 504Br, 470w, 420s
cat_2PBrCl^-	624s, 584m, 572s, 560w, 530s, 500s, 470Br, 430m, 420w
$cat_2PCl_2^-$	640s, 628w, 590m, 578m, 562w, 550w, 540m, 530w, 500s, 470w, 460s, 430s

The frequencies for $cat_2PCl_2^-$ were taken from the spectrum recorded by Reeve.

(d) Acceptor properties towards pyridine.

When pyridine was added to a dilute solution of cat_2PBr in methylene chloride, and its solution spectrum run, a single ^{31}P resonance was observed at 85.5 p.p.m. After a lapse of time, a white precipitate formed, and when the same solution was monitored, no solution peak could be discerned, indicating that complete reaction had occurred. Although two isomers are possible for cat_2PBrpy, the observation of a single resonance implies either that one isomer is formed preferentially or else that there is rapid exchange. The isolated product gave no solid state n.m.r. spectrum, but its i.r. showed a number of new bands below 650 cm^{-1}, which were not present in the cat_2PBr spectrum,

Table 5.2. Analysis confirmed that it was a 1:1 adduct of cat_2PBr and pyridine, formulated as the molecular species.

(e) Acceptor properties towards bipy and phen.

When either bipy or phen was added to a solution of cat_2PBr in methylene chloride, a yellow precipitate was formed, instantly in the case of bipy and therefore no solution peak was observed. In the case of phen, however, two solution peaks were apparent at 29.1 and 90.4 p.p.m. in addition to a small amount of yellow precipitate. These peaks may be assigned to cat_2PBr (unreacted) and the product $cat_2Pphen^+Br^-$. When more phen was added, a single peak was observed at 90.4 p.p.m. indicating that a complete reaction had occurred. When the same sample was run after 1 hour, no signal could be detected and the level of the precipitate had increased in the n.m.r. tube, showing that precipitation was complete. The shift for the cationic species is in good agreement with that reported previously for $cat_2Pphen^+SbCl_6^-$ [15]. The solid state spectra of the complexes isolated were run, but only the bipy complex gave a detectable solid state signal at 85.5 ± 2 p.p.m., and no resonance could be discerned for the phen complex. The i.r. spectra of cat_2PBr and of its complexes have been recorded and the observed frequencies below 650 cm^{-1} are summarised, in Table 5.2. The isolated complexes analysed as $[cat_2Pbipy^+]_2Br^-Br_3^-$ and $[cat_2Pphen^+]_2Br^-Br_3^-$. The Raman spectrum of $[cat_2Pphen]_2^+Br^-Br_3^-$ was recorded below 650 cm^{-1} and a band was observed at 167 cm^{-1}, in good agreement with the reported frequency for Br_3^- [98].

Thus both $catPBr_3$ and cat_2PBr show acceptor properties towards monodentate and bidentate pyridines but not to Br^- ions, in contrast with $catPCl_3$ and cat_2PCl which both reacted with Cl^- ions. Nevertheless cat_2PBr rather surprisingly did form an anionic complex with the chloride ion.

Table 5.2

Infrared frequencies (650 - 250 cm^{-1}) of cat_2PBr and related species in the solid

cat_2PBr	636s, 590w, 578s, 552Br, 538w, 504Br, 470w, 420s, 400w, 370m, 336w, 330w, 306w, 296m
cat_2PBrpy	650s, 620w, 610w, 586w, 572m, 546s, 510w, 504m, 460m, 426s, 366Br, 320m, 306w
$[cat_2Pbipy]_2^+Br^-, Br_3^-$	640s, 616s, 564s, 542s, 526m, 480s, 460w, 440m, 432s, 416w, 400m, 350m, 320w, 300w, 290w, 284w
$[cat_2Pphen]_2^+Br^-, Br_3^-$	646s, 626s, 600s, 572m, 564m, 510s, 500s, 472s, 450s, 438s, 400w, 390w, 350m, 330w, 300w, 280w

3. The acceptor properties of $PhPBr_4$.

(a) Introduction.

Phenyltetrabromophosphorane $PhPBr_4$, was first prepared by Michaelis;[113] chemical shifts of -23.0 p.p.m. in oleum and 4.0 p.p.m. in the solid state have been reported[17,30].

In the present work an attempt was made to investigate its acceptor properties towards Lewis bases. It was prepared by brominating $PhPBr_2$ in methylene chloride. An orange precipitate was formed. This was filtered off and washed with $^{30}/40$ Pet. ether to produce an orange solid.

The ^{31}P n.m.r. solid state spectrum showed a broad resonance at -14.6 p.p.m., with two shoulders at -22.7 and -1.6 p.p.m. No solution shifts could be recorded as this solid was found to be insoluble in all the common solvents available.

(b) Reaction with the bromide ion.

When a tetra-n-alkylammonium bromide was added to a slurry of $PhPBr_4$ in methylene chloride or nitrobenzene, a red solution was observed. Its ^{31}P n.m.r.

spectrum showed a single peak at -153.1 p.p.m., which can easily be assigned to $PhPBr_2$ [36]. This suggests that $PhPBr_4$ reacts with Br^- to give $PhPBr_2$ and the tribromide ion, similar to the behaviour of PBr_5, equation 4.

$$PhPBr_4 + Et_4NBr \longrightarrow PhPBr_2 + Et_4NBr_3 \qquad (4)$$

(c) Reaction with mono- and bidentate pyridines.

The acceptor properties of $PhPBr_4$ towards mono- and bidentate pyridines were investigated without success. A solution of $PhPBr_4$ in neat pyridine gave a single peak at -146.0 p.p.m., which was slightly to higher field of the literature value for $PhPBr_2$. In methylene chloride, a single resonance was seen at -148.4 p.p.m. This might be due to weak complex formation between $PhPBr_2$ and pyridine, similar to that between PCl_3 and pyridine[17]. No bromine colour was observed, presumably because the pyridine-bromine complex is formed, equation 5.

$$PhPBr_4 + 2py \longrightarrow PhPBr_2py + Br_2py \qquad (5)$$

When 2,2'-bipyridine or 1,10-phenanthroline was added to a slurry of $PhPBr_4$ in either methylene chloride or nitrobenzene, no ^{31}P n.m.r. signal was observed, but instead a yellow precipitate formed, which was isolated from methylene chloride in both cases. Analysis and i.r. showed that the product in both instances was $PhPBr_4$, indicating that no coordination was occurring between $PhPBr_4$ and the bidentate ligands used. It can thus be concluded that $PhPBr_4$ has no acceptor properties towards these bases under the experimental conditions, in contrast with $PhPCl_4$ which forms stable six-coordinate complexes[14].

4. The acceptor properties of $PhPBr_3^+BBr_4^-$.

(a) Introduction.

$PhPBr_3^+BBr_4^-$ was isolated from stoichiometric amounts of $PhPBr_4$ and BBr_3 in methylene chloride as a white solid. Its ^{31}P n.m.r. spectrum in nitrobenzene gave a single peak at -24.2 p.p.m., whereas the solid state spectrum showed a broad resonance at -21.1 p.p.m. in good agreement with the solution chemical shift. The presence of the BBr_4^- anion provides an alternative nucleus for n.m.r. investigation. The ^{11}B solution spectrum of this compound in nitrobenzene consisted of a single peak at 38.9 p.p.m., while the solid state spectrum showed a broad peak with a maximum at 38.9 p.p.m., in excellent agreement with the solution value. Its i.r. spectrum was similar to that of $PhPBr_4$ except for a broad band at 584 cm^{-1}, ascribed to the BBr_4^- ion[115,116].

(b) Reaction with bidentate ligands.

Addition of 2,2'-bipyridine or 1,10-phenanthroline to a solution of $PhPBr_3^+BBr_4^-$ in nitrobenzene resulted in the appearance of a yellow precipitate and no detectable solution peak.

$PhPBr_3bipy^+BBr_4^-$ was isolated as a yellow solid from equimolar amounts of $PhPBr_3^+BBr_4^-$ and bipy in methylene chloride. It gave a sharp single peak in the ^{31}P n.m.r. solid state spectrum at 1.6 p.p.m. which is probably due to an impurity in the solid rather than a genuine resonance of the complex, as this compound is expected to give a signal at a much higher field. No solid state ^{11}B spectrum could be obtained for the compound, but it gave a single ^{11}B peak in $PhNO_2$ solution at 42.3 p.p.m., due to the BBr_4^- ion[104,105]. Its i.r. spectrum was very similar to the one recorded for $PhPBr_4$. $PhPBr_3phen^+BBr_4^-$ was isolated as a yellow solid. Its solid state ^{31}P n.m.r. spectrum showed no signal, but its ^{11}B n.m.r. consisted of a broad resonance at 37.7 p.p.m., which was slightly lower than the value recorded for the starting material as well as the values for some BBr_4^- ions reported by Dillon et al[106]. The difference in chemical shift with counter-ion is not surprising, being also observed in ^{31}P n.m.r.[51,54,114]. No solution shift was recorded as the compound was insoluble in all of the common solvents attempted. Its i.r. spectrum was again very similar to that of $PhPBr_4$.

In view of the similarity between these i.r. spectra, the bipy and phen complexes of BBr_3 were isolated and their ^{11}B n.m.r. spectra recorded, in order to discount the possibility that the products isolated from $PhPBr_3^+BBr_4^-$

and bipy (or phen) were mixtures of $PhPBr_4$ and BBr_3bipy (or BBr_3phen). The BBr_3bipy complex was isolated as a yellow solid from stoichiometric amounts of BBr_3 and bipy in CH_2Cl_2. Its ^{11}B n.m.r. spectrum in nitrobenzene gave a single peak at 20.3 p.p.m., ascribed to BBr_2bipy^+. BBr_3phen was isolated as a bright yellow solid from CH_2Cl_2. Its ^{11}B solution spectrum in $PhNO_2$ gave a single resonance at 20.3 p.p.m., indicating that the complex is $BBr_2phen^+Br^-$. This formulation has also been confirmed by analysis. The ^{11}B solid state spectra of these complexes consisted of very broad asymetric signals, and it was not possible to assign specific shifts to the adducts. These spectra (solution and solid) were in marked contrast with the spectrum recorded for $PhPBr_3bipy^+BBr_4^-$ in $PhNO_2$ which showed a single resonance at 42.3 p.p.m. due to BBr_4^- [104,105]. $PhPBr_3phen^+BBr_4^-$ was insoluble in all the common solvents attempted and no solution ^{11}B n.m.r. spectrum could be recorded, but its solid state spectrum consisted of a broad resonance at 37.7 p.p.m., probably due to the anion BBr_4^-. It can thus be concluded that the cations are different in the $PhPBr_4$ and BBr_3 complexes with bipy and (presumably) phen, since otherwise either a single ^{11}B peak would have been observed in the spectrum of the $PhPBr_4$ adduct for the BBr_2bipy^+ cation, or two peaks for BBr_2bipy^+ and BBr_4^-.

The BCl_3.bipy complex was prepared by bubbling BCl_3 into a suspension of bipy in CH_2Cl_2 until all the bipy had dissolved. A small amount of the solution mixture was placed in an n.m.r. tube and its ^{11}B n.m.r. spectrum recorded. Two equally intense signals were observed at 10.3 and 11.2 p.p.m., assigned to the BCl_2bipy^+ cation and the BCl_4^- anion respectively. The BCl_4^- shift is in good agreement with literature values[117-19].

An off-white solid was isolated by removing the solvent in vacuo. Its ^{11}B solid state n.m.r. spectrum gave a broad peak at 32.5 p.p.m., while its nitrobenzene solution spectrum consisted of a single peak at 11.0 p.p.m. This suggests that the second BCl_3 molecule in the complex $BCl_2bipy^+BCl_4^-$ is lost during pumping to give $BCl_2bipy^+Cl^-$, as opposed to the 2:1 complex initially detected in solution. The BCl_3phen complex was isolated from BCl_3 and phen as a white solid from CH_2Cl_2. Its solid state spectrum consisted of a broad resonance at 29.0 p.p.m., whereas its nitrobenzene solution showed a single resonance at 10.1 p.p.m., assigned to the cation BCl_2phen^+, in good agreement with the value recorded for the cation BCl_2bipy^+.

The BCl_2L' (L' = bipy, phen) cations show a marked upfield shift in their solid state spectra compared with the solution values, possibly due to enhanced shielding by the surrounding anions. Thus $PhPBr_3^+BBr_4^-$ does show acceptor properties towards bidentate pyridines, possibly because the resultant complexes are stabilised by immediate precipitation.

5. Experimental.

The preparation of $[catPBr_2py_2]_2^+Br^-,Br_3^-$.

CatPBr (0.76 g, 3.47 mmoles) was dissolved in a small amount of methylene chloride. Bromine (0.2 ml, 3.66 mmole) was added with stirring to produce a pale orange solution. Pyridine (0.56 ml, 6.98 mmoles) was then added cautiously to this solution, and an orange precipitate was instantly formed. The solution was filtered, and the product washed with $^{30}/40$ Pet. ether and dried at the pump to isolate a fine orange solid.

Analysis

Found C = 27.53 H = 2.07 N = 3.92 P = 4.21 Br = 60.96

Calculated C = 27.57 H = 2.01 N = 4.02 P = 4.45 Br = 57.36

$catPBr_2py_2^+Br^-$ requires

C = 35.77 H = 2.61 N = 5.22 P = 5.78 Br = 44.66

The preparation of $[catPBr_2bipy^+]_2Br^-.Br_3^-$.

CatPBr (1.298 g, 5.93 mmoles) was dissolved in a small quantity of methylene chloride. Bromine (0.33 ml, 6.04 mmoles) was added slowly to the above solution by means of a syringe (0.5 ml) with constant stirring. A red solution was formed. 2,2'-bipyridine (0.926 g, 5.93 mmole) was dissolved in the minimum quantity of methylene chloride and added to the above mixture with stirring. An orange precipitate was immediately formed. The solution was then filtered, and the product washed with low boiling petroleum ether and dried in vacuo to yield a bright orange solid, which analysed as $[\text{catPBr}_2\text{bipy}]_2^{+}\text{Br}^{-},\text{Br}_3^{-}$.

Analysis

Found C = 31.60 H = 1.67 N = 4.86 P = 5.10 Br = 51.80

Calculated C = 31.78 H = 1.98 N = 4.68 P = 5.13 Br = 51.18

The preparation of $\text{catPBr}_2\text{phen}^{+}\text{Br}_3^{-}$.

Bromine (0.5 ml, 9.46 mmoles)was added to a solution of catPBr (2.07 g, 9.46 mmoles)in methylene chloride with stirring. To this solution was added a solution of 1,10-phenanthroline (1.708 g, 9.46 mmole) in methylene chloride with constant stirring. A yellow precipitate was immediately formed. The solution mixture was then filtered, the product washed with methylene chloride and 30-40 Pet. ether and then dried in vacuo to isolate a fine yellow solid, which analysed as $\text{catPBr}_2\text{phen}^{+}\text{Br}_3^{-}$.

Analysis

Found C = 30.56 H = 1.89 N = 3.93 P = red Br = 54.90

Calculated C = 30.06 H = 1.67 N = 3.90 P = 4.31 Br = 55.60

The preparation of $\text{catPBr}_2\text{bipy}^{+}\text{BBr}_4^{-}$.

Bromine (0.2 ml, 3.66 mmoles)was added to catPBr (0.843 g, 3.85 mmoles) dissolved in methylene chloride. Boron tribromide (0.37 ml, 3.84 mmoles)was then added to the above solution with stirring. To this mixture was then added bipyridine (0.6 g, 3.85 mmoles) with stirring. A purple solution was formed. The solution was then left to stir for 5 minutes, after which a yellow precipitate formed. The solution mixture was filtered and the product washed with ^{30}/40 Pet. ether to yield a yellow solid.

Analysis

Found C = 24.07 H = 1.62 N = 3.46 P = 3.93 Br = 59.60

Calculated C = 24.45 H = 1.53 N = 3.57 P = 3.95 Br = 61.04

The preparation of $\mathrm{cat_2PBr}$.

An excess of bromine was added to a solution of $\mathrm{cat_2PCl}$ in methylene chloride, giving rise to a very effervescent reaction. The solution was left to stir for a few minutes. The solvent was removed in vacuo leaving a white solid in the flask.

Analysis

Found C = 44.00 H = 2.52 P = 9.50 Br = 24.48

Calculated C = 44.05 H = 2.45 P = 9.48 Br = 24.40

The preparation of $\mathrm{cat_2PBrCl^- Pe_4N^+}$.

$\mathrm{Cat_2PBr}$ (0.448 g, 1.36 mmoles)was dissolved in a small amount of methylene chloride. $\mathrm{Pe_4NCl}$ (0.463 g, 1.38 mmoles)was then added to the above solution. The solvent was removed in vacuo to isolate a white solid.

Analysis

Found C = 59.75 H = 9.14 N = 2.42 P = 4.60 Cl = 5.26 Br = 12.04

Calculated C = 58.15 H = 7.87 N = 2.12 P = 4.69 Cl = 5.38 Br = 12.10

The preparation of $\mathrm{cat_2PBr}$.pyridine.

Pyridine was dripped into an equimolar quantity of $\mathrm{cat_2PBr}$ dissolved in methylene chloride with stirring. A white precipitate was immediately formed. The solution was filtered and the product washed with $^{30}/40$ Pet. ether to isolate a white solid.

Analysis

Found C = 50.85 H = 3.05 N = 4.58 P = 7.60 Br = 19.43

Calculated C = 50.26 H = 3.20 N = 3.45 P = 7.64 Br = 19.68

The preparation of $\mathrm{[cat_2Pbipy]_2^+Br^-,Br_3^-}$.

$\mathrm{Cat_2PBr}$ (0.4767 g, 2.1 mmoles)was dissolved in a small amount of methylene chloride. Bipy (0.333 g, 2.1 mmoles) was added to this solution with stirring.

A yellow precipitate was immediately formed. The solution mixture was then filtered, and the product washed with $^{30}/40$ Pet. ether to isolate a yellow solid, which analysed approximately as $[\text{cat}_2\text{Pbipy}^+]_2\text{Br}^-, \text{Br}_3^-$.

Analysis

Found C = 45.68 H = 3.33 N = 4.83 P = 5.80 Br = 21.42

Calculated C = 46.89 H = 2.84 N = 4.98 P = 5.52 Br = 28.47

The preparation of $[\text{cat}_2\text{Pphen}]_2{}^+\text{Br}^-,\text{Br}_3^-$.

Cat_2PBr (0.324 g, 1.4 mmoles) was dissolved in the minimum quantity of methylene chloride. An equimolar amount of phenanthroline (0.257 g, 1.4 mmoles) in methylene chloride was added to the above solution with stirring. A yellow solution was formed. This solution was placed in a refrigerator overnight, leading to the formation of a yellow precipitate. The solid was then filtered off, and washed with $^{30}/40$ Pet. ether to isolate a fine yellow product, which analysed as $[\text{cat}_2\text{Pphen}^+]_2\text{Br}^-,\text{Br}_3^-$.

Analysis

Found C = 48.24 H = 3.07 N = 4.38 P = 5.33 Br = 26.00

Calculated C = 49.06 H = 2.73 N = 4.77 P = 5.28 Br = 27.26

The attempted preparation of $\text{PhPBr}_3\text{bipy}^+\text{Br}^-$.

2,2'-bipyridine (0.5 g, 3.2 mmoles) was added to a slurry of PhPBr_4 (1.42 g, 3.2 mmoles) in methylene chloride with stirring. A yellow precipitate was observed. This was filtered off and washed with $^{30}/40$ Pet. ether. The yellow solid produced analysed as PhPBr_4.

Analysis

Found C = 14.86 H = 1.01 N = P = 6.92 Br = 74.42

Calculated C = 16.84 H = 1.17 N = P = 7.25 Br = 74.74

The attempted preparation of $\text{PhPBr}_3\text{phen}^+\text{Br}^-$.

1,10-phenanthroline (0.79 g, 4.3 mmoles) was added to a slurry of PhPBr_4 (1.86 g, 4.3 mmoles) in methylene chloride with stirring. An orange precipitate was formed. The solid was filtered off and washed with $^{30}/40$ Pet. ether to isolate a pale yellow product which analysed as $PhPBr_4$.

Analysis

Found C = 15.43 H = 1.36 P = 7.03 Br = 73.80

The preparation of $PhPBr_3^+BBr_4^-$.

Boron tribromide (0.35 mls, 3.5 mmoles) was added cautiously to a slurry of $PhPBr_4$ (1.5 g, 3.5 mmoles) in methylene chloride. The solution was left to stir for 15 minutes. A white precipitate was then observed. This was filtered off and washed with low boiling Pet. ether yielding a white solid.

Analysis

Found C = 9.86 H = 1.04 P = 5.01 Br = 80.60

Calculated C = 10.60 H = 0.74 P = 4.57 Br = 82.47

The preparation of $PhPBr_3bipy^+BBr_4^-$.

$PhPBr_3^+BBr_4^-$ (2.21 g, 3.3 mmoles) was dissolved in methylene chloride. 2,2'-bipyridine (0.52 g, 3.3 mmoles) was added to the above solution with stirring. A yellow precipitate was observed. The solution was left to stir for 30 minutes, then filtered and washed with $^{30}/40$ Pet. ether to yield a yellow solid.

Analysis

Found C = 22.80 H = 1.48 N = 3.40 P = 3.80 Br = 66.84

Calculated C = 22.99 H = 1.56 N = 3.35 P = 3.71 Br = 67.06

The preparation of $PhPBr_3phen^+BBr_4^-$.

$PhPBr_3^+BBr_4^-$ (0.34 g, 0.5 mmoles) was dissolved in methylene chloride. 1,10-phenanthroline (0.1 g, 0.5 mmoles) was then added with stirring. A yellow precipitate was immediately formed. The solution was filtered and washed with $^{30}/40$ Pet. ether to isolate a yellow solid.

Analysis

Found C = 24.89 H = 1.60 N = 3.40 P = 3.64 Br = 64.89

Calculated C = 25.15 H = 1.51 N = 3.26 P = 3.61 Br = 65.19

The preparation of BBr_3bipy.

A solution of BBr_3 (1.4 mls, 14.6 mmoles) in CH_2Cl_2 was added cautiously to a solution of bipy (2.2823 g, 14.6 mmoles) in CH_2Cl_2 with stirring. A vigorous reaction occurred, and a pale yellow precipitate was formed. The solution was left to stir for a few minutes, filtered and washed with $^{30}/40$ Pet. ether to isolate a yellow solid.

Analysis

Found C = 30.21 H = 2.05 N = 6.71 Br = 59.60

Calculated C = 29.56 H = 1.97 N = 6.90 Br = 59.11

The preparation of BBr_3phen.

BBr_3 (0.6 mls, 6.6 mmoles) dissolved in a minimum of methylene chloride was added to a solution of phen (1.182 g, 6.6 mmoles) in methylene chloride. A yellow solution formed, followed by a thick yellow precipitate. The solution was filtered and washed with $^{30}/40$ Pet. ether to isolate a bright yellow solid.

Analysis

Found C = 31.30 H = 2.32 N = 6.00 Br = 54.00

Calculated C = 33.49 H = 1.86 N = 6.51 Br = 55.81

The preparation of BCl_3bipy.

BCl_3 was bubbled into a suspension of bipy in methylene chloride, until all the bipy had gone into solution. A pale brown solution formed. The solvent was removed in vacuo to isolate an off-white solid.

Analysis

Found C = 43.24 H = 2.84 N = 9.86 Cl = 39.90

Calculated C = 43.90 H = 2.93 N = 10.25 Cl = 38.97

The preparation of BCl_3phen.

BCl_3 was bubbled into a solution of phen in CH_2Cl_2. A white precipitate was formed. The solution was filtered and washed with $^{30}/40$ Pet. ether to yield a white solid.

Analysis

Found C = 47.86 H = 2.73 N = 9.34 Cl = 35.16

Calculated C = 48.44 H = 2.69 N = 9.42 Cl = 35.82

CHAPTER SIX

The acceptor properties of organophosphorus (III) halides and pseudohalides.

1. Introduction.

The derivatives of phosphorus (III) halides with all of the halogens replaced by pseudohalides such as SCN, OCN or CN have been well characterised[120]. The acceptor properties of both these compounds and some of the phosphorus trihalides themselves have been investigated recently[18-21]. Thus tetrahalogenophosphates (III) PX_4^- (X = Cl [21] or Br [19]) and cyanohalogenophosphates (III) $P(CN)_{4-n}X_n^-$ (n = 1 or 2; X = Cl, Br or I [18,20]) have been prepared, but the addition of CN^- to $P(CN)_3$ results in a reductive elimination to give $P(CN)_2^-$ and cyanogen[22]. The formation of thermally unstable trimethylamine adducts of phosphorus trihalides $PX_3.NMe_3$ (X = F, Cl or Br) has been reported[23,24]. Adducts of PCl_3 and PBr_3 with pyridine or amides, where no structural information is known[25-9], and the anion obtained from deprotonating a hydridospirophosphorane, have also been described[31]. The acceptor properties of phosphorus (III) halides and pseudohalides PX_3 (X = Cl, Br, CN or NCS) towards the halides or pseudohalides X (X = Cl, Br, I, CN, SCN or OCN) have been investigated by Platt[21], and several new anionic derivatives were obtained. The acceptor properties of phosphorus (III) compounds with an organo-group attached to phosphorus appear not to have been investigated, however.

Organophosphorus dipseudohalides such as $MeP(CN)_2$ and $PhP(CN)_2$ are well established[35,121-24]. Maier[121] reported the X-ray investigation of $MeP(CN)_2$ and showed that the crystals were monoclinic with space group P_{2_1}/n. Britton[122] has used the unit cell dimensions of Maier to calculate an intermolecular P...N distance of 3.05Å. Maier[121] also reported a ^{31}P n.m.r. shift of 81.4 p.p.m. in acetonitrile as solvent, and recorded the i.r. spectrum of the solid between 650 cm^{-1} and 4000 cm^{-1}. Jones and Coskran[123] have published a ^{31}P n.m.r. shift of 81.4 p.p.m. in acetonitrile (which agrees with that obtained by Maier[121]) and have observed two C≡N stretching vibrations in the i.r. spectrum at 2191 and 2095 cm^{-1}.

The i.r. and Raman spectra of solid $MeP(CN)_2$, together with the Raman spectra in CH_3CN solution and in the gas phase, have been recorded by Edwards et al[124], and assigned on the basis of C_s symmetry. By comparison with the spectrum of $P(CN)_3$, the band at 633 cm^{-1} in the condensed phase was assigned to an intermolecular P...N bond.

Various methods of preparation have been reported[35,121,123,125-7], usually involving rather extensive reaction times. In this work, the method of Coskran et al[123] was followed. This method of preparation has been slightly modified by the use of acetonitrile as the reaction medium, which allows the compounds to be formed quickly by simply stirring in a nitrogen atmosphere for about 30 minutes. $MeP(CN)_2$ has previously been prepared using acetonitrile as the solvent, but reflux temperatures were employed for 3 - 5 hours. $EtP(CN)_2$ which has not been reported in the literature was prepared in this work by following an analogous procedure to that described above for $MeP(CN)_2$.

The solid state ^{31}P n.m.r. spectrum of $MeP(CN)_2$ showed a broad resonance with a maximum at ca. 95 p.p.m. There was also a sharp peak superposed at 82.2 p.p.m., probably also due to $MeP(CN)_2$. The presence of the C≡N group has been confirmed by an i.r. band at 2188 cm^{-1} which is in good agreement with the value recorded by Maier[116]. Its ^{31}P n.m.r. shifts in a variety of solvents have been recorded and are tabulated below.

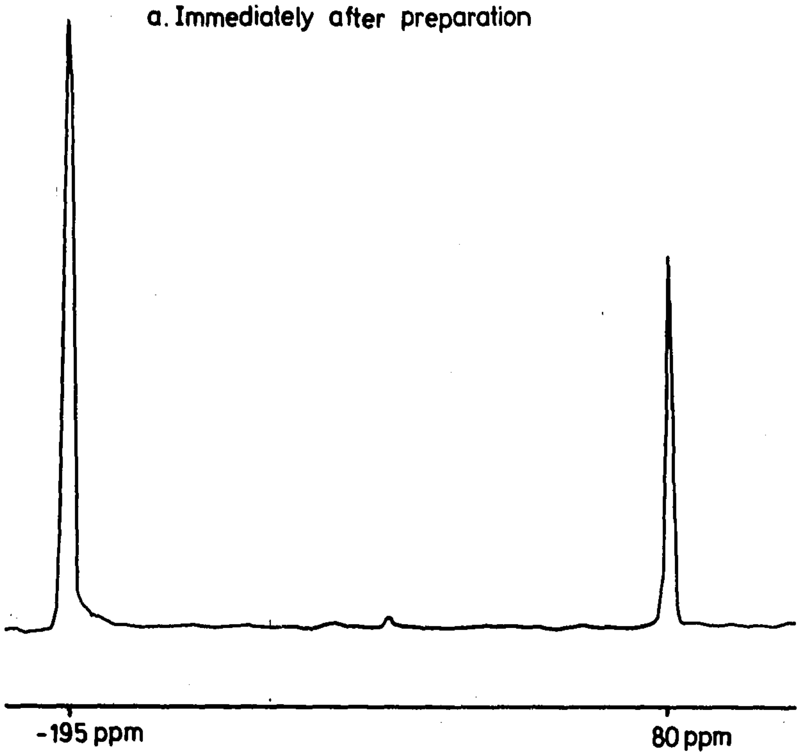
Table 6.1

Shifts of $MeP(CN)_2$ in various solvents

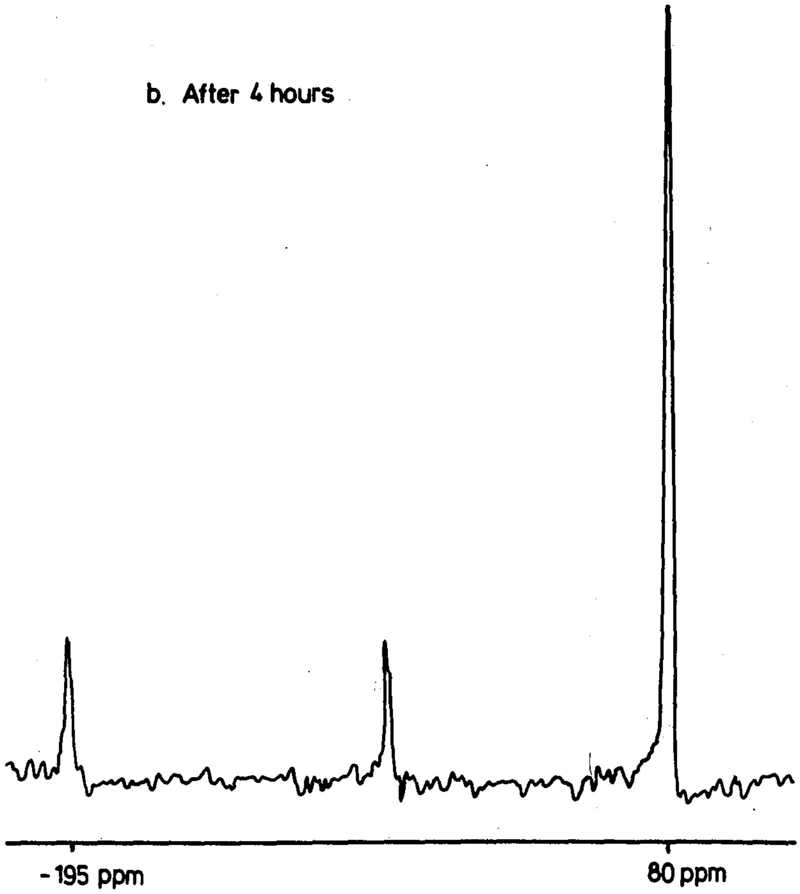
Solvent	Shift (p.p.m.)	Reference
CS_2	82.2	Present work
CH_3NO_2	82.2	Present work
CH_3CN	81.4	121, 123
CH_2Cl_2	79.1	Present work
$PhNO_2$	80.7	Present work

Fig 6.1 ^{31}P n.m.r. spectra of $MePCl_2/AgCN$ systems in CH_2Cl_2

a. Immediately after preparation



b. After 4 hours



A solution of $EtP(CN)_2$ in acetonitrile showed a single signal at 58.0 p.p.m., but its solution in methylene chloride gave a shift of 61.3 p.p.m. Two C≡N stretching vibrations were observed at 2180(s) and 2085(m) cm^{-1} in the i.r. spectrum.

$PhP(CN)_2$ has been described in the literature as a liquid[35] but the present work has shown that it is a solid, with a melting point of 305 K. Its ^{31}P n.m.r. shift of 75.6 p.p.m. in acetonitrile as solvent has been published by Coskran et al[123]. They have also observed two C≡N stretching vibrations in the i.r. spectrum at 2184(s) and 2092(m) cm^{-1}. Chemical shifts of 72.6 and 74.6 p.p.m. have been recorded in methylene chloride and acetonitrile respectively in this work. Its i.r. spectrum has been recorded and two C≡N stretching vibrations at 2246(w) and 2180(s) cm^{-1} were observed. The spectrum showed no absorption at 2092 cm^{-1} as reported by Coskran. This might be due to the fact that the $PhP(CN)_2$ isolated in this work is a solid, as opposed to the liquid described by Coskran. Kirk and Smith have reported that it forms 1:4 and 1:6 adducts with $HCONMe_2$ [35], as shown by ^1H n.m.r. It is also known to form an adduct with chlorine[34], but the product is presumably the phosphorane $PhP(CN)_2Cl_2$.

2. Intermediates in the RPX_2 - AgCN systems (R = Me, Et, Ph, t-Bu; X = Cl or Br).

(a) $MePCl_2$ - AgCN system.

The ^{31}P n.m.r. spectrum of a mixture of $MePCl_2$ and AgCN (< 2:1 AgCN:$MePCl_2$) in CH_2Cl_2 showed two peaks at -191.5 and 79.1 p.p.m., which were assigned to $MePCl_2$ [89] and $MeP(CN)_2$ [121] respectively. When the same solution was re-investigated after 4 hours, a third peak was discerned at -50.0 p.p.m., and the intensities of the other two peaks had reduced, Fig. 6.1. This peak was assigned to the intermediate MePCl(CN).

(b) $EtPCl_2$ - AgCN system.

The $EtPCl_2$ - AgCN system (< 2:1 AgCN:$EtPCl_2$) in CH_2Cl_2 showed three peaks in the ^{31}P n.m.r. spectrum at -196.7 p.p.m. ($EtPCl_2$), -61.3 p.p.m. (EtPCl(CN)), and 61.3 p.p.m. ($EtP(CN)_2$).

(c) $PhPX_2$ - AgCN system (X = Cl or Br).

An analogous behaviour to that of the $EtPCl_2$ - AgCN system was encountered here, with the ^{31}P n.m.r. spectrum showing three peaks. These peaks were readily assigned, Table 6.2.

Table 6.2

^{31}P chemical shifts for the $PhPX_2$ - AgCN systems (X = Cl or Br)

Solvent	CH_2Cl_2	CH_3CN	CH_2Cl_2
X	Br	Cl	Cl
$PhPX_2$	-153.1	-162.7	-162.7
PhPXCN	- 11.4	- 35.5	- 37.1
$PhP(CN)_2$	72.6	74.2	72.6

(d) t-$BuPCl_2$ - AgCN system.

The ^{31}P n.m.r. spectrum of this system (< 2:1 AgCN: t-$BuPCl_2$) showed a single peak at -199.8 p.p.m. due to the starting material[128] in CH_2Cl_2 or CH_3CN. When the same solution was monitored the following day, two other peaks were discerned at -30.7 and 43.6 p.p.m. These peaks were assigned to t-BuPCl(CN) and t-$BuP(CN)_2$ respectively.

3. The acceptor properties of organophosphorus (III) pseudohalides.

(a) The acceptor properties of $MeP(CN)_2$.

(i) $MeP(CN)_2$ - Cl^- system.

Addition of a tetra-n-alkylammonium chloride (Et_4NCl, Pr_4NCl or Pe_4NCl) to the $MeP(CN)_2$ solution in CH_2Cl_2 caused the single peak to move upfield. The ^{31}P n.m.r. spectrum showed a limiting shift value at 101.3 p.p.m., ascribed to the $MeP(CN)_2Cl^-$ ion. A colourless liquid was isolated from a 1:1 molar reaction of $MeP(CN)_2$ and Et_4NCl in CH_2Cl_2. Its ^{31}P n.m.r. spectrum gave a single peak at 101.6 p.p.m. This liquid was placed in a refrigerator and after three weeks colourless crystals were observed. These were filtered off. They analysed as

$MeP(CN)_2Et_4NCl$. When the crystals were redissolved in CH_2Cl_2, a single resonance was seen at 101.6 p.p.m. in the ^{31}P n.m.r. spectrum. Insufficient material was available for any solid state spectrum.

(ii) $MeP(CN)_2 - Br^-$ system.

A mobile equilibrium was established between $MeP(CN)_2$ and Pr_4NBr in CH_2Cl_2, with a limiting shift of 98.4 p.p.m. A colourless liquid was isolated from equimolar amounts of $MeP(CN)_2$ and Bu_4NBr in CH_2Cl_2. Its ^{31}P n.m.r. spectrum showed a single peak at 98.4 p.p.m. A 1:1 molar ratio of $MeP(CN)_2$ and Pr_4NBr in CH_3CN solution yielded a white solid. Its overnight solid state spectrum showed a strong broad resonance with a maximum at ca. 90.0 p.p.m., with three sharp peaks superposed at 92.0(s), 67.8(m) and 25.8(w) p.p.m. There was another sharp peak of higher intensity at -12.9 p.p.m. With this number of scans (16,666), the detection of minor impurities is possible. The most probable assignments are to MePOCl(CN) (-12.9) and $MePO(CN)_2$ (67.8 p.p.m.). The assignment of the resonance at 25.8 p.p.m. is uncertain, while the 92.0 p.p.m. peak is probably the adduct. A small amount of the product dissolved in CH_2Cl_2 gave a single peak at 98.4 p.p.m.

(iii) $MeP(CN)_2 - I^-$ system.

When Pr_4NI was added to a solution of $MeP(CN)_2$ in CH_2Cl_2, the single peak in the ^{31}P n.m.r. spectrum moved upfield until a limiting value of 90.4 p.p.m. was reached, ascribed to the $MeP(CN)_2I^-$ ion. A white solid was isolated from a 1:1 molar ratio reaction of $MeP(CN)_2$ and Pr_4NI in CH_2Cl_2. Its ^{31}P n.m.r. solid state spectrum showed a broad resonance with a maximum at ca. 88.0 p.p.m., with sharper resonances at -12.9(m), 67.8(s) and 83.6(m) p.p.m. This strongly suggests that the first two signals arise from impurities with no iodide present, since these shifts are identical to those seen in the $MeP(CN)_2 - Br^-$ system, and they are assigned to MePOCl(CN) and $MePO(CN)_2$ respectively. The peak at 83.6 p.p.m. is probably due to the adduct.

(iv) $MeP(CN)_2$ - CN^- system.

Addition of Et_4NCN to a solution of $MeP(CN)_2$ in CH_2Cl_2 resulted in the appearance of two signals at 133.8 and -62.9 p.p.m. in the ^{31}P n.m.r. spectrum. When the same sample was re-investigated after 1 hour, only a single peak was observed at -62.9 p.p.m. This suggests that in the initial stages of the reaction $MeP(CN)_3^-$ is formed, which then decomposes in a reductive elimination to give the methylcyanophosphide ion and cyanogen according to equation (1), parallel to the behaviour of $P(CN)_3$ towards $(CN)^-$ [22].

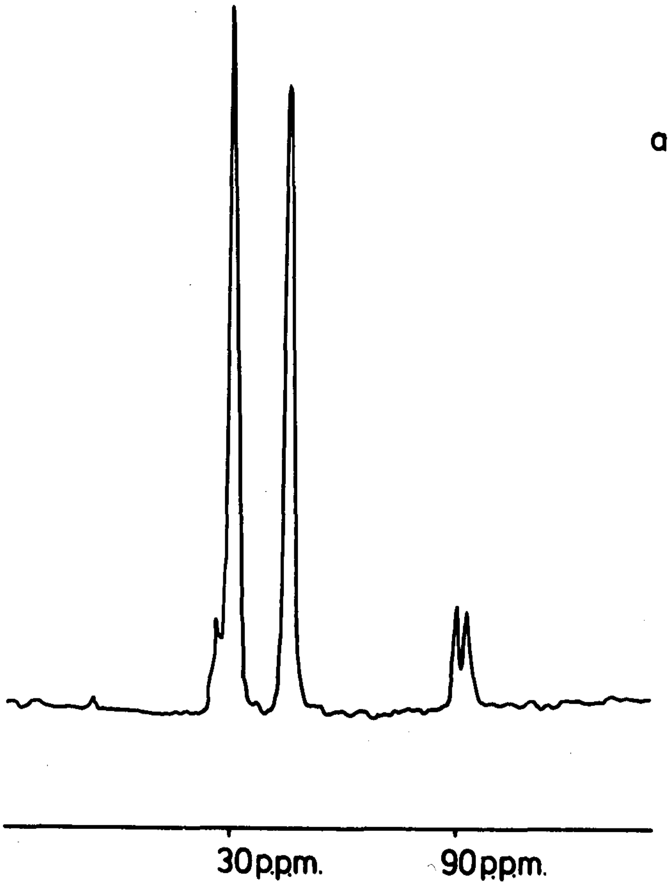
$$MeP(CN)_2 + (CN)^- \longrightarrow MeP(CN)_3^- \longrightarrow MeP(CN)^- + (CN)_2 \qquad (1)$$

Attempts to isolate a solid containing the $MeP(CN)^-$ ion were only partially successful. A dark-reddish liquid was isolated from a 1:1 molar ratio reaction of $MeP(CN)_2$ and Et_4NCN in CH_2Cl_2. Its ^{31}P n.m.r. spectrum gave a single peak at -62.9 p.p.m. This liquid turned into a sticky orange solid in the glove box. Its solid state spectrum was complex, but its solution in CH_2Cl_2 nevertheless gave a single resonance at -62.9 p.p.m. The i.r. spectrum of this solid was not recorded, as it was very sticky and would not mull. Analysis confirmed that it was the expected compound $Et_4N^+MePCN^-$.

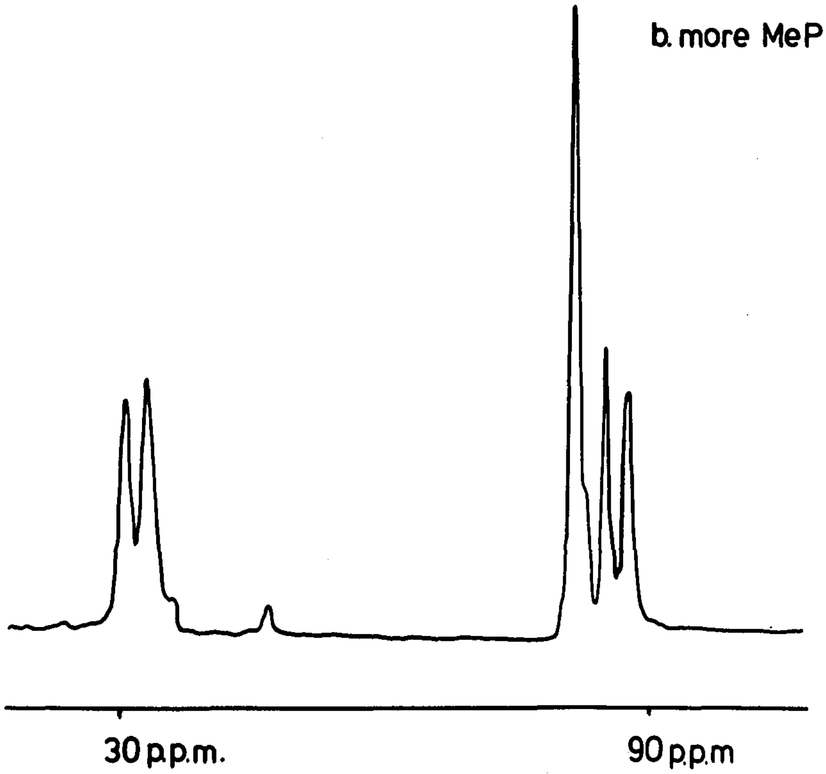
(v) $MeP(CN)_2$ - SCN^- system.

Addition of Et_4NSCN to a solution of $MeP(CN)_2$ in CH_2Cl_2 caused the single peak to move upfield in the ^{31}P n.m.r. spectrum, with a limiting shift of 92.0 p.p.m. Other minor peaks at -12.9 and 70.9 p.p.m. were observed, possibly due to $MeP(O)ClCN$ and $MeP(O)(CN)_2$. A pale yellow solid was isolated from a 1:1 molar ratio of $MeP(CN)_2$ and Et_4NSCN in CH_2Cl_2. A solution of this compound in CH_2Cl_2 gave a single peak at 87.1 p.p.m. Analysis indicated that the product was $MeP(CN)_2Et_4NSCN$. The i.r. spectrum showed a broad absorption between 1960 - 2080 cm^{-1}, indicating the presence of a thiocyanate group. The corresponding band in the uncoordinated Et_4NSCN usually appears at 2060 cm^{-1}, so compound formation has occurred. Insufficient material was available to

Fig 6.2 The ^{31}P n.m.r. spectrum of $HPO(OMe)_2/MeP(CN)_2$ system in CH_2Cl_2



a. more $HPO(OMe)_2$



b. more $MeP(CN)_2$

record the solid state ^{31}P n.m.r. spectrum.

(vi) $MeP(CN)_2$ - $HPO(OMe)_2$ reaction.

When a solution of the phosphite in CH_2Cl_2 was treated with $MeP(CN)_2$, several peaks were observed in the ^{31}P n.m.r. spectrum at -31.6 (doublet, P_A, J_{PP} 117 Hz), -11.3 (doublet, J_{PH} 707 Hz, due to $HPO(OMe)_2$)[36], and 91.1 p.p.m. (doublet, P_B, J_{PP} 117 Hz). The higher field branch of the first doublet is partially obscured by the much more intense lower field resonance of the phosphite doublet. When more $MeP(CN)_2$ was added, two doublets were observed at 30.3 (P_A, J_{PP} 136 Hz) and 92.3 p.p.m. (P_B, J_{PP} 136 Hz) with a third peak at 81.5 p.p.m. ascribed to $MeP(CN)_2$, Fig. 6.2. This suggests that the following reaction occurs, equation (2), in which the compound $Me(NC)P-PO(OMe)_2$ is the

$$MeP(CN)_2 + HPO(OMe)_2 \longrightarrow HCN + Me(NC)P_B-P_AO(OMe)_2 \qquad (2)$$

product rather than an intermediate in the reaction, since excess $MeP(CN)_2$ does not cleave the P-P bond. This is in contrast with the reaction of $P(CN)_3$ with $HPO(OMe)_2$[22].

(vii) Reaction of $MeP(CN)_2$ with $NaPO(OEt)_2$.

When the phosphite was added to a solution of $MeP(CN)_2$ in CH_3CN, the solution spectrum showed two doublets at -26.6 (P_B, J_{PP} 119 Hz) and 90.3 p.p.m. (P_B, J_{PP} 119 Hz). This implies that the following reaction occurs, equation (3).

$$MeP(CN)_2 + NaPO(OEt)_2 \longrightarrow NaCN + Me(NC)P_B-P_AO(OEt)_2 \qquad (3)$$

The magnitude of the coupling constant confirms that there is a direct P-P bond in the product.

(b) The acceptor properties of $EtP(CN)_2$.

(i) The $EtP(CN)_2$ - Cl^- system.

When Et_4NCl was added to a solution of $EtP(CN)_2$ in CH_2Cl_2, an upfield shift of the entire signal was observed. The ^{31}P n.m.r. spectrum showed a limiting shift value of 77.5 p.p.m., ascribed to the $EtP(CN)_2Cl^-$ ion. A viscous liquid was isolated from equimolar amounts of $EtP(CN)_2$ and Et_4NCl in CH_3CN, which analysed as $Et_4N^+EtP(CN)_2Cl^-$. Its ^{31}P n.m.r. spectrum showed a single peak at 78.0 p.p.m., in good agreement with the solution value.

(ii) $EtP(CN)_2$ - Br^- system.

Addition of Pr_4NBr to a solution of $EtP(CN)_2$ in CH_2Cl_2 resulted in an upfield shift of the single peak apparent in the ^{31}P n.m.r. spectrum. A limiting shift was observed of 70.9 p.p.m., ascribed to formation of the $EtP(CN)_2Br^-$ ion. This ion was isolated as its tetra-n-propylammonium salt as a white solid, which analysed as $EtP(CN)_2Br^-Pr_4N^+$. Its ^{31}P n.m.r. spectrum consisted of three resonances at -17.8(s), 54.9(m) and 67.8(s) p.p.m. The peaks at -17.8 and 54.9 p.p.m. could be due to EtPO(Cl)CN and $EtPO(CN)_2$ respectively and the 67.8 p.p.m. peak may be the adduct. When a small amount of this solid was dissolved in CH_2Cl_2, the ^{31}P n.m.r. spectrum showed a sharp single peak at 66.2 p.p.m., indicating that the product maintains the same structure in solution as in the solid state.

(iii) $EtP(CN)_2$ - I^- system.

An analogous situation to that in the $EtP(CN)_2X^-$ systems (X = Cl^- or Br^-) was encountered here. A labile equilibrium was observed to operate, with the chemical shift depending on the amount of the iodide (Pr_4NI) in the system, the limiting shift being 66.2 p.p.m. The ion was isolated as its tetra-n-propylammonium salt as an off-white solid, which analysed as $EtP(CN)_2Pr_4NI$. Its solution in CH_2Cl_2 showed a single ^{31}P n.m.r. peak at 62.9 p.p.m., whereas its solid state spectrum showed two peaks at -17.8 (small) and 62.9 p.p.m. The peak at 62.9 p.p.m. was assigned to the adduct.

(iv) $EtP(CN)_2$ - CN^- system.

Addition of a small amount of Et_4NCN to a solution of $EtP(CN)_2$ in CH_2Cl_2 caused the solution to turn golden yellow. The ^{31}P n.m.r. spectrum showed two peaks at -70.9 and 95.1 p.p.m. When the same solution was run after 2 hours only a single peak was observed at -70.9 p.p.m. in the ^{31}P n.m.r. spectrum. This suggests that in the initial stages of the reaction $EtP(CN)_3^-$ is formed

(δ 95.1 p.p.m.) which then decomposes to $EtP(CN)^-$ with the consequential release of cyanogen, equation (4). Attempts to isolate the product were only

$$EtP(CN)_2 + CN^- \longrightarrow EtP(CN)_3^- \longrightarrow EtP(CN)^- + (CN)_2 \qquad (4)$$

partially successful. A dark brown liquid isolated from a 1:1 reaction of $EtP(CN)_2$ and Et_4NCN in CH_2Cl_2 gave a rather poor analysis (Experimental section), and the second attempt produced a reddish brown liquid which analysed as $EtP(CN)Et_4NCH_2Cl_2$. The presence of CH_2Cl_2 was confirmed by i.r., which showed bands at 1270 and 740 cm^{-1}. This is probably due to the difficulty in effecting complete separation from the solvent.

(v) $EtP(CN)_2$ - SCN^- system.

Addition of Et_4NSCN to a solution of $EtP(CN)_2$ in CH_2Cl_2 caused the single peak to move upfield in the ^{31}P n.m.r. spectrum. A limiting value was established at 66.2 p.p.m., ascribed to the $EtP(CN)_2SCN^-$ ion. The adduct was not isolated.

(vi) $EtP(CN)_2$ - $HPO(OMe)_2$ reaction.

$EtP(CN)_2$ showed no tendency to form adducts with the phosphite in CH_2Cl_2, i.e. the ^{31}P n.m.r. spectrum showed two resonances at -11.3 (doublet, J_{PH} 700 Hz) and 61.3 p.p.m. ($EtP(CN)_2$).

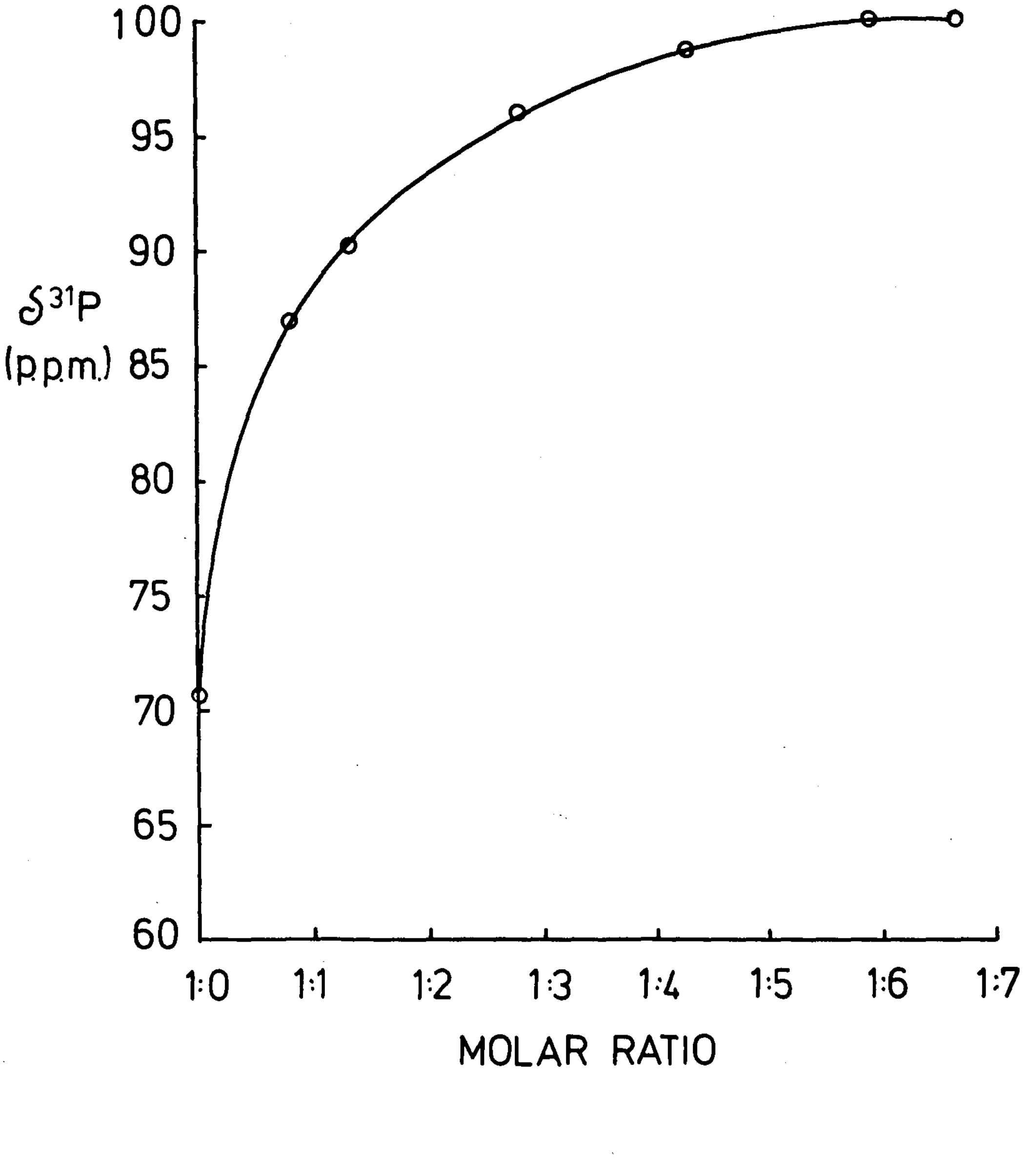
In CCl_4, however, four resonances were observed in the ^{31}P n.m.r. spectrum at -27.5 (doublet, P_A, J_{PP} 158 Hz), -11.3 (doublet, J_{PH} 700 Hz), 61.3 and 77.5 p.p.m. (doublet, P_B, J_{PP} 158 Hz), indicating that a reaction has occurred, equation (5). The two non-equivalent phosphorus atoms interact with one

$$EtP(CN)_2 + HPO(OMe)_2 \longrightarrow HCN + EtNCP_B\text{-}P_AO(OMe)_2 \qquad (5)$$

another to give two doublets at -27.5 and 77.5 p.p.m., with the resonance at 61.3 p.p.m. being assigned to unreacted $EtP(CN)_2$. One of the peaks of the phosphite doublet was partially obscured by the more intense peak from the product at -24.2 p.p.m.

Fig. 6.3.

^{31}P chemical shift of $PhP(CN)_2/Et_4NCl$ solutions in CH_2Cl_2



(c) The acceptor properties of $PhP(CN)_2$.

(i) $PhP(CN)_2$ - Cl^- system.

Addition of a chloride ion donor (Et_4NCl, Pr_4NCl or Pe_4NCl) to a solution of $PhP(CN)_2$ in CH_2Cl_2 gave a slightly yellow solution. The ^{31}P n.m.r. spectra of these solutions showed upfield shifts from that of $PhP(CN)_2$. The limiting shift value observed using Pe_4NCl as the chloride ion donor was 103.3 p.p.m. The compound was initially isolated as the tetra-n-pentylammonium salt. The pale yellow viscous liquid which was obtained gave a single ^{31}P n.m.r. shift at 106.4 p.p.m., in good agreement with the solution limiting shift. With Et_4NCl as the chloride ion donor, a limiting shift of 100.0 p.p.m. was observed. A plot of the variation in chemical shift of the $PhP(CN)_2$ - $PhP(CN)_2Cl^-$ system with the molar ratio of the halide (Et_4NCl) to $PhP(CN)_2$ is shown in Fig. 6.3. Crystals were isolated from a 1:1 molar reaction of Et_4NCl and $PhP(CN)_2$, which analysed as $PhP(CN)_2Cl^-Et_4N^+$. When they were dissolved in CH_2Cl_2, a solution shift of 83.8 p.p.m. was obtained, showing that the complex ion is partially dissociated in solution. Insufficient material was available for a solid state spectrum.

(ii) The $PhP(CN)_2$ - Br^- system.

When a solution of $PhP(CN)_2$ in CH_2Cl_2 was treated with Pr_4NBr, an upfield shift was observed in the ^{31}P n.m.r. spectrum. More bromide was added until a limiting value was established at 90.4 p.p.m., ascribed to the $PhP(CN)_2Br^-$ ion. A yellow liquid was isolated from equimolar amounts of $PhP(CN)_2$ and Bu_4NBr, the ^{31}P n.m.r. spectrum of which gave a major peak at 93.6 p.p.m. with two minor peaks at -1.6 and 51.6 p.p.m., which are tentatively assigned to $PhPOCl(CN)$ and $PhPO(CN)_2$ respectively. $PhP(CN)_2Br^-Pr_4N^+$ isolated from a 1:1 molar ratio of $PhP(CN)_2$ and Pr_4NBr was a viscous liquid with a chemical shift of 87.1 p.p.m. When Et_4NBr was used as the bromide ion donor, a limiting shift value was observed of 82.3 p.p.m., ascribed to the ion $PhP(CN)_2Br^-$. A viscous liquid was isolated from a 1:1 molar ratio reaction of $PhP(CN)_2$ and Et_4NBr.

Its ^{31}P n.m.r. spectrum in CH_2Cl_2 gave a single peak at 82.2 p.p.m. The extent of coordination thus seems to depend on the nature of the cation used as the source of bromide.

(iii) The $PhP(CN)_2 - I^-$ system.

A labile equilibrium was established for $PhP(CN)_2$ and tetra-n-propylammonium iodide in CH_2Cl_2, with a limiting shift of 77.5 p.p.m. for the $PhP(CN)_2I^-$ ion. A viscous yellow liquid was isolated from a 1:1 molar ratio reaction of $PhP(CN)_2$ and Pr_4NI. Its ^{31}P n.m.r. spectrum showed a single peak at 80.4 p.p.m. With Et_4NI no reaction occurred in either CH_2Cl_2 or CH_3CN, possibly due to the insolubility of the iodide in either of these solvents.

(iv) The $PhP(CN)_2 - CN^-$ system.

When a small amount of Et_4NCN was added to a solution of $PhP(CN)_2$ in CH_2Cl_2, a golden yellow solution was observed. The ^{31}P n.m.r. spectrum showed two peaks at -61.3 and 74.2 p.p.m. (unreacted $PhP(CN)_2$). More CN^- gave a single peak at -61.3 p.p.m. in the ^{31}P n.m.r. spectrum. This peak was assigned to $PhP(CN)^-$ and the following mechanism is postulated for the reaction, equation (6), in which the complex $PhP(CN)_3^-$ is very unstable and so immediately

$$PhP(CN)_2 + CN^- \longrightarrow PhP(CN)_3^- \longrightarrow PhP(CN)^- + (CN)_2 \qquad (6)$$

decomposes to $PhP(CN)^-$, thus making its detection impossible in the ^{31}P n.m.r. spectrum. A dark brown liquid which analysed as $PhP(CN)^-Et_4N^+$ was isolated from a 1:1 molar ratio reaction of $PhP(CN)_2$ and Et_4NCN in CH_2Cl_2. Its solution spectrum in CH_2Cl_2 gave a single peak of -62.9 p.p.m.

(v) The $PhP(CN)_2 - SCN^-$ system.

Addition of Me_4NSCN to a solution of $PhP(CN)_2$ in CH_2Cl_2 gave a slightly pinkish solution with Me_4NSCN floating on the surface. The ^{31}P n.m.r. spectrum showed a single peak at 74.2 p.p.m., assigned to unreacted $PhP(CN)_2$, indicating that Me_4NSCN does not react with $PhP(CN)_2$ in this medium, probably due to insolubility. Reaction of $PhP(CN)_2$ with Et_4NSCN in CH_2Cl_2, however, gave a pale yellow solution. Its ^{31}P n.m.r. spectrum showed a single resonance to higher field of the $PhP(CN)_2$ position. A limiting shift of 83.8 p.p.m. was observed, with a minor peak at 46.7 p.p.m. On the following day, the solution had turned dark brown, but no change in the position of the peaks was apparent. In CH_3CN, two signals were observed at 45.3 p.p.m. and 82.2 p.p.m., with the former being of very low intensity.

A viscous liquid was isolated from a 1:1 molar ratio of $PhP(CN)_2$ and Et_4NSCN in CH_2Cl_2. Its ^{31}P n.m.r. spectrum gave a single peak at 85.5 p.p.m., in good agreement with the solution data. Analysis confirmed that it was the 1:1 adduct $Et_4N^+PhP(CN)_2SCN^-$.

(vi) $PhP(CN)_2$ - $HPO(OMe)_2$ reaction.

A solution of $HPO(OMe)_2$ in CH_2Cl_2 showed no reaction with $PhP(CN)_2$, i.e. the ^{31}P n.m.r. spectrum showed two peaks at -11.3 (doublet, J_{PH} = 707 Hz) and 72.6 p.p.m. ($PhP(CN)_2$). A reaction occurred in CCl_4, however, with two peaks observed at -25.1 (doublet, P_A, J_{PP} 117 Hz) and 76.6 p.p.m. (doublet, P_B, J_{PP} 117 Hz), ascribed to the two non-equivalent phosphorus atoms in the reaction product according to equation (7). The product is not apparently

$$PhP(CN)_2 + HPO(OMe)_2 \longrightarrow HCN + Ph(NC)P_B\text{-}P_AO(OMe)_2 \qquad (7)$$

cleaved by excess $PhP(CN)_2$, unlike the reaction of $P(CN)_3$ with the phosphite[22].

(d) The i.r. spectra of several of the organophosphorus (III) cyanide adducts have been recorded in the region 2350 - 1950 cm^{-1}. The adducts and the starting materials showed a common band at ca. 2180 cm^{-1}, ascribed to a C≡N stretching vibration. In addition to this band, another lower frequency vibration was seen in both $MeP(CN)_2$ and $EtP(CN)_2$ adducts. With $PhP(CN)_2$ adducts, a third band was observed at a higher frequency than 2180 cm^{-1}, Table 6.3.

Table 6.3

Infrared stretching vibrations of C≡N groups for the organophosphorus (III) cyanide adducts in the 2350 - 1950 cm^{-1} region

Adduct	Wave number (cm^{-1})
MeP(CN)$_2$	2188(s) 1976(m)
MeP(CN)$_2$.Et$_4$NCl	2184(s) 2060(s)
MeP(CN)$_2$.Pr$_4$NBr	2176(s) 2020(m)
MeP(CN)$_2$.Bu$_4$NBr	2184(s) 2062(s)
MeP(CN)$_2$.Pr$_4$NI	2180(s) 2080(m)
MeP(CN)$^-$ Et$_4$N$^+$	2160(m) 2120 - 2080(s,br)
MeP(CN)$_2$.Et$_4$NSCN	2180(m) 2080 - 1960(s^a,br)
EtP(CN)$_2$	2180(s) 2086(m)
EtP(CN)$_2$.Et$_4$NCl	2180(s) 2046(m)
EtP(CN)$_2$.Pr$_4$NBr	2176(w) 2060(m) 2020(s)
EtP(CN)$_2$.Pr$_4$NI	2180(m) 2068(m) 2020(s)
EtP(CN)$^-$ .Et$_4$N$^+$	2160 - 2070 (s,br)
PhP(CN)$_2$	2246(w) 2180(s)
PhP(CN)$_2$.Et$_4$NCl	2280(w) 2180(m) 2060(s)
PhP(CN)$_2$.Pe$_4$NCl	2248(s) 2190(m) 2052(s)
PhP(CN)$_2$.Pr$_4$NBr	2320(s) 2180(w) 2040(s)
PhP(CN)$_2$.Bu$_4$NBr	2320(m) 2180(m) 2060(s)
PhP(CN)$_2$.Pr$_4$NI	2320(m) 2180(s) 2060(m)
PhP(CN)$^-$ Et$_4$N$^+$	2160 - 2080 (s,br)
PhP(CN)$_2$.Et$_4$NSCN	2280(m) 2182(s) 2080 - 2040^a(s,br)

[a] Partially due to NCS group.

4. The acceptor properties of t-BuP(CN)$_2$.

t-BuP(CN)$_2$ showed no tendency to form adducts with the halide ions (Cl$^-$, Br$^-$ or I$^-$) in CH$_3$CN or CH$_2$Cl$_2$. The ^{31}P n.m.r. spectra showed only a single resonance at 45.8 p.p.m., ascribed to t-BuP(CN)$_2$. No attempts were made to investigate its acceptor properties with CN$^-$ or SCN$^-$.

5. The acceptor properties of R$_2$P(CN) (R = Ph or Me).

Addition of the halide ions (Cl$^-$, Br$^-$ or I$^-$) or cyanide to a solution of Ph$_2$PCN or Me$_2$PCN in either CH$_3$CN or CH$_2$Cl$_2$ did not reveal any new peak or variation in the Ph_2PCN (32.4 p.p.m.) or Me_2PCN (61.3 p.p.m.) positions, indicating that these compounds do not coordinate with halide ions.

6. The acceptor properties of $MePCl_2$.

(a) $MePCl_2 - Cl^-$ system.

The ^{31}P n.m.r. spectrum of a solution of $MePCl_2$ and excess (> 1:1 molar ratio) Et_4NCl in CH_2Cl_2 was recorded over a 40 p.p.m. sweep range. The ^{31}P n.m.r. spectrum showed a quartet at -191.5 p.p.m., J_{PCH} 17 Hz. A minor peak was also observed at -206.7 p.p.m. This peak was ascribed to PCl_4^- [18], formed when the chloride ion reacts with PCl_3, which is a possible impurity in $MePCl_2$. A solution of $MePCl_2$ in CH_2Cl_2 was saturated with Pr_4NCl and cooled, resulting in the formation of crystals. The ^{31}P n.m.r. spectrum of these crystals dissolved in CH_2Cl_2 did not give any signal. Analysis has shown some phosphorus, and an appreciably higher chlorine content than required for Pr_4NCl, indicating that there might be some $Pr_4N^+PCl_4^-$ present in the product which is presumed to be mainly Pr_4NCl.

(b) The $MePCl_2 - Br^-$ system.

Pr_4NBr was added to a solution of $MePCl_2$ in methylene chloride. The ^{31}P n.m.r. spectrum showed only $MePCl_2$. When Bu_4NBr was used, a clear solution formed. Its spectrum showed only the resonance ascribed to $MePCl_2$. $MePCl_2$ thus appears to show no acceptor properties towards bromide ion.

(c) The $MePCl_2 - I^-$ system.

No change in the position of the shift assigned to $MePCl_2$ was observed when Pr_4NI was added to its CH_2Cl_2 solution.

(d) The $MePCl_2 - CN^-$ system.

A vigorous reaction occurred when Et_4NCN was added to a solution of $MePCl_2$ in CH_2Cl_2. The ^{31}P n.m.r. spectrum of the resulting yellow solution showed three resonances at -193.5(s) ($MePCl_2$), -4.9(w) and 95.1(s) p.p.m. When more CN^- was added, only a single peak was apparent at -62.9 p.p.m., probably due to

$MeP(CN)^-$. The -4.9 p.p.m. signal could be $MeP(CN)Cl_2^-$, although there is no direct evidence for this.

The results suggest the formation of $MeP(CN)_2Cl^-$ (95.1 p.p.m.) which then substitutes with more CN^- to give $MeP(CN)_3^-$. This in turn decomposes to give $MeP(CN)^-$ and cyanogen, according to equation (7), as observed in the direct reaction of CN^- with $MeP(CN)_2$.

$$\begin{tikzcd}
MePCl_2 + CN^- \arrow[r] & MePCl(CN) + Cl^- \arrow[r, "CN^-"] & MeP(CN)_2Cl^- \arrow[d, "CN^-"] \\
 & (CN)_2 + MeP(CN)^- & MeP(CN)_3^- + Cl^- \arrow[l]
\end{tikzcd}$$

7. The acceptor properties of $PhPCl_2$.

(a) The $PhPCl_2$ - Cl^- system.

When Et_4NCl was added to a solution of $PhPCl_2$ in CH_2Cl_2, a very exothermic reaction occurred. The ^{31}P n.m.r. spectrum showed only the presence of $PhPCl_2$. Equimolar amounts of Et_4NCl and $PhPCl_2$ were intimately mixed in CH_2Cl_2 and cooled to 243 K, but no crystals formed. Attempts to isolate any product from CH_3CN also failed. It is thus clear that $PhPCl_3^-$, if it exists, does not form under these conditions.

(b) The $PhPCl_2$ - Br^- system.

A clear solution was observed when Pr_4NBr was added to $PhPCl_2$ in CH_3CN or CH_2Cl_2. The ^{31}P n.m.r. spectra showed only one peak at -162.7 p.p.m. in all cases, ascribed to $PhPCl_2$. Attempts to isolate a solid product by mixing stoichiometric amounts of the reactants, followed by cooling to 243 K, did not result in the formation of any crystals.

(c) The $PhPCl_2$ - I system.

A yellow solution was formed when $PhPCl_2$ was added to a solution of Pr_4NI in CH_2Cl_2. Its ^{31}P n.m.r. spectrum showed only $PhPCl_2$, suggesting that $PhPCl_2I^-$ does not form under these conditions.

(d) The $PhPCl_2$ - CN^- system.

Addition of Et_4NCN to a solution of $PhPCl_2$ in CH_2Cl_2 was very exothermic. The ^{31}P n.m.r. spectrum of the pale yellow solution showed 3 peaks at -162.7, 34.0 (small), and 87.1 p.p.m. When more CN^- was added, only a single peak was observed at -62.9 p.p.m., which can be assigned to $PhP(CN)^-$. This suggests that CN^- displaces the chloride to form PhP(CN)Cl, which then reacts with excess cyanide to give $PhP(CN)_2Cl^-$. This in turn presumably reacts with more cyanide to give $PhP(CN)_3^-$ and eventually $PhP(CN)^-$, as described in section 6(d).

$$\begin{tikzcd}
\mathrm{PhPCl_2 + CN^-} \arrow[r] & \mathrm{PhP(CN)Cl + Cl^-} \arrow[r, "\mathrm{CN^-}"] & \mathrm{PhP(CN)_2Cl^-} \arrow[d, "\mathrm{CN^-}"] \\
 & \mathrm{(CN)_2 + PhP(CN)^-} & \mathrm{PhP(CN)_3^- + Cl^-} \arrow[l]
\end{tikzcd} \qquad (8)$$

8. Conclusion.

Compounds of the type $RP(CN)_2$ (R = Me, Et, Ph) have been found to possess acceptor properties towards the halides and pseudohalides X (X = Cl, Br, I or SCN), but their reaction with CN^- results in the formation of $RP(CN)^-$ and the release of cyanogen. $t\text{-}BuP(CN)_2$ and R_2PCN (R = Me or Ph) did not show any tendency to form adducts with the above mentioned ligands, presumably due to the inductive effects of the organo-groups. Similarly the compounds $RPCl_2$ (R = Me or Ph) did not show any acceptor abilities towards these halides, and reacted with CN^- to give $RP(CN)^-$ as the ultimate product. It thus appears that the acceptor properties of these compounds towards the halide and pseudohalide ions follow the sequence:-

$$P(CN)_3 > RP(CN)_2 >> R_2PCN.$$

The acceptor properties are reduced by the presence of electron-supplying groups (CN > Me > t-Bu), and may then be accentuated by introducing electron-withdrawing substituents into the organo-group R in $RP(CN)_2$.

9. Experimental.

The preparation of $MeP(CN)_2$.

$MePCl_2$ (5.4 mls, 60.42 mmoles)was added to AgCN (16.2007 g, 121.00 mmoles) in CH_3CN with stirring. The solution was left to stir for 30 minutes then filtered and the solvent removed in vacuo to isolate a white solid.

Analysis

Found	C = 36.50	H = 3.25	N = 28.45	P = 31.50
Calculated	C = 36.73	H = 3.06	N = 28.57	P = 31.63

The preparation of $MeP(CN)_2.Et_4NCl$.

$MeP(CN)_2$ (0.278 g, 2.8 mmoles)and Et_4NCl (0.470 g, 2.8 mmoles)were dissolved in CH_2Cl_2. The solvent was removed in vacuo leaving a colourless liquid. This liquid was placed in a fridge and fine crystals formed, which were then filtered and washed with $^{30}/40$ Pet. ether.

Analysis

Found	C = 50.02	H = 9.15	N = 15.60	P = 11.46	Cl = 13.80
Calculated	C = 50.09	H = 8.73	N = 15.94	P = 11.76	Cl = 13.47

The preparation of $MeP(CN)_2.Bu_4NBr$.

$MeP(CN)_2$ (0.309 g, 3.2 mmoles)and Bu_4NBr (1.015 g, 3.2 mmoles)were dissolved in CH_2Cl_2. The solvent was removed in vacuo to yield a colourless liquid. Its ^{31}P n.m.r. spectrum gave a single peak at 98.4 p.p.m. There was an insufficient amount of product available for phosphorus and bromine analysis.

Analysis

Found	C = 54.89	H = 10.92	N = 10.62
Calculated	C = 54.23	H = 9.28	N = 9.99

The preparation of $MeP(CN)_2.Pr_4NBr$.

$MeP(CN)_2$ (0.451 g, 4.6 mmoles)and Pr_4NBr (1.232 g, 4.6 mmoles)were intimately mixed in CH_3CN. The solvent was removed in vacuo to isolate a white solid.

Analysis

Found C = 48.61 H = 8.27 N = 11.31 P = 8.60 Br = 20.40

Calculated C = 49.45 H = 8.52 N = 11.54 P = 8.52 Br = 21.98

The preparation of $MeP(CN)_2.Pr_4NI$.

$MeP(CN)_2$ (0.3657 g, 3.7 mmoles)and Pr_4NI (1.169 g, 3.7 mmoles)were dissolved in a small amount of CH_2Cl_2. A yellow solution was observed. The solvent was then removed in vacuo to isolate a white solid.

Analysis

Found C = 43.21 H = 9.37 N = 9.59 P = 8.17 I = 28.70

Calculated C = 43.77 H = 7.54 N = 10.21 P = 7.54 I = 30.88

The preparation of $MeP(CN).Et_4N$.

$MeP(CN)_2$ (0.6085 g, 6.2 mmoles)and Et_4NCN (0.9686 g, 6.2 mmoles)were dissolved in CH_2Cl_2. The solvent was removed in vacuo to produce a viscous orange liquid, which later turned to an orange solid in the box.

Analysis

Found C = 54.00 H = 9.22 N = 19.59 P = 11.90

Calculated C = 56.69 H = 9.06 N = 22.05 P = 12.20

The preparation of $MeP(CN)_2.Et_4NSCN$.

$MeP(CN)_2$ (1.1047 g, 11.3 mmoles)was dissolved in a minimum amount of CH_2Cl_2. Et_4NSCN (2.1192 g, 11.3 mmoles)was added and the solution stirred for a while. The solvent was then removed in vacuo to isolate a yellow solid.

Analysis

Found C = 50.70 H = 19.83 N = 8.72 P = 10.68

Calculated C = 50.35 H = 19.58 N = 8.04 P = 10.84

The preparation of $EtP(CN)_2$.

AgCN (7.5 g, 56.0 mmoles)was added to a solution of $EtPCl_2$ (3.9 mls, 28.0 mmoles) in CH_3CN. The solution was left to stir for 30 minutes, filtered and the solvent removed in vacuo to isolate a white solid.

Analysis

Found C = 42.80 H = 4.72 N = 24.94 P = 27.38

Calculated C = 42.86 H = 4.46 N = 25.00 P = 27.68

The preparation of $EtP(CN)_2.Et_4NCl$.

$EtP(CN)_2$ (0.58 g, 5.2 mmoles) was dissolved in CH_3CN. Et_4NCl (0.8607 g, 5.2 mmoles) was added with stirring. The solvent was then removed in vacuo to isolate a viscous liquid.

Analysis

Found C = 50.74 H = 10.31 N = 14.61 P = 10.70 Cl = 13.40

Calculated C = 51.89 H = 9.01 N = 15.14 P = 11.17 Cl = 12.79

The preparation of $EtP(CN)_2.Pr_4NBr$.

$EtP(CN)_2$ (0.65 g, 5.8 mmoles) and Pr_4NBr (1.543 g, 5.8 mmoles) were dissolved in CH_2Cl_2 (10 mls). The solvent was removed in vacuo to isolate a white solid.

Analysis

Found C = 50.68 H = 11.11 N = 10.08 P = 8.23 Br = 20.80

Calculated C = 50.78 H = 8.73 N = 11.11 P = 8.20 Br = 21.16

The preparation of $EtP(CN)_2.Pr_4NI$.

$EtP(CN)_2$ (0.6183 g, 5.5 mmoles) and Pr_4NI (1.7265 g, 5.5 mmoles) were dissolved in CH_2Cl_2. The solvent was removed in vacuo to yield an off-white solid.

Analysis

Found C = 45.67 H = 7.95 N = 9.62 P = 6.85 I = 29.91

Calculated C = 45.18 H = 7.76 N = 9.88 P = 7.29 I = 29.88

The preparation of $EtP(CN).Et_4N$.

$EtP(CN)_2$ (0.7149 g, 6.4 mmoles) and Et_4NCN (0.9958 g, 6.4 mmoles) were dissolved in CH_2Cl_2. The solvent was removed in vacuo leaving a dark brown viscous liquid.

Analysis

Found C = 53.56 H = 11.01 N = 16.63 P = 11.10

Calculated C = 61.11 H = 11.57 N = 12.96 P = 14.35

(For $EtP(CN)Et_4N$).CH_2Cl_2/a second preparation gave the following analysis.

Found C = 47.48 H = 9.54 N = 13.55 P = 10.83

Calculated C = 47.84 H = 8.97 N = 9.30 P = 10.30

The preparation of $PhP(CN)_2$.

$PhPCl_2$ (11.5 mls, 8.5 mmoles) was treated with AgCN (22.6805 g, 16.9 mmoles) in CH_2Cl_2. The solution was filtered, and the solvent removed in vacuo to isolate a white solid, m.p. 305 K.

Analysis

Found C = 60.26 H = 3.85 N = 17.40 P = 18.84

Calculated C = 60.00 H = 3.12 N = 17.50 P = 19.38

The preparation of $PhP(CN)_2.Pe_4NCl$.

$PhP(CN)_2$ (1.0271 g, 6.4 mmoles) and Pe_4NCl (2.14 g, 6.4 mmoles) were separately dissolved in a minimum amount of CH_3CN. The chloride solution was added to the $PhP(CN)_2$ solution with stirring. The solvent was removed in vacuo, leaving a pale yellow viscous liquid.

Analysis

Found C = 67.84 H = 10.06 N = 8.09 P = 6.25 Cl = 7.00

Calculated C = 68.09 H = 9.93 N = 8.51 P = 6.28 Cl = 7.19

The preparation of $PhP(CN)_2.Et_4NCl$.

$PhP(CN)_2$ (1.9824 g, 12.4 mmoles) was dissolved in methylene chloride (10 mls). Et_4NCl (2.0505 g, 12.4 mmoles) was added with stirring. A slightly yellow solution was formed. The volume of solvent was reduced and the solution placed in a refrigerator until crystals formed. These were filtered off and washed with $^{30}/40$ Pet. ether.

Analysis

Found C = 57.61 H = 9.76 N = 11.10 P = 9.57 Cl = 11.85

Calculated C = 58.99 H = 7.68 N = 12.90 P = 9.52 Cl = 10.91

The preparation of $PhP(CN)_2.Bu_4NBr$.

$PhP(CN)_2$ (0.6646 g, 4.2 mmoles) was dissolved in CH_2Cl_2. Bu_4NBr (1.37 g, 4.2 mmoles) was added with stirring. The solvent was removed in vacuo leaving a pale yellow liquid. Its ^{31}P n.m.r. spectrum showed a major peak at 93.6 p.p.m. ($PhP(CN)_2Br^-$ ion) with other minor resonances at -1.6 and 51.6 p.p.m. Due to the presence of these impurities no attempt was made to analyse this liquid.

The preparation of $PhP(CN)_2.Pr_4NBr$.

$PhP(CN)_2$ (1.552 g, 9.7 mmoles) was dissolved in a small amount of methylene chloride. Pr_4NBr (2.579 g, 9.7 mmoles) was added with stirring and the solution left to stir for 10 minutes. The solvent was removed in vacuo leaving a viscous liquid. This liquid was placed in a refrigerator in the hope that crystals would form, but this did not occur. No analysis was performed on the liquid.

The preparation of $PhP(CN)_2.Et_4NBr$.

$PhP(CN)_2$ (1.9468 g, 12.2 mmoles) was dissolved in a minimum amount of CH_2Cl_2. Et_4NBr (2.5828 g, 12.3 mmoles) was added to the above solution with stirring. The solution was left to stir for a few minutes and the solvent then removed in vacuo to isolate a viscous liquid.

Analysis

Found C = 49.23 H = 8.09 N = 9.05 P = 7.82 Br = 21.20

Calculated C = 51.89 H = 6.76 N = 11.35 P = 8.38 Br = 21.62

The preparation of $PhP(CN)_2.Pr_4NI$.

$PhP(CN)_2$ (2.1 g, 13.1 mmoles) was dissolved in a minimum amount of CH_2Cl_2. Pr_4NI (4.1 g, 13.1 mmoles) was added with constant stirring. The solvent was removed in vacuo, yielding a colourless viscous liquid.

Analysis

Found C = 51.28 H = 7.34 N = 8.40 P = 6.38 I = 26.26

Calculated C = 50.74 H = 6.98 N = 8.88 P = 6.55 I = 26.85

The preparation of PhP(CN).Et_4N.

PhP$(CN)_2$ (1.406 g, 8.8 mmoles)was dissolved in CH_2Cl_2. Et_4NCN (1.38 g, 8.8 mmoles)was then added with stirring. The solvent was removed in vacuo to isolate a dark brown viscous liquid.

Analysis

Found	C = 68.68	H = 8.88	N = 11.88	P = 11.84
Calculated	C = 69.23	H = 9.62	N = 9.23	P = 11.92

The preparation of PhP$(CN)_2$.Et_4NSCN.

Et_4NSCN (1.2925 g, 6.9 mmoles)was added to a solution of PhP$(CN)_2$ (1.10 g, 6.9 mmoles)in CH_2Cl_2. The solvent was removed in vacuo to isolate a colourless viscous liquid which had turned dark green by the following day.

Analysis

Found	C = 55.77	H = 8.50	N = 13.92	P = 8.83	S = 8.96
Calculated	C = 58.62	H = 7.18	N = 16.09	P = 8.91	S = 9.20

The attempted preparation of $Pr_4N^+MePCl_3^-$.

Pr_4NCl (1.9531 g, 8.8 mmoles)was dissolved in CH_2Cl_2. $MePCl_2$ (0.8 ml, 8.8 mmoles)was added slowly with stirring, and a vigorous reaction occurred. The solution was placed in a refrigerator. Fine crystals formed. These were filtered off and washed with $^{30}/40$ Pet. ether.

Analysis

Found	C = 54.10	H = 12.87	N = 4.95	P = 1.60	Cl = 25.10
Calculated	C = 46.08	H = 9.16	N = 4.14	P = 9.16	Cl = 31.46
Pr_4NCl requires					
	C = 65.01	H = 12.64	N = 6.32	P =	Cl = 16.03
$Pr_4N^+PCl_4^-$ requires					
	C = 40.11	H = 7.80	N = 3.90	P = 8.64	Cl = 39.55

The preparation of t-BuP$(CN)_2$.

t-BuPCl_2 (1.7728 g, 11.15 mmoles) was dissolved in methylene chloride. AgCN (3.1494 g, 23.5 mmoles)was added with stirring. The solution mixture was refluxed for 6 hours, filtered and the solvent removed in vacuo to isolate a colourless liquid. Its ^{31}P n.m.r. spectrum gave a single peak at 42.0 p.p.m. No analysis was performed on the liquid.

The preparation of $Ph_2P(CN)$.

Ph_2PCl (4.6 mls, 20.9 mmoles) was dissolved in methylene chloride. AgCN (2.8015 g, 20.9 mmoles) was added with constant stirring. The solution was left to stir for 45 minutes, filtered and the solvent removed in vacuo to isolate a very viscous liquid. Its ^{31}P n.m.r. spectrum in methylene chloride showed a single peak at 32.4 p.p.m. No analysis was performed on the liquid isolated.

The preparation of $Me_2P(CN)$.

Me_2PCl (1.3 ml, 17.8 mmoles) was dissolved in a minimum amount of methylene chloride. AgCN (2.4 g, 17.9 mmoles) was added to the above solution with stirring. The mixture was left to stir for 1 hour, filtered and the filtrate used for the investigation into its acceptor properties. The compound was not isolated because the starting material contained some $MePCl_2$ as impurity which also reacted with AgCN to give $MeP(CN)_2$.

CHAPTER SEVEN

The behaviour of some organophosphorus compounds in sulphuric acid and oleum.

1. Introduction.

The chemical behaviour of phosphates and phosphites under acidic conditions has long been a subject of interest to many investigators[129]. The acidic solvolyses[130,131] and the dealkylation by hydrogen halides[132] of phosphate triesters have been examined in detail, but the chemistry of organophosphorus compounds in sulphuric acid and oleums has been relatively little studied. Gillespie and his coworkers have cited conductometric and cryosopic measurements as evidence for the generation of protonated phosphoric acid $P(OH)_4^+$ in sulphuric acid[133] and disulphuric acid solutions[134]. Their measurements indicated that triethylphosphate and triphenylphosphine oxide are protonated in sulphuric acid solution but that phosphorus oxyfluoride is not[133]. The conductivity of triphenylphosphate in sulphuric acid has been explained in terms of protonation[135]. McFarlane and White[136] have observed by ^1H n.m.r. the protonation at phosphorus of several phosphites and phosphines in 100% H_2SO_4. Olah and McFarland have studied the protonation of trialkyl(aryl)phosphates, trialkyl(aryl)phosphites and dialkylphosphonates in fluorosulphuric acid and in fluorosulphuric acid-antimony pentafluoride solutions using both ^1H and ^{31}P n.m.r.[137]. Protonation of Ph_3PO, $P(OMe)_3O$ and $P(OEt)_3O$ in fluorosulphuric acid has been reported by Paul et al[138]. Dillon and Waddington[139] have studied the behaviour of some inorganic phosphates in strongly acidic solvents by ^{31}P n.m.r.

Sulphonation of the ring as well as protonation has been observed in aryl compounds containing aromatic substituents. Ph_3P has thus been observed to undergo a slow sulphonation in addition to initial protonation when dissolved in 100% H_2SO_4[140]. The reactions of some phosphinates in sulphuric acid and oleum have been investigated by cryoscopy and ^1H n.m.r.[141]. The results indicated that sulphonation followed protonation of the phosphoryl oxygen.

Unlike the aryl systems[140] these workers concluded that the P-OH groups were sulphonated to give P-OSO_3H units. Dillon et al have recently investigated the chemistry of a number of phenyl organophosphorus species and some related alkyl compounds in 100% H_2SO_4, oleums, and $HSClO_3$ [30,142,143]. 25 oleum in particular has proved to be a useful solvent for phosphonium salts containing either inorganic and/or organic groups, enabling important structural information to be obtained in solution[143]. ^{31}P n.m.r. spectroscopy has shown, for example, that the 'compound' $PhPCl_2Br_2$, made by reaction of $PhPCl_2$ with bromine[144], contains the whole series of mixed cations $[PhPCl_{3-n}Br_n]^+$ $(0 \leqslant n \leqslant 3)$[143].

All the results indicate that tetravalent phosphoryl compounds are protonated on the phosphoryl oxygen atom, whereas tervalent compounds protonate at the phosphorus atom.

The present work is mainly to examine the chemistry of some organophosphorus (V) halides in 100% H_2SO_4 and 25 oleum solutions by ^{31}P n.m.r. spectroscopy.

2. Present Work.

(a) $MePBr_4$ and $\overset{+}{MePBr_3}\overset{-}{BBr_4}$.

The ^{31}P n.m.r. spectrum of $MePBr_4$ in 25 oleum showed three resonances at -74.2(w), -53.3(s), and -30.7(m) p.p.m. These peaks were assigned as in Table 7.1.

Table 7.1

δ ^{31}P (p.p.m.)	Assignment
-74.2	$MeP(OH)ClBr^+$
-53.3	$MeP(OH)Br_2^+$
-30.7	$MePBr_3^+$

The peak for the chloro-species arises from MePClBr present in the starting material. After a period of one month an additional signal was observed at

-43.6 p.p.m. This peak must be assigned to either $MeP(OH)_2Br^+$ or the final product $MeP(OH)_3^+$. The shift is in good agreement with the value of -43. p.p.m. for $MeP(OH)_3^+$ in 25 oleum reported by Dillon et al[145], but the shift of $MeP(OH)_2Br^+$ may well be similar in 25 oleum in view of the results for the $MePOBr_2$/MePOClBr mixture in 100% H_2SO_4, described below. The alternative possibility is that the species $MeP(OH)_2Br^+$ solvolyses faster than its precursors, as observed in other systems[30], and its concentration remains below the detection limit. Two months later the peak at -74.2 p.p.m. had disappeared. The change in the relative intensities of the other three signals was -54.9(w), -45.3(s), and -31.5(mw) p.p.m. When the same solution was reinvestigated after a further month, the same three resonances were observed, indicating that the solvolysis of the P-Br bonds was occurring slowly.

$MePBr_3^+BBr_4^-$ was prepared as an off-white solid from $MePBr_4$ and BBr_3. Its solid state spectrum gave a broad resonance at -27.5 p.p.m. whereas its solution in nitrobenzene showed a single resonance at -30.7 p.p.m., attributed to the $MePBr_3^+$ ion. The presence of the BBr_4^- anion provides an alternative nucleus for n.m.r. investigation. The ^{11}B solution spectrum of this compound in nitrobenzene consisted of a single signal at 37.7 p.p.m., while the solid state spectrum showed a broad peak at 41.8 p.p.m., in good agreement with the solution value and with literature data[104,105,106]. Its solution in 25 oleum showed two resonances at -29.1(vs) and -62.9(w) p.p.m. These signals were assigned to $MePBr_3^+$ and $MePClBr_2^+$ respectively. The presence of $MePClBr_2^+$ arises from MePClBr which was an impurity in the starting material $MePBr_2$. The sample was heated in a water bath until reaction ceased. This was indicated when the ^{31}P n.m.r. spectrum consisted of only one signal at -45.8 p.p.m., ascribed to the final solvolysis product $MeP(OH)_3^+$.

(b) $MePOBr_2$/MePOClBr mixture.

$MePOBr_2$/MePOClBr was isolated as a yellow liquid. Its ^{31}P n.m.r. spectrum showed two signals at -25.8(w) and -6.5(s) p.p.m., assigned to MePOClBr and

$MePOBr_2$ respectively. Its ^{31}P n.m.r. spectrum in 25 oleum consisted of two resonances at -72.6(w) and -53.3(s) p.p.m., assigned to $MeP(OH)ClBr^+$ and $MeP(OH)Br_2^+$ respectively. The peaks were readily assigned in this instance from the relative peak intensities in the starting material. Species such as MePOClBr and $MePOBr_2$ may be only partially protonated in these acidic solvents, the extent of protonation depending on the concentration of the solute and the acid strength of the medium[30,142,143,145]. They are represented in the protonated form above and subsequently for clarity. A single ^{31}P n.m.r. signal was observed for the exchanging system in each case, the degree of protonation being reflected in the downfield shift relative to the parent (unprotonated) compound[30,142,143,145].

In 100% H_2SO_4 four resonances were observed at -61.3(w), -46.0(vs), -36.4(mw) and -25.8(s) p.p.m., assigned as below (Table 7.2).

Table 7.2

δ ^{31}P (p.p.m.)	Assignment
-61.3	$MeP(OH)_2Cl^+$
-46.0	$MeP(OH)_3^+$
-36.4	$MeP(OH)Br_2^+$
-25.8	$MeP(OH)_2Br^+$

The resonances at -61.3 and -46.0 p.p.m. agree well in shift with values reported previously for these species in H_2SO_4 [30,145], and the remaining assignments seem reasonable in view of the relative peak intensities and the probable solvolytic path. Solvolysis is clearly much more rapid in 100% H_2SO_4 than in 25 oleum, as expected, and this accounts for the failure to observe a signal attributable to $MeP(OH)ClBr^+$. The signals for $MeP(OH)Br_2^+$ and $MeP(OH)_2Br^+$ are at appreciably higher field than in 25 oleum, in accordance with less extensive protonation in the more weakly acidic solvent. The P-Br bond is expected to solvolyse faster than the P-Cl bond, so the solvolysis routes for the two components of the mixture are probably

$$MeP(OH)Br_2^+ \xrightarrow{100\%\ H_2SO_4} MeP(OH)_2Br^+ \xrightarrow{100\%\ H_2SO_4} MeP(OH)_3^+$$

$$MeP(OH)BrCl^+ \xrightarrow{100\%\ H_2SO_4} MeP(OH)_2Cl^+ \xrightarrow{100\%\ H_2SO_4} MeP(OH)_3^+ .$$

These conclusions are entirely in keeping with the above results.

(c) $MePCl_2Br_2$.

Methyldichlorodibromophosphorane is a white solid which showed a broad solid state resonance at -85.6 p.p.m. in the ^{31}P n.m.r. spectrum. This solid dissolved in both 25 oleum and 100% H_2SO_4 with effervescence to yield red-orange solutions. The ^{31}P n.m.r. spectra showed peaks assignable to cationic species in the series $[MePCl_nBr_{3-n}]^+$ $(0 \leqslant n \leqslant 3)$. In 25 oleum the ^{31}P n.m.r. spectrum showed signals which can be assigned as below (Table 7.3).

Table 7.3

δ ^{31}P (p.p.m.)	Assignment
-120.9	$MePCl_3^+$(w) [30,50]
- 95.1	$MePCl_2Br^+$(s)
- 75.8	$MeP(OH)ClBr^+$(s)
- 64.5	$MePClBr_2^+$(m)
- 54.9	$MeP(OH)Br_2^+$(w)
- 30.7	$MePBr_3^+$(m)

These assignments are in good agreement with published data where available, while other shifts compare well with data obtained in this work using independent reactions. The assignment of the peaks at -75.8 and -54.9 p.p.m. to $MeP(OH)ClBr^+$ and $MeP(OH)Br_2^+$ respectively was confirmed by dissolving a mixture of $MePOClBr/MePOBr_2$ in 25 oleum as described in the previous section, after 5 days the $MePCl_2Br_2$ solution in 25 oleum showed signals at -95.1, -74.2, -64.5, -45.7 and -29.1 p.p.m. The intensities of these peaks had reduced considerably except for the new peak at -45.7 p.p.m. which had grown with time. The presence of this signal assignable to $MeP(OH)_2Br^+$ or $MeP(OH)_3^+$ [145], is understandable in terms of solvolysis. After two weeks only a single peak was observed at -45.7 p.p.m., ascribed to the final solvolysis product, $MeP(OH)_3^+$.

The ^{31}P n.m.r. spectrum in 100% H_2SO_4 showed signals which are assigned below, Table 7.4.

Table 7.4

δ ^{31}P (p.p.m.)	Assignment
-120.9(w)	$MePCl_3^+$
- 95.1(m)	$MePCl_2Br^+$
- 74.2(m)	$MeP(OH)Cl_2^+$
- 64.5(s)	$MePClBr_2^+$
- 59.6(mw)	$MeP(OH)ClBr^+$
- 43.6(vw)	$MeP(OH)Br_2^+$
- 30.7(s)	$MePBr_3^+$

The shifts for the cations $[MePCl_nBr_{3-n}]^+$ are in excellent agreement with the values in 25 oleum, and that for $MeP(OH)Cl_2^+$, which is expected to be the first solvolysis product of both $MePCl_3^+$ and $MePCl_2Br^+$, agrees well with the previous result of -72 p.p.m. in 100% H_2SO_4 [145]. The other assignments appear reasonable from a consideration of the relative peak intensities and the expected solvolytic paths of the cations. When the same sample was monitored after a day, the signal at -120.9 p.p.m. had almost disappeared, that at -74.2 p.p.m. had increased somewhat in intensity, and there was a weak signal at -48.4 p.p.m., possibly due to $MeP(OH)_3^+$. A shift of -48.0 p.p.m. has been obtained for this ion in 100% H_2SO_4 [145]. When this sample was re-investigated after a month only one resonance was observed at -48.4 p.p.m., ascribed to the final solvolysis product $MeP(OH)_3^+$ [30,145].

(d) $\underline{Me_2PBr_5 \text{ and } Me_2PBr_2^+BBr_4^-}$.

Me_2PBr_5 is an orange solid with a chemical shift of -75.8 p.p.m. in both nitrobenzene and acetonitrile solution, ascribed to the $Me_2PBr_2^+$ ion. The probable structure of the compound is thus $Me_2PBr_2^+Br_3^-$. The presence of the Br_3^- ion has been confirmed by its Raman spectrum which showed a band at 169 cm^{-1}, ascribed to Br_3^- [98]. A broad resonance was recorded at -72.6 p.p.m. in the solid state spectrum. When the compound was dissolved in either 25 oleum or 100% H_2SO_4, a vigorous reaction occurred with effervescence and evolution of heat, and the subsequent appearance of a red-orange solution. Liquid bromine was deposited at the bottom of the n.m.r. tube in 100% H_2SO_4. The ^{31}P n.m.r. in 100% H_2SO_4 showed signals at -74.2(vs), -85.5(w) and -92.0(mw) p.p.m., which were assigned as below (Table 7.5).

Table 7.5

δ ^{31}P (p.p.m.)	Assignment
-92.0	$Me_2P(OH)Br^+$
-85.5	$Me_2P(OH)_2^+$
-74.2	$Me_2PBr_2^+$

These assignments are in good agreement with independent data described below or earlier. After 6 days the ^{31}P n.m.r. spectrum showed a single peak at -85.5 p.p.m., assigned to the completely solvolysed product. No change in the position of the single peak was observed when the same solution was re-investigated after two months. In contrast with the data obtained from 100% H_2SO_4, 25 oleum gave only two signals at -96.0(m) and -74.2(s) p.p.m., ascribed to the partial solvolysis product $Me_2P(OH)Br^+$ and $Me_2PBr_2^+$ respectively, and showing that the rate of solvolysis is much slower in 25 oleum than in 100% H_2SO_4. This is in keeping with previous work on halogenophosphorus compounds in these solvents[30,142,143,145]. When this solution was re-investigated later, only a single resonance was observed at -85.5 p.p.m. in the ^{31}P n.m.r. spectrum, ascribed to the completely solvolysed product. Elemental bromine was also observed at the bottom of the n.m.r. tube.

To confirm the above assignments, the compound $Me_2PBr_2^+BBr_4^-$ was prepared as a white solid by reaction of Me_2PBr_5 and BBr_3. Its solid state spectrum showed a broad resonance at -70.9 p.p.m., in good agreement with the solid state spectrum recorded for Me_2PBr_5. The ^{11}B n.m.r. of this solid consisted of a broad resonance at 59.7 p.p.m., whereas its solution in $PhNO_2$ gave a single peak at 39.4 p.p.m. The solution value is in good agreement with literature data[104-6], and the solid state shift is similar to that reported for Et_4NBBr_4 [106]. Its dissolution in 25 oleum was violent and yielded a pale brown solution. The initial ^{31}P n.m.r. spectrum showed signals at -95.1(m), -87.1(w) and -74.2(s) p.p.m. Little change was observed when the solution was re-investigated after a week, but after 2 months only one peak was observed at -85.5 p.p.m. The spectral data is thus consistent with the following reaction scheme, and shows that slow solvolysis occurs in this medium. Liquid

$$\underset{-74.2\ \text{p.p.m.}}{Me_2PBr_2^+} \xrightarrow[\text{oleum}]{25} \underset{-95.1\ \text{p.p.m.}}{Me_2P(OH)Br^+} \longrightarrow \underset{-85.5\ \text{p.p.m.}}{Me_2P(OH)_2^+}$$

bromine was also liberated in this reaction.

(e) $\underline{Me_2POBr}$.

This compound was isolated as a dark red liquid by bubbling SO_2 into a solution of Me_2PBr_5 in CH_2Cl_2 and removing the solvent in vacuo. Its ^{31}P n.m.r. spectrum consisted of a single peak at -72.6 p.p.m. Its solution in 100% H_2SO_4 showed only a single resonance at -83.8 p.p.m., assigned to $Me_2P(OH)_2^+$ which is the final solvolysis product. In 25 oleum the spectrum gave a single peak at -89.5 p.p.m., ascribed to $Me_2P(OH)Br^+$. Nine months later when the same solution was re-investigated a single peak was observed at -86.4 p.p.m. which is due to the final solvolysis product $Me_2P(OH)_2^+$.

(f) $\underline{Me_2PCl_3}$.

The ^{31}P n.m.r. spectrum of Me_2PCl_3 in 25 oleum showed a number of peaks, assigned as shown in Table 7.6.

Table 7.6

δ ^{31}P (p.p.m.)	Assignment
-124.2(s)	$Me_2PCl_2^+$ [50]
-106.4(m)	$Me_2P(OH)Cl^+$
- 85.5(w)	$Me_2P(OH)_2^+$

The peak at -124.2 p.p.m. was assigned to $Me_2PCl_2^+$ in good agreement with the chemical shift reported by Dillon et al[50], while the signal at -85.5 p.p.m. was assigned to the complete solvolysis product $Me_2P(OH)_2^+$ and that at -106.4 p.p.m. to $Me_2P(OH)Cl^+$. No change in the position of the peaks was detected when the same solution was monitored after a further two months. In 100% H_2SO_4 three signals were also observed at -123.3(s), -106.4(s) and -86.4(m) p.p.m., assigned as above.

(g) $\underline{Me_2PClBr_2}$.

Me_2PClBr_2 is a white solid, its solid state spectrum showed a broad resonance at -112.9 p.p.m. It dissolved in 25 oleum with effervescence to give an orange solution. The ^{31}P n.m.r. spectrum showed a number of peaks, assigned as shown in Table 7.7.

Table 7.7

δ ^{31}P (p.p.m.)	Assignment
-124.2(w)	$Me_2PCl_2^+$
-109.6(s)	Me_2PClBr^+ and $Me_2PCl(OH)^+$
- 96.0(vs)	$Me_2P(OH)Br^+$
- 75.8(m)	$Me_2PBr_2^+$
- 55.6(m)	$MeP(OH)Br_2^+$

The assignment of the peak at -124.2 p.p.m. agrees with published work[50], while the assignments of the resonances at -96.0 and -55.6 p.p.m. are based on the results obtained from the ^{31}P n.m.r. solution spectra of Me_2POBr, and both $MePBr_4$ and $MePCl_2Br_2$, respectively, in 25 oleum. The assignment of the shift at -75.8 p.p.m. to $Me_2PBr_2^+$ is based on the data obtained from solutions of Me_2PBr_5 and $Me_2PBr_2^+BBr_4^-$ in 25 oleum. The signal at -109.6 p.p.m. may then reasonably be attributed to Me_2PClBr^+ as confirmed by subsequent work, although it probably also has a contribution from $Me_2P(OH)Cl^+$.

The 100% H_2SO_4 solution showed a more complicated spectrum, and assignment of peaks to particular species is given in Table 7.8. When the same solution was re-investigated after 5 weeks, only two signals could be

Table 7.8

δ ^{31}P (p.p.m.)	Assignment
-124.2(w)	$Me_2PCl_2^+$
-106.4(vs)	Me_2PClBr^+ + $Me_2P(OH)Cl^+$
- 92.7(w)	$Me_2P(OH)Br^+$
- 86.4(s)	$Me_2P(OH)_2^+$
- 74.2(m)	$Me_2PBr_2^+$
- 56.5(mw)	$MeP(OH)ClBr^+$
- 39.6(m)	$MeP(OH)Br_2^+$
- 30.7(w)	$MeP(OH)_2Br^+$ or $MePBr_3^+$

discerned at -86.4 and -48.4 p.p.m., ascribed to the final solvolysis products $Me_2P(OH)_2^+$ and $MeP(OH)_3^+$ for dimethyl and monomethyl systems respectively. The assignment of some peaks to compounds with only one methyl group in both 25 oleum and 100% H_2SO_4 is explained by the fact that the starting material Me_2PCl contained some $MePCl_2$, despite efforts to separate the two liquids by distillation. This was confirmed by recording the ^{31}P n.m.r. spectrum of the starting material. This observation enabled the assignments to be made for the initial spectrum in 100% H_2SO_4.

(h) Me_2PCl_3/Me_2PBr_5 system in 25 oleum.

The n.m.r. study of the re-organisation of triply connected monophosphorus compounds in which the exchangeable substituents were chlorine, bromine and phenyl groups has been described by Fluck et al[146]. Halogen exchange reactions of phosphorus (V) halides and oxyhalides in 25 oleum have been investigated by Dillon et al[147] by means of ^{31}P spectroscopy. The species were found not to exchange unless a suitable source of halide ion was present. In this work, the Me_2PCl_3/Me_2PBr_5 system was investigated in 25 oleum. The ^{31}P n.m.r. spectrum showed signals at -122.6(s) ($Me_2PCl_2^+$), -108.6(s) (Me_2PClBr^+), -93.5(m) and -72.6(m) p.p.m. ($Me_2PBr_2^+$). The signal at -93.5 p.p.m. was assigned to $Me_2P(OH)Br^+$ which is a partial solvolysis product of $Me_2PBr_2^+$. After 2 months the same number of peaks was observed with the peak at -93.5 p.p.m. having increased in intensity relative to the other peaks. The results show that exchange does occur between $Me_2PCl_2^+$ and $Me_2PBr_2^+$ in 25 oleum to form Me_2PClBr^+ and that solvolysis is slow in this instance.

(i) $\underline{Me_3PBr_2 \text{ and } Me_3PBr^+BBr_4^-}$.

Me_3PBr_2 was isolated as a yellow solid. Its solution spectrum in nitrobenzene gave a single peak at -66.2 p.p.m., and the solid state spectrum showed a broad resonance at -67.8 ± 1 p.p.m., attributed to the Me_3PBr^+ ion. It dissolved in 25 oleum with effervescence to yield a pale orange solution. Its ^{31}P n.m.r. spectrum showed two signals at -67.8(m) and -106.4 p.p.m. These peaks were easily assigned to Me_3PBr^+ and $Me_3P(OH)^+$ respectively. No change in the spectrum was observed after a day, but when the solution was monitored after a week only one signal was observed at -106.4 p.p.m., ascribed to $Me_3P(OH)^+$ and consistent with the complete solvolysis of the P-Br bond.

In 100% H_2SO_4, a vigorous reaction occurred and a pale yellow orange solution formed. Its ^{31}P n.m.r. spectrum showed two signals at -66.2(w) and -88.7(s) p.p.m. The signal at -66.2 p.p.m. was assigned to Me_3PBr^+ while the signal at -88.7 p.p.m. was assigned to $Me_3P(OH)^+$ which is the solvolysis product. After a day, the intensity of the downfield signal had increased relative to the upfield resonance, and a week later the spectrum showed only a single resonance at -90.4 p.p.m., due to $Me_3P(OH)^+$.

The downfield shift of 16.0 p.p.m. for $Me_3P(OH)^+$ on going from 100% H_2SO_4 to 25 oleum is not unreasonable since the extent of protonation will depend on the acid strength of the solutions[148,149]. Hence the following reaction sequence can be postulated.

$$Me_3PBr^+ \xrightarrow[\text{25 oleum}]{\text{100\% } H_2SO_4} Me_3P(OH)^+$$

The adduct $Me_3PBr^+BBr_4^-$ showed a broad resonance at -64.5 p.p.m. in the ^{31}P n.m.r. spectrum. A solution spectrum in nitrobenzene gave a single peak at -66.2 p.p.m., in good agreement with the solid peak. The ^{11}B n.m.r. spectrum of the solid showed a broad peak at 55.7 p.p.m., whereas the solution spectrum in $PhNO_2$ gave a single peak at 39.4 p.p.m. The solution value is in good agreement with literature data[104-6], and the solid shift is very similar to that reported for Et_4NBBr_4[106].

A solution of the adduct in 25 oleum showed signals at -66.2(vs), -79.1(vw) and -114.6(m) p.p.m. The resonance at highest field was easily assigned to Me_3PBr^+, but the assignment of the other two peaks was not easy, since this compound is expected to show two peaks only, due to Me_3PBr^+ and the solvolysis product $Me_3P(OH)^+$. The peak at -114.6 p.p.m. could be assigned to $Me_3P(OH)^+$ although the shift is rather low. The weak resonance at -79.1 p.p.m. was unexpected and no attempt was made to assign it.

3. Conclusion.

25 oleum and 100% H_2SO_4 have proved to be useful solvents for phosphonium salts containing either inorganic and/or organic groups, enabling important structural information to be obtained in solution. ^{31}P n.m.r. spectroscopy has shown that the 'compound' $MePCl_2Br_2$ and Me_2PClBr_2 both contain a series of mixed cations $[MePCl_{3-n}Br_n^+]$ and $[Me_2PCl_{2-n}Br_n^+]$ respectively. Solvolysis of phosphorus-halogen bonds in these solvents has been found to occur, with the P-Br bond usually showing a greater tendency to solvolyse than the P-Cl bond in mixed compounds, as expected from the bond strengths. Direct exchange of the halogens (Cl, Br) between $Me_2PCl_2^+$ and $Me_2PBr_2^+$ in 25 oleum to form Me_2PClBr^+ has been established in this work. Direct exchange between phosphorus halides in these acidic media has not been reported before except in the presence of halide ions or hydrogen halide molecules[147].

Comparison of the results for bromo-phosphorus compounds with those for their chloro-analogues[30] suggests that solvolysis is faster for the former group in both 100% H_2SO_4 and 25 oleum. This is at least partly because the HBr liberated by partial solvolysis of either a bromo-phosphonium ion or a tetrabromoborate may then be oxidised by the solvent to give bromine and a sulphur (IV) species such as H_2SO_3, equations (7.1, 7.2), leading to a reduction in the acid strength and an increased rate of solvolysis.

$$2HBr + H_2SO_4 \longrightarrow Br_2 + H_2SO_3 + H_2O \qquad (7.1)$$

$$2HBr + H_2S_2O_7 \longrightarrow Br_2 + H_2SO_3 + H_2SO_4 \qquad (7.2)$$

Support for this conclusion is provided by the observation of liquid bromine or a bromine colour in several of the reactions described above. HCl on the other hand, is not oxidised to chlorine by sulphuric acid or oleum. A further factor is the greater bond strength of a P-Cl bond than of a P-Br bond, as mentioned above in the solvolysis of mixed species.

4. Experimental.

The preparation of $MePBr_2$.

$MePCl_2$ (19 mls, 0.2 mmoles)was placed in a two-necked flask. PBr_3 (13.5 mls, 0.2 mmoles)was then added and the solution stirred for 10 minutes. The mixture was distilled and the fraction which distilled over at 139 - 140°C was collected. Its ^{31}P n.m.r. spectrum showed a major peak at -184.0 p.p.m. ($MePBr_2$) with traces of PBr_3 (-227.4 p.p.m.) and MePBrCl (-190.0 p.p.m.)[36].

The preparation of $MePOBr_2$.

$MePBr_4$ (3 gm, 8.2 mmoles) was suspended in CH_2Cl_2. SO_2 was bubbled through until $MePBr_4$ had completely dissolved. The solvent was then removed in vacuo to yield a yellow liquid. The ^{31}P n.m.r. showed that the liquid was $MePOBr_2$ (δ -6.5 p.p.m.)[36].

The preparation of $MeP(O)Br_2/MeP(O)ClBr$ mixture.

A mixture of $MePBr_4$ and $MePClBr_3$ was suspended in CH_2Cl_2. SO_2 was bubbled through until a yellow solution formed. The solvent was removed in vacuo leaving a pale yellow liquid. Its ^{31}P n.m.r. spectrum consisted of two resonances at -25.8 p.p.m. (MeP(O)ClBr) and -6.5 p.p.m. ($MeP(O)Br_2$)[36].

The preparation of $Me_2P(O)Br$.

Me_2PBr_5 (3.51 g, 7.6 mmoles) was dissolved in CH_2Cl_2. SO_2 was bubbled into the above solution until the solution turned purple. The solvent was then removed in vacuo to isolate a dark red liquid. Its ^{31}P n.m.r. spectrum consisted of a single resonance at -72.6 p.p.m.

Sample Preparation.

Solutions for investigation were prepared in a dry box by placing the appropriate phosphorus compound in an n.m.r. tube and adding carefully the proper acid by a dropping pipette. In many instances instantaneous reaction occurred with elemental bromine being deposited on the bottom of the tube. For reliable results to be obtained, scrupulously anhydrous conditions were used to avoid any aerial hydrolysis. The samples were then monitored by ^{31}P n.m.r. The investigation was continued over varying periods of time depending on the particular reaction involved. Observation was stopped only when reaction had ceased, or after the course of the reaction had been established.

CHAPTER EIGHT

Azido- and cyano- derivatives of some organophosphorus (V) compounds.

1. Azido- derivatives of some organophosphorus (V) compounds.

(a) Introduction.

In spite of the fact that a number of fully-substituted azido- derivatives of organophosphorus compounds has been known for a long time[150], it was not until 1978 that detailed studies of likely mixed azido- halogeno- species or decomposition products were reported by Dillon et al[151]. Polymeric phosphazenes $(Br_2PN)_n$, $(C_6H_5(Cl)PN)_n$ and $((C_6H_5)_2PN)_n$ have been synthesised by reacting NaN_3 with the corresponding trivalent phosphorus halides at specific temperatures[152]. Photolysis with ultra violet light of hydrogen azide (HN_3) dissolved in phosphorus trichloride between 195 and 206 K gave a viscous liquid with the stoichiometry $(P_5N_8Cl_9)_4$[153]. No evidence for the formation of azido-substituted phosphorus (III) compounds was found in either case, although PCl_2N_3 was considered as a likely intermediate in the formation of the tetramer.

Dillon et al[154] have identified the complete series of azidochlorophosphates $PCl_{6-n}(N_3)_n^-$ in solution by ^{31}P n.m.r. spectroscopy. The azido-containing cations $(CH_3)_{4-n}P(N_3)_n^+$ [155] and $(C_6H_5)_{4-n}P(N_3)_n^+$ [156] ($0 \leqslant n \leqslant 4$) have also been described and their ^{31}P n.m.r. chemical shifts recorded[156,157].

(b) Azido- derivatives of monoethyl- and monophenyltrichlorophosphonium salts

When the salts $C_2H_5\overset{+}{P}Cl_3\overset{-}{S}bCl_6$ and $C_6H_5\overset{+}{P}Cl_3\overset{-}{S}bCl_6$ were treated with LiN_3 in CH_3NO_2 solution, resonances upfield from those of the starting materials were observed in the ^{31}P n.m.r. spectrum. These signals were readily assigned to the cationic species as in Table 8.1.

Table 8.1

δ ^{31}P (p.p.m.) of $C_2H_5PCl_{3-n}(N_3)_n^+$ and $C_6H_5PCl_{3-n}(N_3)_n^+$ ($0 \leqslant n \leqslant 3$) cations in CH_3NO_2

n	0	1	2	3
δ $C_2H_5PCl_{3-n}(N_3)_n^+$	-128.9	-92.0	-62.9	-51.6
δ $C_6H_5PCl_{3-n}(N_3)_n^+$	-103.3	-72.6	-51.6	-35.5

The chemical shifts for the monophenyltrichlorophosphonium species are in good agreement with those recorded by Platt[21] for the $C_6H_5PCl_3^+BCl_4^-$ salt, while the value of -35.5 p.p.m. for the fully-substituted cation is in excellent agreement with the value reported by Schmidt et al[156]. When this solution was re-investigated after four days, the ^{31}P n.m.r. spectrum showed a number of resonances at -103.3(w), -72.5(s), -51.6(m), -43.6(m), -32.4(w) and -21.1(w) p.p.m., the resonances at -43.6 and -21.1 p.p.m. being assumed to arise from a decomposition. The peak at -32.4 p.p.m. might also be due to decomposition product, although it could arise from $PhP(N_3)_3^+$. The solution of $C_2H_5PCl_{3-n}(N_3)_n^+$, on the other hand, gave a single resonance at -38.7 p.p.m., possibly due to the expected decomposition product $(C_2H_5(Cl)PN)_3$ or a related phosphazene.

(c) Azido- derivatives of dimethyl- and diethyldichlorophosphonium salts.

When LiN_3 was added to a CH_3NO_2 solution of $(CH_3)_2PCl_2^+SbCl_6^-$ or $(C_2H_5)_2PCl_2^+SbCl_6^-$, three peaks were observed in the ^{31}P n.m.r. spectrum. These were readily assigned to the $R_2PCl_{2-n}(N_3)_n^+$ $(0 \leqslant n \leqslant 2)$ cations as indicated in Table 8.2.

Table 8.2

δ ^{31}P (p.p.m.) of $R_2PCl_{2-n}(N_3)_n^+$ $(0 \leqslant n \leqslant 2)$ (R = CH_3 or C_2H_5) cations in CH_3NO_2

n	0	1	2
δ $(CH_3)_2PCl_{2-n}(N_3)_n^+$	-124.2	-100.0	-77.0
δ $(C_2H_5)_2PCl_{2-n}(N_3)_n^+$	-138.7	-108.0	-82.2

The chemical shift for the fully-substituted cation $(CH_3)_2P(N_3)_2^+$ was in good agreement with the value reported by Schmidt et al[156]. With the addition of more azide, the ^{31}P n.m.r. solution spectrum of $(C_2H_5)_2PCl_2^+$ showed a single resonance at -82.2 p.p.m., ascribed to the fully-substituted cation $(C_2H_5)_2P(N_3)_2^+$. This means that complete substitution of the azide into the $(C_2H_5)_2PCl_2^+$ cation can be achieved before any significant decomposition occurs. After four days the ^{31}P n.m.r. spectrum showed a further upfield resonance at -64.5 p.p.m. besides the -82.2 p.p.m. peak. This new peak was ascribed to a decomposition product $((C_2H_5)_2PN)_n$. When the $(CH_3)_2PCl_{2-n}(N_3)_n^+$ system was monitored after five days, its ^{31}P n.m.r. spectrum showed two peaks at -77.5(s) p.p.m. for the fully-substituted cation and -58.0(s) p.p.m., probably due to a decomposition product such as $((CH_3)_2PN)_n$.

(d) Azido- derivatives of $MePCl_4$.

When a solution of $MePCl_4$ in nitromethane was treated with LiN_3, a vigorous reaction occurred. The reaction was left to subside and the ^{31}P n.m.r. spectrum of the solution recorded. Two resonances were observed at -53.3(s) and -43.6(m) p.p.m., assigned to the $CH_3P(N_3)_3^+$ ion[156,157] and a decomposition product. After a week the solution was monitored and the spectrum showed only two resonances at -42.0(s) and -29.1(w) p.p.m., ascribed to the decomposition products.

(e) Azido- derivatives of $EtPCl_4$.

Addition of LiN_3 to a nitromethane solution of $EtPCl_4$ was accompanied by a vigorous reaction. The ^{31}P n.m.r. spectrum of the solution showed resonances downfield from that of the starting material, readily assigned to the azido- substituent species. These chemical shifts are given in Table 8.3, and are identical with those for the $SbCl_6^-$ salt given in Table 8.1.

Table 8.3

δ ^{31}P (p.p.m.) of $EtPCl_{3-n}(N_3)_n^+$ $(0 \leqslant n \leqslant 3)$ cations in CH_3NO_2

n	0	1	2	3
δ $C_2H_5PCl_{3-n}(N_3)_3^+$	-128.9	-92.0	-62.9	-51.6

When the spectrum of the same solution was re-recorded after a week, four resonances were observed at -59.6(s), -42.0(m), -25.8(m) and 6.5(w) p.p.m. These resonances probably arise from decomposition products, except the signal at -59.6 p.p.m. which might be due to the $C_2H_5PCl(N_3)_2^+$ cation.

(f) Reaction of LiN_3 with $PhPCl_5^-$.

A solution of $Et_4\overset{+}{N}PhPCl_5^-$ was prepared by the addition of excess Et_4NCl to a solution of $PhPCl_4$ in either methylene chloride or nitromethane. Treatment of this solution with NaN_3 or LiN_3 was accompanied by rapid decomposition in which a colourless gas was evolved. The reaction was left to subside and the solution spectrum recorded. Two resonances were observed at -43.6 and -35.5 p.p.m. With more azide, other peaks were observed at -29.0 and -19.4 p.p.m. besides the peak at -35.5, while the peak at -43.6 p.p.m. was no longer present. Further addition of LiN_3 resulted in the appearance of new peaks to higher field at -17.8, -12.9 and -9.8 p.p.m. When the solution spectrum was re-recorded the following day, the same number of peaks was observed with the same relative intensities. These peaks were assumed to arise from decomposition products as they are in the correct region for phenyl-substituted phosphonitrilic trimer derivatives[158]. The shifts are in good agreement with those of the decomposition product peaks from $PhPCl_{3-n}(N_3)_n^+$ cations recorded by Platt[21], except for the peak at -9.8 p.p.m. which was not visible in his spectrum.

(g) Reaction of $EtPCl_5^-$ and $MePCl_5^-$ with LiN_3.

Addition of LiN_3 to a solution of either $EtPCl_5^-$ or $MePCl_5^-$ (prepared by adding excess chloride to $EtPCl_4$ or $MePCl_4$ until a limiting shift was reached) in nitromethane was accompanied by rapid decomposition. In the case of $EtPCl_5^-$, a single peak was observed at -38.7 p.p.m. in the ^{31}P n.m.r. spectrum, while the $MePCl_5^-$ solution showed two resonances at -42.0 and -32.4 p.p.m. After six days, the ^{31}P n.m.r. spectrum of the $EtPCl_5^-$ solution showed three resonances at -38.7, -27.5 and -16.2 p.p.m., assumed to arise from decomposition products.

Replacement of a chlorine group by an organo-group (Me, Et or Ph) thus seems to enhance the decomposition of the azido- anions as compared with the relative kinetic stability of the hexa-azidophosphate ion and its precursors $PCl_{6-n}(N_3)_n^-$ $(0 \leqslant n \leqslant 5)$[154].

(h) Experimental.

All the reactions were carried out inside the glove box. A small amount of the compound under investigation was placed in an n.m.r. tube. A minimum amount of the requisite solvent was added, followed by cautious addition of the azide. For violent reactions, the reaction was allowed to subside before sealing the tube and recording the solution ^{31}P n.m.r. spectrum. Isolation of the azido- derivatives was not attempted because of their potential explosive nature.

The preparation of $Et_4\overset{+}{N}PhP\overset{-}{Cl_5}$.

$PhPCl_4$ (1.3124 g, 5.2 mmoles) and a stoichiometric amount of Et_4NCl (0.8688, 5.2 mmoles) were separately dissolved in CH_2Cl_2. The chloride solution was added to the $PhPCl_4$ solution with stirring. After complete addition of the chloride the solution was left to stir for 10 minutes. The solvent was then removed in vacuo to isolate a fine white solid.

Analysis

	C	H	N	P	Cl
Found	C = 39.86	H = 6.30	N = 3.14	P = 7.32	Cl = 42.50
Calculated	C = 40.43	H = 6.02	N = 3.37	P = 7.46	Cl = 42.72

The preparation of $PhP\overset{+}{Cl_3}Sb\overset{-}{Cl_6}$.

$PhPCl_4$ (2.4763, 9.9 mmoles) and antimony (V) chloride (1.3 ml, 9.9 mmoles) were separately dissolved in a small amount of methylene chloride. The antimony (V) chloride solution was added slowly to the $PhPCl_4$ solution with stirring. The solution mixture was left to stand for a few minutes. The white precipitate was then filtered, washed with methylene chloride and low boiling petroleum ether to isolate a fine white solid. Its solution in $PhNO_2$ gave a single peak at -103.4 p.p.m. No analysis was performed on this solid.

2. Reaction of $MePCl_5^-$ with the cyanide ion (CN).

Successive small amounts of AgCN were added to a strong solution of $Et_4N^+MePCl_5^-$ (prepared by adding excess Et_4NCl to a solution of $MePCl_4$) in CH_2Cl_2 and recording the ^{31}P n.m.r. spectrum after each addition. Resonances were observed upfield from the $MePCl_5^-$ signal, in addition to some signals from decomposition and hydrolysis products. From the changes in the relative intensities of the peaks in the six-coordinate region with the amount of cyanide added, it was possible to assign them to particular species, as shown in Table 8.7.

Table 8.7

$\delta\ ^{31}P$ (p.p.m.) for $MePCl_{5-n}(CN)_n^-$ ions in CH_2Cl_2 solution

n	0	1	2	3	4	5
$\delta\ ^{31}P$	204.7	217.7[a]	267.5	296.6	315.9	333.7
		224.0*			325.5	

* more abundant isomer

[a] see text.

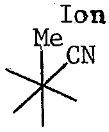
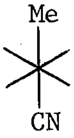
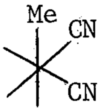
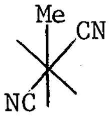
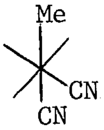
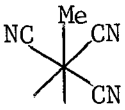
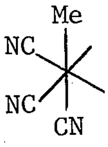
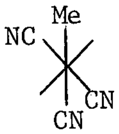
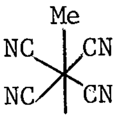
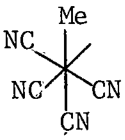
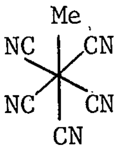
The initial spectrum of the mixture with a small amount of AgCN added did not show the peak at 217.7 p.p.m., but this was observed as a minor signal in one of the later spectra. There was some doubt as to whether it was genuine, but it could be due to the less abundant isomer of $MePCl_4(CN)^-$. Only one isomer was observed for n = 2 and 3, although there are three possible configurations in each case.

No attempt was made to isolate the various mixed chlorocyanides, but the reaction of $Et_4N^+MePCl_5^-$ with excess AgCN (1:> 5) in CH_2Cl_2 gave an orange solid which analysed as $Et_4NMeP(CN)_5$. Its CH_2Cl_2 solution spectrum consisted of a major peak at 333.7 p.p.m. and a minor impurity peak at -17.8 p.p.m. Its i.r. spectrum showed absorption bands at 2200(s), 2166(w) and 2060(m), characteristic of the C≡N bond. Reactions of various molar ratios of $MePCl_5^-$ with AgCN did not give a single anionic product. For instance a 1:2 reaction in CH_3NO_2 gave a number of peaks at 225.7(m), 269.1(vs), 298.2(m), 319.5(w) and 327.2(m) p.p.m., as well as some impurity signals. A 1:4 reaction in CH_3CN showed a number of resonances at 267.5(vs), 296.6(vs), 317.5(w) and 325.5(m) p.p.m., whereas a 1:5 molar ratio reaction of these compounds in CH_3CN gave a spectrum with resonances at 315.9(vs), 327.1(s) and 333.7(m) p.p.m., ascribed to the two isomers of $MePCl(CN)_4^-$ and $MeP(CN)_5^-$ respectively.

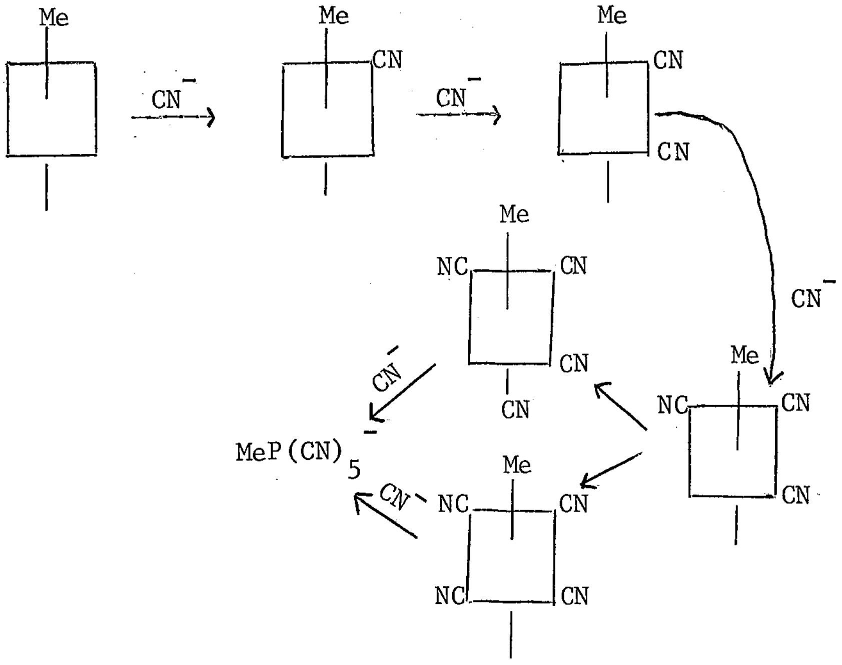
Table 8.8 gives the values of the ^{31}P chemical shifts, calculated via the approximation of Pairwise additivity, according to the method of Vladimirov and Malinowski[159]. In an octahedron, there are 12 interactions with at most six possible types for three different monodentate ligands A, B and C (A:A, A:B, A:C, B:B, B:C and C:C). In the case of $MePCl_4(CN)^-$, however, there are only four types of interactions, i.e. Cl:Cl, Me:Cl, CN:Cl and Me:CN. The Cl:Cl term was calculated as 24.85 p.p.m. from the shift of PCl_6^-, on the assumption that terms can be transferred from one octahedral complex to another. The Me:Cl term was similarly evaluated as 1.48 p.p.m. from the limiting shift of $MePCl_5^-$, and the CN:Cl term as 27.19 p.p.m. from the $PCl_{6-n}(CN)_n^-$ series[160]. The $MePCl_4(CN)^-$ ion can exist in two isomeric forms, with the CN^- either trans or cis to the methyl group. For a trans isomer, there are no Me:CN interactions and its chemical shift can then be calculated as 214.1 p.p.m., in reasonable agreement with the minor peak observed at 217.7 p.p.m. in one of the later ^{31}P n.m.r. spectra of the $MePCl_5^-/CN^-$ system. The shift at 224.0 p.p.m. is therefore assumed to be due to the cis isomer, enabling the Me:CN term to be evaluated as 13.74 p.p.m. If the CN:CN term is taken as 36.88 p.p.m. from the $PCl_{6-n}(CN)_n^-$ series[160], the shifts for all the other possible isomers may then be calculated as shown in column A of Table 8.8. It is apparent from the table that the calculated values are not in good agreement with the observed shifts for n = 2-5. The breakdown of this approach is perhaps not surprising, having been observed before by Platt[21] in the $PCl_{6-n}(CN)_n^-$ series and in related fluoro-systems with cyano-groups present, and may arise from distortion of the regular octahedral structure. Since the $MePCl_5^-$ ion is not completely associated in CH_2Cl_2 even in the presence of excess chloride ion, the chemical shift of the first substitute was checked in $PhNO_2$ also, in case the $MePCl_4(CN)^-$ ion dissociated to any extent in CH_2Cl_2, thus giving a low chemical shift and a low value for the Me:CN term. Pe_4NCl was added to a solution of $MePCl_4$ in $PhNO_2$ until the limiting shift of 204.7 p.p.m. was reached, and AgCN was then added. The ^{31}P solution spectrum contained a number of peaks at 198.2(s) ($MePCl_5^-$), 225.7(s), ascribed to cis-$MePCl_4(CN)^-$, 267.5(m), 298.2(ms), 317.5(s) and 335.3(m) p.p.m. Within experimental error the values are very similar for the two solvents, suggesting that the cyano-species are predominantly associated in solution. If the Me:CN value of 15.44 p.p.m. from the shift of $MePCl_4(CN)^-$ in $PhNO_2$ is used, the calculated shifts are as given in column B of Table 8.8. This gives a marginal improvement for the species where n = 2, 3 or 4, but even poorer agreement than before for n = 5. Alternatively if the Me:CN term is taken as 13.74 p.p.m. and the experimental shift for $MeP(CN)_5^-$ then used to obtain a revised value for the CN:CN term of 34.84 p.p.m., the values given in column C are obtained, which give a poorer fit than column A for n = 2, 3 and 4. Despite these limitations, some deductions can be made from the data. The results suggest that $MePCl_3(CN)_2^-$ probably has the first structure shown in Table 8.8, with cis cyano-groups and a chlorine trans to the methyl group since this isomer has the highest calculated shift. Similarly, the most probable isomer for $MePCl_2(CN)_3^-$ is the one with three cyano- groups cis to the methyl, since this isomer has the highest calculated shift. Both isomers of $MePCl(CN)_4^-$ were detected, and the initially more abundant isomer (δ315.9 p.p.m.) may be the one with the additional CN trans to the methyl group, although the values calculated from pairwise interactions are quite close in this instance.

Table 8.8

$\delta\ ^{31}P$ (p.p.m.) predicted from Pairwise interactions for $MePCl_{5-n}(CN)_n^-$ ions

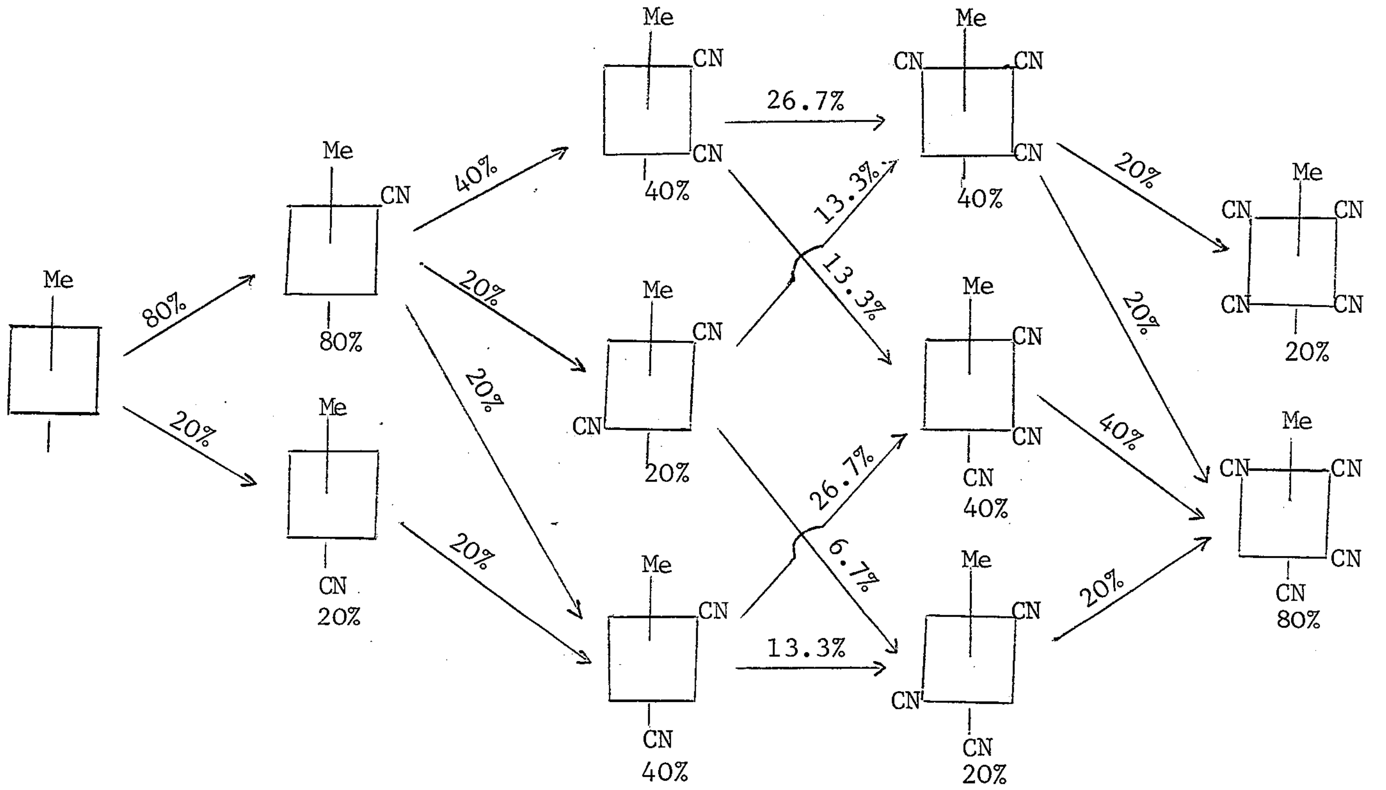
Ion	Calculated $\delta\ ^{31}P$ (p.p.m.)			Experimental $\delta\ ^{31}P$ (p.p.m.)
	A	B	C	
	224.0	225.7	224.0	224.0
	214.1	214.1	214.1	217.4
	250.6	254.0	248.6	267.5
	243.3	246.7	243.3	
	240.7	242.4	238.7	
	277.3	282.4	273.2	
	274.7	278.1	268.6	296.6
	267.3	270.7	263.3	
	311.2	318.0	303.1	325.5
	308.7	313.8	298.5	315.9
	350.0	356.8	333.5	333.7

These conclusions are supported by a statistical consideration of the system, as shown in Fig. 8.1. The cis isomer of $MePCl_4(CN)^-$ is more likely to be formed than the trans isomer, since there are four P-Cl bonds cis and only one trans to the methyl group. The experimental results indicate that one isomer of $MePCl_4(CN)^-$ is formed almost exclusively. Only one isomer was detected for $MePCl_3(CN)_2^-$, and the statistically more probable configuration starting from cis $MePCl_4(CN)^-$ is with the two cyano-groups cis and Cl trans to methyl. Substitution into this isomer leads preferentially to the isomer of $MePCl_2(CN)_3^-$ with all the cyano-groups in the equatorial plane. Again only one species was observed, for which this structure has been deduced from pairwise additivity. Both isomers of $MePCl(CN)_4^-$ are now equally likely to be formed by substitution into this starting material, and both were observed, although not in equal quantities. While the results indicate that the statistical predictions are not followed exactly, since all isomers would then be seen, and that the methyl group and/or the cyano-groups may therefore exert directive effects leading to the preferential formation of particular isomers, the structural deductions are entirely compatible from the two approaches. The suggested pattern of substitution is thus as shown in scheme 8.1.



Scheme 8.1

Fig. 8.1. Statistical Pattern of Substitution in the MePCl$_5^-$/CN$^-$ System



3. Reaction of cyanide with $Et_4NPhPCl_5$.

$Et_4N^+PhPCl_5^-$ was prepared by adding an excess of Et_4NCl to a solution of $PhPCl_4$ in CH_2Cl_2. Small amounts of AgCN were then added and the ^{31}P n.m.r. spectrum recorded after each addition. New resonances were observed upfield from the $PhPCl_5^-$ signal. These peaks were assigned as in Table 8.9 from the changes in their relative intensities with the quantity of cyanide added.

Table 8.9

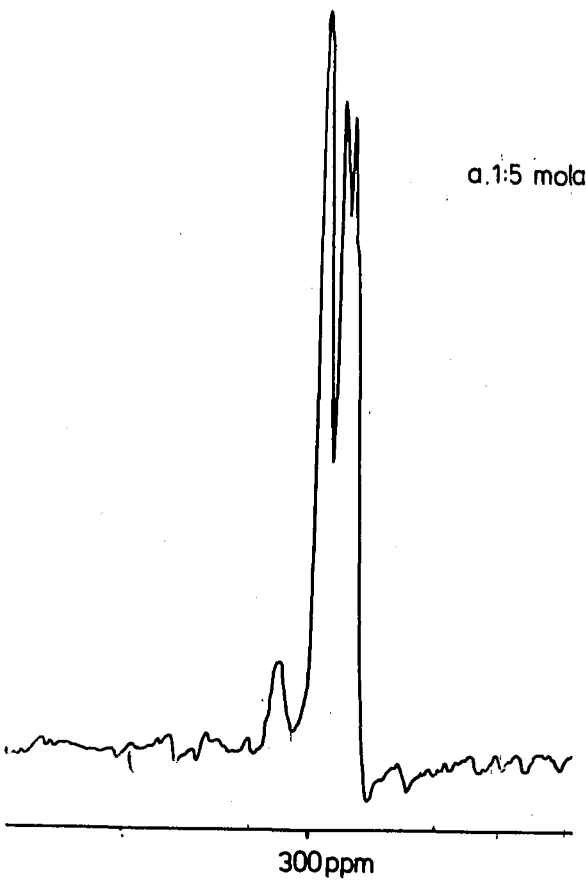
δ ^{31}P (p.p.m.) for $PhPCl_{5-n}(CN)_n^-$ ions in CH_2Cl_2 solution

n	0	1	2	3
δ ^{31}P	172.6	224.4	259.5	299.8
			277.3*	309.5
			285.3	314.2

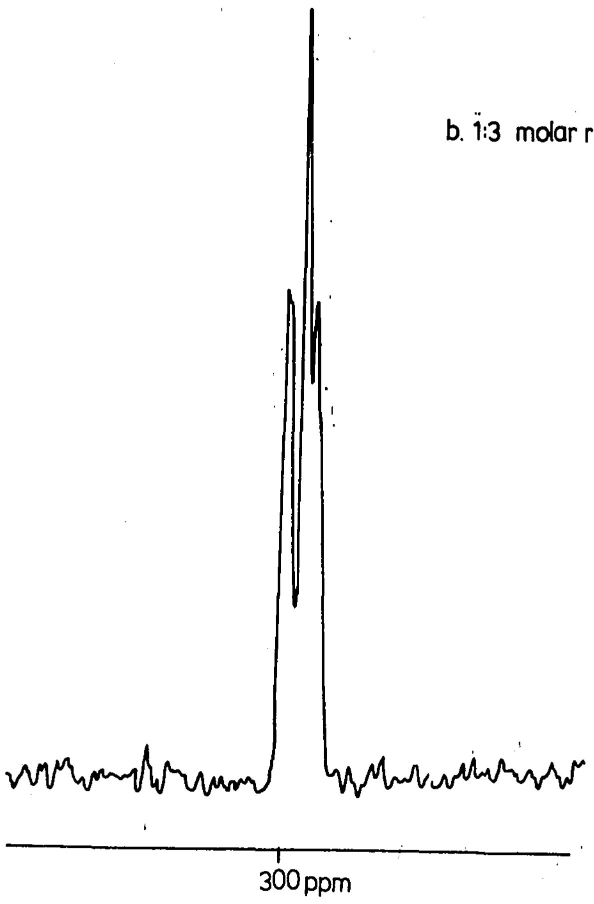
* observed in a redissolved solution of $PhPCl_3(CN)_2^-$

In solutions with a small amount of AgCN present the resonance at 259.5 p.p.m. was more intense than that at 285.3 p.p.m., but the latter became much more intense than the former with the addition of more cyanide, as the intensity of the signal at 224.4 p.p.m. declined. This behaviour is discussed below. The anions were relatively stable in solution and attempts were made to isolate some of them. The reaction of $PhPCl_5^-$ with AgCN in a 1:2 ratio in CH_2Cl_2 gave fine crystals which analysed approximately as $PhPCl_3(CN)_2^-$. When they were redissolved in CH_2Cl_2 and their ^{31}P n.m.r. spectrum recorded, a number of resonances were observed at 227.3(m), 262.8(s), 277.3(mw), 288.6(w), 302.9(s), 311.1(ms) and 314.1(ms) p.p.m., ascribed to the cis isomer of $PhCl_4(CN)^-$, the three isomers of $PhPCl_3(CN)_2^-$ and the three isomers of $PhPCl_2(CN)_3^-$ respectively. A 1:3 molar ratio reaction of $PhPCl_5^-$ and AgCN in CH_2Cl_2 gave fine crystals which when redissolved in CH_2Cl_2 gave resonances at 301.5(s), 309.5(vs) and 314.2(s) p.p.m. in the ^{31}P n.m.r.

Fig. 8.2 ^{31}P nmr spectra of $Et_4N^+PhPCl_2(CN)_3$



a. 1:5 molar reaction



b. 1:3 molar reaction

spectrum. These peaks were assigned to the three possible isomers of the expected anion $PhPCl_2(CN)_3^-$. Substitution of cyanide into $PhPCl_5^-$ seems to stop at $PhPCl_2(CN)_3^-$. This was confirmed by the product isolated from a 1:5 molar ratio reaction of $PhPCl_5^-$ with AgCN in CH_2Cl_2. The crystals which were isolated showed three resonances at 301.5(vs), 309.5(s) and 314.2(s) p.p.m. in the ^{31}P n.m.r. spectrum when re-dissolved in CH_2Cl_2. These signals are identical in shift to the ones obtained from a 1:3 molar ratio reaction although they differ in relative intensity (Fig. 8.2), and are assigned to the three isomers of $PhPCl_2(CN)_3^-$. Analysis also confirmed that the product was $Et_4NPhPCl_2(CN)_3$. The i.r. spectra of the two products showed a marked resemblance except for minor differences in the region below 400 cm^{-1} (Table 8.10). This is expected since the relative amounts of the isomers were different in the two compounds as observed in the ^{31}P n.m.r. spectra above.

Table 8.10

I.r. spectra of some $PhPCl_{5-n}(CN)_n^-$ ions (650 - 250 cm^{-1})

$Et_4N^+PhPCl_5^-$		614(mw), 586(mw), 562(s), 540(s), 510(s), 450(w), 400Br, 320(v), 294(s), 280(w), 260(w)
$Et_4N^+PhPCl_3(CN)_2^-$		620(vw), 580(s), 550(s), 530(v), 512(w), 500(vw), 490(w), 454(s), 430(s), 404(m), 390(m), 380(s), 340(m), 320(m), 280Br
$Et_4N^+PhPCl_2(CN)_3^-$	(a)	620(vw), 582(s), 550(s), 530(m), 500(vw), 490(w), 460(s), 430(s), 390(s), 380(m), 340(m), 320(s), 280Br
	(b)	620(m), 590(vs), 560(s), 538(s), 502(w), 490(m), 460(m), 434(s), 400(vw), 380(s), 326(m), 280(w)

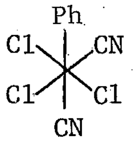
(a) isolated from a 1:3 molar ratio reaction

(b) isolated from a 1:5 molar ratio reaction

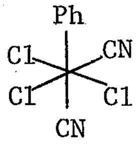
The $PhPCl_5^-$ - CN^- system clearly differs in several respects from the $MePCl_5^-$ - CN^- system. More of the possible isomers are observed in the phenyl series, and substitution appears to stop at the $PhPCl_2(CN)_3^-$ stage, just as in the PCl_6^- - CN^- system where the two isomers of $PCl_3(CN)_3^-$ are very stable and resistant to further substitution[21]. This stability was attributed to the position of CN^- in the spectrochemical series, which could lead to a lowering in energy of the unoccupied 3d t_{2g} orbitals on phosphorus and hence to P-Cl π-bonding by donation from filled orbitals on Cl [16]. Like $PCl_3(CN)_3^-$ the $PhPCl_2(CN)_3^-$ ion proved to be resistant to hydrolysis, and its ^{31}P n.m.r. spectrum was unchanged by exposure to the laboratory atmosphere for 4 hours. The phenyl group is capable of taking part in π-bonding, unlike the methyl group, and this tendency, together with their differing electronic effects, may possibly account for the difference in reactivity between $MePCl_2(CN)_3^-$ and $PhPCl_2(CN)_3^-$.

The observations that chemical shifts are in general higher for a given value of n in the $PhPCl_{5-n}(CN)_n^-$ series than in the $MePCl_{5-n}(CN)_n^-$ series, and that the Ph:Cl pairwise additivity term as deduced from the limiting shift of $PhPCl_5^-$ [14] is even smaller (1.05 p.p.m.) than the Me:Cl term, suggest that the Ph:CN term should be appreciably larger than the Me:CN term, even though the experimental shifts for the predominant isomers of the first substitute $RPCl_4(CN)^-$ are very similar. Accordingly the Ph:CN term was derived as 26.2 p.p.m. from the value of 314.2 p.p.m. for the isomer of $PhPCl_2(CN)_3^-$ with the highest shift, which was assumed to have the structure with three coplanar CN groups and Cl trans to phenyl. The shifts calculated on this basis and using the Cl:Cl, Cl:CN and CN:CN terms from the $PCl_{6-n}(CN)_n^-$ series[160] are given in column A of Table 8.11. A second set of values was derived by taking the weighted average for the Ph:CN term from the shifts of the three isomers of $PhPCl_2(CN)_3^-$, and these are presented in column B. Although the numerical agreement is only moderate, the data again enable some structures to be deduced. The single isomer detected for $PhPCl_4(CN)^-$ is assigned a cis configuration since this is the most probable product, although the experimental shift is between the calculated values for the cis and trans isomers. The experimental value could be rather low if the $PhPCl_4(CN)^-$ ion dissociates to any extent, like $PhPCl_5^-$ in CH_2Cl_2, so the experiment was repeated in $PhNO_2$ as solvent, by adding AgCN to a solution of $Et_4N^+PhPCl_5^-$ in the presence of excess Et_4NCl. Resonances at 225.7(s), 262.8(mw), 286.9(m), 302.9(s), 309.5(s) and 314.2(ms) p.p.m. were observed in the six-coordinate region, in general in good agreement within experimental error with the shift values in CH_2Cl_2. Thus either the cyano- complexes are essentially associated in both solvents, or else the $PhPCl_4(CN)^-$ ion dissociates to a similar extent in CH_2Cl_2 and $PhNO_2$. (A shift value of 227.3 p.p.m. was obtained for the first substitute in one or two instances.)

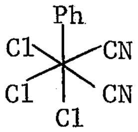
The two signals (259.5, 285.3 p.p.m.) assigned to isomers of $PhPCl_3(CN)_2^-$ from the substitution reaction are interesting in that the signal at 259.5 p.p.m. was initially more intense, but the one at 285.3 p.p.m. increased rapidly in intensity with the addition of more cyanide, as the intensity of the signal at 224.4 p.p.m. decreased. A possible explanation is that both isomers of $PhPCl_4(CN)^-$ are initially formed but the trans isomer is not detected in solution because it is rapidly substituted by more CN^- to give the isomer



of $PhPCl_3(CN)_2^-$, with a shift of 259.5 p.p.m. Substitution into cis - $PhPCl_4(CN)^-$ then leads predominantly to the isomer of $PhPCl_3(CN)_2^-$ with two cis CN groups and Cl trans to phenyl (δ 285.3 p.p.m.) as shown by the statistical treatment which is identical for reaction of cyanide with $MePCl_5^-$ or $PhPCl_5^-$. Some support for this hypothesis is provided by the pairwise calculations, which give the nearest value to 259.5 p.p.m. for



and the nearest value to 285.3 p.p.m. for

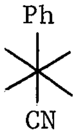
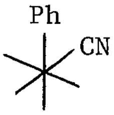
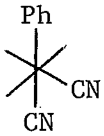
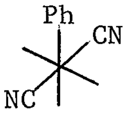
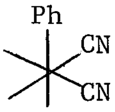
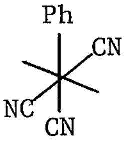
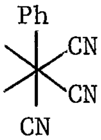
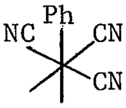


A small peak at 277.3 p.p.m. observed in the spectrum of the re-dissolved 1:2 reaction product is assigned to the third isomer of $PhPCl_3(CN)_2^-$, in keeping with the intermediate shift value calculated from pairwise additivity. All three isomers of $PhPCl_2(CN)_3^-$ were observed, and the structures are assigned as shown in Table 8.11 on the basis of the pairwise calculations.

The breakdown of the pairwise additivity method in this system is probably again due to large distortions from octahedral symmetry about the phosphorus atom as more CN groups are introduced. This approach assumes that the Cl:Cl interaction in PCl_6^- can be treated as being the same as in the anions $PhPCl_3(CN)_2^-$, $PhPCl_2(CN)_3^-$, etc., i.e. that terms can be transferred from one six-coordinate compound to another and that the successive replacement of Cl^- by CN^- does not affect the Cl:Cl or Ph:Cl values. This may not necessarily be true, although terms have been successfully transferred in other six-coordinate systems previously, such as the PCl_5py-N_3^- series where the Cl:Cl, Cl:N_3 and N_3:N_3 terms were taken from the PCl_6^- - N_3^- system[161], and the $NbCl_nBr_{5-n}MeCN$ series where Cl:Cl, Cl:Br and Br:Br terms were transferred from the $NbCl_{6-n}Br_n^-$ system[57].

Table 8.11

δ ^{31}P (p.p.m.) predicted from pairwise interactions for $PhPCl_{5-n}(CN)_n^-$ ions

Ion	Calculated δ ^{31}P (p.p.m.)		Experimental δ ^{31}P (p.p.m.)
	A	B	
	212.4	212.4	224.4
	235.2	237.9	
	251.9	254.6	259.5
	267.3	272.7	277.3
	274.7	280.1	285.3
	291.4	296.8	299.8
	298.8	304.2	309.5
	314.2	322.3	314.2

4. Experimental.

The preparation of $Et_4N^+MeP(CN)_5^-$.

$Et_4NMePCl_5$ (3.318 g, 9.4 mmoles) was dissolved in CH_3NO_2. AgCN (6.484 g, 48.4 mmoles) was added with stirring. The solution was left to stir for 1 hour. The orange solution was filtered and the solvent removed in vacuo to isolate an orange solid.

Analysis

Found C = 54.81 H = 9.71 N = 26.22 P = 9.90

Calculated C = 54.90 H = 7.52 N = 27.45 P = 10.13

The attempted preparation of $Et_4N^+PhPCl_3(CN)_2^-$.

$Et_4NPhPCl_5$ (1.651 g, 3.97 mmoles) was dissolved in a small amount of CH_2Cl_2. AgCN (1.0814 g, 8.07 mmoles) was added with stirring. The solution was left to stir for 1 hour and filtered. The volume of the solvent was reduced in vacuo and the solution placed in the fridge. Fine crystals formed. These were filtered off and washed with low boiling petroleum ether.

Analysis

Found C = 48.00 H = 6.82 N = 9.96 P = 8.2 Cl = 25.78

Calculated C = 48.42 H = 6.31 N = 10.59 P = 7.8 Cl = 26.86

The preparation of $Et_4N^+PhPCl_2(CN)_3^-$.

$Et_4NPhPCl_5$ (4.97 g, 11.96 mmoles) was dissolved in CH_2Cl_2. AgCN (4.815 g, 35.96 mmoles) was added with stirring. The solution was left to stir for 2 hours and then filtered. The volume of the solvent was reduced in vacuo and the remaining solution placed in a fridge. Fine white crystals were formed. These were filtered off and washed with $^{30}/40$ Pet. ether.

Analysis

Found C = 54.03 H = 7.16 N = 13.54 P = 8.20 Cl = 14.40

Calculated C = 52.71 H = 6.46 N = 14.47 P = 8.01 Cl = 18.35

The attempted preparation of $Et_4\overset{+}{N}PhP(CN)_5^-$.

$Et_4NPhPCl_5^-$ (3.8476 g, 9.3 mmoles) was dissolved in CH_2Cl_2. AgCN (6.2043 g, 46.3 mmoles) was added with stirring. The solution was left to stir for about 2 hours and then filtered. The amount of the solvent was reduced in vacuo and the solution placed in the fridge. The fine white crystals which formed were filtered off and washed with $^{30}/40$ Pet. ether. These analysed approximately as $Et_4\overset{+}{N}PhCl_2(CN)_3^-$.

Analysis

Found C = 51.95 H = 8.48 N = 17.21 P = 8.10 Cl = 16.80

Calculated C = 52.71 H = 6.46 N = 14.47 P = 8.01 Cl = 18.35

CHAPTER NINE

Conclusions and discussion.

The alkyl-substituted phosphoranes $MePCl_4$ and $EtPCl_4$ have been shown to possess acceptor properties towards chloride and pyridine ligands. The chloride adducts were found to dissociate to some extent in solution, showing that an equilibrium exists between the parent compound and the phosphate ion.

$$RPCl_4 + Cl^- \rightleftharpoons RPCl_5^- \text{ (R = Me or Et)} \qquad (1)$$

The introduction of more than one alkyl group into the compounds $R_nPCl_{4-n}^{+}Cl^{-}$ reduces the acceptor abilities to such an extent that no detectable adduct formation occurs. This is presumably due mainly to the inductive effects of the organo-groups. The acceptor properties of the chlorophosphonium salts $[RPCl_3]^+[SbCl_6]^-$ towards bidentate pyridines have been systematically examined and six-coordinate adducts which exist in two isomeric forms have been found.

No addition compounds of phenyltetrabromophosphorane have been reported. Addition of bromide ion to its solution in either methylene chloride or acetonitrile resulted in its decomposition to $PhPBr_2$ and the tribromide ion. It does not form adducts with mono- or bidentate pyridines, but the complex $Ph\overset{+}{P}Br_3\overset{-}{B}Br_4$ has been found to possess acceptor properties towards the bidentate ligands 2,2'-bipyridine and 1,10-phenanthroline.

The catechyl derivatives of phosphorus (V) bromide, $catPBr_3$ and cat_2PBr exhibit acceptor properties towards mono- and bidentate pyridines, unlike PBr_5 and $PhPBr_4$, for which no six-coordinate adducts have been reported. The acceptor properties of PBr_5 have not as yet been investigated but it is unlikely to form-six-coordinate compounds mainly because it is unstable with respect to PBr_3 and bromine in organic solvents. The ability of catechyl groups to enhance the acceptor properties of phosphorus (V) bromides is probably due to a number of factors. The six-coordinate species will show less geometric strain than their five-coordinate precursors, since the catechyl groups like to be planar and this can be achieved in an octahedron more readily than in a trigonal bipyramidal or square pyramidal structure[17]. The oxygens of the catechyl groups are also more electron-withdrawing than either aryl groups or bromines, facilitating nucleophilic attack at phosphorus. There may also be less steric hindrance from a firmly-held chelated ligand than from aromatic groups such as phenyl, although this factor is unlikely to be of major importance.

Compounds of the type $RP(CN)_2$ (R = Me, Et, Ph) possess acceptor properties towards the halide and pseudo-halide ions X (X = Cl, Br, I or SCN), but undergo reductive elimination when reacted with cyanides to give $RP(CN)^-$ and cyanogen. On the other hand $t\text{-}BuP(CN)_2$, R_2PCN and $RPCl_2$ show no tendency to form adducts with the above-mentioned ligands, except $RPCl_2$ (R = Me or Ph) which reacts with cyanide (CN^-) to give $RP(CN)^-$ as the ultimate product. The inability of these compounds to form adducts is again probably due to the inductive effects of the organo-groups.

25 oleum and 100% H_2SO_4 have proved very useful solvents for phosphonium salts with either inorganic and/or organic groups present, enabling important structural deductions to be made in solution. ^{31}P nuclear magnetic resonance spectroscopy has revealed that the 'compounds' $MePCl_2Br_2$ and Me_2PClBr_2 both contain a series of mixed cations $[MePCl_{3-n}Br_n^+]$ and $[Me_2PCl_{2-n}Br_n^+]$ respectively. Solvolysis of phosphorus - halogen bonds in these solvents has been shown to occur, with the P-Br bond usually having a greater tendency to solvolyse than the P-Cl bond in mixed compounds, as expected from the bond strengths. Direct halogen (Cl, Br) exchange between $Me_2PCl_2^+$ and $Me_2PBr_2^+$ in 25 oleum to form Me_2PBrCl^+ has been established for the first time. Halogen exchange has not been observed before in these acidic media except in the presence of halide ions or hydrogen halide molecules[147].

Comparison of the results for bromo-phosphorus compounds with those for their chloro-analogues[30] in these highly acidic media suggests that solvolysis is much more pronounced for the former group in both 100% H_2SO_4 and 25 oleum. This is at least partly because the hydrogen bromide liberated by partial solvolysis of either a bromo-phosphonium ion or a tetrabromoborate ion may then be oxidised by the solvent to give bromine and a sulphur (IV) species such as H_2SO_3, resulting in a reduction in the acid strength and an increased rate of solvolysis. Support for this conclusion is provided by the observation

$$\text{P-Br} + H_2SO_4 \longrightarrow \text{P-OH} + HBr + SO_3 \tag{2}$$

$$2HBr + H_2SO_4 \longrightarrow Br_2 + H_2SO_3 + H_2O \tag{3}$$

$$\text{or } 2HBr + H_2S_2O_7 \longrightarrow Br_2 + H_2SO_3 + H_2SO_4 \tag{4}$$

of liquid bromine or a bromine colour in several of the reactions described in Chapter Seven. Hydrogen chloride on the other hand, is not oxidised to chlorine by sulphuric acid or oleum. A further factor is the greater bond strength of a P-Cl bond compared to a P-Br bond, as mentioned above.

Stepwise addition of azide to methylene chloride or nitroethane solutions of the organophosphate ions $MePCl_5^-$, $EtPCl_5^-$ and $PhPCl_5^-$ yielded decomposition products only, whereas cyanides give the fully substituted ion $MeP(CN)_5^-$ from $MePCl_5^-$, as well as the intermediate species. In the case of $PhPCl_5^-$ substitution by CN^- seems to stop at $PhPCl_2(CN)_3^-$.

The present work has shown that ^{31}P n.m.r. spectroscopy is an invaluable tool for the investigation of phosphorus-containing species, although the final structural proof, especially in cases of ambiguity, may rest on other methods such as Raman and i.r. spectroscopy, and, for isolable compounds, elemental analysis and (for chloro- compounds) ^{35}Cl n.q.r. spectroscopy.

Future work.

The acceptor properties of organophosphorus (III) compounds have not been intensively studied and much remains to be done in this field. The Lewis acidity of compounds such as $MeP(NCS)_2$ and $MeP(NCO)_2$ towards the halides or pseudo-halides X (X = Cl, Br, I, NCS or NCO) can be investigated and compared with the acceptor properties of $RP(CN)_2$ (R = Me, Et or Ph) studied in this work and with the work of Platt on PX_3 [21] (X = NCS, NCO or CN) compounds. The compounds $RP(CN)_2$ (R = Me, Et or Ph) have been shown to add on NCS^- and may well react also with the cyanate ion to give $RP(CN)_2NCO^-$, for which O- and N-bonded isomers are possible. All thiocyanato- derivatives of phosphorus so far reported seem to be bonded through nitrogen.

The $RP(CN)^-$ (R = Me, Et or Ph) anions have only been isolated as viscous liquids, although the $MeP(CN)^-$ salt solidified on standing. The introduction of a more electronegative group into the organo-group R, e.g. $ClCH_2P(CN)^-$ or $CF_3P(CN)^-$, may enhance the stability of these species and could possibly lead to their isolation as solids. Similarly the presence of an electronegative group might stabilize better $RP(CN)_2X^-$ compounds, some of which have either been isolated in this work as liquids or have tended to dissociate to some extent in solution.

Reaction of $RP(CN)_2$ (R = Me, Et or Ph) with halogens or pseudo-halogens may be interesting, since the probable oxidation products can exist in different isomeric forms such as $RP(CN)_2Cl^+Cl^-$, $RPCl_2(CN)^+CN^-$ or $RP(CN)_2Cl_2$ (molecular) in the case of reaction with chlorine. The oxidation of $RP(CN)^-$ (R = Me, Et or Ph) anions with halogens, interhalogens or pseudo-halogens also merits further investigation, and may lead to unusual phosphorus (III) and phosphorus (V) products.

Substitution of NCO^-, NCS^- or CN^- (in the case of $EtPCl_5^-$) into the $RPCl_5^-$ anions (R = Me, Et or Ph) can be investigated and compared with the results for the cyano- and azido- analogues obtained in this work.

The reactions of organofluorophosphorus (V) species such as RPF_5^- or $RPF_{5-n}Cl_n^-$ with pseudo-halides could also be studied. Since the P-F bond is strong, direct substitution into RPF_5^- is unlikely, but ions of this type may undergo exchange reactions with phosphorus (III) or phosphoryl pseudo-halides[21]. The preparation of the mixed species $RPF_{5-n}Cl_n^-$ might pose some synthetic problems, but these ions are likely to undergo substitution reactions in which Cl is replaced by pseudo-halides such as N_3^-, CN^- or NCS^-. Organofluorophosphates could be studied in solution by ^{19}F as well as ^{31}P n.m.r. spectroscopy, which would help in assigning configurations to the isomers observed.

APPENDIX ONE

Departmental colloquia and first-year induction course for post-graduates. The colloquia marked (*) were the ones attended by the author.

1. University of Durham chemistry colloquia.

Academic year 1978-1979.

12 December.	Professor C.J.M. Stirling (University of Bangor), "Parting is such sweet sorrow - the leaving group in organic chemistry".
31 January.	Professor P.D.B. de la Mare (University of Auckland, New Zealand), "Some pathways leading to electrophilic substitution".
*14 February.	Professor B. Dunnel (University of British Columbia), "The application of n.m.r. to the study of motions of molecules in solids".
14 March.	Dr. J.C. Walton (University of St. Andrews), "Pentadienyl radicals".
28 March.	Dr. A. Reiser (Kodak Ltd.), "Polymer photography and the mechanism of cross-link formation in solid polymer matrices".
25 April.	Dr. C.R. Patrick (University of Birmingham), "Chlorofluoro carbons and stratospheric ozone: an appraisal of the environmental problem".
1 May.	Dr. G. Wyman (European Research Office, U.S. Army), "Excited state chemistry of indiqoid dyes".
2 May.	Dr. J.D. Hobson (University of Birmingham), "Nitrogen-centred reactive intermediates".
*8 May.	Professor A. Schmidpeter (Institute of Inorganic Chemistry, Munich University), "Five-membered phosphorus heterocycles containing dicoordinate phosphorus".
9 May.	Professor G. Maier (Lahn Giessen University), "Tetra-tert-butyltetrahedrane".

9 May.	Dr. A.J. Kirkby (University of Cambridge), "Structure and reactivity in intramolecular and enzymic catalysis".
*16 May.	Dr. J.F. Nixon (University of Sussex), "Some recent developments in platinum-metal phosphine complexes".
23 May.	Dr. B. Wakefield (University of Salford), "Electron transfer in reaction of metals and organometallic compounds with polychloropyridine derivatives".
13 June.	Professor I. Ugi (University of Munich), "Synthetic uses of super nucleophiles".
25 September.	Professor R. Soulen (South Western University, Texas), "Applications of HSAB theory to vinylic halogen substitution reactions and a few copper coupling reactions".

Academic year 1979-1980.

21 November.	Dr. J. Müller (University of Bergen), "Photochemical reactions of ammonia".
28 November.	Dr. B. Cox (University of Stirling), "Macrobicyclic cryptate complexes: dynamics and selectivity".
5 December.	Dr. G.C. Eastmand (University of Liverpool), "Synthesis and properties of some multicomponent polymers".
12 December.	Dr. C.I. Ratcliffe, "Rotor motions in solids".
*18 December.	Dr. K.E. Newman (University of Lausanne), "High pressure multinuclear n.m.r. in the elucidation of mechanism in fast simple inorganic reactions".
30 January.	Dr. M. Barrow (University of Edinburgh), "The structures of some simple inorganic compounds of silicon and germanium-pointers to structural trends in group IV".
6 February.	Dr. J.M.E. Quirke (University of Durham), "Degradation of chlorophyll- in sediments".

23 April.	B. Grievson B.Sc. (University of Durham), "Halogen radiopharmaceuticals".
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 (University of Swansea), "Medium and structural effects on solvolytic reactions".
10 July.	Professor D. Des Marteau (University of Heidelberg), "New developments in organonitrogen fluorine chemistry".

Academic year 1980-1981.

19 September.	Dr. C.D. Wagner (University of Berkeley, California), "Identification of chemical states by spectral features in ESCA".
8 October.	Professor T. Fehlner (Notre Dame University, Indiana, U.S.A.), "Metalloboranes - cages or coordination compounds".
15 October.	Dr. R. Alder (University of Bristol), "Doing chemistry inside cages - medium ring bicyclic molecules".
*12 November.	Dr. M. Gerloch (University of Cambridge), "Magneto-chemistry is about chemistry".
19 November.	Dr. T. Gilchrist (University of Liverpool), "Nitroso-olefins as synthetic intermediates".
*3 December.	Dr. J. Connor (University of Manchester), "Thermochemistry of transition metal compounds".
18 December.	Dr. R.F. Evans (University of Brisbane, Australia), "Some recent communications to the editor of Australian Journal of failed chemistry".
4 February.	Professor S.F.A. Kettle (University of East Anglia), "Variations in the molecular dance at the crystal ball".

25 February.	Dr. K. Bowden (University of Essex), "The transmission of polar effects of substituents".
*4 March.	Dr. S. Cradock (University of Edinburgh), "Pseudolinear pseudohalides".
11 March.	Dr. J.F. Stoddart (I.C.I. Ltd./University of Sheffield), "Stereochemical principles in the design and function of synthetic molecular receptors".
*17 March.	Professor W. Jencks (Brandeis University, Massachusetts, "When is an intermediate not an intermediate"?
*18 March.	Dr. P.J. Smith (International Tin Research Institute), "Organotin compounds - a versatile class of organometallic derivatives".
6 May.	Professor M. Szwarc F.R.S. (University of California), "Mechanisms of ionic polymerisation, living and dormant polymers".
10 June.	Dr. J. Rose (I.C.I. Plastic Division), "New engineering plastics".
17 June.	Dr. P. Moreau (University of Montpellier), "Recent results in perfluoroorganometallic chemistry".
24 June.	Dr. S.A.R. Knox (University of Bristol), "Coordination and reactivity of organic species at dinuclear metal centres".
26 June.	Professor A.P. Schaap (Office of U.S. Naval Research, London), "Mechanisms of chemiluminescence and photooxygenation".

2. Durham University Chemical Society.

Academic year 1978-1979.

10 October.	Professor H.C. Brown (Purdue University), "The tool of increasing electron demand in the study of cationic processes".

*19 October.	Mr. F.C. Shenton (Public Analyst, Co. Durham), "There is death in the pot".
26 October.	Professor W.J. Albery (Imperial College, London), "Photogalvanic cells for solar energy conversion".
9 November.	Professor A.R. Katritzky (University of East Anglia), "Some adventures in heterocyclics".
16 November.	Dr. H.C. Fielding (Mond Division, I.C.I.), "Fluorochemical surfactants and textile finishes".
23 November.	Dr. C. White (Sheffield University), "The magic of chemistry".
18 January.	Professor J.C. Robb (Birmingham University), "The plastics revolution".
8 February.	Mr. C.G. Dennis (Vaux Ltd.), "The art and science of brewing".
1 March.	Professor R. Mason (Government Scientific Advisor), "The scientist in defence policy".
10 May.	Professor G. Allen (Chairman, S.R.C.), "Neutron scattering for polymer structures".

Academic year 1979-1980.

18 October.	Dr. G. Cameron (University of Aberdeen), "Synthetic polymers - twentieth century polymers".
25 October.	Professor P. Gray (University of Leeds), "Oscillatory combustion reactions".
1 November.	Dr. J. Ashby (I.C.I. Toxicological Laboratory), "Does chemically-induced cancer make chemical sense".
8 November.	J.H. Turnbull (R.M.C. Shrievenham), "Luminescence of drugs".
*15 November.	Professor E.A.V. Ebsworth (University of Edinburgh), "Stay still, you brute: the shape of simple silyl complexes".
24 January.	Professor R.J.P. Williams (University of Oxford), "On first looking into biology's chemistry".

14 February.	Professor G. Gamlen (University of Salford), "A yarn with a new twist - fibres and their uses".
*21 February.	Dr. M.L.H. Green (University of Oxford), "Synthesis of highly reactive organic compounds using metal vapours".
28 February.	Professor S.F.A. Kettle (University of East Anglia), "Molecular shape, structure and chemical blindness".
6 March.	Professor W.D. Ollis (University of Sheffield), "Novel molecular rearrangements".

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16 October.	Dr. D. Maas (Salford University), "Reactions a go-go".
23 October.	Professor T.M. Sugden (Cambridge University), "Reactions in flames".
30 October.	Professor N. Grassie (Glasgow University), "Inflammability hazards in commercial polymers".
6 November.	Professor A.G. Sykes (Newcastle University), "Metalloproteins: an inorganic chemists approach".
13 November.	Professor N.N. Greenwood (Leeds University), "Metalloborane chemistry".
*4 December.	Rev. R. Lancaster, "Fireworks".
22 January.	Professor E.A. Dawes (Hull University), "Magic and mystery through the ages".
29 January.	Mr. H.J.F. Maclean (I.C.I. Agricultural Division), "Managing in the chemical industry in the 1980's".
5 February.	Professor F.G.A. Stone (University of Bristol), "Chemistry of carbon to metal triple bonds".
12 February.	Dr. I. Fleming (University of Cambridge), "Some uses of silicon compounds in organic synthesis".
7 May.	Professor M. Gordon (University of Essex), "Do scientists have to count"?

3. First year induction course.

Series of lectures arranged by the department for the benefit of the postgraduate students.

Department 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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