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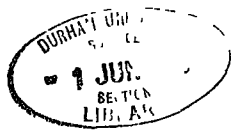
ASPECTS OF THE COORDINATION CHEMISTRY OF PHOSPHORUS(V) CHLORO-COMPOUNDS

by

R. N. Reeve B.A. B.Sc.

A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE UNIVERSITY OF DURHAM

APRIL 1975



DECLARATION

The work described in this thesis was carried out in the University of Durham between September 1971 and April 1974. This work 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.

ACKNOWLEDGMENTS

I would like to thank my supervisor, Dr. K. B. Dillon, for his continual help and encouragement, and Dr. R. J. Lynch for many helpful discussions and for running the n.q.r. spectra quoted in this work. I would also like to thank the other members of the research group, M. P. Nisbet and J, Lincoln, and members of the inorganic chemistry department for useful help and discussion, R. Coult for the large number of elemental analyses he performed, and Dr. D. Clark for the use of the Dupont curve analyser.

Thanks are also given to Mrs G. W. Parker for typing the thesis, and to Peabody Holmes Limited for assistance during the typing.

ABSTRACT

Acceptor properties of several phosphorus(v) chloro-compounds have been studied by solution and solid state ^{31}P n.m.r. techniques, using pyridine, 1,10-phenanthroline, 2,2'-dipyridyl and chloride ions as ligands. Six co-ordinate adduct formation has been detected in most systems.

As reported previously[1], phosphorus pentachloride forms a molecular 1:1 adduct with pyridine. Bidentate pyridines produce $PCl_4(L\text{-}L)^+ PCl_6^-$ (L-L = 2,2'-dipyridyl or 1,10-phenanthroline). Non-stoichiometric adducts $PCl_4phen^+(PCl_6^-)_{1-x} Cl^-_x$ ($x < 1$) disproportionate on dissolution to the 2:1 complex.

$PCl_4^+ SbCl_6^-$ reacts with pyridine in nitrobenzene to give the equilibrium

$$PCl_4(pyridine)_2^+ SbCl_6^- \rightleftharpoons PCl_5\text{.pyridine} + SbCl_5\text{.pyridine}$$

Solid $PCl_4(pyridine)_2^+ SbCl_6^-$ has been successfully isolated, however. Solution-stable adducts $PCl_4(L\text{-}L)^+ SbCl_6^-$ are formed with bidentate pyridines.

Phenyltetrachlorophosphorane $PhPCl_4$, catechyl phosphorus trichloride $(C_6H_4O_2)PCl_3$ and bis-catechyl phosphorus monochloride $(C_6H_4O_2)_2 PCl$ yield chloride ion adducts which are partially dissociated in solution. Each has been isolated as a solid. These phosphoranes also form molecular 1:1 adducts with pyridine, of which only $PhPCl_4$.pyridine dissociates in solution. In the presence of excess pyridine, $(C_6H_4O_2)PCl_2(pyridine)_2^+Cl^-$ and $(C_6H_4O_2)_2P(pyridine)_2^+ Cl^-$ equilibrate with the 1:1 adducts. The acceptors slowly produce cationic adducts with bidentate pyridines viz. $PhPCl_3(L\text{-}L)^+ Cl^-$, $(C_6H_4O_2)PCl_2(L\text{-}L)^+ (C_6H_4O_2)PCl_4^-$ and $(C_6H_4O_2)_2P(dipyridyl)^+ Cl^-$.

Similar cationic adducts $Z_4P(L\text{-}L)^+ MCl_6^-$ are rapidly formed by addition of bidentate ligands to $PhPCl_3^+ SbCl_6^-$, $PhPCl_3^+ PCl_6^-$, $(C_6H_4O_2)PCl_2^+ SbCl_6^-$ and $(C_6H_4O_2)_2P^+ SbCl_6^-$. The solid hexachloroantimonate adducts possess unexpected stability to water and moist air. Pyridine adducts $Z_4P(pyridine)_2^+ SbCl_6^-$ are formed with $(C_6H_4O_2)PCl_2^+ SbCl_6^-$ and $(C_6H_4O_2)_2P^+ SbCl_6^-$ but not with $PhPCl_3^+ SbCl_6^-$.

Preliminary experiments with methyltetrachlorophosphorane ($MePCl_4$) show the formation of $MePCl_5^-$ on addition of chloride ions.

The addition of substituted pyridines to PCl_5 and $PCl_4^+ SbCl_6^-$ has been investigated. 3- and 4-substituted non-methylated pyridines yield complexes, but 2-substituted pyridines show a much lower tendency to co-ordinate. Methyl pyridines are attacked by the phosphorus species in solution.

Reactions of the type

$$R_3P + PCl_5 \longrightarrow R_3PCl_2 + PCl_3$$

$$R_3PCl_2 + PCl_5 \longrightarrow R_3PCl^+ PCl_6^-$$

have also been studied. By variation of the reaction stoichiometry, either R_3PCl_2 or $R_3PCl^+ PCl_6^-$ may be prepared. With $PhPCl_2$, however, only $PhPCl_3^+PCl_6^-$ has been isolated.

Reference

1. I. R. Beattie, M. Webster. J. Chem. Soc. 1731 (1961)

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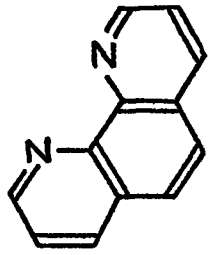
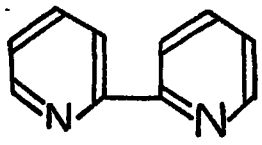
Abbreviations used in this work

py = pyridine or a substituted derivative of this, according to context.

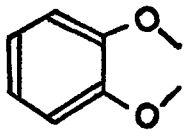
phen = 1,10-phenanthroline



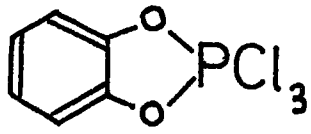
dipy = 2,2'-dipyridyl



cat = catechyl



e.g. $catPCl_3$ =



prop = n-propyl, n- C_3H_7

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

e.g. $pent_4N^+ Cl^-$ = $(n\text{-}\ C_5H_{11})_4N^+ Cl^-$

S/N = Signal/Noise

CHAPTER 1

INTRODUCTION

1. Co-ordination Chemistry of Phosphorus (v) Compounds

Many examples are known of the co-ordination of neutral and anionic monodentate ligands to group VB pentahalides [1], e.g. $PF_5.Me_2O$ [2], $SbCl_5$.pyridine [3], $SbCl_5Br^-$ [4-6], $AsCl_6^-$ [7] (derived from the unknown $AsCl_5$), and PCl_5.pyridine [8]. The resulting six co-ordinate complexes possess octahedral structures. Six co-ordinate cationic species are also known in which a bidentate ligand is co-ordinated to MCl_4^+, e.g. PCl_4 phen$^+$, $SbCl_4$ phen$^+$ [9] (phen = 1,10-phenanthroline), and have been postulated where MCl_4^+ is co-ordinated by two monodentate ligands e.g. $PCl_4py_2^+$ [10] (py = pyridine), $SbCl_4(MeCN)_2^+$ [11].

The range of adducts isolated [1] varies greatly with the acceptor, partly indicating the attention each compound has received, but also reflecting the acceptor properties of the molecule. For example, nitrobenzene is found to complex with antimony pentachloride [1] but not with phosphorus pentachloride [12]. PF_5 and $SbCl_5$ form adducts with a large variety of nitrogen, oxygen and other donors [1]. PCl_5, on the other hand, is a very weak acceptor, forming well-established complexes with only a few ligands.

Phosphorus pentachloride has long been known to have the stable solid structure $PCl_4^+ PCl_6^-$ [13,14], in which one molecule of phosphorus pentachloride acts as a chloride ion acceptor towards a second molecule. It was later thought that the hexachlorophosphate ion might only exist in this salt [12,15]. The discovery of tetraethyl ammonium

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hexachlorophosphate [16] subsequently showed the ion to have an existence independent of PCl_4^+. A large number of hexachlorophosphates have since been prepared.

e.g. $\left[Cl_3 P = N - PCl_3\right]^+ PCl_6^-$ [17]; $(C_7H_7^+)_2 Cl^- PCl_6^-$ [11,18]

Nonetheless phosphorus pentachloride is a poor chloride ion acceptor, forming the hexachlorophosphate ion only in the absence of competing reactions. The chloride ion acceptor strength of a number of Lewis acids, measured using Ph_3CCl as donor in benzoyl chloride solvent, decreases in the order

$SbCl_5 > FeCl_3 > GaCl_3 > SnCl_4 > BCl_3 > ZnCl_2 >$
$TiCl_4 > SbCl_3 > AlCl_3 > PCl_5$ [19]

From a study of the heats of formation of a number of pyridine adducts [20], phosphorus pentachloride was found to be a very weak acid compared with other inorganic halide acceptors. The order of increasing acceptor strength is:

$PCl_5 < PCl_4F \leqslant BF_3 < PCl_3F_2 < SbCl_5 \sim BCl_3 < BBr_3$

The heat of reaction of phosphorus pentachloride and pyridine in nitrobenzene was determined as 24.5-26.5 kcal/mole [20], whereas that of antimony pentachloride and pyridine is 28.3 kcal/mole. A similar order was found by Hensen and Sarholtz [21] from a study of the ultra violet spectra of the pyridine adducts:

$HCl < BF_3 = SiF_4 = PCl_5 < AlCl_3 < AlBr_3 < BCl_3$
$< SiHCl_3 < GeCl_4 < BBr_3 < SiCl_4 < SiBr_4$

./.

The adduct PCl_5.pyridine is discussed in more detail in Chapter 3 section 1(i).

Adducts of phosphorus pentachloride with bidentate pyridines are also known. The adduct $PCl_4phen^+Cl^-$ [22] has been characterised by its infra red spectrum and molecular weight measurements. $(PCl_4dipy^+)(Cl^-)_{0.67}(PCl_6^-)_{0.33}$ has been characterised [23] by solid state and solution ^{31}P n.m.r. spectroscopy. Few other adducts of phosphorus pentachloride have well established structures. Complexes with methyl acetamides and methyl formamides [24,25] have been investigated by infra red spectroscopy. The 1:1 complex between phosphorus pentachloride and dimethyl nitrosoamine was studied by ^1H n.m.r. spectroscopy [26]. Other complexes have been characterised by elemental analyses alone. The known species are shown in Table 1, together with their postulated formulae. With the exception of PCl_5.pyridine and the substituted formamide and acetamide complexes there is little physical evidence for the structures given. The difficulty in precise formulation of the complexes occurs because of the ease of ionisation of the P-Cl bond, and also to the existence of the hexachlorophosphate ion. Thus it is possible for the 1:1 complex between phosphorus pentachloride and pyridine to have the structures.

PCl_5.py, $PCl_4py^+ Cl^-$, $PCl_4py_2\ ^+PCl_6^-$

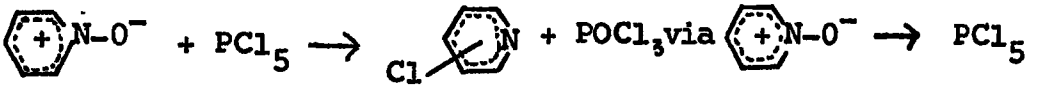
The structure may also vary in different phases, or in solution in different solvents. For instance the parent compound, phosphorus pentachloride has a completely molecular structure in non polar solvents [48], but in nitrobenzene there is an equilibrium between PCl_5, $PCl_4^+PCl_6^-$, and $PCl_4^+Cl^-$ species [49].

A review of the addition compounds of phosphorus pentachloride up to December 1964 is given by Webster [1]. More general reviews of the chemistry of phosphorus halides are given by Payne [50] and Kolditz [51].

If the tetrachlorophosphonium ion is generated by formation of a salt with a chloride ion acceptor (e.g. $PCl_5 + SbCl_5 \rightarrow PCl_4^+SbCl_6^-$ [11]), it appears that complexes of the type $PCl_4X_2^+SbCl_6^-$ (X = pyridine, tetrahydrothiophene, tetrahydrofuran) may be temporarily stable in solution [10]. $PCl_4phen^+SbCl_6^-$ has also been isolated [9].

The weak acceptor properties are probably of great importance in organic chemistry where phosphorus pentachloride has found considerable use as a chlorinating agent. Many of the reactions have been postulated to proceed via intermediate adducts. Examples of the reactions are given below:

(i) $R - C(=O)(OR) + PCl_5 \rightarrow R - C(=O)Cl$ via $R - C(=O \rightarrow PCl_4^+)(OR)\ Cl^-$ [52]

(ii)  53

(iii) $R - OH + PCl_5 \xrightarrow[AlCl_3]{py} R - Cl$ via $PCl_4py_2^+AlCl_4^-$ 54

Several factors may contribute to the smaller range of phosphorus pentachloride complexes known, compared with, say, phosphorus pentafluoride. The high electronegativity of fluorine is thought to help charge distribution and also to contract high energy vacant orbitals (probably the 3d orbitals [55], although suggestions [56] have been made that other orbitals may be involved) sufficiently for energetically favourable hybridisation to form octahedral complexes. Chlorine has a lower electronegativity than fluorine but a far greater size. The large size of five chlorine atoms around a single phosphorus may hinder the formation of a sixth weak co-ordinate bond (steric crowding has been proposed with organofluorophosphorane adducts [57]). The ease of ionisation of phosphorus-chlorine bonds must also be considered. Phosphorus(v) chlorine species often possess ionic structures containing chloride ions (e.g. $Bu_3PCl^+Cl^-$ [58]). Moreover where molecular structures are found (e.g. $PhPCl_4$ [59]) a chloride ion may be easily removed by very weak acceptors (e.g. chlorine [60]). Thus the addition of a donor may give a transient complex, but P-Cl bond fission results giving free chloride ions, which are then able to attack the ligand. This is the mechanism suggested for the

conversion of pyridine N-oxides into chloro-pyridines by means of phosphorus pentachloride [53]. A final factor which may be involved is the ability of phosphorus pentachloride to chlorinate a number of potential ligands. Triphenyl phosphine thus reacts

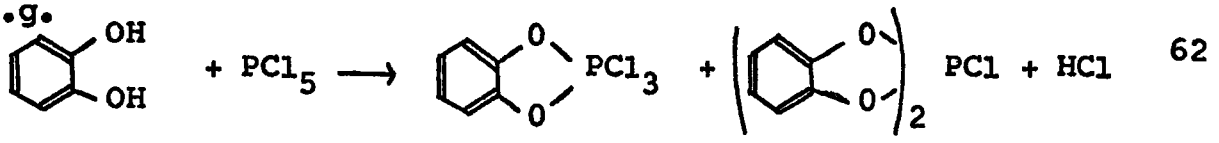
$$Ph_3P + 2PCl_5 \longrightarrow Ph_3PCl^+PCl_6^- + PCl_3 \quad 61$$

Phosphine oxides behave in an analogous manner

$$Ph_3PO + 2PCl_5 \longrightarrow Ph_3PCl^+PCl_6^- + POCl_3 \quad 33$$

Ligands may also not be used if they contain N-H or O-H bonds as hydrogen chloride is immediately liberated.

e.g.



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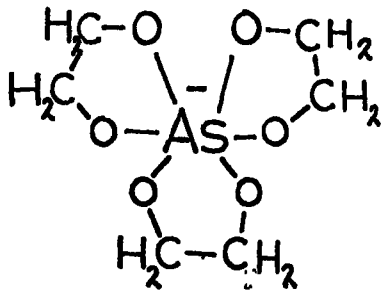
c.f. however the proposed complexes with piperidine [25,32] and N-methyl acetamide [24,25].

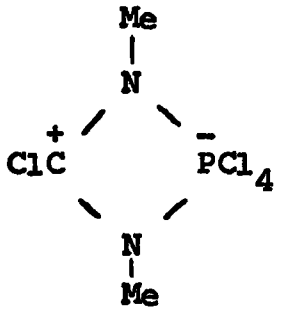
The acceptor properties of phosphorus pentachloride and phosphorus pentafluoride have not been fully investigated, and some of the apparent differences between the two systems may be due to this reason.

A number of six co-ordinate phosphorus(v) species are now knownwhich contain no halide atoms. These are listed in Appendix I. All the complexes so far discovered contain at least two bidentate molecules and contain mainly P-C or P-O bonds. The large number of phosphorus complexes reported of this type is due to their ease of detection by ^{31}P n.m.r. techniques. Similar complexes are known with other central atoms but have been relatively little investigated.

e.g.  63

2. Present Work

The purpose of the present work was to investigate the acceptor properties of phosphorus pentachloride and some of its organic derivatives. Only one well characterised example of an organo chloro phosphorus(v) complex was previously known [64] viz.



Its ^{31}P n.m.r. shift [64] of +202 ppm is indicative of the six co-ordinate environment of the phosphorus (see Chapter 1 section 3(i)). Substituted chlorophosphates have been postulated from conductance or hydrolysis investigations [65-67]. The proposed species have however, not been further substantiated e.g. ref.68. A ^{31}P n.m.r. investigation of the tentatively proposed mixed phenoxychlorophosphates [69] did not distinguish these species from the more likely hexachlorophosphate ion.

With sufficiently strong halide acceptors it has been found that acceptor properties are retained where one or more of the halides are replaced by alkyl or aryl groups. The substitution of organic groups progressively decreases the Lewis acidity of the molecule [57,70,71]. Thus in the PF_5 series, PF_6^- [72], $MePF_5^-$ [70,73], $Me_2PF_4^-$ [74] but not $Me_3PF_3^-$ are known. Similarly $PhPF_5^-$ [73,75] and $Ph_2PF_4^-$ [70], but not $Ph_3PF_3^-$, have been prepared. PF_5.pyridine [76] is a stable complex, but $PhPF_4$.pyridine [57] is only partially associated in solution. It was therefore interesting to discover whether the weak acceptor phosphorus pentachloride retained acceptor properties on successive substitution of the chlorines by organic groups. The degree of substitution possible whilst still retaining acceptor properties would then reflect the acceptor strength of phosphorus pentachloride.

Organo-chloro phosphorus(v) species

A large number of compounds is known in which one or more of the chlorines of phosphorus pentachloride have been substituted by organic groups (e.g. Ref.77). The compounds may have a five co-ordinate molecular structure R_xPCl_{5-x}, or one of the chlorines may be ionised, giving a salt-like structure $(R_xPCl_{4-x})^+ Cl^-$. Indeed, in many cases the structure may depend on the physical state of the compound as with phosphorus pentachloride itself. Thus methyl tetrachlorophosphorus(v) is ionic in the solid state but in solution in polar and non polar solvents is predominantly if not completely molecular (Ref.78: See also Chapter 4 Section 3(ii)).

Trends in structure may be found within groups of compounds. An ionic formulation becomes more likely as more chlorines are replaced by less electronegative organic groups. This is illustrated by the chloro phenyl phosphorus(v) series:

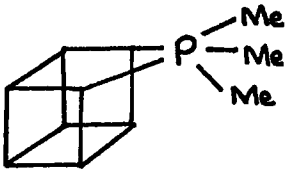
TABLE 2

STRUCTURES FOUND IN THE SERIES

Ph_xPCl_{5-x} (x = 1-4)

Formula	Structure in Solid	Nitrobenzene solution
$PhPCl_4$	$PhPCl_4$ [59]	$PhPCl_4$ [60]
Ph_2PCl_3	Ph_2PCl_3 [59]	Mainly Ph_2PCl_3 [60]
Ph_3PCl_2	$Ph_3PCl^+Cl^-$ [59]	Ph_3PCl_2 and $Ph_3PCl^+Cl^-$ [60,58]
Ph_4PCl	$Ph_4P^+Cl^-$ [59]	$Ph_4P^+Cl^-$ [23]

Ring strain effects have been postulated as encouraging phosphorane structures. Despite attempts at synthesis, pentamethyl phosphorane Me_5P has not been prepared.[79] The compound



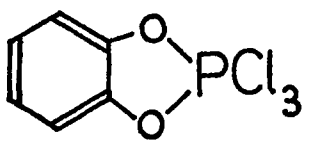
is quite stable [79-81], however, where the ring strain is thought to be relieved by 5 co-ordination. If the ring occupies axial/equatorial positions in the trigonal bipyramid then the preferred $\hat{CPC}$ angle will be 90°.

This is much closer to the sterically imposed angle of $\sim 85^{o}$ than found in a tetrahedral arrangement where the preferred angle is $109^{o}\ 28'$ [81].

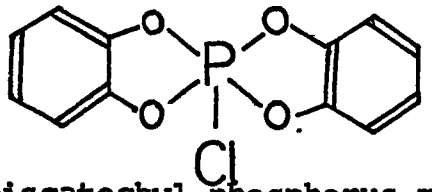
Range of Compounds Studied

The compounds studied were resticted to those with a molecular 5 co-ordinate structure, at least in solution, and to hexachloroantimonate salts of the cations from these species. These compounds were thought to be the most likely species to exhibit co-ordination properties. A five co-ordinate structure from a molecular orbital description necessarily involves hybridisation utilising higher energy vacant orbitals. If the orbitals were of sufficiently low energy for this to occur, it was thought that little further energy would be necessary for further hybridisation to form a six-co-ordinate adduct. No hybridisation involving high energy vacant orbitals is necessary to form four co-ordinate structures, and these orbitals might thus be too high in energy to form six co-ordinate complexes readily.

The co-ordination properties of phosphorus pentachloride were studied in depth with a variety of ligands. The simple substituted derivative, phenyl tetrachlorophosphorane, $PhPCl_4$, was then investigated, as were the catechyl derivatives, catechyl phosphorus trichloride, $C_6H_4O_2PCl_3$ and biscatechyl phosphorus monochloride, $(C_6H_4O_2)_2PCl$.



catechyl phosphorus trichloride



biscatechyl phosphorus monochloride

(The non systematic names for these species are used throughout this work in order to emphasise that they are simple derivatives of PCl_5 with two or four of the chlorines replaced by catechyl groups. This is not apparent in their systematic nomenclature as 1,3,2-benzodioxaphosphole derivatives).

The tris catechyl phosphate ion is well-known (c.f. Appendix I). By investigating the above compounds it was hoped to produce the intermediate catechyl PCl_4^- and catechyl$_2$ PCl_2^- ions as well as pyridine, dipyridyl, and phenanthroline adducts.

Other species including methyl tetrachlorophosphorane and diphenyltrichlorophosphorane were studied in less detail to provide comparisons with the above species.

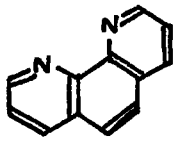
The cations derived from the above species were also studied. As previously mentioned, PCl_4^+ salts may be formed by reacting a large number of inorganic chloride ion acceptors with phosphorus pentachloride [1,82]. Even the 1:1 $AsCl_5$ ($AsCl_3 + Cl_2$) : PCl_5 adduct originally thought to be $AsCl_4^+PCl_6^-$ [83,84] has now been shown to be $PCl_4^+AsCl_6^-$ [48,85,86]. In a similar way organo-chlorophosphonium salts may be produced from the corresponding phosphorane, e.g. Ref.59.

Hexachloroantimonate salts were chosen for investigation. These compounds were readily produced by simple addition of the components in methylene chloride solution. Although highly insoluble in non polar solvents they were readily soluble in nitrobenzene. Antimony pentachloride is an extremely strong chloride ion acceptor and formed salts

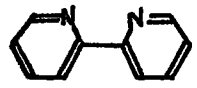
with even the catechyl derivatives (See Chapter 5). In addition the work of Beattie, Livingston, and Webster [10] on the addition compounds of PCl_4^+ using $PCl_4^+SbCl_6^-$ could be directly confirmed. The species studied were $PCl_4^+SbCl_6^-$, $PhPCl_3^+SbCl_6^-$, $(C_6H_4O_2)PCl_2^+SbCl_6^-$ and $(C_6H_4O_2)_2P^+SbCl_6^-$. $PhPCl_3^+$ was also investigated as its hexachlorophosphate salt $PhPCl_3^+PCl_6^-$.

The preparation of the parent phosphoranes and their hexachloroantimonate salts is described in Chapter 2.

The range of ligands investigated was mainly restricted to those types forming well-characterised compounds with phosphorus pentachloride, namely pyridine and simple substituted derivatives of it, bidentate pyridines 1,10 -phenanthroline and 2,2'-dipyridyl,



1,10-phenanthroline



2,2'-dipyridyl

as well as chloride ions derived mainly from tetraalkyl ammonium chlorides. Tetra-n-pentyl ammonium chloride was the most extensively used chloride ion source. The large cation made the salt soluble in non polar (e.g. carbon tetrachloride) as well as polar solvents. It provided a large cation to help stabilise any weakly bound large anions formed. It is also very easy to dry, the lower tetraalkyl ammonium chlorides being very difficult to obtain anhydrous (especially tetra-n-butyl ammonium chloride). Sometimes

tetra-n-propyl ammonium chloride was used, in addition to a number of other chloride ion sources.

Nitrobenzene was found to be a suitable solvent both for molecular and ionic complexes and was generally used in this work. The solvent is known not to react with phosphorus pentachloride even at elevated temperatures [87]. Methylene chloride was also commonly used for molecular complexes but ionic species were generally insoluble in this medium. No difficulty was found in the use of the solvent even though methylene bromide and iodide react with pyridine under very mild conditions [88].

3. Techniques Used

(i) ^{31}P n.m.r. spectroscopy

a) Solution

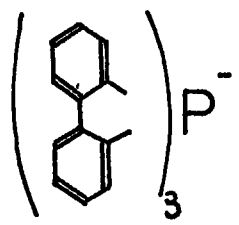
^{31}P nuclear magnetic resonance spectroscopy is ideally suited for the study of changes in the co-ordination of phosphorus(v) compounds. ^{31}P chemical shifts cover a range of greater than 600 ppm [89]. Three co-ordinate compounds span the whole range of shifts. Species with higher co-ordination numbers do, however, fall within specific ranges. Within particular classes of compounds (e.g. organo chlorophosphorus species) the co-ordination number may be deduced from the chemical shift. In general (this is not easily applicable to phosphorus (III) compounds where the shielding of the nucleus is greatly affected by bond angles) the greater the co-ordination number of the phosphorus the greater is the nuclear

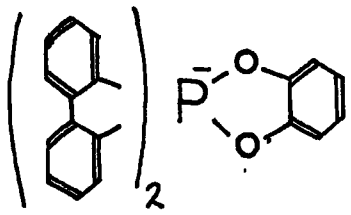
shielding and so the higher is the chemical shift. The chemical shift also increases with increasing negative charge on phosphorus. This is illustrated by the shifts (relative to 85% aqueous phosphoric acid) of phosphorus-chlorine species, $POCl_3$ being included as an example of a neutral, four co-ordinate chloro-species.

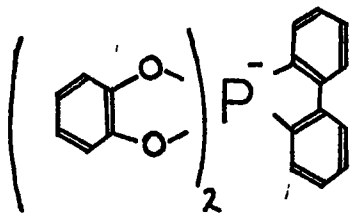
PCl_3	PCl_4^+	$POCl_3$	PCl_5	PCl_6^-
-219	-86	-2.5	+83	+296 ppm

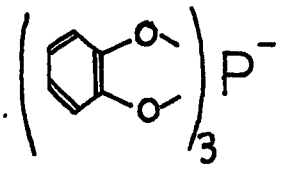
Organo chloro-compounds tend to have a smaller range of chemical shifts. A value of between -220 and -120 ppm may be ascribed to a three co-ordinate species, one between about -120 and -20 ppm to a four co-ordinate species, between about -10 and +85 ppm to a five co-ordinate species and any shift greater than +85 ppm to a six co-ordinate species. Thus the formation of a six co-ordinate adduct is immediately apparent from the chemical shift. PCl_5.pyridine, for instance, has a chemical shift of about + 233 ppm [23,31]. With compounds containing oxygen ligands the range of shifts is somewhat compressed, probably due to the ability of the oxygen ligand to accommodate part of the formal charge from phosphorus. Thus the shift of five co-ordinate P-O compounds usually falls between 0 and + 60 ppm [89] whilst the shift range of 6 co-ordinate compounds is between + 80 and + 110 ppm.

Mixed species appear to have shifts between the two extreme species e.g. the series


+ 186.6 ppm


+ 147 ppm


+ 106 ppm


+ 82 ppm

The second advantage of ^{31}P n.m.r. spectroscopy for the study of co-ordination is that hydrolysis or oxidation products do not interfere with the observation of the spectra. The signals from these species are usually well-removed from areas of interest. Hydrolysis of phosphorus(v) chloro-compounds generally proceeds via the oxychloride [90] then in a stepwise manner to the corresponding acid [91].

e.g. $PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$

$\downarrow H_2O$

$POCl_2(OH)$

$\downarrow H_2O$

$POCl(OH)_2$

$\downarrow H_2O$

H_3PO_4

(In the particular case of phosphorus pentachloride pyrophosphoryl chloride, $P_2O_3Cl_4$, is also produced [92]).

When the extent of hydrolysis is small, as observed in this work, the reaction proceeds only to the oxychloride. These species have chemical shifts between about -50 and 0 ppm, outside the ranges for six co-ordinate products or for starting materials. N.m.r. data for the main hydrolysis products are summarised in Appendix 2.

The main disadvantage of ^{31}P n.m.r. spectroscopy is its lack of sensitivity. Although the ^{31}P isotope in phosphorus is in 100% natural abundance, the nuclear properties of phosphorus make ^{31}P n.m.r. only 6.6% as sensitive as ^{1}H n.m.r. spectroscopy for equal numbers of nuclei. Single ^{31}P n.m.r. peaks were found in this work, any coupling with nuclei in the organic groups being unresolvable. Proton signals are often split by coupling. The signals are, however, generally far sharper than phosphorus signals. The lack of sensitivity of phosphorus may be partially compensated by utilising 8.5 mm diameter n.m.r. tubes, instead of the 5 mm diameter tubes used for proton n.m.r., but even so the signal is often not visible on a single scan of the spectrum. Signal enhancement can, however, be conveniently achieved by signal averaging, using a computer of average transients (C.A.T.).

b) Solid State

The large shifts found in ^{31}P nuclear magnetic resonance make feasible the study of co-ordination by solid state n.m.r. spectroscopy. Although lines in solid state spectra are very broad making peak maxima only measurable to a few ppm the large shift on change of co-ordination number makes this degree of accuracy sufficient to discern the

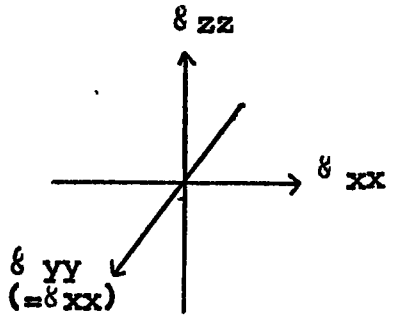
state of co-ordination of the species.

Andrew [93,94] showed that the solid state spectrum of phosphorus pentachloride consisted of two lines at -91 and +282 ppm attributable to PCl_4^+ and PCl_6^- respectively. A modified broad line spectrometer was used in which the compound was spun at high velocity at an angle of 54° 44' to the magnetic field [95]. Under these conditions the dipole-dipole interaction is minimised. Phosphorus pentachloride and several other compounds containing PCl_4^+, or PBr_4^+ ions were studied by Wieker and Grimmer using a conventional broad line n.m.r. spectrometer [86,96-98]. Dillon and Waddington studied a variety of phosphorus compounds using a high resolution n.m.r. spectrometer with spectrum accumulation [99]. Signals were often sufficiently narrow to observe by this technique [99], which has subsequently been used to characterise the mixed $PCl_xBr_{4-x}^+$ ions [100]. These have also been observed with a broad line spectrometer [101]. The paper reporting this discusses the relative advantages and disadvantages of broad line and high resolution techniques for solid state ^{31}P n.m.r. measurements. The high resolution technique has also been applied to R_3PX_2 species [102] (X = halogen), to P_2Cl_9Br, [103] and to $POCl_3$ adducts [104].

The lines observed are generally broad, widths at half-peak height of about 50 ppm (~1200 Hz) being typical, and symmetrical in shape. The broadness is mainly due to the effect of dipole-dipole interactions. With freely

rotating molecules, as in solutions, these effects are averaged out producing much sharper lines. Dipolar broadening in the solid state is generally so great as to mask any other effects, such as anisotropy of the chemical shift tensor. As the chemical shifts in ^{31}P n.m.r. spectroscopy are very dependent on the environment of the phosphorus (shifts of up to 600 ppm) compared to the more commonly used nucleus ^{1}H (shifts of 25 ppm), under certain circumstances anisotropic effects may become apparent. These would then give the line an unsymmetrical appearance and cause further broadening. Although only a few instances of spectra showing this effect have been reported [105-109] examples are known in the spectra of phosphorus(v) species [109]. The possibility must therefore be taken into account.

Consider a single crystal containing molecules of axial symmetry in unique crystallographic environments. Two of the three principle values of the tensor will be equal.

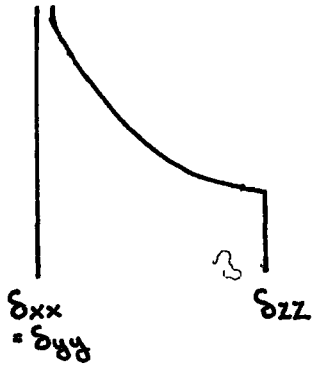


If the n.m.r. spectrum of the single crystal is observed in the yz plane and the crystal is rotated through 360° about the x axis, the chemical shift will progress slowly from

$\delta_{yy} \longrightarrow \delta_{zz} \longrightarrow \delta_{yy} \longrightarrow \delta_{zz} \rightarrow \delta_{yy}$

A similar progression will occur when observed in the xz plane and rotated about the y axis. When observed in the xy plane and rotated about the symmetry (z) axis, however, the shift remains at a constant value of $\delta_{xx} = \delta_{yy}$. Such an investigation has been undertaken with the ^{13}C spectrum of calcite [106].

A powder can be considered as a large number of randomly orientated molecules, the n.m.r. absorption being the sum of the absorptions over all possible orientations. Theoretical line shapes have been given by Andrew and Tunstall [108]. The absorptions are dominated by the $\delta_{xx} = \delta_{yy}$ shift.



Theoretical lineshape

Experimental curves have an asymmetric appearance

Experimental lineshape

The line is somewhat broader than expected for an isotropic shift. The average shift, as found in solution, will not be the absorption maximum, but

an average of the principle values [106].

i.e. δ soln = $\frac{1}{3}$ (δ zz + 2 δ xx)

This can be significant since the shift difference of the components in, for example, P_4O_{10} is 265 ppm [109].

Since no non spherically symmetric octahedral complexes have been previously studied the size of this effect is unknown. No asymmetry of the signal is observed with related organo chloro-phosphonium ions [23], however, and this effect may therefore be negligible for fairly symmetrical species.

(ii) Infra-red spectroscopy

Phosphorus-chlorine stretching frequencies occur in the infra-red spectrum between 658 and 420 cm^{-1} [110,111]. They are usually strong absorptions. Their position and number depend strongly on the environment of the phosphorus-chlorine bond and are thus ideal for characterisation of complexes in the solid state. In addition the spectra of the starting materials are well-known. Infra red spectroscopy thus provides a quick check on whether any starting material is present in the product.

TABLE 3

CHARACTERISTIC i.r. FREQUENCIES OF P-Cl STARTING MATERIALS AND HYDROLYSIS PRODUCTS

PCl_4^+	653 cm^{-1}	Ref.110
PCl_6^-	449 cm^{-1}	Ref,110
$POCl_3$	581, 485 cm^{-1}	Ref.112 (581 cm^{-1} peak is the stronger)

Although the region of the infra red spectrum between 660 and 420 cm^{-1} is in general free from C-H and C-C absorptions, bands in this region may also be found from P-Ph [113] groups. Although bands from the complexes cannot then be easily assigned to particular vibrations, the spectrum in this region is still extremely useful for "fingerprinting".

Many of the complexes prepared in this work are ionic, and have been synthesised with more than one counter-ion. Spectra of the ionic species would be expected to be quite similar even with different counter ions. The infra red spectra then provided a means of confirming the presence of similar species in the complexes.

(iii) ^{35} Cl Nuclear quadrupole resonance spectroscopy

The ^{35} Cl n.q.r. spectra of several of the complexes were determined by Dr. R. J. Lynch in order to obtain further information about their solid state structures. N.q.r. signals occur by resonance between the non-degenerate energy levels of a nuclear quadrupole interacting with an asymmetric electric field gradient. Thus for the completely symmetrical chloride ion no absorption is found. A chlorine atom produces a ^{35} Cl ($I = 3/2$) signal at 54.87 MHz. For chlorines within a molecule signals are found between 54.87 and 0 MHz, dependent on the character of the X-Cl bond. The simplest interpretation of the frequency value gives the position by [114],

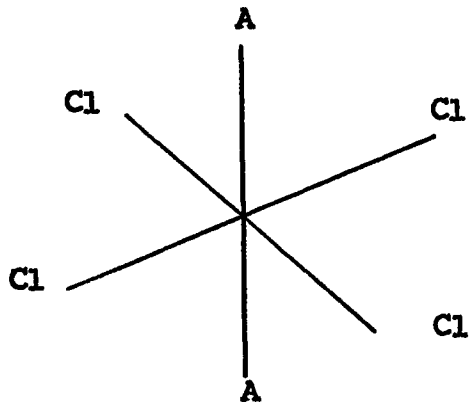
$$\frac{\nu \text{ molecule}}{\nu \text{ chlorine atom}} = (1-S)\sigma - \pi$$

where S is the amount of S-p hybridisation and σ and π are the relative amounts of the σ and π characters of the X-Cl bond. Each chemically distinct chlorine atom will give a separate signal. In addition crystallographical inequivalencies may further split these lines. Thus in solid $PCl_4^+PCl_6^-$ (at 77K) separate signals are found for PCl_4^+ and PCl_6^- but each of these signals is a multiplet [115-117]. For solid, molecular, PCl_5 separate signals are found [116] for the axial and equatorial chlorines.

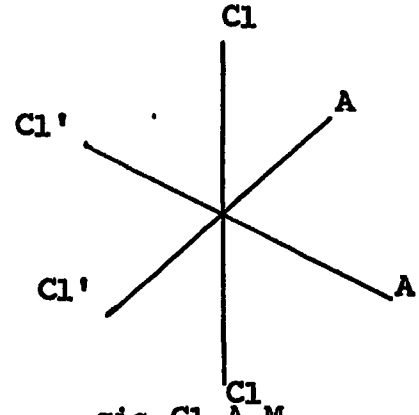
As ^{37}Cl also possesses a nuclear quadrupole (I = 3/2), resonances may also be detected from this nucleus. These occur at $\frac{1}{1.2688}$ of the frequency of the ^{35}Cl lines but have only 25% of the intensity. They are thus not used for signal detection but are useful in deciding whether a particular resonance is from ^{35}Cl or from another quadrupolar nucleus. Little ambiguity was found in this work. The other quadrupoles present absorbed in different frequency ranges (^{14}N, ^{79}Br, ^{81}Br) or were present in environments differing only slightly from spherical symmetry so that the resonance frequencies would be close to zero ($SbCl_6^-$ at 77K produces in many cases a multiplet due either to symmetrical $SbCl_6^-$ in a variety of crystal sites, or to a distorted octahedron. In this latter case there will be a slight field gradient at the ^{121}Sb or ^{123}Sb nucleus).

It is, in theory, possible to distinguish between certain isomers in the solid state using n.q.r. techniques.

For an octahedral complex Cl_4A_2M, when the A atoms are trans to each other all the chlorines are equivalent. One group



trans Cl_4A_2M



cis Cl_4A_2M

of lines should then be seen in the ^{35}Cl n.q.r. spectrum. If the A atoms are cis the chlorines split into two chemically distinct pairs, depending on whether the chlorines are trans to another chlorine or to A. Two groups of lines of approximately equal intensity are then expected in the spectrum. An example of such a system is a $PCl_4py_2^+$ species.

The technique may only be used in the solid state, however, and is particularly sensitive to imperfections or strains in the crystal structure [115]. In many compounds the technique is too insensitive to detect signals. Other compounds may have to be annealed at just below their melting points. Thus, although a potentially extremely useful technique, at present it has severe experimental disadvantages in its application as a method of determining structures.

CHAPTER 2

EXPERIMENTAL

1. Methods Used

(i) Glove Box Techniques

All reactions were carried out under an atmosphere of dry nitrogen, because of the great sensitivity of the starting materials and products, particularly in solution, to water. Similarly the phosphorus-containing reactants and products were stored under nitrogen in closed containers.

Reactions were generally performed in a glove box continuously purged with dry nitrogen. The glove box was equipped with two entry ports; a large port and a smaller "quick entry" port. The large port was purged with nitrogen for at least 30 minutes before opening to the glove box. The "quick entry" port was either evacuated using an external water pump, or flushed with nitrogen by means of the excess pressure in the glove box. A large dish of phosphorus pentoxide was kept exposed in the box to remove final traces of water. The surface of the phosphorus pentoxide was reformed each time it developed a skin. An external water pump could be attached to a filter apparatus inside the glove box, so that reactions and product isolation could be carried out completely within the box.

A short vacuum line was sometimes used for drying processes. The line was equipped with rotary and mercury diffusion pumps. The latter could be by-passed on the line if required.

Moisture-sensitive materials were weighed outside the glove box in stoppered sample tubes.

(ii) Preparation of Starting Materials

a) Phosphorus Pentachloride

This was purchased from May and Baker Limited and used without further purification.

b) Phenyltetrachlorophosphorane

Phenyltetrachlorophosphorane was prepared by J. Lincoln, according to the procedure of Michaelis [118] but with methylene chloride added as a diluent.

Phenyldichlorophosphine was diluted with methylene chloride. Chlorine was slowly bubbled into the cooled solution until a slight excess was present, as shown by a yellow colouration in the solution. The solvent was then evaporated under vacuum to produce large white moisture-sensitive crystals.

The preparation was repeated several times on scales yielding up to 40g product.

Although phenyltetrachlorophosphorane has a tendency to take up excess chlorine according to the equation [119,60]

$$PhPCl_4 + Cl_2 \longrightarrow PhPCl_3^+ Cl_3^-$$

no contamination was detected, samples all giving ^{31}P n.m.r. shifts in solution of about + 43 ppm (see Chapter 4 Section 1(i)). Any contamination by the trichloride would lower the chemical shift [60]. The presence of $PhPCl_3^+$ ions in the solid state was undetectable by i.r. spectroscopy (Chapter 4 Section 1(i)). It would thus seem that the excess chlorine is removed by pumping.

Typical analyses: C,28.46; H,2.51; P,12.44; Cl,55.0%

$C_6H_5PCl_4$ requires: C,28.84; H,2.02; P,12.39; Cl,56.8%

c) Catechyl phosphorus trichloride

(2,2,2-trichloro-1,3,2-benzodioxaphosphole)

Samples of the compound were either obtained commercially (Aldrich Chemicals Limited) or were synthesised as below (see also Chapter 3 Section 3(i) b).

Typical preparation - 13.129g (75.048 mmole) catechyl phosphorus monochloride were mixed with an approximately equal volume of methylene chloride. 15.648g (75.124 mmole) finely powdered phosphorus pentachloride were slowly added in portions, dissolving each portion almost completely before addition of the next. The resulting clear yellow solution was then evaporated almost to dryness at room temperature on a vacuum line. Drying was completed on the filter pump. The slightly yellowish white crystals were not washed as they were found to be extremely soluble even in 30/40 pet ether. Yield = 16.948g = 92.0% as $C_6H_4O_2PCl_3$.

Typical analysis Found: C,28.67; H,1.72; P,12.66; Cl,43.20

$(C_6H_4O_2)PCl_3$ requires C,29.24; H,1.64; P,12.98; Cl,43.12

o-phenylene phosphorochloridite was obtained by the water-catalysed reaction of catechol with phosphorus trichloride [120], and was performed by J. Lincoln.

d) Biscatechyl phosphorus monochloride

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

This compound was prepared according to the optimum procedure of Ramirez [62].

Typical preparation - 27.304g (131.19 mmole) phosphorus pentachloride were stirred in 80ml dry benzene for 20 minutes. 27.32g (248.1 mmole) catechol (recrystallised from toluene by J. Lincoln) were quickly added in portions, as a solid, allowing the reaction to subside between each addition. After heating at 60-80° for one hour, the solution was transferred to the glove box and the pure-white solid filtered, washed with diethyl ether and dried at the pump. Yield = 30.318g = 86.5% as $(C_6H_4O_2)_2PCl$.

Typical analyses Found: C,50.72; H,3.01; P,10.64; Cl,12.70. $(C_6H_4O_2)_2PCl$ requires C,50.99; H,2.86; P,10.96; Cl,12.55.

Some of the samples were recrystallised from a 50/50 benzene/hexane mixture in order to reduce contamination by small amounts of impurity, probably $(C_6H_4O_2)POH$ (see Chapter 5 Section 4(i)).

e) Diphenyltrichlorophosphorane

(See also Chapter 3 Section 3(i) b)

10.096g (48.462 mmole) powdered phosphorus pentachloride were slowly dissolved in a mixture of about 9ml (11.1g 49.9 mmole) diphenylchlorophosphine and 50ml methylene chloride. The solution was stirred. After about 5 minutes a precipitate started to form. After 2 hours the pure white solid was filtered, washed with a little methylene chloride, then 30/40 pet ether and dried at the pump and

finally under vacuum. Yield = 9.506g = 71.7% as Ph_2PCl_3
Analyses Found: C,48.03; H,4.16; P,11.10; Cl,37.01.
Ph_2PCl_3 required C,49.43; H,3.46; P,10.62; Cl,36.48.

Ph_3PCl_2 was prepared by J. Lincoln by the chlorination of triphenylphosphine [121] in carbon tetrachloride.

f) $MePCl_3^+AlCl_4^-$ and $MePCl_4$

The complex $MePCl_3^+AlCl_4^-$ was prepared by J. Lincoln from methyl chloride, phosphorus trichloride and aluminium chloride according to the method of Clay [122,123]. This was reduced by aluminium powder in the presence of dry potassium chloride [124] to methyldichlorophosphine, which was then chlorinated in methylene chloride solution to give methyltetrachlorophosphorane.

g) $PhPCl_2Br_4$

This preparation followed the procedure of Meisenheimer [125] to produce $PhPCl_2Br_2$.

2.4ml (7.5g 49 mmole) bromine dissolved in carbon tetrachloride were slowly run into 6.4ml (8.5g 48 mmole) $PhPCl_2$ also in carbon tetrachloride, the total volume of solvent used being approximately 90ml. At first a sticky solid formed, but as the addition continued this became a bright yellow precipitate. Stirring was continued for several minutes. The solid was then filtered, washed with 30/40 pet ether, and dried at the pump, and then under vacuum.

Analyses Found: C,17.37; H,1.25; P,7.91; Cl,13.1; Br,66.54. $PhPCl_2Br_4$ requires C,14.45; H,1.01; P,6.21; Cl,14.22; Br,64.10.

h) Hexachloroantimonate salts

Each of the salts formed was found to attack Apiezon grease. Antimony pentachloride was purchased from Hopkin and Williams Limited.

$PCl_4^+ SbCl_6^-$

This was prepared by the method of Schmidtpeter and Brecht [126].

Typical preparation - 8.7ml (20g 67 mmole) antimony pentachloride were slowly dripped into 14.163g (67.996 mmole) phosphorus pentachloride dissolved in 170ml methylene chloride. This produced a thick white precipitate in a very exothermic reaction. The solid was filtered, washed with methylene chloride and 30/40 pet ether and dried at the pump. Drying was completed on a vacuum line.

Yields were quantitative. The preparation was repeated many times on scales yielding up to 35g product. With the larger scale preparations the solvent began to boil due to the exothermic nature of the reaction. Although undesirable inside a glove box, there was no effect on the product.

$PCl_4^+ SbCl_6^-$ could be stored in a stoppered flask, under nitrogen, for long periods, if all traces of solvent had been removed.

$PhPCl_3^+ SbCl_6^-$

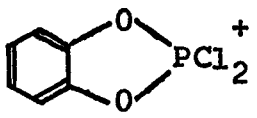
This was prepared according to the method of Ruff [127]. One of the two preparations was performed by J. Lincoln.

Inside the glove box 9.5ml (22g 74 mmole) antimony pentachloride in 37ml methylene chloride were slowly added to 5ml (6.60g 37 mmole) phenyldichlorophosphine in 55ml methylene chloride. The solution was left to stand for a few minutes. The precipitate was then filtered, washed with methylene chloride and 30/40 pet ether, dried at the pump and then on a vacuum line, producing fine white crystals.

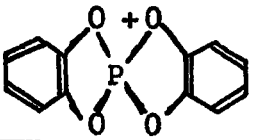
Yield = 15.30g = 76% as $PhPCl_3^+ SbCl_6^-$

Analyses Found: C,12.97; H,1.03; P,5.52; Cl,58.2

$PhPCl_3^+ SbCl_6^-$ requires C,13.13; H,0.92; P,5.64; Cl,58.13



$SbCl_6^-$ and



$SbCl_6^-$

These were produced from the parent phosphorane and antimony pentachloride in a similar manner to the preparation of $PCl_4^+ SbCl_6^-$.

The white compounds produced were extremely sensitive to moisture, turning yellow within seconds on exposure to the glove box atmosphere, then black. Hence they were stored in sealed containers immediately after removal of the solvent. Even in a stoppered container inside the glove box the solids could only be stored for a few days. The decomposition appeared to be catalysed by contact with metal spatulas, glass spatulas being used in the preparations. C,H,N analyses were not attempted as these involved use of metal capsules. Since $cat_2P^+SbCl_6^-$ attacked gelatin, P and Cl analyses were carried out in glass capsules.

(a) 3.35ml (7.84g 26.2 mmole) antimony pentachloride were added to 6.406g (26.08 mmole) catechyl phosphorus trichloride in a small quantity of methylene chloride. The precipitate was filtered and washed with 30/40 pet ether, producing a white solid.

Analyses Found: P,6.52; Cl,52.37

$(C_6H_4O_2)PCl_2^+ SbCl_6^-$ requires P,5.86; Cl,52.00

(b) 2.31ml (5.41g 18.1 mmole) antimony pentachloride mixed with about 7ml methylene chloride were added to 5.194g (18.38 mmole) biscatechyl phosphorus monochloride dissolved in the minimum quantity of methylene chloride. For a few seconds the solution remained yellow, then a thick precipitate formed. The solid was quickly isolated as it seemed to decompose in solution, producing a very dark colour in the liquid. The precipitate was filtered, washed with 30/40 pet ether, and dried under vacuum to produce an off-white, almost fawn solid.

Yield = 7.684g = 72.9% as $cat_2P^+ SbCl_6^-$

Analyses Found: P,5.28; Cl,36.8

$cat_2P^+ SbCl_6^-$ required P,5.62; Cl,38.6

i) $PCl_4^+AlCl_4^-$

The preparation follows the procedure of Petro and Shore [128]. 4.25g (20.4 mmole) finely ground phosphorus pentachloride and 2.83g (21.2 mmole) aluminium chloride (sublimed under vacuum to produce a light yellow solid)

were each dissolved in the minimum quantity of redistilled grade methylene chloride. The aluminium chloride solution, which was dark and contained a small amount of white solid (there seemed little difficulty in producing light coloured solutions in test experiments with reagent grade methylene chloride), was added to the phosphorus pentachloride solution, producing, after a few seconds, a white precipitate. This was filtered, washed with methylene chloride and 30/40 pet ether and dried at the pump.

Yield = 4.97g = 71.4% as $PCl_4^+AlCl_4^-$.

Analyses Found: P,9.16; Cl,83.5; Al,7.94

$PCl_4^+AlCl_4^-$ requires P,7.07; Cl,83.0; Al,7.90.

j) Phosphines

Triphenylphosphine, purchased from R. Emanuel Limited, was recrystallised from acetone by J. Lincoln.

Phenyldichlorophosphine, purchased from Eastman-Kodak as a yellowish liquid, was distilled by J. Lincoln to produce a colourless liquid.

Diphenylchlorophosphine (ICN - K and K Labs Inc), tributylphosphine (Aldrich Chemicals Limited), and dimethyloctadecylphosphine (kindly donated by Dr. A. F. Childs of Messrs. Albright and Wilson Limited) were used without further purification.

(iii) Ligands

The pyridine was Karl Fisher reagent grade (Hopkins and Williams Limited) and was used without further drying. 2,2'-dipyridyl was used as supplied (Koch-Light Limited A.R. grade). 1,10-phenanthroline was obtained anhydrous (R. Emanuel Limited) but before use was left in a

desiccator for several days over concentrated sulphuric acid and was stored open inside this desiccator.

Other pyridines were the best available commercial grade and were inspected by infra red spectroscopy to see if they contained excessive amounts of water, which gives an absorption at 3200-3500 cm^{-1}. 2-picoline, 2,4,6-collidine and 2-chloropyridine were distilled from potassium hydroxide pellets [129] and were subsequently stored under nitrogen. The solid pyridines usually contained no detectable moisture.

Tetra-n-propyl ammonium chloride and tetra-n-pentyl ammonium chloride, purchased from Eastman Kodak Limited, were dried under vacuum for several hours at 100°C and were then stored and handled entirely under nitrogen. Their infra red spectra showed no trace of water after the drying procedure. Tetraethyl ammonium chloride was purchased (Schuhardt Limited) as specified to contain 5-7% water.

(iv) Adducts

a) Nitrogen bases

Reactions and adduct formation were initially monitored in solution by ^{31}P nuclear magnetic resonance spectroscopy. Once reactions had been established attempts were made to isolate the solid complexes. Although the pyridine adducts could probably be precipitated from non polar solvents such as carbon disulphide (c.f. literature preparation of PCl_5.pyridine[8]) such solvents were not usually employed, because of the insolubility of likely contaminants. Any trace of hydrolysis of the chlorophosphoranes produces hydrogen chloride which

immediately attacks the pyridine to give the corresponding pyridinium chloride. This either precipitates as such, or in the case of phosphorus pentachloride at least, may react further to form the corresponding chlorophosphate salt.

e.g. $PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$

$py + HCl \longrightarrow pyH^+Cl^-$

$pyH^+Cl^- + PCl_5 \longrightarrow pyH^+PCl_6^-$

Hydrolysis reactions producing hexachlorophosphates were investigated with phosphorus pentachloride and 2,4,6-collidine (Chapter 3 section 1(ii)a). As the hydrolysis contaminants were found to be soluble in polar solvents preparation of the adducts in these media was attempted. A further advantage was that the complexes crystallised rather than precipitated out of solution, making them less likely to contain impurities, and also giving them a less strained crystal structure which would help n.q.r. investigations. Solvents which were not quickly attacked during the reaction were limited to nitrobenzene, nitromethane, and nitroethane. The latter two solvents were often slowly attacked. If, however, the solid was removed from solution as quickly as possible, there was little contamination of product. In a few instances, where any initial partial hydrolysis product could be clearly distinguished from the more slowly precipitating adduct (e.g. $cat_2Pdipy^+ Cl^-$), or where solvates were formed in nitrobenzene (e.g. $catPCl_2dipy^+ catPCl_4^-$)

reactions were also carried out in methylene chloride. The absence of hydrolysis products in solids produced was confirmed by the lack of a broad $\overset{+}{N}$-H absorption in their i.r. spectra. Pyridinium chloride, for instance, has two absorptions at 2840 and 2740 cm^{-1} [130]. Bis 2,4,6-collidinium chloride hexachlorophosphate (Chapter 3 Section 1(ii)a) has a broad absorption with peaks at about 2560 and 2600 cm^{-1}.

Hydrogen chloride tended to build up in the glove box because of hydrolysis of the phosphorus chloro-compounds by residual traces of water. This hydrogen chloride immediately attacked pyridine to form the corresponding pyridinium chloride, which then tended to fill the glove box with white fumes and also to contaminate the reaction solution. Two methods were used to combat this. A few reactions were performed under a nitrogen atmosphere outside the glove box, and the reaction vessel then transferred inside. This was unsatisfactory when using nitromethane or nitroethane since the solvent was slowly attacked. Thus transfer had to be via the quick entry port which restricted the flask to small volumes (less than about 40ml). Complete handling of reactions under nitrogen in closed systems outside a glove box becomes relatively cumbersome with the quantities of materials required. At least 3g product were necessary for the ^{35} Cln.q.r. and ^{31} P n.m.r. solid state investigations, and the average yield in any preparation was only about 60%.

A technique was later developed for conducting the reaction entirely inside a glove box.

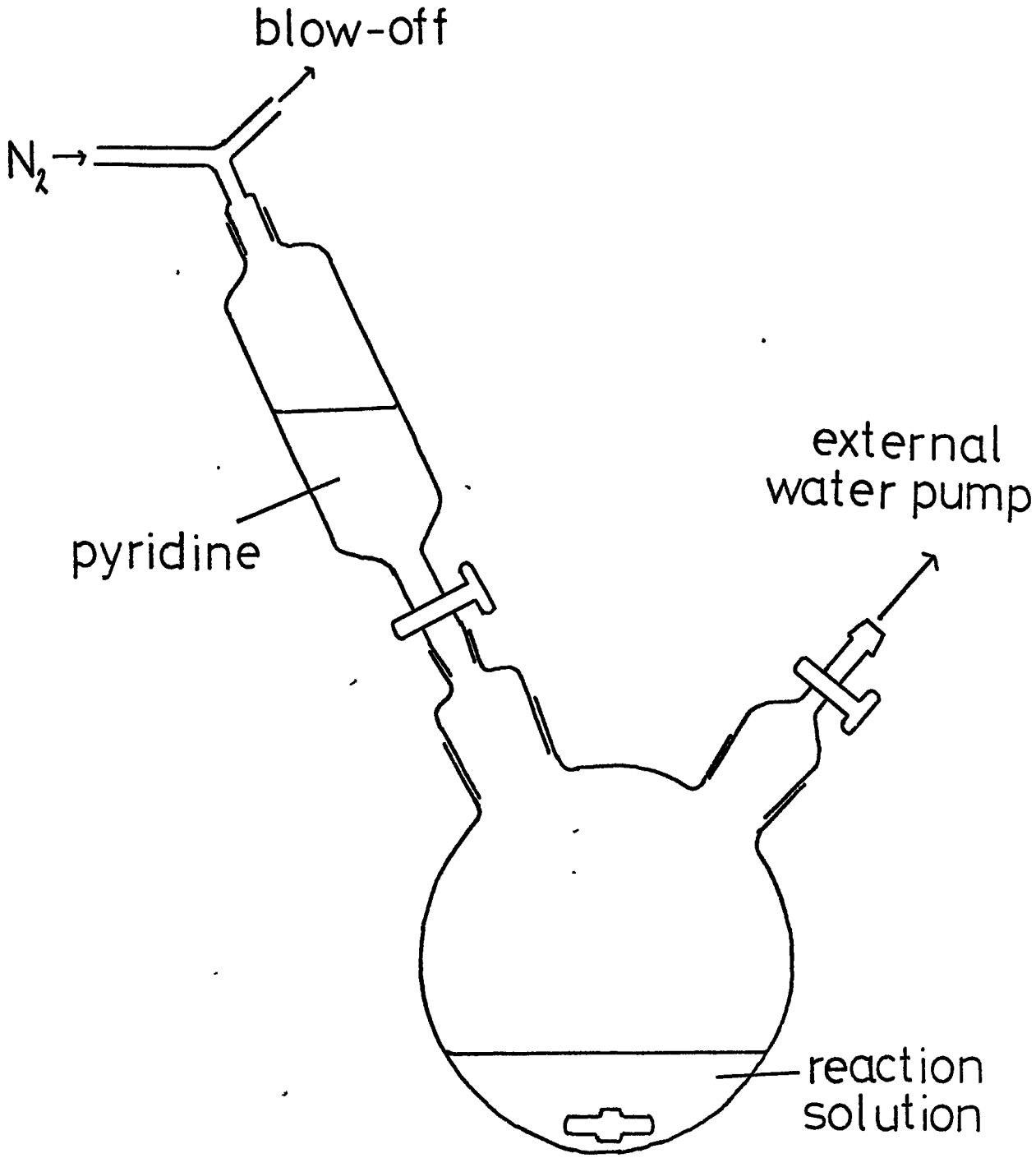


Fig 1 Glove box apparatus for reactions involving liquid pyridines

A gas tight system was erected inside the box (Figure 1) using quickfit apparatus, the pyridine being introduced into the box inside the stoppered dropping funnel. The pyridine was drawn into the reaction vessel under reduced pressure using suction from the external water pump, thus without contaminating the glove box atmosphere. After all the pyridine had reacted the apparatus was dismantled and the solid isolated by conventional glove box techniques.

The above apparatus was only necessary when handling liquid pyridines. Reactions involving solid pyridines were performed in stoppered flasks in the glove box with the minimum exposure of the free pyridine to the box atmosphere. Moist solids containing dipyridyl or phenanthroline had to be manipulated by glass spatulas. The ligands were found to attack metal spatulas, producing bright red complexes which could contaminate the product.

b) Chloride adducts

Few of the above difficulties applied where chloride ions were used as ligands. Non polar as well as polar solvents could be used.

Some of the adducts were partially dissociated in solution and would not crystallise out at room temperature. The use of non polar solvents increased the dissociation. Two techniques were then developed.

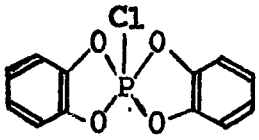
The adduct could be formed by fusing an intimate mixture of the compounds. It then contained no phosphorane contaminant but was discoloured by products from organic side reactions. The method was useful in preparing samples

for physical investigations where the absence of starting materials was important.

Aryl chloro phosphorus(v) species tend to decompose at elevated temperatures [131]. By conducting the heating and cooling as quickly as possible, decomposition was kept to a minimum. The temperature to which the mixtures were heated depended on the lowest-melting component in the mixture.

TABLE 4

M.pt. AND STABILITY OF VARIOUS STARTING MATERIALS

Compound	m.pt.	Thermal stability
$(C_5H_{11})_4N^+ Cl^-$	137° *	See below
$C_6H_5PCl_4$	73° [118]	Almost no change on heating to 100° partial decomposition at 140° complete when heated to 180° [132].
$(C_6H_5)_2PCl_3$	194-200° [133]	Decomposes on melting [133]
	166-8° [134]	-

*present work

Quaternary ammonium salts often show no precise melting point but decompose on heating [135].

e.g. $(Et_2\overset{+}{N}Me_2)\ Cl^- \longrightarrow Et_2NMe + MeCl$

No study has been made with tetrapentyl ammonium chloride. It was found here that the anhydrous salt had a sharp melting point at 137°C. In the Ph_2PCl_3 + $pent_4N^+Cl^-$ system

(Chapter 4 Section 3(i)) where no adduct formation occurred, the quaternary ammonium salt was recovered with little loss.

Secondly, if equimolar quantities of the quaternary ammonium salt and phosphorane were dissolved in methylene chloride, cooling of the solution could increase the extent of adduct formation by moving the equilibrium

$$R_4N^+Cl^- + Z_5P \rightleftharpoons R_4N^+ Z_5PCl^-$$

to the right. The solvent could then be slowly evaporated under vacuum. Although this method was not prone to side reactions, unless the cooling was sufficient and the rate of evaporation slow enough, the adduct was likely to be contaminated with starting materials. Thus the two methods were complementary.

In a number of favourable cases the adducts were isolable by the conventional technique of mixing the components in a suitable solvent at room temperature.

Preparation of specific compounds is described in more detail in the appropriate chapters.

(v) Solvents

Methylene chloride - Redistilled grade (BDH Limited) was dried and stored over mesh 4A molecular sieve under nitrogen.

Nitrobenzene - Analar grade (BDH Limited) nitrobenzene was distilled from phosphorus pentoxide and stored over molecular sieve under nitrogen.

30/40 pet ether - This was used as supplied (A.R. grade BDH Limited). The solvent was used to wash and dry complexes.

All reactants (with the exception of catechyl phosphorus trichloride) and complexes were found to be insoluble in

this solvent. Since 30/40 pet ether is immiscible with nitro-solvents it proved best to have the solid as dry as possible before washing, or to give a preliminary wash with methylene chloride or benzene.

Nitromethane - Eastman spectroscopic grade was used. This was found to be more slowly attacked than other grades. The solvent was dried and stored over mesh 4A molecular sieve.

Nitroethane - This was dried and stored over mesh 4A molecular sieve.

Benzene and diethyl ether were stored over sodium. Approximately 24 hours before use fresh sodium was added to ensure a completely dry solvent.

1,2-dichloroethane was distilled from phosphorus pentoxide.

Carbon tetrachloride was stored over phosphorus pentoxide.

Acetonitrile was stored over mesh 4A molecular sieve.

Chloroform was either used as reagent grade (containing about 1% ethanol) or was freshly distilled from phosphorus pentoxide (see text for which grade was used in any particular experiment).

Symtetrachloroethane, technical grade, was distilled from calcium sulphate [136]. The colourless distillate turned yellow over a period of days. The technical grade solvent turned yellow on addition of pyridine. This did not occur after distillation.

Tetrahydrofuran was supplied freshly dried as a laboratory service. The tetrahydrofuran was stood over potassium hydroxide pellets, and then refluxed with potassium until

the addition of benzophenone produced a permanent blue-purple colour. The liquid was then distilled into a flask containing lithium aluminium hydride and distilled from there when required for use.

Tetrahydrothiophene was dried by storage over calcium hydride c.f. Ref.137.

Other compounds used in this work were the best available commercial grade and were used without further purification. These included bromine, phosphorus tribromide, cycloheptatriene and sodium tetraphenylborate.

(vi) Analyses

Carbon, hydrogen and nitrogen were determined as a laboratory service by microcombustion with a Perkin Elmer 240 Elemental Analyser. The reliability of the machine was variable. A satisfactory analysis was usually considered to be within 0.5% of the theoretical analysis, together with satisfactory phosphorus and chlorine analyses.

The phosphorus and chlorine analyses were considered more reliable. These and the other analyses below were performed by R. Coult. A sample (about 40mg) weighed in a gelatin capsule was decomposed by heating with sodium peroxide in a nickel Parr bomb. The residue was washed out, acidified with concentrated nitric acid and made up to 100ml with distilled water. For phosphorus a suitable aliquot was treated with ammonium molybdate - ammonium vanadate reagent and the absorbance measured at 420 μ using a SP500 spectrophotometer. Chlorine was determined by potentiometric titration. A

suitable aliquot was titrated against $\frac{N}{100}$ silver nitrate solution using Ag, AgCl electrodes in an acetone medium.

Interference occurred in the analysis of a number of 2,2'-dipyridyl or 1,10-phenanthroline complexes by the formation of a red colour in the solution. This was presumably due to incomplete decomposition of the ligand which then complexed with free metal ions.

Direct estimation of 2,2'-dipyridyl was performed for a number of samples. The complexes were decomposed by dissolving in water. The dipyridyl was then estimated spectrophotometrcially at 522μ as its ferrous salt.

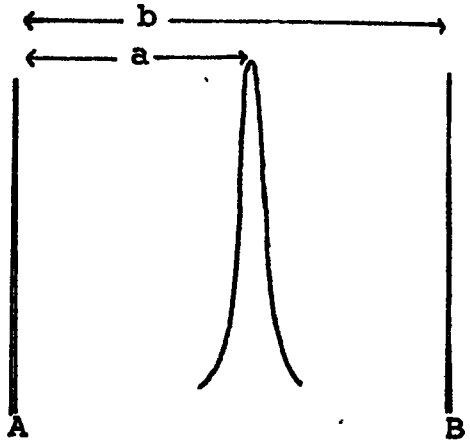
Bromine and iodine were determined iodometrically following a Schoniger Oxygen Flask combustion of the compound as described by Ingram [138]. Aluminium was determined by atomic absorption spectroscopy.

2. ^{31}P nuclear magnetic resonance spectroscopy

^{31}P nuclear magnetic resonance spectra were obtained using a Perkin Elmer R10 high resolution n.m.r. spectrometer operating at 24.29 MHz. The spectrometer embodies a permanent magnet of field 14,000 Gauss (1.4 Tesla). In order to scan larger fields than possible on the conventional spectrometer (200 ppm), a modification had been introduced to extend the maximum sweep width to 367 ppm. The sweep with this modification was linear for about 70% of the range then departed progressively from linearity. The modification was especially useful in the recording of spectra of solids.

The computer of average transients (C.A.T.) was triggered by the revolving recorder drum at the beginning of each sweep. The signal from the output amplifier was fed into an analogue/digital converter and was accumulated in the computer. After processing the accumulated spectrum was fed back into the R10 and could be plotted on the chart recorder. Samples were enclosed in 8.5mm outside diameter non spinning tubes, closed with neoprene bungs covered with paraffin film (using "parafilm" tape).

Phosphorus trioxide, P_4O_6, was used as an external reference. Shifts are quoted, however, with respect to 85% aqueous phosphoric acid, P_4O_6 then having a shift of -112.5 ppm [139]. Shifts to lower field of H_3PO_4 are taken as negative. Allowance was made for the non-linearity of the wide sweep by recording the reference signals on either side of the experimental peak using the field shift, and calculating the experimental shift from the distance of the experimental peak from the references, and the known separation of the reference peaks, i.e.



The separation of the reference peaks A and B is, say

1 kc/s $\equiv$ 16.67 ppm

Shift of experimental peak from A

$$= \frac{a}{b} \times 16.67 \text{ ppm}$$

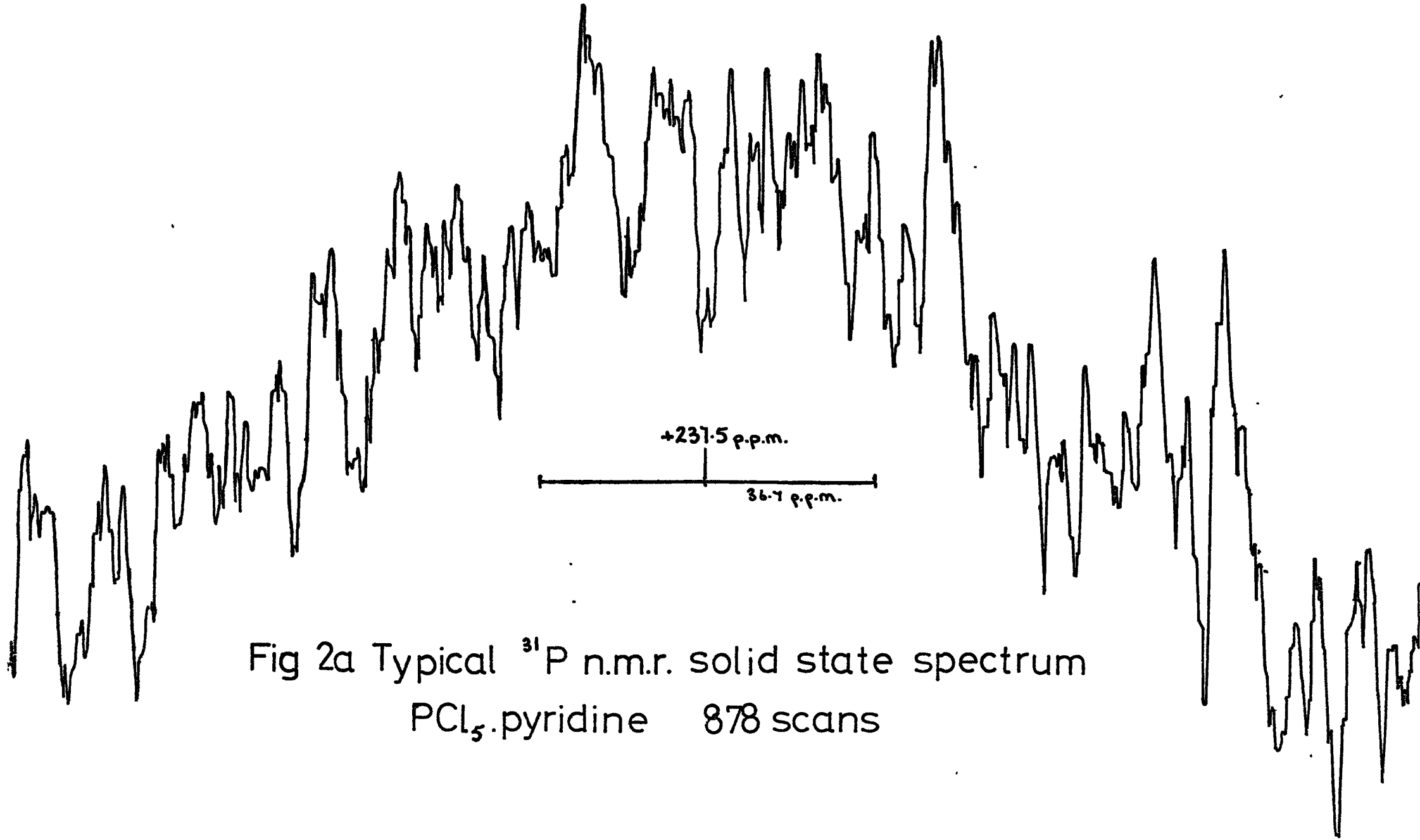


Fig 2a Typical ^{31}P n.m.r. solid state spectrum

PCl_5.pyridine 878 scans

Saturated solutions were generally used. The n.m.r. spectra were normally first run over a large range covering the six co-ordinate region and, if possible, the hydrolysis product region, using the wide sweep facility, then run over a narrower range (60 or 100 ppm) to obtain accurate shift data. In favourable circumstances the signals appeared easily on a single scan, but with only slightly soluble complexes up to about 200 accumulated scans were necessary. Spectra were accumulated until the signal/noise level was at least ~15:2.

Comparison of the areas of two peaks was achieved either by weighing the traced peaks accurately or by comparing the ideal areas using a Dupont 310 curve analyser.

Solid spectra were obtained by leaving the spectrometer to accumlate overnight, up to 1024 scans. Wide sweep was usually necessary to show the complete peak. A typical spectrum is shown in Figure 2A. A similar radiofrequency level was used as for solutions. Solids usually had to equilibrate in the machine for about 30 minutes before they had stabilised enough to start the accumulation. In order to determine peak maxima two techniques were used. The first consisted of drawing an "ideal" curve through the spectrum by hand, then determining the peak centroid by the centre of the absorption at various heights on the peak, measured parallel to the baseline. The peak maximum was taken as the average of a number

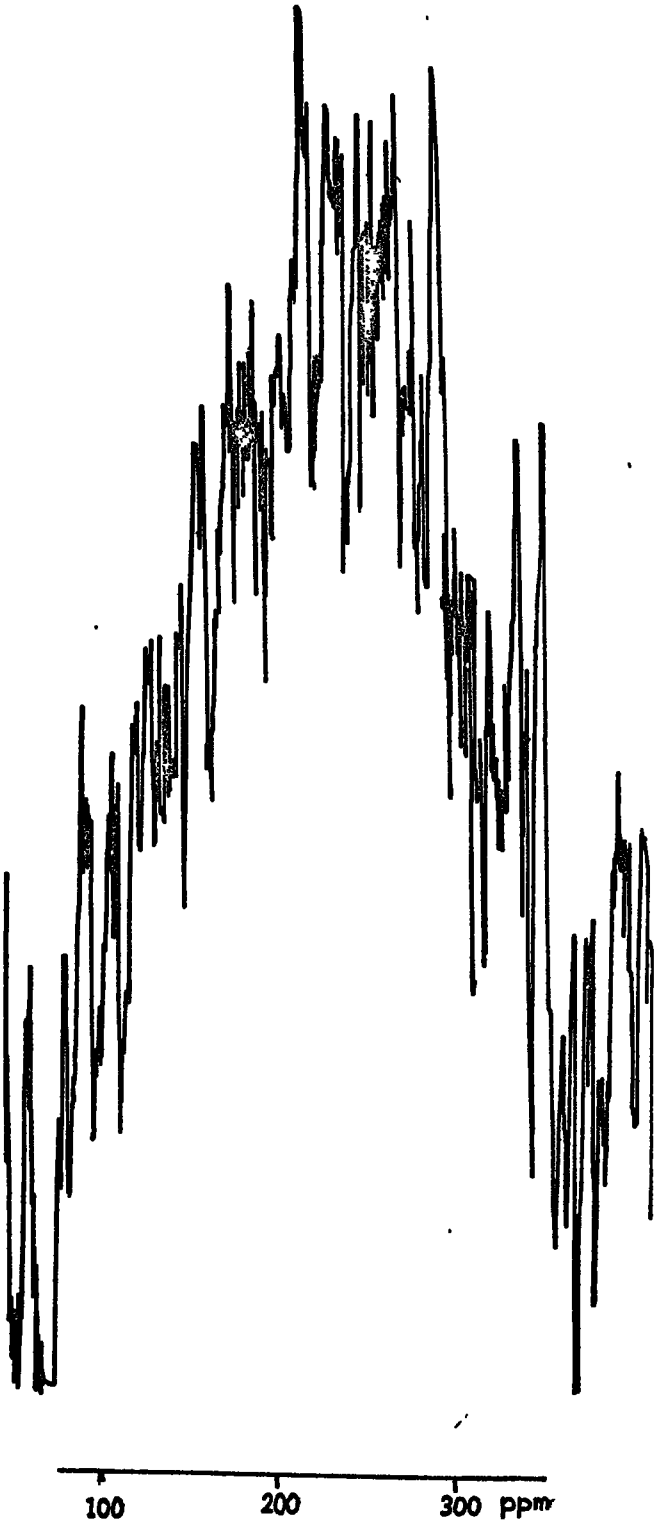


Fig 2b PCl_5.pyridine read out at a speed suitable for curve-fitting

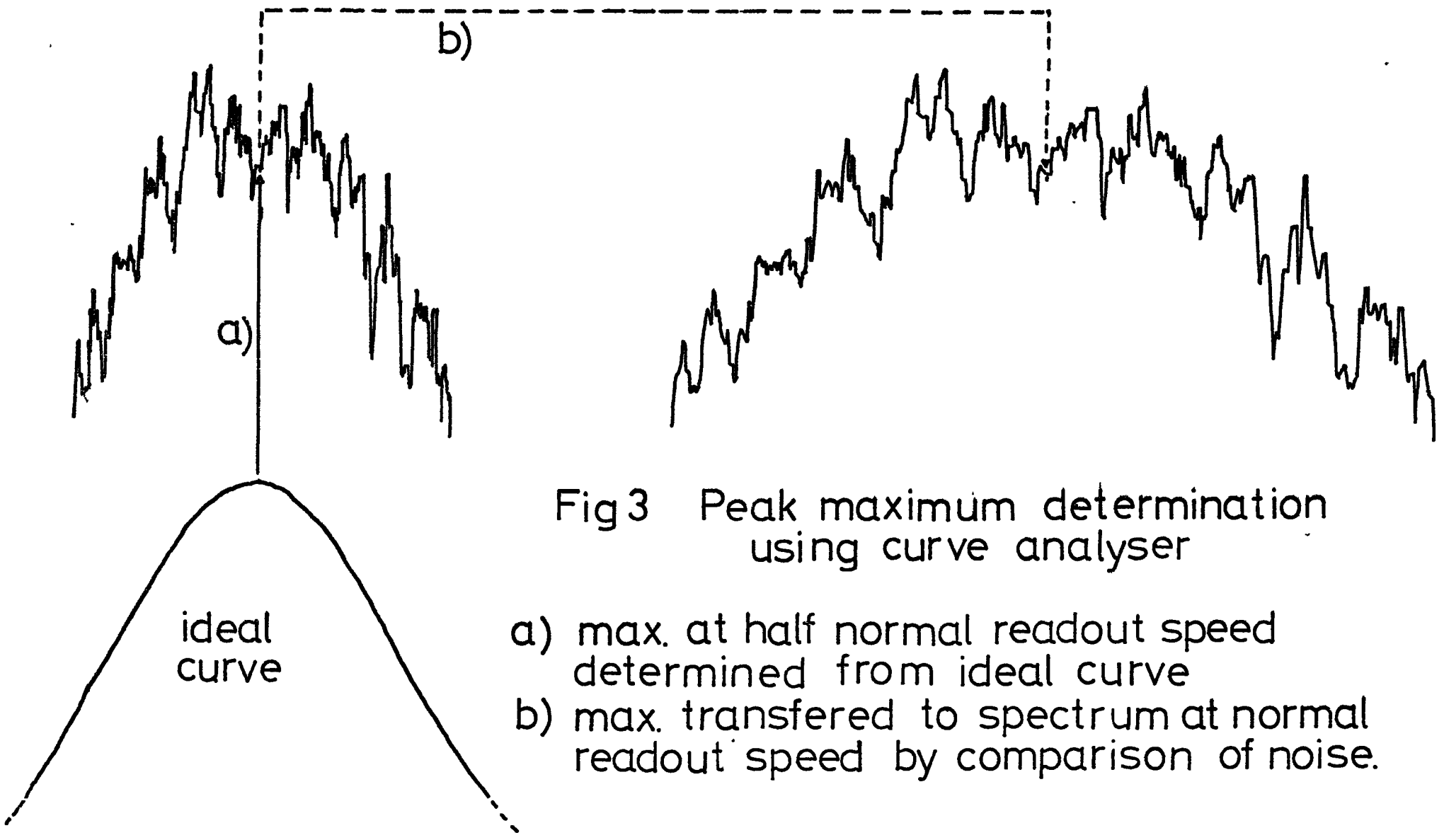


Fig 3 Peak maximum determination using curve analyser

a) max. at half normal readout speed determined from ideal curve
b) max. transfered to spectrum at normal readout speed by comparison of noise.

of these values. The second technique involved simulating the spectrum on the Dupont 310 curve analyser. The maximum of this ideal peak was then determined visually. In order to fit the analyser conveniently the spectrum was recorded at $\frac{1}{2}$ or $\frac{1}{4}$ of the normal drum speed, making the peak sharper (many of the spectra shown in this work are read out at these speeds. The effect on the spectra can be seen by comparing figures 2a and b). The maximum was then marked on the experimental peak. A similar position was then marked on a spectrum read out at the normal drum speed by comparison of its position relative to the noise on the peak. The shift of the peak was then calculated, this being only possible on a spectrum read out at normal speed. This procedure was repeated a number of times for each overnight accumulation.

The above procedure is exemplified in Figure 3.

With the exception of only the sharpest, most distinct peaks several independent overnight runs were made for each sample. The error limits were determined from the spread either of the separate calculated values or of the average values determined from separate runs. The accuracy of the determinations depended on the width of the signal and the signal/noise ratio, and also to the degree of slope on the baseline. A sloping baseline is caused by the gradual drift in balance of the sample during the run. Slightly sloping baselines can be almost completely compensated in both techniques described above, but a larger slope tends to distort the spectrum beyond

compensation. A positive slope tends to give a peak with an apparent shift higher than its true value and a negative slope a lower shift. The effect of sample drift becomes more pronounced the broader the signal, or where there is only a small amount of phosphorus in the sample.

The operating temperature of the spectrometer was $34.2^{\circ}C$.

3. Other Spectroscopic Techniques

(i) Infra Red Spectroscopy

Infra red spectra of solids were run as nujol mulls from 4000 to 250 cm^{-1} using a Perkin Elmer 457 grating spectrometer. The nujol was stored over sodium. Phosphorus-chlorine compounds were found to attack unprotected caesium iodide plates which were necessary to give spectra to 250 cm^{-1}. Mulls were run in potassium bromide plates to give spectra from 4000 to 650 cm^{-1}, and then in caesium iodide plates protected with polythene sheets (giving absorptions below 1000 cm^{-1} at 712 and 722 cm^{-1}) to give spectra between 650 to 250 cm^{-1}. Except where otherwise stated all spectra were run at a medium scan rate (18 mins over the range 4000-250 cm^{-1}).

Solution i.r. spectra were run in KBr solution cells with a 0.1 mm spacing between the plates. Saturated, or near saturated solutions were used.

(ii) ^{35} Cl Nuclear Quadrupole Resonance

N.q.r. spectra were recorded on a Decca spectrometer by Dr. R. J. Lynch. 16mm outside diameter ampoules were usually used. Liquid nitrogen temperatures were necessary

for signal detection. All spectra quoted in this work were run at 77K. Slow overnight scans between about 36 and 23 MHz were first run to detect the signals in the region expected for ^{35}Cl resonances of chlorine bonded to phosphorus. Narrower scans were then run to give a more accurate signal position. Zeeman modulation was used throughout. The line shape produced by the spectrometer was a mixture of the first and second derivative of the absorption curve. Due to their probable thermal instability, annealing of the samples at an elevated temperature was not attempted.

CHAPTER 3

PHOSPHORUS PENTACHLORIDE AND ITS DERIVATIVES

1. PCl_5.Pyridine and Related Complexes

(i) Introduction

The 1:1 complex between phosphorus pentachloride and pyridine was first mentioned by Holmes [27] in 1953. Gutmann [28] in 1954 also noted its formation. The first detailed account, however, was given by Beattie and Webster [8] in 1961. Earlier work either gave results which would not have detected the presence of addition compounds [140] or yielded pyridinium chloride mixtures by partial hydrolysis of the reactants [3]. The former paper does, however, show the great resistance of the pyridine ring to attack by phosphorus pentachloride, heating in a sealed tube at 210-220° for 15-20 hours being necessary. Refluxing in phosphoryl chloride has very little effect.

Beattie and Webster isolated the moisture-sensitive 1:1 complex from carbon disulphide solution [8]. They measured its infra red and Raman spectra and found it to be undissociated in benzene and acetonitrile [11,29]. Holmes [20,30] measured the heat of reaction in nitrobenzene solution (24.5-26.5 kcal/mole) and, using cryoscopy and conductivity measurements, suggested that the adduct was molecular in that solvent. Latscha [31] and Dillon [23] measured the ^{31}P n.m.r. chemical shift of phosphorus pentachloride in neat pyridine solution ($\delta^{31}P$ + 234, + 233.2 ppm respectively) attributing this peak to the molecular complex. Dillon [23] also found a value of + 232.6 ppm for the complex in dichloroethane

and investigated the PCl_5/2-chloropyridine and PCl_5/3-picoline systems. The "PCl_5.pyridine" complex of Wieker, Grimmer and Kolditz [141] appears from their ^{31}P n.m.r. shift (+ 296 ppm solid, + 310 ppm acetonitrile solution) to be a hexachlorophosphate salt, probably pyridinium hexachlorophosphate. Acetonitrile attacks phosphorus pentachloride at room temperature [142] and so may also react with the complex. Other workers, however, have found no difficulty in using acetonitrile solutions [11].

R. C. Paul and co-workers [25,32] prepared PCl_5.pyridine, PCl_5.quinoline, PCl_5.3-picoline and PCl_5.4-picoline and reported infra red and conductance measurements (the latter in nitrobenzene solution). The conductance data suggest that the PCl_5/pyridine complex is ionic, in contrast with Holmes' conclusions [20]. Their infra red spectrum of PCl_5.pyridine does not agree with that of Beattie and Webster [11].

As has been mentioned in Chapter 1 section 1, Hensen and Sarholtz [21] observed the ultra violet spectrum of PCl_5.pyridine, comparing it with other adducts of pyridine. A shorter list was also mentioned from the heats of formation of several pyridine adducts [20]. Lehr and Schwarz [33] compared the reactivity of ammonium chloride with PCl_6^-, PCl_5.pyridine, PCl_5 and PCl_4^+ and found that reactivity increases with Lewis acidity along the series,

$$PCl_6^- < py.PCl_5 < PCl_5 < PCl_4^+$$

In contrast Zhivukhin et al. [34] found that the reactivity of phosphorus pentachloride with ammonium chloride increases on addition of pyridine. This would suggest the complex to have the structure $PCl_4py^+Cl^-$.

Finally PCl_5.pyridine has been mentioned in a patent concerning α-olefin homopolymerisation [35].

A 1:1:1 complex of phosphorus pentachloride with pyridine and phosphoryl chloride is known [28]. On the basis of conductivity titrations it is formulated as $C_5H_5N.POCl_2^+PCl_6^-$. A 5:1 complex of isoquinoline with phosphorus pentachloride has been reported [143]. The elemental analysis of a complex of this stoichiometry would be very similar, however, to that of the more probable isoquinoline hydrochloride, formed as a hydrolysis product.

Deveney and Webster [9,22] have isolated a 1:1 complex of phosphorus pentachloride with 1,10-phenanthroline. From cryoscopic and conductivity measurements, and also by comparison of its infra red spectrum with that of $PCl_4phen^+SbCl_6^-$ [9,22], they formulated the complex as $PCl_4phen^+Cl^-$. Dillon [23] has isolated a 1.33:1 complex of phosphorus pentachloride with dipyridyl, the solid ^{31}P n.m.r. spectrum of which shows an asymmetric peak at + 292.4 ppm with a pronounced shoulder to lower field. This complex gives ^{31}P n.m.r. peaks in nitrobenzene solution at + 191.3 ppm and + 299.0 ppm. The latter is attributed to PCl_6^- and the former to the PCl_4^+ ion co-ordinated by two nitrogen atoms, rendering the complex ionic (c.f. the shift of the PCl_5.pyridine complex at + 233 ppm). PCl_4dipy^+ has also been mentioned as a private communication by Webster in reference 29.

Thus, with the exception of the work of Paul, Sehgal and Chanda [25,32] and that of Zhivukhin et al, [34] the results suggest that PCl_5.pyridine is molecular and undissociated

both in the solid and also in solution, whilst adducts with bidentate pyridines appear to be ionic. The exact formulation of these latter complexes appears to differ with differing ligands however.

Of the complexes of phosphorus pentachloride with other donors, "$Ph_3PO.PCl_5$" appears from its ^{31}P n.m.r. spectrum (δ^{31}P -67.2, +297.0) [39] to be $Ph_3PCl^+PCl_6^-$. Shifts for the Ph_3PCl^+ and PCl_6^- ions have been reported as -66 and +295 ppm respectively [31,58]. Indeed $Ph_3PCl^+PCl_6^-$ has been prepared from Ph_3PO and PCl_5 [33]. Similarly "$(n\text{-}C_4H_9)_3PO.PCl_5$" ($\delta^{31}$P -103.5, +296.0) [39] appears to be $(n\text{-}C_4H_9)_3PCl^+ PCl_6^-$, the shifts of these ions being reported as -102 and +295 ppm [31,58]. The analyses do, however, correspond to the adducts [39]. Frazer et al. [41] isolated the complex between Ph_3PO and PCl_5 but from its infra red spectrum formulated the complex as $Ph_3PCl_2.POCl_3$. If dissociated in solution this would show signals attributable to Ph_3PCl^+ (-66 ppm) and $POCl_3$ (-2 ppm) [89].

(ii) Present Work

a) Solution Investigations

PCl_5.pyridine is thus well established. To extend knowledge of this type of complex, solutions of phosphorus pentachloride with various substituted pyridines were investigated using ^{31}P n.m.r. techniques. It was hoped to discover any change of behaviour with respect to substitution, together with any trends in the n.m.r. shift. The effect on adduct formation of either lowering the

basicity of the pyridine or having large α substituents on the pyridine ring, was also studied.

A large variety of substituted pyridines was investgiated (see Table 5), falling into the categories of methyl pyridines (2,4,6-collidine, 2- and 3-picoline); sterically unhindered pyridines of weaker basicity than pyridine itself (3-F,Cl,Br,I,CN pyridine, 4-CN , 3,5 di-Cl-pyridine, pyrazine); and hindered 2-substituted pyridines of low basicity (2-F,Cl,Br,CN pyridine). In addition a bidentate pyridine, 1,10-phenanthroline, was investigated.

Solutions were generally made up with a large excess of pyridine in order to increase the possibility of complex formation with weak bases. For some low basicity pyridines, and for the 2-substituted methyl pyridines solutions were also made up containing equimolar quantities of the reactants.

The results are shown in Table 5. The pyridines are arranged in order of the pKa values of their conjugate acids. This was used to give an approximate relative measure of basic strength for monodentate pyridines without regard to larger steric effects as expected for complexation with phosphorus pentachloride.

TABLE 5

SOLUTION INVESTIGATIONS OF

PCl_5/PYRIDINE REACTIONS

	pKa [144]	$\delta^{31}P$	Solvent ℓ
2,4,6-collidine	7.4	-217.0 (PCl_3)	1:1 in $PhNO_2$
3,5-lutidine	6.2*	adduct insoluble	-
2-picoline	5.9	-217.3 (PCl_3)	1:1 in $PhNO_2$
3-picoline	5.6	+228.0 ‡	neat
pyridine	5.2	+228.0	neat
1,10-phenanthroline	pK_1 4.9	+190.6 +299.0	sat $PhNO_2$
		+193.3 +298.6	1:1 in $PhNO_2$
3-I pyridine	3.3	+229.7	sat $PhNO_2$
3-F pyridine	3.0	+229.3	neat
3-Br pyridine	2.9	+228.3	neat
3-Cl pyridine	2.8	+228.6	neat
4-CN pyridine	1.9	+227.5	sat $PhNO_2$
3-CN pyridine	1.4	+228.1	sat $PhNO_2$
pyrazine	0.8	+224.9	sat $PhNO_2$
		+219.1	1:1 in $PhNO_2$
3,5-diCl pyridine	0.7*	+222.7	sat $PhNO_2$
		+170.2	1:1 in $PhNO_2$
2-Br pyridine	0.8	+83.0	neat
2-Cl pyridine	0.6	+109.1	neat
		+84.8	1:1 in $PhNO_2$
2-CN pyridine	-0.3	+170.8	neat
		+171.3	1:1 in $PhNO_2$
2-F pyridine	-0.4	+184.7 +296.7	neat
		+77.8	1:1 in $PhNO_2$

Peaks due to slight hydrolysis are not tabulated.

ℓ solvent either neat pyridine, nitrobenzene saturated with pyridine, or containing equimolar quantities of pyridine and PCl_5

‡ a peak at -203.3 ppm slowly appears

* pKa's from ref.145

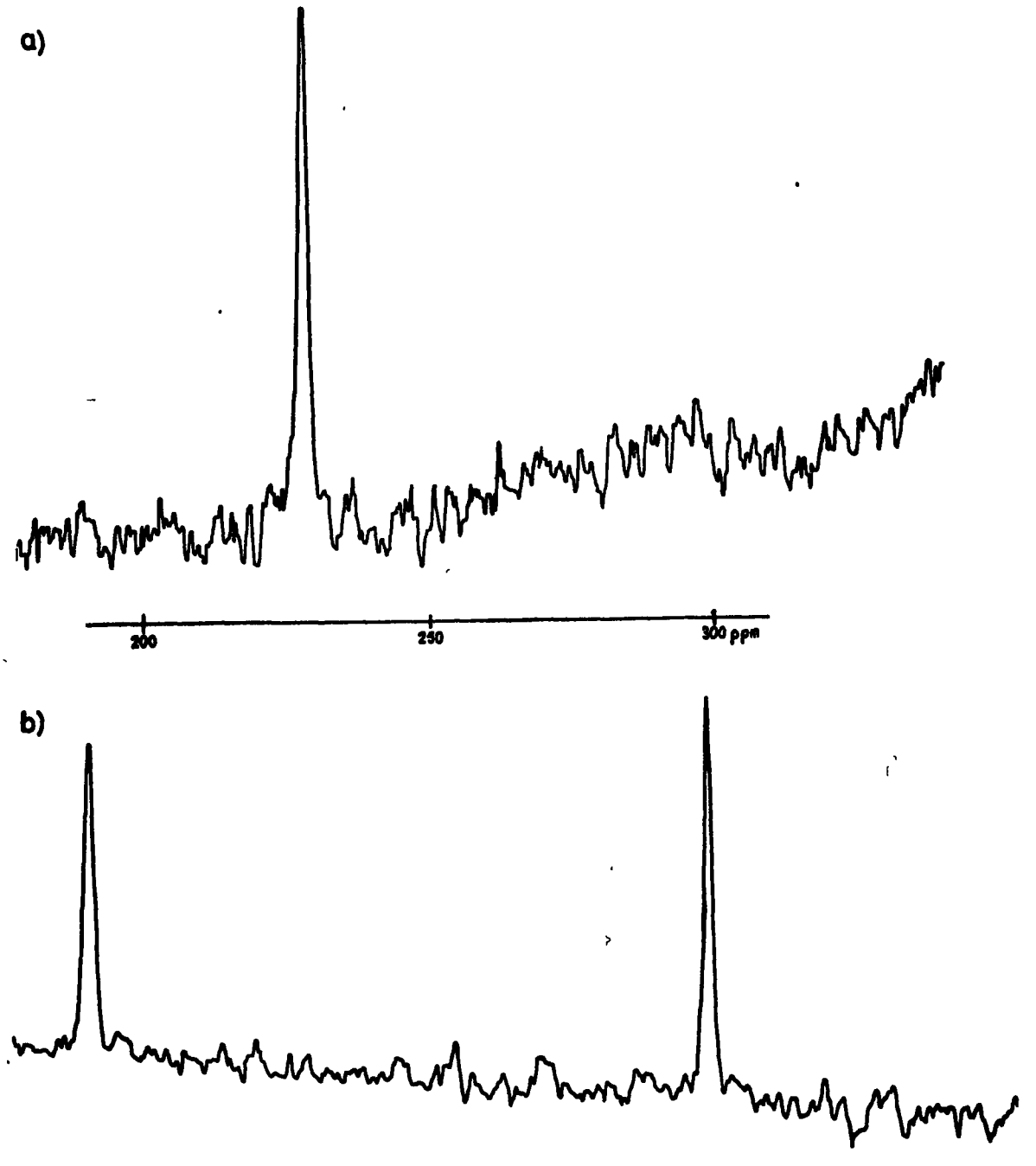


Fig 4 ^{31}P n.m.r. solution spectra

a) PCl_5 in 3-bromopyridine 109 scans
b) PCl_5 in nitrobenzene saturated with 1,10-phenanthroline 87 scans

The results compare well with the existing values.

TABLE 6

KNOWN RESULTS FOR PCl_5/PYRIDINE MIXTURES

	$\delta^{31}P$	Ref.
PCl_5/2-Cl pyridine	+97.2 ppm	23
PCl_5/pyridine	+233.2	23
PCl_5.pyridine	+234	31
PCl_5/pyridine in $PhNO_2$	+226.6	23
PCl_5/pyridine in $C_2H_4Cl_2$	+231.5	23
PCl_5/3-picoline in $C_2H_4Cl_2$	+231.5	23
PCl_5/dipyridyl in $PhNO_2$ *	+189, +293	23

* The solution was made up by dissolving the solid complex PCl_5 1.33. dipy

Bidentate pyridines give peaks in the ^{31}P n.m.r. spectrum at around +190 and +296 ppm, both in the 6-co-ordinate region (Fig. 4). The latter peak is attributable to PCl_6^-, whilst the lower field peak is attributable to PCl_4dipy^+ or PCl_4phen^+, with the dipyridyl and phenanthroline acting as bidentate ligands. The ^{31}P n.m.r. spectra of the complexes $PCl_4phen^+ SbCl_6^-$ and $PCl_4dipy^+SbCl_6^-$ described in Chapter 3 Section 2(ii)a, also show peaks at about +190 ppm attributable to these cations. The rigid structure of 1,10-phenanthroline would make monodentate co-ordination highly unlikely. Even with the more flexible 2,2'-dipyridyl, few structures have been proposed where

only one nitrogen co-ordinates to a particular atom [146-151], and none have been conclusively determined.

The ratio of the areas underneath the PCl_4phen^+ and PCl_6^- peaks are approximately equal both when the solution contains equimolar quantities of phosphorus pentachloride and phenanthroline, and when an excess of phenanthroline is present. The species present in solution are then $PCl_4phen^+PCl_6^-$ and free phenanthroline. The 1:1 complex is not found even when free phenanthroline is present. Disproportionation was found to occur when complexes of the composition $PCl_4phen^+(PCl_6^-)_{1-x}\ Cl^-_x$ were dissolved in nitrobenzene,

$$PCl_4phen^+\ (PCl_6^-)_x\ Cl^-_{1-x} \rightarrow \left(\frac{1+x}{2}\right) PCl_4phen^+PCl_6^- + \frac{1-x}{2}\ phen$$

This will be discussed more fully in Chapter 3 section 1(ii).

The conclusion that $PCl_4phen^+PCl_6^-$ is the stable solution species contrasts with the work of Webster and Deveney [22]. They dissolved the solid 1:1 complex in nitrobenzene and found the structure to be $PCl_4phen^+Cl^-$, using molecular weight and cryoscopic measurements. With these techniques very dilute solutions must be used, whereas with ^{31}P n.m.r. spectroscopy very concentrated solutions are required. The discrepancy could be explained by a change in structure on dilution, as is the case of phosphorus pentachloride itself [49]. At very low concentrations the dominant equilibrium is,

$$PCl_5 \rightleftharpoons PCl_4^+ + Cl^-$$

whereas at higher concentrations

$$2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$$

predominates.

Pyridine, 3-X pyridine (X=F,Cl,Br,I,CN), 4-CN pyridine

Phosphorus pentachloride with excess of a monodentate pyridine substituted only in the 3, 4 or 5 position gave a single ^{31}P n.m.r. peak between +228.0 and +229.7 ppm, about 38 ppm upfield from the positions of PCl_4dipy^+ and PCl_4phen^+ (Figure 4). The large positive shifts indicate that six co-ordinate species are formed, while the shift difference from the cationic complexes is compatible with their formulation as molecular compounds e.g. $PCl_5.py$. Similar shifts found with the solid state complexes further suggest that the peaks are due to a distinct molecular forms and not to an equilibrium between say $PCl_4py_2^+$ and PCl_6^- (Chapter 3 section 1(ii)b). Indeed the solution peaks are found not to exchange with the corresponding $PCl_4py_2^+$ species (Chapter 3 section 2(ii)a).

The chemical shift seems little affected by the electronegativity of the pyridine ring. There is no observable trend in the shifts of the $PCl_5.py$ complexes, the 2 ppm spread of shifts being within the sum of experimental error and solvent effects. The constant shift of the species also indicates that under these conditions the complexes are completely undissociated. Any dissociation would lead either to the appearance of a ^{31}P n.m.r. line attributable to free PCl_5 (molecular PCl_5 being the easiest of the phosphorus pentachloride species to detect in nitrobenzene solution by ^{31}P n.m.r. spectroscopy) or would move the peak downfield from the

position of $PCl_5.py$ as it exchanges with free PCl_5. The narrow range together with the similarity of the shifts of PCl_4dipy^+ and PCl_4phen^+ suggest that ^{31}P n.m.r. may be used to distinguish closely related 6 co-ordinate structural types.

Where investigated the complexes were completely associated even when there was no excess of pyridine, similar shifts to those in Table 5 being found. The solutions were produced by the equilibrium of $PCl_4L_2^+ SbCl_6^-$ (Chapter 3 section 2(ii)a) according to the equation,

$$PCl_4L_2^+SbCl_6^- \rightleftharpoons PCl_5.L + SbCl_5.L$$

$PCl_5.L$ must be produced with no excess of ligand, L. $SbCl_5.L$ would be expected to be completely associated, as antimony pentachloride is an extremely strong Lewis acid [1]. Unfortunately due to the insolubility or lack of formation of the corresponding $PCl_4L_2^+SbCl_6^-$ complex, the method could not be used to generate the $PCl_5.L$ complex, where L = 3-CN or 4-CN pyridine.

When the solid $PCl_5.L$ complex is dissolved in nitrobenzene (L = pyridine, 3-Cl, 3-Br pyridine) shifts are found at about + 230 ppm or higher, again indicating that no dissociation is occurring. This is discussed more fully in Chapter 3 section 1(ii)b.

The shift order

$$PCl_4py_2^+ < PCl_5.py < PCl_6^-$$

is consistent with an increase of the shielding on phosphorus by an increase in its negative charge.

The similarity of the shifts in nitrobenzene solutions of phosphorus pentachloride saturated with 3- and 4-cyanopyridine to those of the other unhindered pyridines indicates that similar species are present in the solution and thus similar co-ordination is found i.e. through the ring nitrogen atom. This mode of co-ordination is generally found [152,153] due to the greater nucleophilic power of the pyridine nitrogen over the cyano nitrogen [152]. Further co-ordination through the cyano group would not be expected due to the low acidity of phosphorus pentachloride and also to the excess of the cyanopyridine present. It is, however, known to occur with stronger acceptors, such as tin tetrachloride in the absence of excess cyanopyridine [153]. Bridging cyanopyridines are then found.

Pyrazine; 3,5 di Cl pyridine

Pyrazine and 3,5-dichloropyridine give slightly lower shifts with phosphorus pentachloride (+ 224.9 + 222.7 ppm respectively) than the pyridines previously discussed. In order to discover whether the shifts of the complexes are genuinely different or merely due to slight dissociation of the complexes, solutions containing equimolar amounts of pyridine and phosphorus pentachloride were made up. If the peak is due to an equilibrium then the shift will be at much lower field under these conditions. With pyrazine a single sharp line is found at +219.1 ppm, with 3,5-dichloropyridine at +170.2 ppm. The large shift

difference in this latter case is almost certainly due to exchange between free phosphorus pentachloride and the complex. In a 1:1 solution of phosphorus pentachloride and 3,5-dichloropyridine the complex is then about 60% associated. The pyrazine system is more ambiguous. The slightly lower value for the shift may be due to slight dissociation but may also be due to the pyrazine being less than 100% pure, the PCl_5/pyrazine ratio then becoming less than 1:1. The latter explanation is almost certainly valid. PCl_5.pyrazine produced by the partial decomposition of $PCl_4(pyrazine)_2^+SbCl_6^-$, thereby containing equimolar quantities of reactants has a shift of +224.2 ppm (Chapter 3 section 2(ii)a). The pyrazine complex may have a slightly different shift compared with other pyridine complexes because it has a slightly different structure. It will, however, be expected under the reaction conditions still to co-ordinate through only one nitrogen. As with the 3- and 4-cyanopyridines, although co-ordination through two as well as one site is known [154,155] this would not be expected with a molar ratio of pyridine : PCl_5 of 1:1 or greater.

With boron Lewis acids a correlation has been made between the ^{11}B n.m.r. shift of a complex and the basicity of the ligand [156,157]. If this correlation also holds for ^{31}P n.m.r., it would explain the lower shift of the pyrazine complex, but as no trends in shift were found for the more basic pyridines, the correlation does not seem applicable to these systems.

The ligands used for the ^{11}B correlation [156] did not overlap sufficiently with the ligands used here for a more direct comparison.

The 3,5-dichloropyridine ligand has its bulky substituents far removed from the nitrogen. The partial formation of the complex must then be ascribed to the lowering of the basicity of the nitrogen by the electron withdrawing capacity of the chlorines, and not to their steric effects. This provides the only definite example where co-ordination is lowered by electronic effects, the other systems described later being ambiguous because steric effects may play a large part.

3,5-dichloropyridine is a slightly weaker base towards protons than pyrazine, In 1:1 solutions of the pyridines and phosphorus pentachloride, however, the pyrazine complex is the more completely formed. The differences in the pKa's of the pyridines are only slight, however.

Although very broad lines are found with other low basicity pyridines and PCl_5 in a 1:1 molar ratio, even when the 3,5-dichloropyridine complex is almost entirely formed and excess pyridine is present, a very broad line is produced (~12 ppm width at half peak height, several times broader than normally found). This is ascribed to relatively slow exchange between free phosphorus pentachloride and the complex.

2-X Pyridine (X = F,Cl,Br,CN)

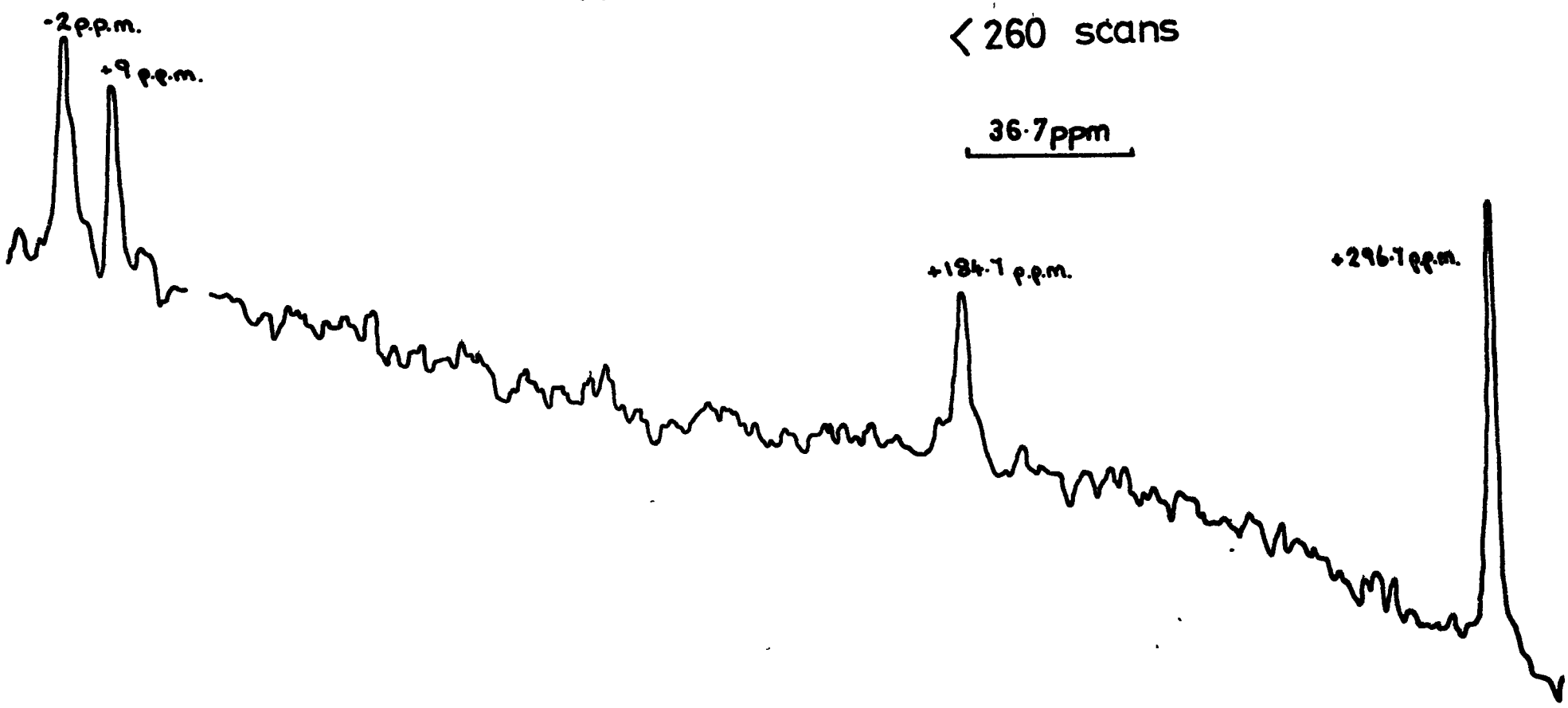
The shifts of phosphorus pentachloride dissolved in these pyridines cover a wide range from + 83 to + 190 ppm.

The shift in 2-bromopyridine is only slightly higher than the range of values found for molecular PCl_5 (+ 80 ± 2 ppm [23,158,159]). In 2-chloropyridine a higher shift of + 109.1 ppm is found, whereas the shift in 2-fluoropyridine is about + 185 ppm. When spectra are run with equimolar amounts of phosphorus pentachloride and the pyridine in nitrobenzene each gives a broad peak at about + 80 ppm. Free PCl_5 appears to be exchanging with the complex,

PCl_5 + 2-halpyridine $\rightleftharpoons$ PCl_5.2-halpyridine

with the complex being incompletely formed even with a large excess of pyridine, and being formed to only a very small extent with equimolar quantities of reactants. Although the peak positions from the 1:1 molar ratios of the reactants (and also in neat 2-bromopyridine) are very close to that of free PCl_5 in nitrobenzene (+ 82 ppm), the n.m.r. signals are very broad (2-chloropyridine ~16 ppm, 2-fluoropyridine ~30 ppm width at half peak height), even broader than the signal of molecular PCl_5 in nitrobenzene, (the PCl_5 resonance in nitrobenzene is broadened by exchange with small amounts of PCl_4^+ and PCl_6^- present in solution). This would suggest that some interaction between the pyridine and phosphorus pentachloride does take place. With excess pyridine the lines are narrower, especially in the 2-fluoropyridine case, indicating that the exchange rate has increased. The difference between the observed value for phosphorus pentachloride in 2-chloropyridine (+ 109.1 ppm) and that obtained by Dillon [23] (+ 97.2 ppm) can be attributed to different phosphorus pentachloride concentrations in the two solutions.

Fig 5 ^{31}P n.m.r. solution spectrum of PCl_5 in 2-F pyridine



The relative order of the chemical shifts of the different 2-halopyridine solutions is consistent with the dominating effect which is hindering co-ordination being steric. The hindrance to complex formation from the 2 position would be greatest for 2-bromopyridine and least for 2-fluoropyridine. The electron withdrawing effects of the halide atoms seem less important. 2-bromopyridine is a much stronger base with respect to protons than 2-fluoropyridine. Thus if electronic effects were dominant the 2-bromopyridine complex would be stronger, and so more completely formed than that with 2-fluoropyridine

<u>decreasing basicity</u>

$PCl_5 \cdot$2-Brpyr $PCl_5 \cdot$2-Clpyr $PCl_5 \cdot$2-Fpyr

<u>increasing steric hindrance</u>

<u>decreasing complex formation</u>

The above arguments assume that, in neat pyridine, the pyridine is in such an excess that differences in phosphorus pentachloride concentration will have no effect on the relative order of the shifts found.

The 2-fluoropyridine solution initially presented difficulties in interpretation, due to partial hydrolysis. The spectrum is shown in Figure 5. The shift of +185 ppm would seem to indicate a cationic species present and this would seem to be confirmed by the presence of PCl_6^-, designating the species as $PCl_4(2\text{-Fpyr})_2^+ PCl_6^-$. However the PCl_6^- signal is much larger than the "cation" peak and also is of approximately equal intensity to peaks

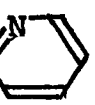
around 0 ppm. The presence of PCl_6^- may then be explained as due to partial hydrolysis forming 2-fluoropyridinium hexachlorophosphate (c.f. Chapter 2 section 1(iv)a). The +185 ppm peak is coincidentally in the $PCl_4py_2^+$ region, as is also shown by its movement to +77.8 ppm when equimolar amounts of reactants are present. As before, the peak may be assigned to exchange between PCl_5.2-Fpyridine and free PCl_5. As no indication of cationic species have been found with non-hindered monodentate pyridines and phosphorus pentachloride it is not unreasonable to suppose that a neutral species is partially formed here and with the other 2-halopyridines. The steric effects would be larger on forming a cationic species containing two hindered pyridines than with a neutral complex. Few studies have been made concerning the donor properties of 2-fluoropyridine [160-163] but none would indicate any anomalous properties compared to other pyridine donors.

The second equilibrating species would seem to be molecular PCl_5. It would, however, be very difficult to decide, using n.m.r. techniques, whether one equivalent of the weakly co-ordinating 2-halopyridine suppresses the partial ionisation of PCl_5 into $PCl_4^+PCl_6^-$ which occurs in nitrobenzene solution [49]. With free phosphorus pentachloride in nitrobenzene it is difficult to detect PCl_4^+ [23] whereas the more easily detectable PCl_6^- [23] will probably be found anyway if a pyridine is present, due to slight hydrolysis (Chapter 2 section 1(iv)a).

2-cyanopyridine would at first sight fit into the above discussion since the complex gives a peak at +170.8 ppm. When the pyridine and phosphorus pentachloride are in equimolar quantities in nitrobenzene, however, the peak does not move appreciably. The shift is also very similar to that found when a 1:2 molar ratio of $PCl_4^+SbCl_6^-$ and 2-CNpyridine is investigated. Peaks are found at +18.0, +107.3 and +173.4 ppm (Chapter 3 section 2(ii)a). Thus the peak is due to a single non-equilibrating species.

In transition metal chemistry 2-cyanopyridine may co-ordinate through either the pyridine [164] or the cyano nitrogen [152,165]. The latter mode of co-ordination has been ascribed to steric factors making the cyano nitrogen preferable although the pyridine nitrogen has a greater nucleophilic power [152]. Evidence has been given that when co-ordination occurs through the pyridine nitrogen there is perhaps also π interaction of the cyano group [166]. π interaction would, however, not be expected with a phosphorus acceptor.

The ^{31}P n.m.r. shift of +170.8 ppm indicates a 6 co-ordinate species. The shift is, however, very different from that of PCl_5.pyridine indicating a different mode of co-ordination. This would suggest co-ordination through the cyano group,

$PCl_5 \longleftarrow N\equiv C-$ 

the other peaks found with PCl_4^+ then being

$PCl_4(N\equiv C-$ $)_2^+$ and $PCl_4(N\equiv C-$ $)^+$

However acetonitrile has been found not to co-ordinate to phosphorus pentachloride. At -40°C phosphorus pentachloride in this solvent is ionic and unco-ordinated [167]. At room temperature they react [142], producing, amongst other species, PCl_6^-. Solutions of $PCl_4^+SbCl_6^-$ in acetonitrile contain unco-ordinated PCl_4^+ (Chapter 3 section 2).

As solutions of phosphorus pentachloride in 2-cyanopyridine were very dark coloured, reaction rather than addition may have occurred, but it is difficult to see what 6 co-ordinate species would be produced. Reaction, rather than addition between phosphorus pentachloride and cyanides has been shown to occur in cases where there is a hydrogen atom adjacent to the cyano group [142]. Dillon, [23] however, noted peaks in the ^{31}P n.m.r. spectrum of phosphorus pentachloride in benzonitrile which could be explained either in terms of reaction, or in terms of partial co-ordination

$$PCl_4^+ + PhCN \rightleftharpoons PCl_4.PhCN^+$$

In no case reported, however, have any solution stable six co-ordinate species other than PCl_6^- been found. 3- and 4-cyano pyridines also give no indication whatsoever of similar reactions occurring.

Thus, although the results would suggest co-ordination through the cyanide group, since this mode of co-ordination to phosphorus has been previously unknown, further confirmation would seem to be necessary. The isolation of the pure complex as a solid would help because the complex could then be characterised by analysis, and infra red spectroscopy, the latter technique confirming the mode of co-ordination.

Solution infra red spectroscopy was not attempted due to the possibility of side reactions other than co-ordination having occurred.

Methyl Pyridines

The methyl pyridines differ in behaviour from the ones discussed above. With the 2 substituted methyl pyridines no adduct formation is observable, the clear yellow solutions darkening within minutes. The solutions were stable enough to run the ^{31}P n.m.r. spectrum only after the reaction had subsided, the only reaction peak observable (with 2-picoline δ^{31} P-217.3; 2,4,6-collidine δ^{31} P-217.0) then being ascribable to phosphorus trichloride.

Slightly different results are obtained using methyl pyridines substituted in other than the 2-position. 3,5-lutidine forms an insoluble stable 1:1 adduct with phosphorus pentachloride. 3-picoline dissolves phosphorus pentachloride to form a clear yellow solution which darkens more slowly than that with 2-picoline. A peak at +228 ppm ascribable to the adduct is, however, found but a peak slowly appears at -203.3 ppm. Even after several days, however, the 6 co-ordinate peak has not completely disappeared. The -203.3 ppm peak is attributable to slight co-ordination of phosphorus trichloride with excess 3-picoline.

$$PCl_3 + \text{3-picoline} \rightleftharpoons PCl_3.\text{3-picoline}$$

The equilibrium occurring between phosphorus trichloride and its pyridine adduct was confirmed by running a spectrum of phosphorus trichloride in excess pyridine. A peak was found of varying shift depending on the concentration, but

of the above order of magnitude. The equilibration did not occur with the other systems described since no excess of pyridine was present. Complexes of phosphorus trichloride with pyridines are known in the solid state [32,168,169] but their solution behaviour has not been investigated. The similar Me_3N-PCl_3 system has, however, been investigated by ^{31}P n.m.r. spectroscopy [170], shifts of up to +33.8 ppm from the position of PCl_3 then being found, and the formation of $Me_3N.PCl_3$ being deduced.

Reactions involving chlorination of the pyridine seem to have occurred. Steric hindrance from the 2-substituted group appears to weaken the P ← N bond and so lower the energy needed for further reaction. If complexes are formed with 2-methyl pyridines they quickly decompose.

Complicated reactions of 2- (but not 4-) picolines are known to occur with other acceptor molecules, e.g. trimethyl aluminium [171], but with phosphorus pentachloride chlorination may also take place. With the much stronger and larger Lewis acid antimony pentachloride a 1:1 complex is formed with 2-picoline but the heat of formation is lower than that of the pyridine and 4-picoline adducts [20]. With longer chain 2-substituted pyridine complexes further reaction may occur [20]. Steric effects are also shown by phosphorus pentafluoride only partially associating with 2,4,6-collidine at 25°, but forming a stable complex with pyridine [76].

The reaction of phosphorus pentachloride with the methyl pyridines is rather surprising in view of the usual stability of the pyridine ring to attack [140]. The ring is probably

activated by the electron donor ability of the methyl groups. The precise course of the reaction was not, however, investigated further. Because of the possibility of partial hydrolysis, it was not easy to distinguish whether the large PCl_6^- peaks, observable in many cases, were due to hydrogen chloride being produced during the course of the reaction, or being due to partial hydrolysis,

i.e. via $R\text{-}H + PCl_5 \rightarrow R\text{-}Cl + PCl_3 + HCl$

or via $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

$py + HCl + PCl_5 \rightarrow pyH^+PCl_6^-$

Although it was difficult to dry the methyl pyridines completely in some cases it was found that the PCl_6^- peak was much more intense than the $POCl_3$ peak, suggesting the former mechanism.

Discussion

An almost identical series of substituted pyridine ligands has been used by Perkampus and Krüger [163] in studying the acceptor properties of BF_3, $AlBr_3$ and H^+. By monitoring the proton n.m.r. shift of the pyridine they were able to observe the amount of co-ordination occurring. Solutions were made up with a 1:2 molar ratio of pyridine to Lewis acid. With boron trifluoride, complex formation took place even in the presence of 2 substituents (2-F,Cl,Br,CN pyridine). With aluminium tribromide, however, only a small amount of the $AlBr_3$ was complexed. The extent of complex formation was in the order

$CN < Cl < F < Br$

No reactions other than addition were found with the methyl pyridines studied (2-, 3-picoline). With other non-hindered ligands (pyridine, 4-CN, 3-Cl, 3-Br pyridine) complete formation of complexes took place.

Except for the methyl pyridines, and 2-cyanopyridine, phosphorus pentachloride behaves in many ways in an analogous manner to aluminium tribromide with respect to steric effects. Boron trifluoride, being a much smaller molecule is not so prone to steric effects and produces stable complexes with 2 substituted pyridines, even though PCl_5 (approximately the same acceptor strength towards pyridine on the Hensen, Sarholtz [21] scale) and $AlBr_3$ (a much better acceptor on the same scale) do not.

Hydrolysis Difficulties

As was described in Chapter 2 section 1(iv)a hydrogen chloride produced by traces of hydrolysis will add to the pyridine to produce pyridinium chloride, or pyridinium hexachlorophosphate. The PCl_6^- was detected in some spectra as a small peak in relation to PCl_5.pyridine, with no other peak of comparable intensity attributable to a phosphorus-containing cation. In a number of systems small peaks also appeared in the spectrum between -5 and +12 ppm e.g. PCl_5 in pyridine (-3.7, +10.6 ppm), PCl_5 in 3-Cl pyridine (-5.6, +4.2, +8.1 ppm), PCl_5 in 2-Cl pyridine (-3.8 ppm). These, are almost certainly due to partial hydrolysis products (Appendix 2). When excess pyridine is used, if any of these peaks were due to, say, PCl_4py^+, a larger $PCl_4py_2^+$ peak would also be expected to appear,

this cation being well characterised with $PCl_4^+SbCl_6^-$ (Chapter 3 section 2(ii)). Such peaks are not found.

The above scheme of hydrolysis was illustrated by isolating 2,4,6-collidinium chloride hexachlorophosphate mixed salts from PCl_5 and 2,4,6-collidine in undried carbon tetrachloride. The precipitation was instantaneous, the collidine having little time to react with the phosphorus pentachloride as found in the solution work discussed earlier.

b) Solid State Investigations

Monodentate Pyridines

The similarity between the solid state [29] and solution [11] infra red spectra of PCl_5.pyridine, as found by Beattie et al. suggests that the complex is molecular in the solid state. In order to confirm this, and to extend the structural information, several complexes were isolated, namely PCl_5.pyridine, PCl_5.pyridine. $2PhNO_2$, PCl_5. 3-X pyridine (X = Cl, Br, I), and PCl_5. 3,5-lutidine. Details of the preparations and analyses are given in Chapter 3 section 1(ii)c.

Chemical properties and structure

All the solids analysed as 1:1 complexes.

PCl_5.pyridine is a white moisture-sensitive crystalline solid (m.pt 194-201°C), moderately soluble in methylene chloride and nitrobenzene. The complex was also isolated as the bisnitrobenzene solvate, a fine white powder, when

prepared from nitrobenzene solution. Physical techniques described later show the phosphorus is co-ordinated by the pyridine and not nitrobenzene.

PCl_5. 3-Cl pyridine and PCl_5. 3-Br pyridine (m.pt 141-7°) were isolated as white solids. The 3-Cl pyridine complex was moderately soluble in nitrobenzene whereas the 3-Br pyridine complex was only slightly soluble. The infra red spectrum of PCl_5. 3-Br pyridine was unchanged after keeping a sample under nitrogen for about 15 months, showing the stability of the complex at room temperature.

PCl_5. 3-I pyridine (m.pt 163-5°) is a slightly cream coloured solid. Once isolated it seemed completely insoluble in nitrobenzene. It has, however, been detected in solution by ^{31}P n.m.r. techniques when produced in situ (Chapter 3 section 2(ii)a). The complex also seems slightly soluble in the presence of excess 3-iodopyridine (Chapter 3 section 1(ii)a)

PCl_5. 3,5-lutidine is a stable white powder insoluble in nitrobenzene. Its stability as a solid contrasts sharply with that of the methyl pyridine complexes in solution.

The complexes gave broad symmetric ^{31}P n.m.r. solid state signals (see Figures 2a and b) in the region between +210 and +240 ppm (Table 7).

TABLE 7

^{31}P n.m.r. SOLID STATE SHIFTS FOR PCl_5.PYRIDINE COMPLEXES

	$\delta^{31}P$
PCl_5.pyridine	+224.7 ± 4.1
PCl_5.pyridine. $2PhNO_2$	+228.5 ± 2
PCl_5. 3,5-lutidine	+215.9 ± 12.9
PCl_5. 3-Cl pyridine	+235.8 ± 7.3
PCl_5. 3-Br pyridine	+236.2 ± 10.2
PCl_5. 3-I pyridine	-

Difficulty was found with the 3-halopyridines in that no spectra were obtained with horizontal baselines because of drift during the accumulation. This effect was so great with the 3-I pyridine complex that no reliable shift could be determined. Shifts quoted in Table 7 are averaged from spectra with the most horizontal baseline and "best shaped" Gaussian peak.

The solid shifts are very similar to the corresponding solution values and thus show that the complexes are molecular in the solid state. If the compounds had the structure $PCl_4py_2^+PCl_6^-$ they would show a sharp asymmetric peak at about +296 ppm (compare the spectra of $PCl_4dipy^+ PCl_6^-$ and $PCl_4phen^+ PCl_6^-$, Figures 7 and 10). There is no change in structure between solution and the solid state as there is for phosphorus pentachloride itself. The solid state spectra of the complexes are somewhat broader than are found with PCl_6^-. This may be attributed to a

lowering of the symmetry of the species and also the proximity of the nitrogen quadrupole to the phosphorus atom. Other effects altering the linewidth may be due to a significant variation in the interdipolar distances. As interaction strength varies as the cube of the interdipolar distance slight changes have a great effect.

The similarity of the shift of $PCl_5.py.2PhNO_2$ to those of the other pyridine complexes would suggest similar co-ordination i.e. by the pyridine. The nitrobenzene would thus appear to be only loosely attached in the crystal lattice, in the form of molecules of crystallisation.

The complexes were dissolved in nitrobenzene to give the following shifts.

TABLE 8

CHEMICAL SHIFTS OF REDISSOLVED PCl_5.PYRIDINE COMPLEXES

	$\delta^{31}P$	Solvent	$\delta^{31}P$ PCl_5 in neat pyridine (from Table 5)
PCl_5.pyridine	+231.5	$PhNO_2$	+228.0
	+229.4	CH_2Cl_2	
PCl_5. 3-Cl pyridine	+248.1	$PhNO_2$	+228.6
PCl_5. 3-Br pyridine	+234.8	$PhNO_2$	+228.3
PCl_5. 3-I pyridine	Insoluble	$PhNO_2$	-

The shifts are larger than in neat pyridine solution. They are also larger than when the complexes were produced in nitrobenzene solution by the equilibrium from the $PCl_4py_2^+SbCl_6^-$ complex, shifts of +226.3 to +229.6 ppm

then being found (Chapter 3 section 2(ii)a). The shifts of the redissolved pyridine and 3-bromopyridine complexes are, however, still within the range of literature values already quoted (Table 6). The 3-chloropyridine complex, however, gives a higher value. The large difference may be due to the complex being in rapid equilibrium with a second species. The only other species probable in this system, having a greater shift than PCl_5. 3-Cl pyridine, is PCl_6^- (δ^{31} P +296 ppm). Partial hydrolysis may therefore have occurred in solution, producing phosphoryl chloride and 3-chloropyridinium hexachlorophosphate. The PCl_5. 3-Cl pyridine and PCl_6^- could then exchange. However no large phosphoryl chloride peak was found in the solution. On making a tube up of (2,4,6-collidinium)$_2Cl^-$,PCl_6^- and PCl_5.pyridine in nitrobenzene two separate peaks due to the different phosphorus species were found, showing no rapid equilibration between the species. If, however, hydrogen chloride is bubbled through PCl_5.pyridine the peak moves slowly to higher field. This is presumably due to a slow reaction to produce $pyH^+PCl_6^-$, but this reaction in itself provides difficulties, in that exchange must be rapid for a single peak to be formed, yet the reaction proceeds very slowly, a period of days being required to go even halfway to completion.

TABLE 9

INFRA RED SPECTRA OF PCl_5.PYRIDINE COMPLEXES 650-250cm^{-1}

	State	Ref.												
PCl_5.py	solid	29				503s	484s	455s 440s		350w	310mw	289mw	266vw	253m
	Nujol Mull	11	641vw	606vw	584w		484sbr	432sbr						
"	"	32	625s					425s						
"	"		642m	610w	588w[b]		484sbr	440s		352w	312w	292w	268w	253w
PCl_5.py. $2PhNO_2$	"		642m	612w	591w[b]		485sbr	432sbr	398w[a]	349w	312w		c.	
PCl_5.3,5-lutidine	"		638w	615w	588w[b]	538m	527m	496s	470sbr	438sbr	348m	299w	278w	
PCl_5. 3-I pyridine	"		654w	620w	591m[b]	518m	508m	488s	450sbr			c.		
PCl_5. 3-Br pyridine	"		650m	618w	589m[b]	521m	512m	488s	448sbr	402s	362m	350w	327w	290w
PCl_5. 3-Cl pyridine	"		652w	622w	592m	532m	526m	492s	448sbr			c.		

a. $PhNO_2$ frequency

b. $POCl_3$ hydrolysis impurity

c. Spectra 650-350 cm^{-1} using KBr windows

Infra red spectra

The i.r. spectra of the complexes below 650 cm^{-1} are given in Table 9. Lines in this region are mainly due to P-Cl (and perhaps P-N) vibrations. There are large differences from the spectrum of $PCl_4^+PCl_6^-$ (Chapter 1 section 3(ii)). The absorptions found are mainly below 500 cm^{-1}, in the lower end of the region where P-Cl vibrations are found, indicating weakening of the P-Cl bonds by co-ordination of the pyridine. The intense bands almost certainly obscure the ligand modes in this region (frequencies of the free ligands are given in Table 24, Chapter 3 section 2(ii)b).

Weak or medium lines appear with some of the complexes in the region 642-654 cm^{-1}. These appear to be genuine and not due to PCl_4^+ impurity. The 642 cm^{-1} line appeared in all samples of PCl_5.pyridine at constant intensity relative to the other lines and was also reported by Beattie and Webster [11]. Several transition metal complexes also have absorptions in this region which have been attributed to a pyridine ring vibration [172].

The spectrum of PCl_5.pyridine is in good agreement with the spectrum reported by Beattie et al. [11,29]. According to their assignment of the spectrum the intense absorptions in the region 520-350 cm^{-1} are mainly due to P-Cl vibrations with little or no contribution from the P-N bond. These spectra do not, however, correspond to that found by Paul, Sehgal and Chanda [32].

With the exception of the peaks due to nitrobenzene the spectrum of PCl_5.pyridine.$2PhNO_2$ is very similar to that of PCl_5.pyridine, even below 650 cm^{-1}, showing that the co-ordination is similar in both complexes and that the co-ordinated ligand is pyridine. The only difference below 650 cm^{-1}, a small peak at 398 cm^{-1}, may be attributed to nitrobenzene. Throughout the range 4000-250 cm^{-1} the nitrobenzene frequencies were unperturbed from those found in free nitrobenzene, showing that it is only very loosely bound, as a solvate molecule. For co-ordinated nitrobenzene in $SbCl_5$.$PhNO_2$, Grossman [173] found that of the two strong bands at 1575 (presumably a printing mistake for 1525 cm^{-1} c.f. refs. 174,175) and 1340 cm^{-1} (unsymmetric and symmetric $-NO_2$ stretching vibrations respectively), the 1575 cm^{-1} band disappeared on co-ordination, whilst the 1340 cm^{-1} band moved to 1335 cm^{-1}. Driessen et al. [176] showed that, for transition metal complexes, the infra red spectrum of the nitrobenzene ligand between 2000 and 700 cm^{-1} was identical with that of free nitrobenzene, whereas some changes appeared below this frequency. Instead of one band at 676 cm^{-1}, two bands appeared at 682 and 669 cm^{-1}. The medium strong band at 420 cm^{-1} was substituted by two bands at 430 cm^{-1} (w) and 413 cm^{-1} (m). The strong band at 397 cm^{-1} disappears on complexing whilst a band at 365 cm^{-1} appears. The band at 532 cm^{-1} moves 2-20 cm^{-1} to higher frequency according to the complex.

TABLE 10

SELECTED i.r. PEAKS OF FREE, CO-ORDINATE AND SOLVATE NITROBENZENE

Free $PhNO_2$	1575(1525?)	1340	676	532	420	397
Transition metal complexes			682 669	534-552	430 413	365
$bCl_5 \cdot PhNO_2$	-	1335				
$Cl_5 \cdot py \cdot 2PhNO_2$	1525	a	a	a	a	398

a-obscured by Nujol, P-Cl, or pyridine frequencies.

Unfortunately most of the low frequency bands are obscured by the P-Cl stretching frequencies. A small shoulder does, however, occur at 398 cm^{-1} (c.f. 397 cm^{-1} of free nitrobenzene). There are similarly no changes in the spectrum between 1500 and 1600 cm^{-1}.

Nitrobenzene solvates were often found in the complexes prepared in this work, and in all instances except $PCl_4(4\text{-}CNpyr)_2{}^+SbCl_6{}^- \cdot 2PhNO_2$, where the 676 cm^{-1} nitrobenzene band splits into two bands at 676 and 683 cm^{-1} (Chapter 3 section 2(ii)b), the nitrobenzene frequencies are unperturbed from those of free nitrobenzene.

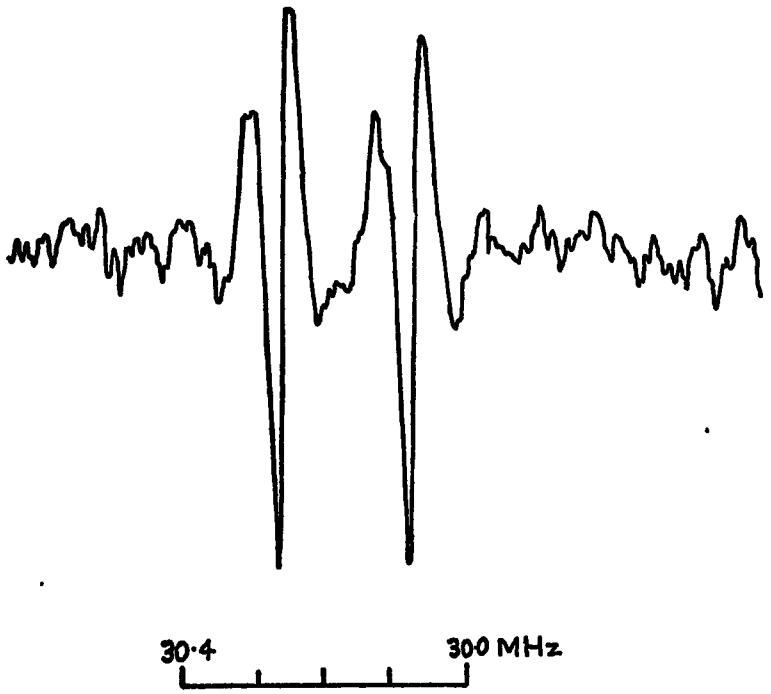
The P-Cl stretching frequencies in $PCl_5 \cdot$pyridine and its solvate are unresolved due to the broadness of the lines in a nujol mull of the solid. In the substituted pyridine complexes, however, the lines are considerably sharper allowing greater resolution.

Of the ligand vibrations in pyridine complexes, the 601 and 403 cm^{-1} bands have been the most used in characterisation [172,177,178]. Both these lines move to higher frequencies on complexing. Unfortunately the 403 cm^{-1} band is unidentifiable in PCl_5.pyridine amongst the strong P-Cl stretches. Beattie et al [11,29] assume it to be underneath the broad 440 cm^{-1} band. The 601 cm^{-1} band moves to 610 cm^{-1} in PCl_5.pyridine and to 612 cm^{-1} in its nitrobenzene solvate. This shift is lower than is found with transition metal complexes [172]. A second useful band for identification of complex formation in phosphorus chloride complexes would seem to be the strong 1583 cm^{-1} band. This moves to 1610 cm^{-1} in PCl_5.pyridine. The band is found at 1624 cm^{-1} in BCl_3.pyridine [130] and 1625-1660 cm^{-1} in transition metal complexes [172]. Once again the shift is smaller in the PCl_5 complex. Other bands show shifts in frequencies generally similar to those found with BCl_3.pyridine [130] and in most cases within the range of shifts found for transition metal pyridine complexes [172].

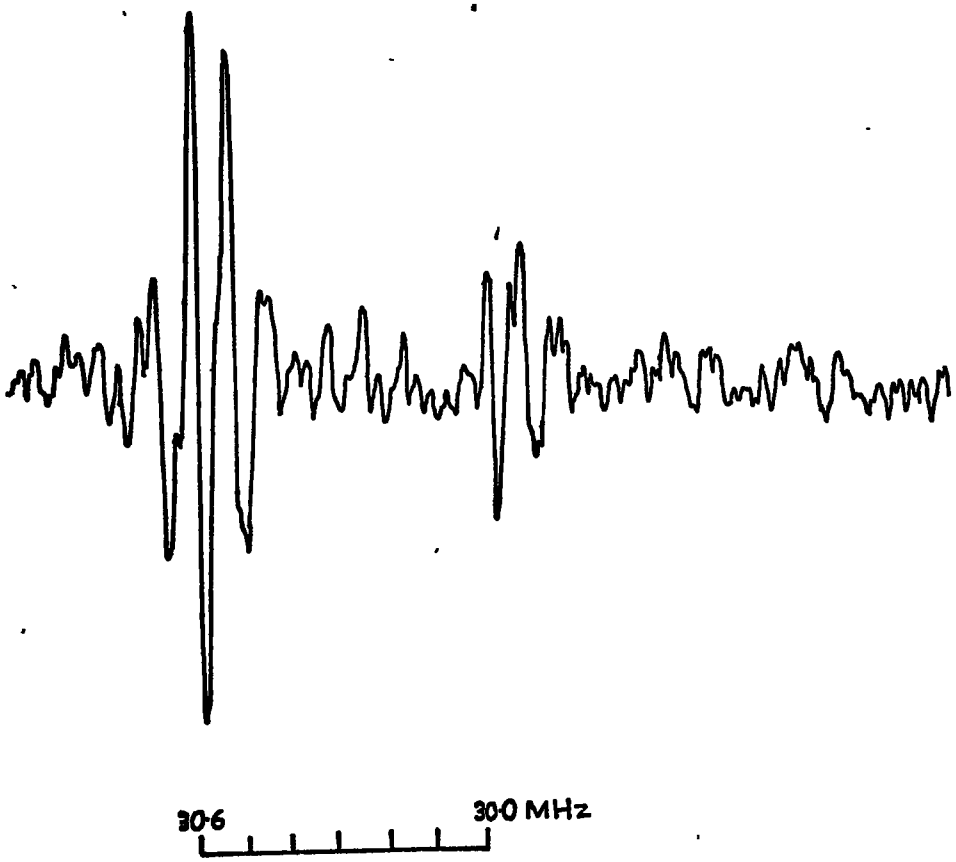
N.Q.R. Spectra

The ^{35}Cl N.Q.R. spectra of a number of these complexes were run by Dr. R. J. Lynch. The spectra would be expected to consist of two sets of lines, of intensity ratio 4:1, corresponding to chlorines cis and trans to the pyridine ligand. The results are shown in Table 11. They roughly agree with the above prediction. With PCl_5.pyridine,

Fig 6 ^{35}Cl n.q.r. spectra



a) PCl_5 .pyridine (2nd sample)



b) PCl_5 .3-bromopyridine

however, the line intensities were only slightly different from 1:1 (Figure 6). Crystal splitting effects (Chapter 1 section 3(III)) may be up to 0.5 MHz, spanning almost the whole of the spectra found here. The PCl_5.pyridine spectrum may then be due to the cis line being split into two of more components, thus masking the weak trans line. If the trans line is also split into two or more components the lines may be too weak to observe even if not masked. No other line attributable to the trans chlorine was detected between 35 and 23.7 MHz.

TABLE 11

^{35} Cl n.q.r. SPECTRA OF PCl_5.PYRIDINE COMPLEXES

	MHz	Signal/noise	Position of chlorine relative to pyridine
PCl_5.3,5-lutidine	30.04	3.5:1	trans
	29.70	5.5:1	cis
PCl_5.pyridine.$2PhNO_2$	29.93	2.2:1	trans
	30.41	7.2:1	cis
PCl_5.pyridine(Sample 1)	30.05	4.0:1	
	30.24	5.3:1	
PCl_5.pyridine (Sample 2)	30.065	5.9:1	
	30.26	6.1:1	
PCl_5.3-Br pyridine	29.94	3.6:1	trans
	30.57	9.4:1	cis

The ^{37} Cl lines expected would be in general very weak and were not investigated.

If the cis and trans assignments are correct, the trans frequency remains approximately constant at about

30 MHz with change in pyridine ligand. There is a much larger change for the cis chlorines, the stronger the base, the lower the frequency becomes. Too few samples were investigated to discern whether this trend was significant. One relatively stationary line and a changing line is also found with $(PCl_4(py)_2)^+$ complexes discussed in Chapter 3 section 2(ii)b, but in this case interpretation is helped by the larger separation of the lines.

Whatever the detailed interpretation of the spectrum, it can be seen that there is only a small difference between the cis and trans frequencies and in turn the signals are not shifted significantly from the position of PCl_6^-.

TABLE 12

^{35}Cl n.q.r. FREQUENCIES FOR VARIOUS PHOSPHORUS CHLORINE SPECIES

Species	ν MHz	Av	Ref
PCl_4^+	Four lines between 32.29 and 32.62	32.44*	117
PCl_5	29.24, 29.27(ax) 33.75(equat)		116
PCl_6^-	Six lines between 28.40 and 30.58	29.88*	117

*As found in crystalline $PCl_4^+PCl_6^-$

In the simplest interpretation of ^{35}Cl n.q.r. frequencies the frequency of a line is given by [114]

$$\frac{\nu \text{ molecule}}{\nu \text{ chlorineatom}} = (1-s)\sigma - \pi$$

as described in Chapter 1 section 3(iii). In a hexaco-ordinate

phosphorus species all the low lying orbitals are used in bonding and so the π character of the bond would be expected to be very small. The frequency of the line is thus a measure of the σ character of the P-Cl bond, which in turn will depend on the σ characteristics of the other bonds to phosphorus. Thus the similarity of the frequencies of PCl_6^- and PCl_5.py reflects the similarity of the donor properties of pyridine and chloride towards PCl_5. This is chemically not unreasonable, the relative donor properties of chloride and pyridine being found to be approximately equal, the order depending on the particular system studied. In some systems pyridine will even displace chlorine from a five co-ordinate compound to give a cation of type $R_4Ppy_2^+$ (see Chapter 5 section 3(ii)b).

The spectrum of $SbCl_5$.pyridine was run for comparison with the above spectra. The spectrum, however, was very weak, showing a single line at 24.85 MHz (signal/noise 2:1). The line was of such low intensity that detection of the trans line would not be easy. There are signs of a possible line near 24.4 MHz. This would indeed indicate only small differences between the cis and trans chlorines as found with PCl_5.pyridine.

The only systematic investigation of six co-ordinate adducts of a non transition metal chloride has been the investigation of tin tetrachloride adducts (with mainly oxygen donors) by Maksyutin et al [179]. Here the cis - trans splittings were somewhat larger than found with the

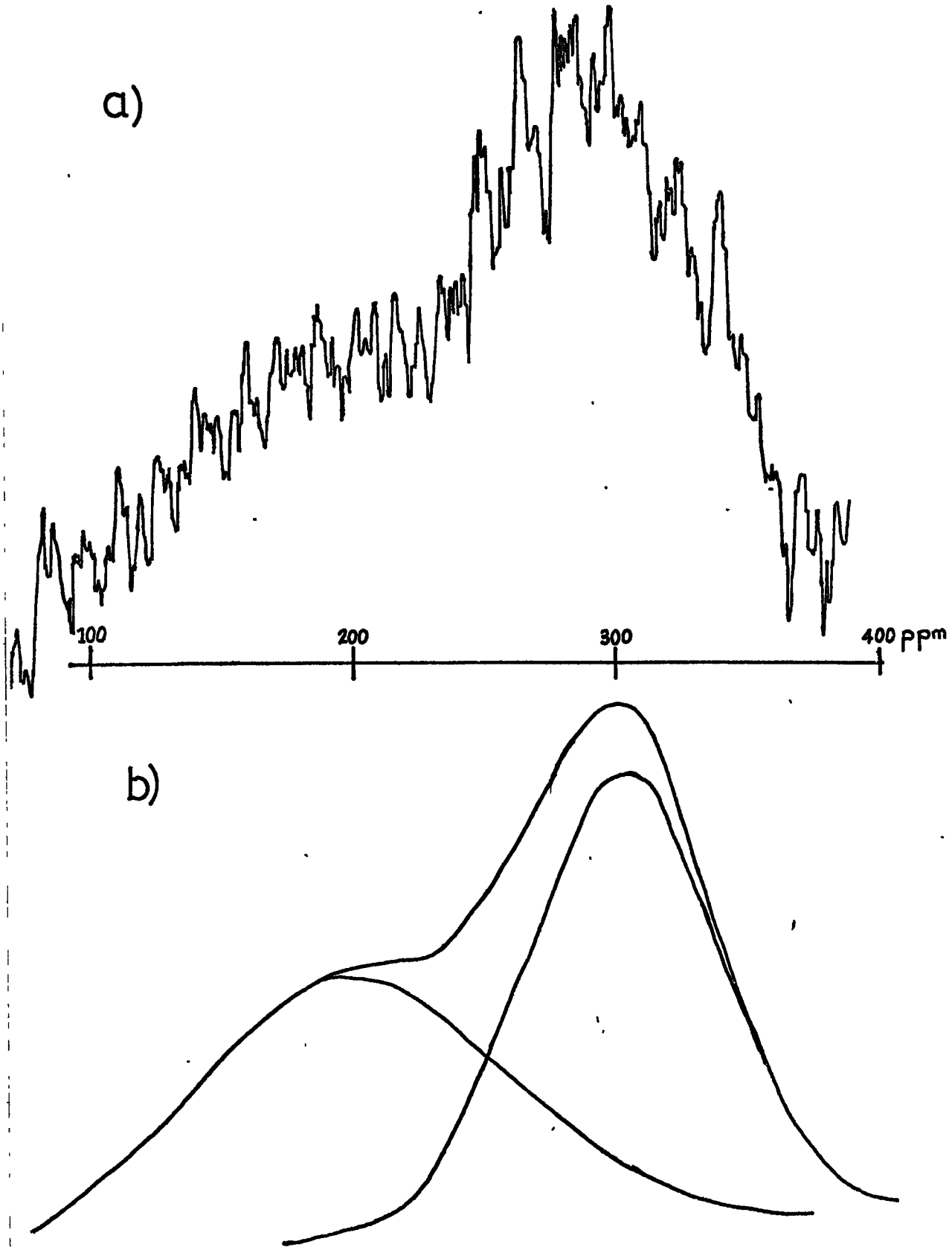


Fig 7 ^{31}P n.m.r. solid state spectrum of $PCl_4 phen^+ PCl_6^-$
a) experimental curve
b) deconvoluted spectrum

phosphorus-chlorine complexes, ranging from 1.5 to 3.0 MHz. The cis chlorines occurred at higher frequency than the trans chlorine, as found in two of the three unambiguous cases above. Maksyutin found a correlation between the splitting of the cis and trans lines and the average shift of the lines. No correlation is found from the limited data in this work, however. The smaller splittings compared with the tin complexes are consistent with the phosphorus being a poorer transmitter of inductive effects than tin. The poor transmission characteristics of phosphorus have been previously observed [180].

Bidentate Pyridines

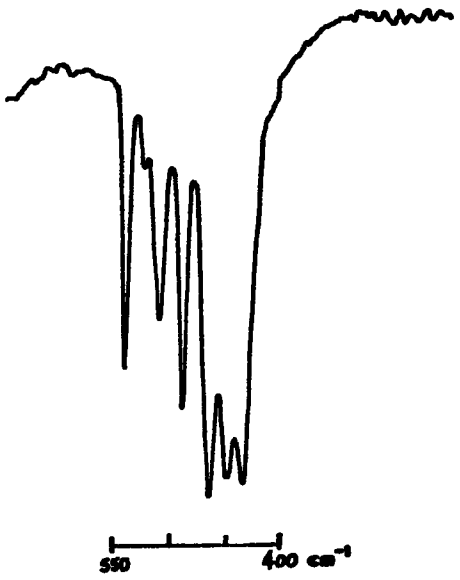
In order to gain a more complete understanding of the complexes formed between phosphorus pentachloride and bidentate pyridines attempts were made to isolate several of these complexes in the solid state.

1,10-Phenanthroline

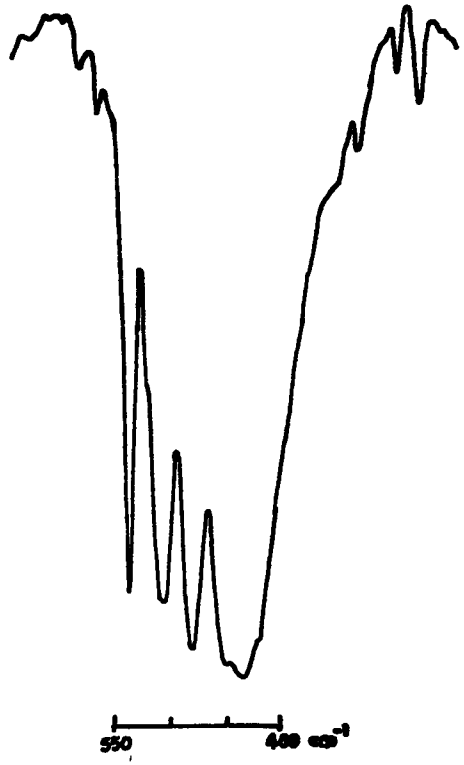
As the solution stable species between phosphorus pentachloride and phenanthroline in nitrobenzene is the 2:1 complex attempts were made to isolate this species by crystallisation from a polar solvent. When phosphorus pentachloride and 1,10-phenanthroline are dissolved in nitroethane in the correct stoichiometric proportions, a solid crystallises out of solution which analyses as the 2:1 complex. The ^{31}P n.m.r. solid state spectrum shows an asymmetric peak (Figure 7) which can be deconvoluted (assuming two peaks present of equal area)

Fig 8 I.R. Spectra

a) $PCl_4phen^+(PCl_6^-)_{0.214}Cl^-_{0.786}$



b) $PCl_4phen^+ PCl_6^-$



c) $PCl_4phen^+ PCl_6^-$ exposed to atmosphere overnight

to give peaks at +198.7 ± 10.4 ppm and +298.3 ± 2 ppm. This confirms the solid state structure as $PCl_4phen^+PCl_6^-$. The resolution of the solid state lines is possible due to the large difference in linewidths between PCl_4phen^+ and PCl_6^-. Indeed the spectrum is dominated by the PCl_6^- peak.

The literature preparation [22] to produce the 1:1 PCl_5/phenanthroline complex was repeated. The complex precipitates on mixing the components in benzene solution. An off-white solid was formed, but this did not analyse as a 1:1 complex. The formula best corresponding to the analytical data (Chapter 3 section 1 (ii)c) was $PCl_4^+phen\ (PCl_6^-)_{0.214}\ Cl^-_{0.786}$. By reversing the order of addition of the components so that the phenanthroline was added to the phosphorus pentachloride solution, a complex of formula $PCl_4phen^+\ (PCl_6^-)_{0.324}\ Cl^-_{0.676}$ was produced. The solid state ^{31}P n.m.r. spectrum of the former complex indeed showed a peak attributable to PCl_6^-, together with a shoulder to lower field attributable to PCl_4phen^+.

The infra red spectra of the PCl_5/phenanthroline complexes in the region below 650 cm^{-1} (Figure 8) consist of a broad absorption at 438 cm^{-1} attributable to the PCl_6^- ion, together with other lines at higher frequencies ascribed to PCl_4phen^+. Comparison with the spectrum of $PCl_4phen^+SbCl_6^-$ discussed in Chapter 3 section 2(ii)b shows additional lines due to PCl_4phen^+ to be expected in the same region of the spectrum as the hexachlorophosphate line. These lines are partially resolved in the 1+x:1

complexes but are less so in the 2:1 complex because of the greater relative intensity of the PCl_6^- peak. The similarity of the spectra below 650 cm^{-1} to each other and to the spectrum of $PCl_4phen^+SbCl_6^-$ (after allowance for the different counter ions) confirms similar co-ordination of the phosphorus.

Due to bands from the PCl_4phen^+ ion being present in the region 460-430 cm^{-1}, it is difficult to deduce from the published infra red spectra [22] whether PCl_6^- is present in the 1:1 complex of Deveney and Webster [22].

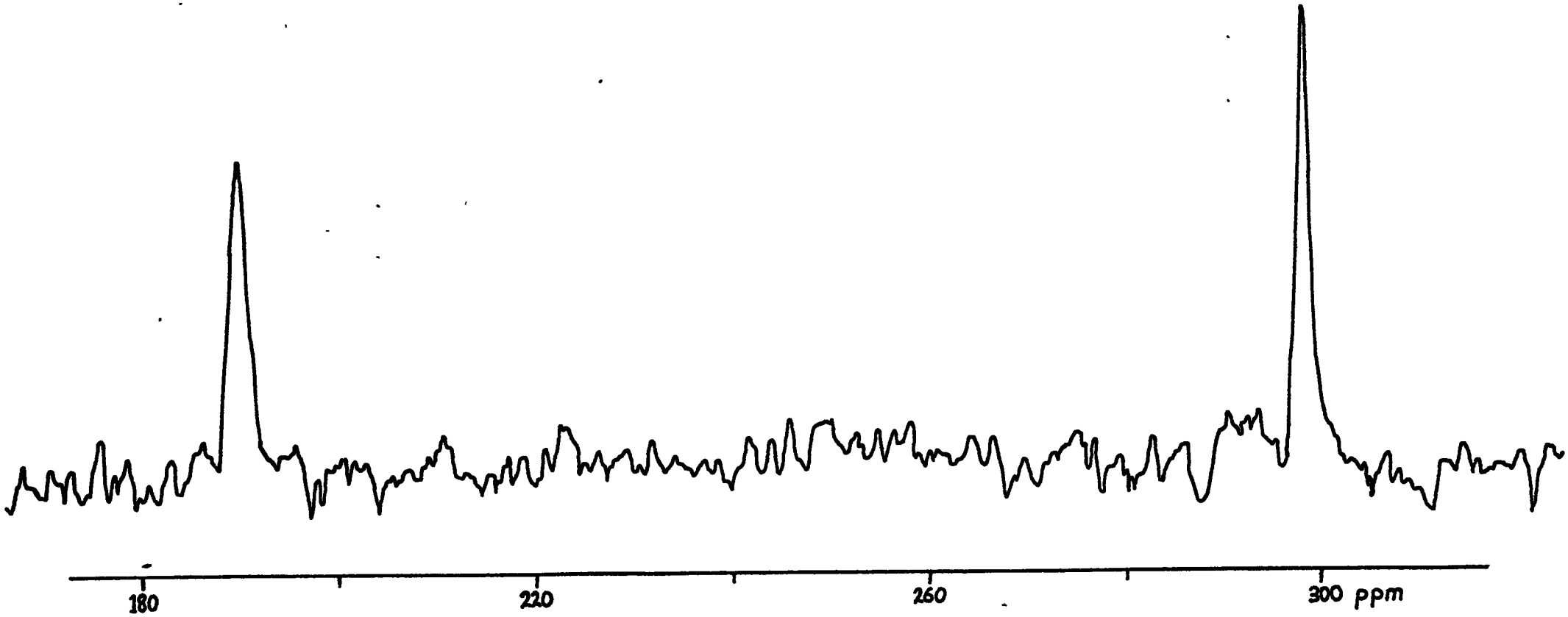
TABLE 14

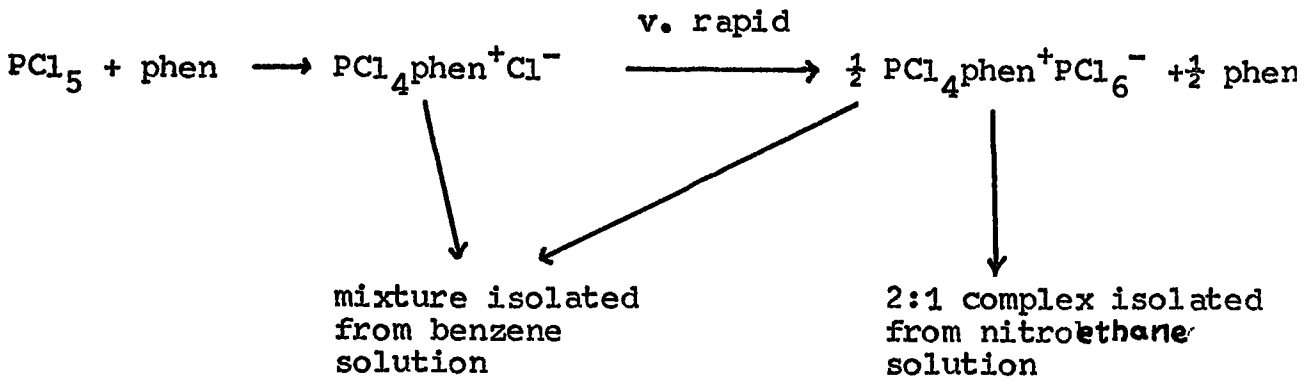
i.r. SPECTRA OF PCl_5/phen COMPLEXES 550-350 cm^{-1}

$Cl_4phen^+Cl^-$ [22]	532m	503m	480m	460s	450sh	439vs	392vw
Cl_4phen^+ $PCl_6^-)_{0.324}$ $Cl^-_{0.676}$	542s	527m	511s	488s	467s	452s	438s
Cl_4phen^+ $PCl_6^-)_{0.214}$ $Cl^-_{0.786}$	541s	525m	509s	488s	466s	449s	437s
$Cl_4phen^+PCl_6^-$	539s	525sh	508s	482s	(452sh,	438s,	422sh)

The isolation of the two different phenanthroline complexes may be explained by the immediate formation of $PCl_4phen^+Cl^-$ on dissolution of equimolar quantities of reactants and a subsequent disproportionation to the 2:1 complex. The complexes are so very insoluble in benzene that they precipitate before this process is complete. Presumably Deveney and Webster [22], using their particular isolation techniques, were able to isolate the 1:1 complex before disproportionation started.

Fig 9 ^{31}P n.m.r. solution spectrum of $PCl_4phen^+(PCl_6^-)_{0\cdot324}Cl^-_{0\cdot676}$ in nitrobenzene 133 scans





In polar solvents, attack may occur directly on the $PCl_4^+ PCl_6^-$ present in solution. The complexes may be expected to have at least a slight solubility in these solvents, and thus have time to disproportionate before crystallisation.

On dissolution of either the non stoichiometric complexes, or the $PCl_4phen^+PCl_6^-$ complex, in nitrobenzene, the ^{31}P n.m.r. spectrum showed peaks of approximately equal intensity corresponding to PCl_4phen^+ and PCl_6^- thus confirming the stable solution species to be $PCl_4phen^+ PCl_6^-$ even in the presence of excess phenanthroline (Fig. 9).

TABLE 13

^{31}P n.m.r. SHIFTS AND RELATIVE INTENSITIES OF PCl_5/PHENANTHROLINE SYSTEMS IN NITROBENZENE

System	$\delta^{31}P$		Relative area
excess phen + PCl_5	+190.6	+299.0	1:1.06
1:1 phen + PCl_5	+193.3	+298.6	1:0.91
$PCl_4phen^+PCl_6^-$	+192.7	+299.1	1:1.03
$PCl_4phen^+(PCl_6^-)_{0.324}Cl^-_{0.676}$	+193.4	+302.2	1:1.17
$PCl_4phen^+(PCl_6^-)_{0.214}Cl^-_{0.786}$	+192.4	+299.2	1:0.95

The accuracy of measurement of relative areas in these systems was sufficient to render these all approximately 1:1.

A possible explanation for the discrepancy in solution data from that found by Deveney and Webster has already been described (Chapter 3 section 1(ii)a). No formulation of their complex in solution other than 1:1, even allowing for the possibility of contamination by hydrolysis products, would give an average molecular weight of 182. Similarly, even if the non stoichiometric solids isolated here were in fact 1:1 complexes, contaminated with phenanthrolinium hexachlorophosphate, this would not explain the solution formulation as PCl_4phen^+ with an equimolar amount of PCl_6^-. Due to the use of non polar solvents in the preparations the possibility of contamination of the complexes by precipitated hydrolysis products (see Chapter 3 section 1(ii)a) was checked in the infra red spectrum. In practice none were found.

The behaviour of the non-stoichiometric phenanthroline complexes is somewhat different from that of the analogous $(PCl_4dipy)^+(PCl_6^-)_{0.33}\ Cl^-_{0.67}$ complex of Dillon [23]. In nitrobenzene solution the peak attributable to PCl_6^- seemed somewhat less intense than the PCl_4dipy^+ peak, indicating only slight disproportionation occurred in solution. Due to the low signal/noise ratio after 140 scans precise relative areas could not be found. The solution was not stable in the n.m.r. probe. Slow disproportionation may have been taking place, this being incomplete when the spectrum was run. Reactions of bidentate pyridines with five and six co-ordinate phosphorus species have indeed been found to proceed slowly and may be monitored by

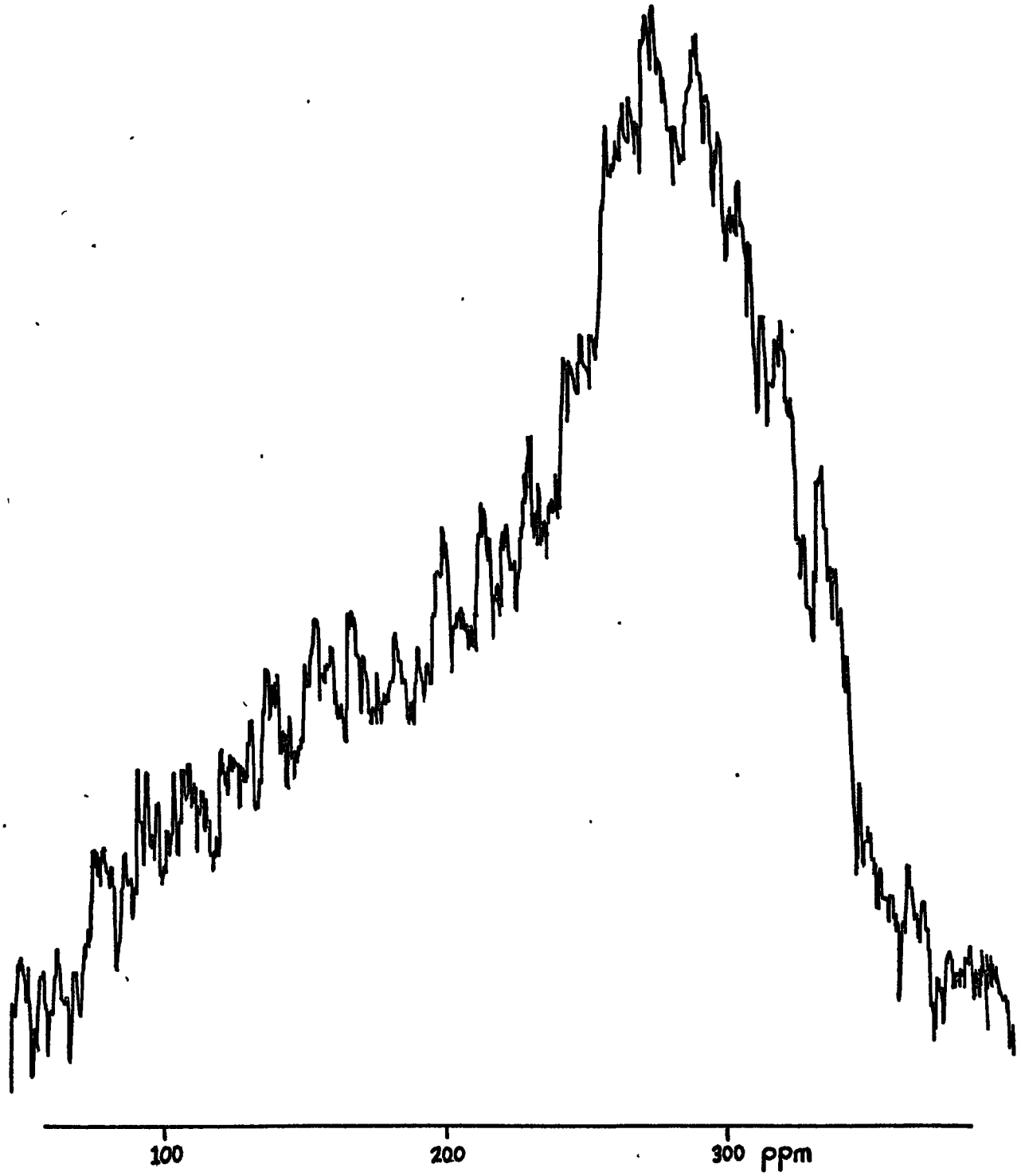


Fig 10 ^{31}P n.m.r. solid state spectrum of . $PCl_4dipy^+ PCl_6^-$ overnight accumulation

^{31}P n.m.r. technique (see especially Chapter 5), so this may not be unreasonable.

Hydrolysis Behaviour of $PCl_4phen^+PCl_6^-$

On exposure of $PCl_4phen^+PCl_6^-$ to the atmosphere there was a slight evolution of hydrogen chloride. After leaving exposed to the air overnight, however, the compound was still a powder and not a viscous solution of phosphoric acid, as is generally found in hydrolysis of compounds with phosphorus-chlorine bonds. The infra red spectrum showed little difference in the phosphorus chlorine region except for the disappearance of the broad band at about 435 cm^{-1} attributable to PCl_6^- (Fig.8). The hexachlorophosphate ion would seem to have hydrolysed leaving the cation unaffected.

$$PCl_4phen^+PCl_6^- \xrightarrow[air]{moist} PCl_4phen^+Cl^- + H_3PO_4 + HCl$$

The spectrum below about 650 cm^{-1} is sharp. Above this value, although the peaks may still be identifiable with the unhydrolysed complex they are broadened considerably. It would thus seem that the cation is partially attacked. The analogous complex $PCl_4phen^+SbCl_6^-$ is completely unaffected by exposure to air whereas tetraethylammonium hexachlorophosphate rapidly hydrolyses (contrast the slower rate of hydrolysis of tetraalkylammonium hexachloroantimonates [181]).

2,2'-Dipyridyl

When phosphorus pentachloride and 2,2'-dipyridyl are dissolved in nitromethane in the correct stoichiometric ratio, crystals appear which analyse as the 2:1 complex. The solid state ^{31}P n.m.r. spectrum (Fig.10) shows a narrow peak at +291.9 $\pm$ 5.1 ppm with a shoulder to lower field at +181.4 $\pm$ 6.8

(assuming two peaks of equal intensity). Dillon [23] found a similar spectrum for $PCl_4dipy^+(PCl_6^-)_{0.33}\ Cl^-_{0.67}$. The similarity is due to the domination of the spectrum by the sharp PCl_6^- peak, even when present in smaller amounts compared to the PCl_4dipy^+.

The infra red spectrum of $PCl_4dipy^+PCl_6^-$ below 600 cm^{-1} consisted mainly of a line slightly split into two at 517 and 510 cm^{-1} and a broad absorption at 437 cm^{-1}. This latter absorption may be attributed to PCl_6^-. Studies of $PCl_4dipy^+SbCl_6^-$ (Chapter 3 section 2(ii)b) show, however, that there are also several less intense lines hidden by this band which, together with the 517 and 510 cm^{-1} absorptions, are attributable to the PCl_4dipy^+ cation.

c) Experimental

Preparation of n.m.r. samples

Solutions of phosphorus pentachloride in liquid pyridines were made up by saturating the pyridine with powdered phosphorus pentachloride at room temperature. 2-cyanopyridine was first melted and the phosphorus pentachloride dissolved in this. The solution produced remained liquid at n.m.r. temperature (34$\frac{1}{2}$°C).

Nitrobenzene solutions containing excess pyridine were made up by saturating the nitrobenzene with the pyridine, then saturating this solution with phosphorus pentachloride. 1:1 molar ratio solutions were made up by dissolving the pyridine in a little nitrobenzene, adding this solution to solid phosphorus pentachloride, then adding more nitrobenzene with stirring until little or no solid remained.

The n.m.r. spectra were run as soon as the solutions stabilised in the n.m.r. machine, generally up to about 1½ hours after making up. PCl_5.pyridine complexes equilibrating with $PCl_4py_2^+ \cdot SbCl_6^-$ in solution have however, been shown to be stable for many months (Chapter 3 section 2(ii)a).

With the exception of the methylpyridine, phenanthroline, 3-fluoro, and 2-cyanopyridine systems, the solutions were yellow. The methyl pyridine solutions turned dark red-brown within minutes. Solutions containing excess 1,10-phenanthroline and 2-cyanopyridine were dark red coloured, whilst that from 3-fluoropyridine was almost colourless. The solution containing approximately 1:1 2-cyanopyridine and phosphorus pentachloride, although originally yellow, slowly darkened overnight at n.m.r. temperatures, producing a distinct red tinge to the solutions.

2-picoline and 2,4,6-colline were found to produce excessive hydrolysis when phosphorus pentachloride was dissolved in the neat pyridine solution even after the pyridines had been distilled from KOH pellets. Solutions were then made up in nitrobenzene solution with equimolar amounts of reactants. Significant amounts of hydrolysis were still seen to occur producing n.m.r. peaks at around 0 ppm along with peaks attributable to the hexachlorophosphate ion. The only other case in which significant amounts of hydrolysis were found was with phosphorus pentachloride in neat 2-fluoropyridine, already discussed (Chapter 3 section 1(ii)a)

Molar ratios of pyridine to phosphorus pentachloride used in the stoichiometric solutions were as follows:

TABLE 15

2,4,6-collidine	~1.01:1	2-Cl pyridine	~1.09:1
2-picoline	~1.02:1	2-CN pyridine	1.07:1
1,10-phenanthroline	1.15:1	2-F pyridine	1.08:1
pyrazine	1.01:1	3,5-diCl pyridine	1.05:1

The slight hydrolysis, which always occurs, will decrease the ratio of pyridine to phosphorus pentachloride. Assuming that PCl_6^- will form preferentially to PCl_5.pyridine, one equivalent of water will remove three equivalents of phosphorus pentachloride but only two equivalents of pyridine.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

$$2HCl + 2PCl_5 + 2py \longrightarrow 2pyH^+PCl_6^-$$

The solubility of the complexes, as shown by the ^{31}P n.m.r. peak intensity in saturated solution, varied greatly from one compound to another, being visible on a single scan in some cases (phosphorus pentachloride in pyridine) but needing up to 150 scans in other cases e.g. phosphorus pentachloride with excess 3-iodo pyridine.

Spectra were scanned from about -10 to +360 ppm, and additionally between -300 and +50 ppm if reaction was seen to occur. Narrower sweeps were used (50 or 100 ppm with monodentate pyridines, 200 ppm with bidentate pyridines) for accurate shift determination.

Preparation of complexes

PCl_5.pyridine. $2PhNO_2$

Under a continuous stream of nitrogen 3.41g (16.4 mmole) finely powdered PCl_5 were stirred in 14ml nitrobenzene to form

a saturated solution containing some undissolved PCl_5. 1.32 ml (16.4 mmole) pyridine were slowly added. An exothermic reaction occurred and a white precipitate immediately formed. Stirring was continued until all the solid PCl_5 had reacted (about 10 minutes). The solution was then transferred to the glove box, the solid filtered and washed with 30/40 pet ether, and dried at the pump.

The absence of PCl_5 impurity was shown by there being no infra red band at 654 cm^{-1} (PCl_4^+).
Yield = 6.36g = 95% based on $PCl_5.C_5H_5N.2C_6H_5NO_2$
Analysis: Found C,35.54; H,2.67; N,7.84; P,5.96; Cl,35.8
PCl_5.pyridine.$2PhNO_2$ requires C,37.92; H,2.79; N,7.82; P,5.77; Cl,33.04.

PCl_5.pyridine

a) Preferred method

In the glove box reaction apparatus (Chapter 2 section 1(i)) 10.930g (52.4 mmole) PCl_5 were stirred in 45ml nitromethane to form a saturated solution containing some undissolved PCl_5. 4.4ml (54.6 mmole) pyridine were slowly dripped in under reduced pressure. Stirring was continued for about 10 minutes to ensure all the PCl_5 had reacted, producing a cloudy white precipitate. A little extra pyridine was added to ensure completion of reaction. Before the solution had time to darken greatly (due to attack of PCl_5.pyridine on solvent) the solid was filtered off, washed twice with small amounts of benzene, then twice with 30/40 pet ether to produce snowy-white flaky crystals. The absence of PCl_5 as impurity was shown by there being no band in the

infra red spectrum at 654 cm^{-1} due to PCl_4^+.

Yield = 9.67g = 64% based on $PCl_5.C_5H_5N$

Analysis: Found C,19.73; H,2.59; N,6.70; P,10.40; Cl,61.3;

PCl_5.pyridine requires C,20.85; H,1.74; N,4.87; P,10.76;

Cl,61.7.

b) A saturated solution of PCl_5 was made up in warm ($\sim 30^{\circ}C$) nitromethane, in a tube small enough to be placed in the quick entry port of the glove box. Excess pyridine was added, and the slight pyridinium chloride fog was blown off with a continuous stream of nitrogen. The tube was then sealed, the stopper covered with "Parafilm" as an added protection, shaken and cooled under running water. White crystals came out of solution. After the outside of the tube was thoroughly dried, the "parafilm" was removed and the tube transferred into the glove box via the quick entry port. The white flaky solid was then filtered and dried at the pump.

Yield = 0.922g = 32.5% based on $PCl_5.C_6H_5N$

Analysis: Found C,20.74; H,2.09; N,4.56, P,10.36; Cl,60.4

PCl_5.pyridine requires C,20.85; H,1.74; N,4.87; P,10.76;

Cl,61.7.

<u>PCl_5.3,5-lutidine</u>

In the glove box reaction apparatus 8.302g (39.8 mmole) PCl_5 were dissolved in 120 ml nitrobenzene. 4.27g (39.9 mmole) 3,5-lutidine were slowly dripped into the stirred solution under reduced pressure. During the addition a white precipitate formed. The reaction was exothermic. Stirring was continued for a few minutes, then the solution was left for about

10 minutes to cool. The solid was then filtered, washed with methylene chloride then 30/40 pet ether, and dried at the pump.

Yield = 8.54g = 68.1% based on PCl_5.3,5-lutidine

Analysis: Found C,28.05; H,3.41; N,4.85; P,9.87; Cl,55.70; PCl_5.3,5-lutidine requires C,26.65; H,2.88; N,4.44; P,9.82; Cl,55.70.

PCl_5.3-X pyridine (X = Cl, Br, I)

Inside the glove box a saturated solution of PCl_5 in the required solvent (see below) was made up in a tube capable of fitting in the quick entry port. The tube was then brought out of the glove box, and approximately the requisite amount of the halopyridine was added under a continuous stream of nitrogen, either as neat liquid (3-chloro, 3-bromo pyridines), or as a saturated solution in the solvent used (3-I pyridine). The tube was then shaken to start rapid crystallisation. The tube was transferred into the glove box via the quick entry port, and the solid filtered, washed with 30/40 pet ether, and left to dry for a few minutes at the pump, then dried on a vacuum line for more than one hour.

PCl_5.3-Cl pyridine - nitroethane used as solvent

Analysis: Found C,18.69; H,1.38; N,4.34; P,9.61; Cl,65.5; PCl_5.3-Cl pyridine requires C,18.66; H,1.26; N,4.35; P,9.63; Cl,66.1

PCl_5.3-Br pyridine - nitroethane used as solvent

Analysis: Found C,17.17; H,1.58; N,3.91; P,8.2; Cl,49.3; Br,22.1; PCl_5.3-Br pyridine requires C,16.40; H,1.10; N,3.82; P,8.48; Cl,48.4; Br,21.8.

PCl_5.3-I pyridine - nitromethane used as solvent.

Analyses: Found C,14.80; H,1.25; N,3.34; P,7.42; Cl,42.40; I,30.5; PCl_5.3-I pyridine requires C,14.53; H,0.98; N,3.39; P,7.50; Cl,42.90; I,30.71.

$PCl_4phen^+(PCl_6^-)_x\ Cl^-_{1-x}$

1. 2.813g (13.5 mmole) finely powdered PCl_5 were dissolved with stirring in 100ml dry benzene. 2.434g (13.5 mmole) phenanthroline were dissolved in a few ml of dry benzene. The phenanthroline solution was added to the PCl_5 solution with stirring, forming at first a white precipitate then a yellowish suspension. The suspension was filtered off, washed with 30/40 pet ether, then dried on the vacuum line for about one hour giving an off-white powder.

Yield = 3.03g = 68.8% as $PCl_4phen^+(PCl_6^-)_{0.324}\ Cl^-_{0.676}$

Analysis: Found C,32.63; H,2.59; N,6.50; P,9.21; Cl,53.75; $PCl_4phen^+(PCl_6^-)_{0.324}\ Cl^-_{0.676}$ requires C,31.61; H,1.78; N,6.15; P,9.00; Cl,51.48.

2. This is the method used by Deveney and Webster to produce $PCl_4phen^+Cl^-$ [22].

2.78g (13.3 mmole) PCl_5 dissolved in 79ml benzene was added to 2.42g (13.4 mmole) phenanthroline dissolved in the minimum quantity of benzene. The off-white powder was isolated as above.

Yield = 3.64g = 80.9% as $PCl_4phen^+(PCl_6^-)_{0.214}\ Cl^-_{0.786}$

Analyses: Found C,34.26; H,1.87; N,5.87; P,8.85; Cl,51.58; $(PCl_4phen^+)(PCl_6^-)_{0.214}\ Cl^-_{0.786}$ requires C,33.29; H,1.87; N,6.47; P,8.68; Cl,49.69.

$PCl_4phen^+PCl_6^-$

Saturated solutions of PCl_5(3.87g; 18.6 mmole) and phenanthroline (1.72g; 9.5 mmole) in nitroethane were made up in the glove box. The PCl_5 solution was quickly added to the phenanthroline solution with stirring. The light red brown solution was left without stirring for about 2 minutes during which time crystals appeared in the solution. The off-white crystals were then separated, washed with methylene chloride, then 30/40 pet ether, and dried at the pump.

Yield = 2.94g = 51.6% as $PCl_4phen^+PCl_6^-$

Analysis: Found C,23.92; H,1.37; N,5.10; P,10.21; Cl,59.34; $PCl_4phen^+PCl_6^-$ requires C,24.15; H,1.35; N,4.70; P,10.38; Cl,59.42.

$PCl_4dipy^+PCl_6^-$

In the glove box saturated solutions of PCl_5 (5.65g; 27.1 mmole) and dipyridyl (2.11g; 13.5 mmole) were made up in nitromethane. The dipyridyl solution was added to the PCl_5 solution with stirring. Off-white crystals rapidly formed. These were filtered off, washed with 30/40 pet ether, and dried at the pump.

Yield = 3.56g = 55.5% as $PCl_4dipy^+PCl_6^-$

Analyses: Found C,19.27; H,1.61; N,4.59; P,10.31; Cl,60.7; dipyridyl, 28.80; $PCl_4dipy^+PCl_6^-$ requires C,20.97; H,1.41; N,4.89; P,10.82; Cl,61.91; dipyridyl, 27.27.

Bis(2,4,6-Collidinium) chloride hexachlorophosphate

6.50g (31.2 mmole) PCl_5 were dissolved in 250ml of undried carbon tetrachloride. Under a continuous stream of nitrogen, an equimolar quantity of 2,4,6-collidine was added with stirring. A thick white precipitate almost immediately formed in the solution. This was filtered off and dried.

Yield = 6.64g

Analyses: Found C,37.17; H,4.94; N,4.97; P,5.25; Cl,46.96; $(C_8H_{11}NH^+)_2\ Cl^-PCl_6^-$ requires C,36.7; H,4.58; N,5.36; P,5.92; Cl,47.4.

The compound was characterised by infra red spectroscopy (one broad P-Cl stretch at 448 cm^{-1} ; broad ^+N-H frequency at 2555 cm^{-1}), and by ^{31}P n.m.r. in the solid state (δ^{31}P 298.7 ppm) and nitrobenzene solution (δ^{31}P 297.5 ppm), these peaks being attributable to the hexachlorophosphate ion.

The analogous compound $(pyH^+)_2Cl^-PCl_6^-$ has been prepared by Beattie et al [182]. The exact stoichiometry of the collidinium salt, however, varied with the conditions of preparation. The preparative route used here is similar to that used by Van der Meulen and Hellen [183] to produce $pyH^+\ BF_4^-$.

$SbCl_5$.pyridine

The preparation follows the procedure of Hutton and Webb [3].

2.0ml (24.8 mmole) pyridine in 20ml of chloroform, which had been previously distilled from phosphorus pentoxide, were slowly added to a solution of 4.8ml (9.8g, 32.86 mmole) antimony pentachloride in 50ml of chloroform. The off white product was filtered, washed with hot chloroform and dried under vacuum.

Yield = 5.65g = 60.2% as $SbCl_5.py$

i.r. spectrum 400-300 cm^{-1}:358 cm^{-1} str, 348 cm^{-1} str. c.f.

Beattie et al [11] 353 vs br, 344 vs br.

Analyses: Found C,15.1; H,1.84; N,3.35; Cl,51.4 $SbCl_5.py$

requires C,15.9; H,1.34; N,3.70; Cl,46.9.

2. Acceptor Properties of the Tetrachlorophosphonium ion : Tetrachlorophosphonium Hexachloroantimonate $PCl_4^+SbCl_6^-$

(i) Introduction

The 1:1 adduct of phosphorus pentachloride and antimony pentachloride has been long known [1,184], and its formation in non aqueous solvents investigated using a variety of physical techniques [16,185,186]. The conductivity of the complex in solution and its high sublimation temperature (321°C) immediately suggested a salt-like structure [187]. Its i.r. and Raman spectra show the formulation of the complex to be $PCl_4^+SbCl_6^-$ in both solid state [11,188,189] and solution [11].

The complex is a white solid, readily soluble in nitrobenzene, nitromethane and nitroethane but insoluble in methylene chloride. It does not react with acetonitrile in solution, at least for many hours, in marked contrast with phosphorus pentachloride [142]. The solid state ^{31}P n.m.r. spectrum of the complex shows a single peak at -88.3 ppm [99], attributable to PCl_4^+. The shift is -87.9 ppm in nitromethane or nitroethane [126]. Shifts of -87.2 in acetonitrile and -85.8 in nitrobenzene have been found in this work, visible on a single scan in saturated solution. The complex is then completely ionic in solution. The ^{35}Cl n.q.r. spectrum at 77K consists of two sets of lines attributable to PCl_4^+ and $SbCl_6^-$ [115].

TABLE 16

N.q.r. SPECTRUM OF $PCl_4^+SbCl_6^-$ AT 77K

ν ^{35}Cl MHz	ν ^{37}Cl MHz	Assignment
22.80		$SbCl_6^-$
23.02		$SbCl_6^-$
31.87	25.15	PCl_4^+
32.35	25.50	PCl_4^+
32.51	25.63	PCl_4^+

Although thermally stable [187], the complex is very water sensitive. Hydrolysis by traces of moisture was found to produce phosphoryl chloride and a black solid.

The complex may be conveniently prepared by reaction of antimony pentachloride with one equivalent of phosphorus pentachloride [190,126,11] or with half an equivalent of phosphorus trichloride [127].

$$PCl_3 + 2SbCl_5 \longrightarrow PCl_4^+SbCl_6^- + SbCl_3$$

The first method was used in this work (Chapter 2 section 1(ii)h). Reviews of the investigations of $PCl_4^+SbCl_6^-$ are given by Webster [1] and Kolditz [187].

The acceptor properties of PCl_4^+ in the complex $PCl_4^+SbCl_6^-$ were demonstrated by Beattie, Livingston and Webster [10]. I.r. spectra indicated the formation of $PCl_4py_2^+SbCl_6^-$ in acetonitrile solution as well as for similar tetrahydrofuran and tetrahydrothiophene complexes. These temporarily stable complexes could not be isolated as solids. A cis configuration for $PCl_4py_2^+$ was at first deduced, but it was later shown

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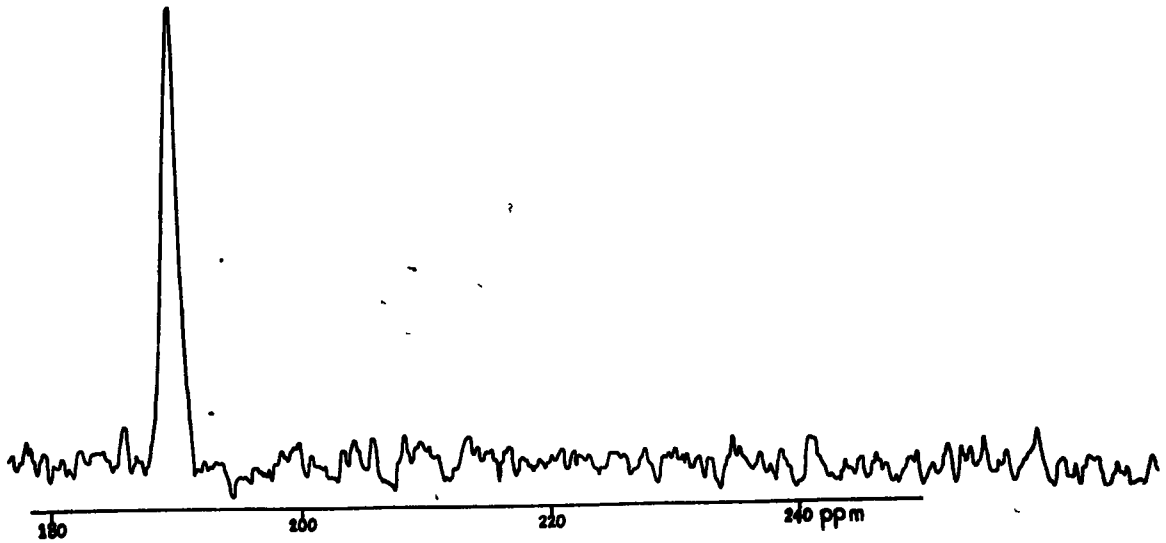
that insufficient evidence was available to confirm the stereochemistry [29]. No evidence was found for the formation of a stable PCl_4py^+ species [10].

A stable solid $PCl_4phen^+SbCl_6^-$ has been prepared [10]. Its i.r. spectrum was similar to that of the complex $PCl_4phen^+Cl^-$ [10,22], showing similar species to be present. Other examples of PCl_4^+ acting as an acceptor include PCl_4dipy^+ [29], and $PCl_4dipy^+ (PCl_6^-)_{0.33}(Cl^-)_{0.67}$ [23].

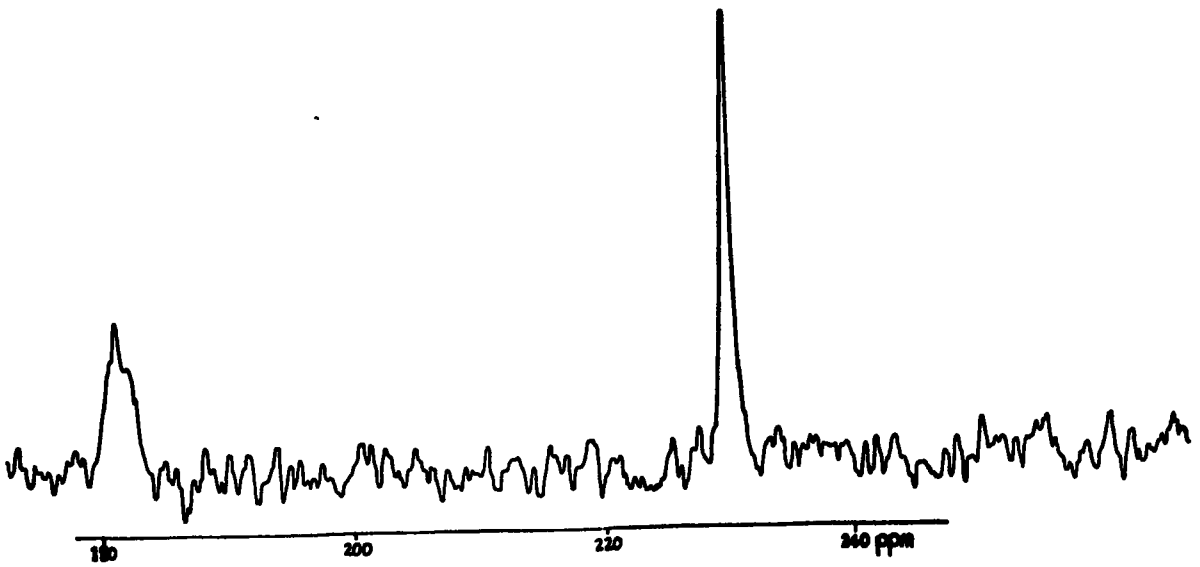
The 1:1 adduct of phosphorus pentachloride and aluminium trichloride has an ionic formulation, $PCl_4^+AlCl_4^-$, both in the solid state [128,189,110] and in solution [191]. Although the first solid state ^{31}P n.m.r. spectrum suggested a covalent structure [97], this has since been shown to be in error [23]. The solid gives a ^{31}P n.m.r. peak at -87 ppm [23], attributable to PCl_4^+, whereas the solution spectrum gives a shift at -86.5 ppm [191]. $PCl_4^+AlCl_4^-$ was used in this work to determine the effect of the counter ion on the reaction between PCl_4^+ and pyridine. The complex was prepared by mixing the components in methylene chloride c.f. ref. 128. It is extremely soluble in nitrobenzene.

Mixtures of phosphorus pentachloride, aluminium trichloride (or ferric chloride) and pyridine have been used to effect Walden inversion chlorinations in organic compounds [54]. Before the general availability of physical techniques Hückel and Pietrok [54] postulated intermediates such as $PCl_4py^+AlCl_4^-$ and $PCl_4py_2^+Cl^-$;

Fig 11 ^{31}P nmr solution spectra



a) $PCl_4^+SbCl_6^-$ + 2 equivs dipyridyl in nitrobenzene 30 scans



b) $PCl_4^+SbCl_6^-$ + 2 equivs pyridine in nitrobenzene
5 days after making up 64 scans

(ii) Present Work

a) Solution investigations

Reactions of $PCl_4^+SbCl_6^-$ with a number of monodentate and bidentate pyridines were investigated in nitrobenzene solution by ^{31}P n.m.r. techniques to determine the precise nature of the reaction and the stability of the cationic species $PCl_4L_2^+$ (L = monodentate pyridine) or PCl_4L^{1+} (L^1 = bidentate pyridine). It was hoped to compare the products with the molecular complexes of PCl_5 and pyridines (Chapter 3 section 1(ii)) and thus compare the relative acceptor properties of PCl_4^+ and PCl_5.

A nitrobenzene solution containing equimolar proportions of 2,2'-dipyridyl and $PCl_4^+SbCl_6^-$ gave a single ^{31}P n.m.r. line at +190.5 ppm, similar to the value of +189 ppm found by Dillon [23] for PCl_4dipy^+ in $PCl_4dipy^+(PCl_6^-)_{0.33}Cl^-_{0.67}$, and distant from the position of PCl_6^-. The formation of $PCl_4dipy^+SbCl_6^-$ is then confirmed. Solutions containing dipyridyl and $PCl_4^+SbCl_6^-$ in 1.5:1 and 2:1 proportions (Fig.11) gave similar ^{31}P n.m.r. spectra (δ^{31}P +190.4, +189.6 ppm respectively), showing that no further dipyridyl co-ordinates when excess of the ligand is present. The solutions showed no signs of further reaction over many months, contrasting with the slow equilibration found with complexes of monodentate pyridines as described below. Solutions containing equimolar proportions of phenanthroline and $PCl_4^+SbCl_6^-$ produced a single ^{31}P n.m.r. peak at +191.5 ppm (compare the value of +192.7 ppm found with $PCl_4phen^+PCl_6^-$ in Chapter 3 section 1(ii)b) attributable to PCl_4phen^+.

Solutions containing $PCl_4^+SbCl_6^-$ and various monodentate pyridines were then made up in a 1:2 molar ratio. The range of substituted pyridines investigated was identical with that used in the work on phosphorus pentachloride adducts (Chapter 3 section 1(ii)a). The results are given in Table 17.

TABLE 17

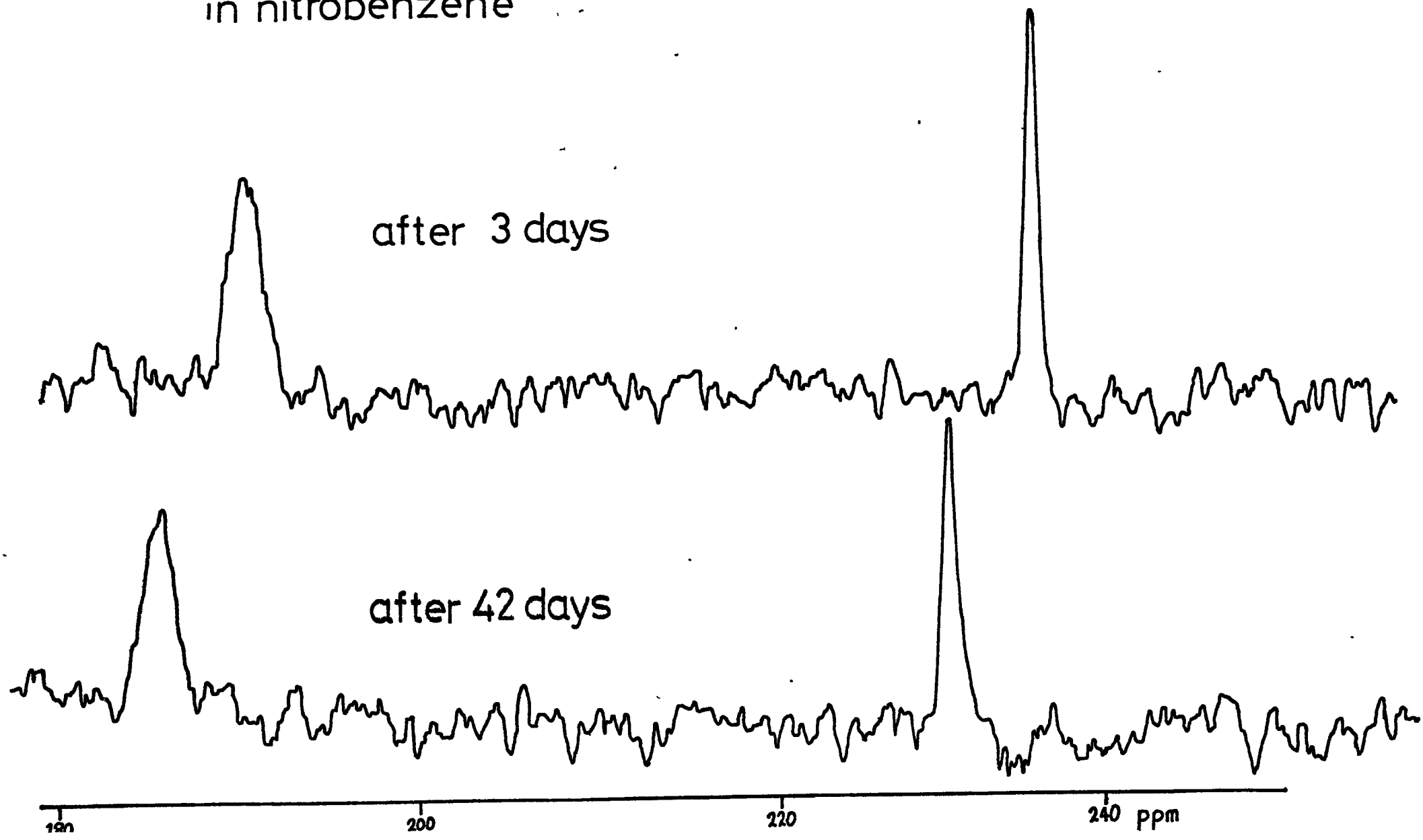
RESULTS OF ADDITION OF PYRIDINE TO $PCl_4^+SbCl_6^-$

	pKa	$PCl_4^+SbCl_6^-$ + 2 pyridine in nitrobenzene ^{31}P n.m.r. shift	c.f. PCl_5 + pyridine Table 5
2,4,6-collidine	7.4	-218.5(PCl_3)	-217.0 *
3,5-lutidine	6.2	adduct insoluble	
2-picoline	5.9	-218.1(PCl_3)	-217.3 *
3-picoline	5.6	adduct sparingly soluble	
pyridine	5.2	+180.8 +229.6	+228.0
1,10-phenanthroline *	4.9	+191.5	+193.3 +298.6 *
2,2'-dipyridyl *	4.4	+190.5	+189 +293.0
3-I pyridine	3.3	+188.0 +231.6	+229.7
3-F pyridine	3.0	+184.0 +225.0	+229.3
3-Br pyridine	2.9	+184.9 +229.7	+228.3
3-Cl pyridine	2.8	+182.5 +226.3	+228.6
4-CN pyridine	1.9	adduct insoluble	
3-CN pyridine	1.4	no 6 co-ordinate adduct Peaks -6.0, -3.6	+228.1
Pyrazine	0.8	+180.7 +224.2	+219.1 *
3,5-diCl pyridine	0.7	-86.4 (PCl_4^+)	+170.2 *
2-Br pyridine	0.8	-87.1 (PCl_4^+)	+83.0
2-Cl pyridine	0.6	-86.7 (PCl_4^+)	+84.8 *
2-CN pyridine	-0.3	+18.0 +107.3 +173.4	+171.3 *
2-F pyridine	-0.4	-86.4 (PCl_4^+)	+77.8 *

* ^{31}P shifts for equimolar quantities of reactants in $PhNO_2$
Others for solutions containing excess pyridine

‡ Equimolar quantities of $PCl_4^+SbCl_6^-$ and bidentate pyridine used

Fig 12 ^{31}P n.m.r. solution spectrum of $PCl_4^+SbCl_6^-$ + 2 equivs 3-I pyridine in nitrobenzene

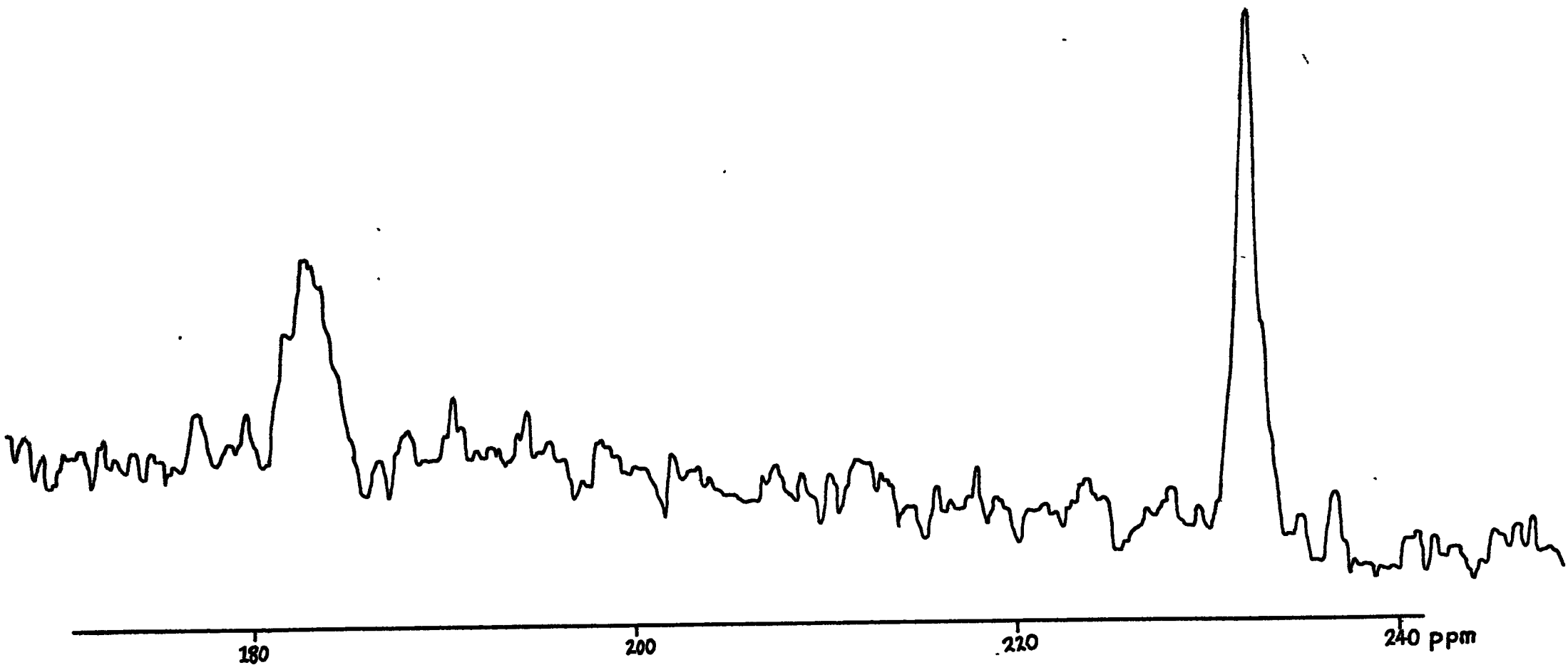


Pyridine, 3-X pyridine (X = Cl, Br, I)

The solution containing pyridine itself and $PCl_4^+SbCl_6^-$ in a 2:1 molar ratio took several hours to stabilise in the n.m.r. spectrometer. Two peaks were then visible, at +180.8 ppm and +229.6 ppm (Fig.11). By analogy with the shifts of PCl_4phen^+ and PCl_4dipy^+ the low field peak can be attributed to $PCl_4py_2^+$, whilst the higher field peak has a similar shift to that found for $PCl_5.py$ [23,31]. The appearance of two peaks was also found to be a general feature of the solutions containing 3-halopyridines, as was the instability of the solutions in the n.m.r. machine for several hours. This instability is presumably due to the slow reaction of the $PCl_4py_2^+$ species initially formed to give $PCl_5.py$.

With 3-iodopyridine the ^{31}P n.m.r. spectrum was strong enough to be visible on a single scan, making observation of the spectrum possible immediately after preparation of the solution. The spectrum then showed a simgle peak at +188.1 ppm, with no peak visible at higher field. A peak at about +230 ppm slowly appeared and grew with respect to the $PCl_4(3\text{-Ipy})_2^+$ peak. Over a period of several months the reaction proceeded no further than the two species being present in approximately equal proportions (Fig.12). An equilibrium thus appears to be established. The equilibration seemed general with the pyridines. $PCl_4py_2^+SbCl_6^-$ is immediately formed but slowly equilibrates with $PCl_5.py$ and presumably $SbCl_5.py$. Antimony pentachloride may complex [1] with both pyridine and nitrobenzene.

Fig 13 ^{31}P n.m.r. solution spectrum of PCl_5.pyridine + $SbCl_5$.pyridine in nitrobenzene



The pyridine complex is much stronger than the nitrobenzene complex, however, and may be synthesised in nitrobenzene solution.

In order to determine whether an equilibrium is really established, and to test the feasibility of one product of the equilibration being $SbCl_5.py$, a 1.00:1.03 solution of $PCl_5.py$ and $SbCl_5.py$ was made up in nitrobenzene solution (for preparation of $SbCl_5.py$ see Chapter 3 section 1(ii)c). Reaction was seen to occur, the ^{31}P n.m.r. spectrum after one day showing two lines, at +181.7 ppm and +232.0 ppm, attributable to $PCl_4py_2^+$ and $PCl_5.py$ respectively (Fig.13). The resulting spectrum must then be due to an equilibrium, since this has been approached from each direction in turn.

$$PCl_4py_2^+SbCl_6^- \rightleftharpoons PCl_5.py + SbCl_5.py$$

To determine the equilibrium position, the relative proportions of $PCl_4L_2^+$ and $PCl_5.L$ were measured by comparing the areas of the ^{31}P n.m.r. peaks, as given in Table 18.

TABLE 18

RELATIVE AREAS OF $PCl_5.py$ AND $PCl_4py_2^+$ SPECIES IN VARIOUS SYSTEMS

a) 1:1 $PCl_5.py$: $SbCl_5.py$ in nitrobenzene

Time after making up	$\delta^{31}P$		Relative areas
1 day	+181.7	+232.0	54:46
1 month	+182.4	+231.1	57:43

b) 2:1 pyridine : $PCl_4^+ SbCl_6^-$ in nitrobenzene

1 day	+180.7	+229.5	59:41
5 days	+181.2	+230.1	44:56

c) 2:1 3-iodopyridine : $PCl_4^+SbCl_6^-$ in nitrobenzene

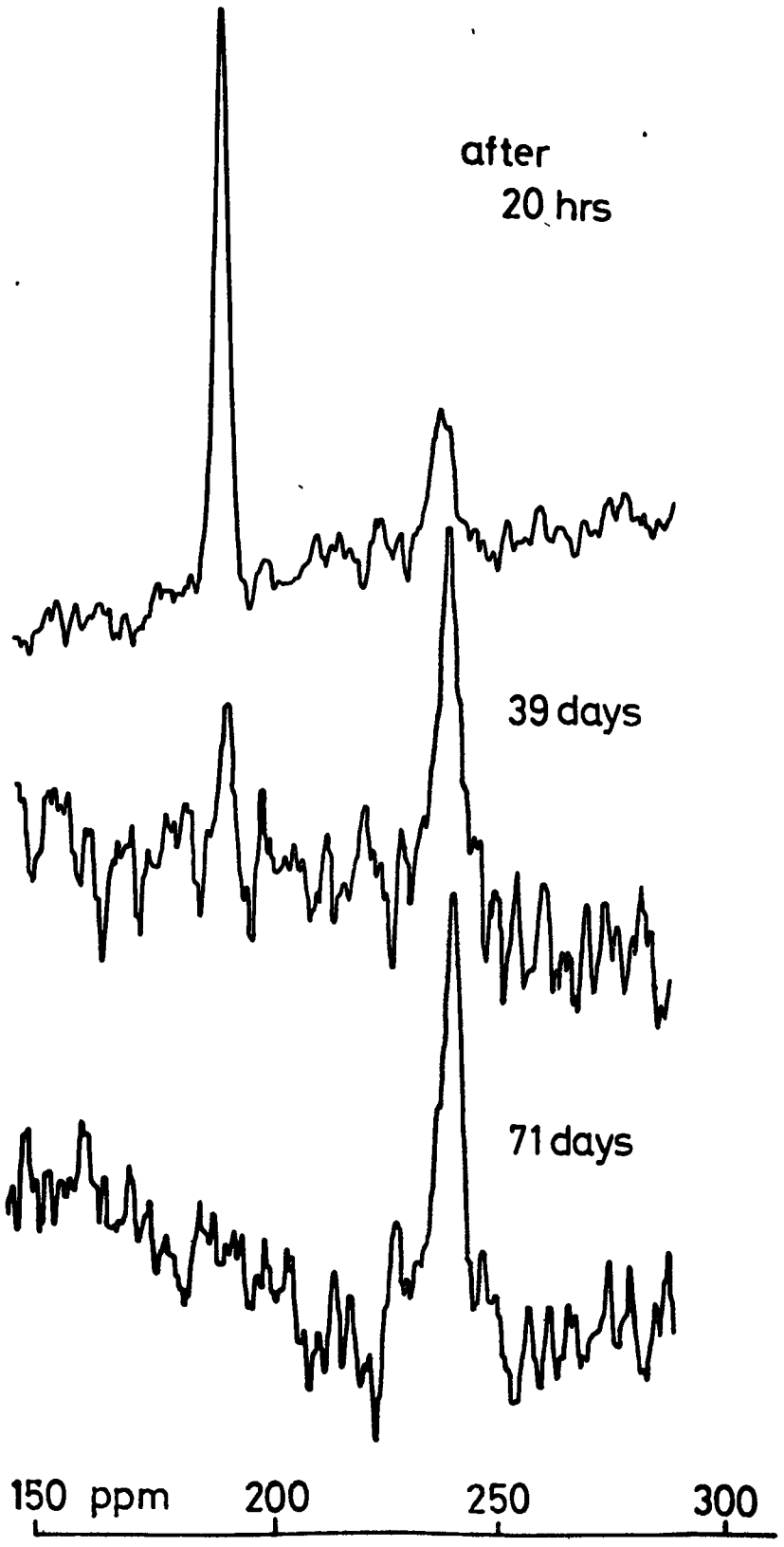
3 days	+190.4	+233.8	53:47
42 days	+185.6	+229.3	52:48

The equilibrium position from the PCl_5.py/$SbCl_5$.py mixture is about 57:43 $PCl_4py_2^+$: PCl_5.py, agreeing with the value from pyridine and $PCl_4^+SbCl_6^-$ after less than one day. However, after 5 days the latter solution appeared to have reacted further. This seems difficult to explain unless hydrolysis of one component has occurred, thus disturbing the equilibrium position.

The 3-iodopyridine equilibrium was investigated only from the direction of 3-iodopyridine and $PCl_4^+SbCl_6^-$. The equilibrium ratio $PCl_4(3\text{-I pyr})_2^+$: PCl_5.(3-I pyr) appears to be about 52;48. The difference between the ratios in the pyridine and 3-iodopyridine systems is probably within experimental error. However, for the very weak base, pyrazine, discussed later, the $PCl_4py_2^+$ peak was undetectable after several days, the equilibrium being completely over to the side of PCl_5.pyrazine.

Solutions after the equilibrium between $PCl_4py_2^+SbCl_6^-$ and PCl_5.py has been established are stable over many months. The instability of the $PCl_4py_2^+SbCl_6^-$ solution, as found by Beattie, Livingston, and Webster [10], may thus have been due to their not leaving sufficient time for equilibrium to be attained. Furthermore, the acetonitrile used as solvent may attack the reactants. Although $PCl_4^+SbCl_6^-$ seems stable at room temperature in acetonitrile solution, the reaction to produce the adduct may generate enough energy to cause attack on the solvent. The complexes are very moisture-sensitive in solution. Unless water is thoroughly excluded, reaction may be due to hydrolysis. This sensitivity

Fig 14 ^{31}P nmr solution spectrum of $PCl_4^+AlCl_4^-$ +2equivs pyridine in nitrobenzene



to moisture contrasts with the relative stability of the solid complexes towards moisture, as discussed in Chapter 3 section 2 (ii)b.

A nitrobenzene solution containing $PCl_4^+AlCl_4^-$ and pyridine in a 1:2 molar ratio after a few hours showed little sign of a peak attributable to PCl_5.pyridine, although the peak due to $PCl_4py_2^+$ was clearly visible. After one day two peaks corresponding to $PCl_4py_2^+$ and PCl_5.py were found (δ^{31} P +182.2, +230.4). The cation peak slowly lost intensity with respect to the neutral peak, however, until it had disappeared completely (Fig.14). Thus the reaction

$$PCl_4py_2^+AlCl_4^- \longrightarrow PCl_5.py + AlCl_3.py$$

apparently proceeds to completion. The position of the equilibrium between $PCl_4py_2^+$ and PCl_5.py thus appears to depend on the nature of the anion. With a suitable anion the original adduct may possibly be completely stable, perhaps with a non chlorine containing anion such as PF_6^-, or with an ion such as ClO_4^-.

The species present in the solutions used by Hückel and Pietrok [54] to effect Walden inversions, for freshly mixed reagents at least, are thus $PCl_4py_2^+AlCl_4^-$ together with PCl_5.py and $AlCl_3$.py.

3-CN pyridine, 4-CN pyridine, pyrazine

When 4-cyanopyridine was used as ligand the solvated adduct $PCl_4(4\text{-CNpyr})_2^+ SbCl_6^- . 2PhNO_2$ immediately precipitated. Hence no solution data on the complex could be obtained. The solution containing 3-cyanopyridine and $PCl_4^+SbCl_6^-$ in a 2:1 molar ratio was found to contain no six co-ordinate species. Reproducible ^{31} P n.m.r. peaks were found at

-6.0 and -3.6 ppm, unfortunately in the hydrolysis product region of the spectrum. The 3-cyanopyridine was shown by infra red spectroscopy to contain no detectable moisture. Indeed no difficulty was found with hydrolysis in the system PCl_5/3-CN pyridine (excess) in nitrobenzene (Chapter 3 section 1(ii)a). The peak at -3.6 ppm is very close to the position of phosphoryl chloride (-2.2 ppm) [89]. The peak at -6.0 ppm is more difficult to explain. This may be due to a genuine five co-ordinate adduct, $PCl_4(3\text{-CNpy})^+$, although no conclusive evidence has been found in other systems for formation of such species.

Pyrazine behaves in a similar fashion to the 3-halo pyridines in showing both cationic and neutral peaks initially. The cation peak was very broad, however, probably because of slow exchange with PCl_4^+, and after several days had disappeared completely, leaving only the resonance attributable to PCl_5.pyrazine.

3,5-dichloropyridine

A 2:1 3,5-dichloropyridine/$PCl_4^+SbCl_6^-$ solution shows a single peak at -86.4 ppm assigned to unco-ordinated PCl_4^+. In order to make sure that the PCl_4^+ion was not in equilibrium with a small amount of the co-ordinated form the high field region was accumulated for about 240 scans. No peak was, however, discernible. This contrasts sharply with the 1:1 3,5-dichloropyridine/PCl_5 solution in nitrobenzene where the adduct is about 60% associated (Chapter 3 section 1(ii)a). It provides the only evidence found for differences in the acceptor properties of PCl_5 and PCl_4^+ and suggests PCl_5 is a

slightly better acceptor than PCl_4^+. As the substituents are in the 3 and 5 ring positions steric effects are minimal. The difference in acceptor properties may be attributable to the extra orbital hybridisation energy needed for co-ordination in the case of PCl_4^+. For a covalently bonded PCl_5 trigonal bipyramid hybridisation including d orbitals must be postulated. With four co-ordinate PCl_4^+, however, no d orbital participation is necessary, since sp^3 hybridisation alone would produce a tetrahedral molecule. d orbital contributions may of course still occur, if this is energetically worthwhile in the system.

Unlike the solutions in which co-ordination occurs, $PCl_4^+SbCl_6^-$/2 x 3,5-dichloropyridine is stable in nitrobenzene. It has no tendency to form the phosphorus pentachloride adduct. For the equilibrium with the PCl_5 adduct to be established it would thus seem that a PCl_4^+ adduct needs first to be formed.

$$PCl_4^+SbCl_6^- + 2(3,5\text{-diClpyr}) \not\rightleftharpoons PCl_5\cdot(3,5\text{-diClpyr}) + SbCl_5\cdot(3,5\text{-diClpyr})$$
$$\Downarrow\Uparrow$$
$$PCl_5 + 3,5\text{-diClpyr}$$

For the reaction to the PCl_5 complex to be favourable the energy gained from formation of the adducts must compensate for the dissociation of $PCl_4^+SbCl_6^-$,

$$PCl_4^+SbCl_6^- \longrightarrow [\ PCl_5 + SbCl_5\ ] \xrightarrow{2py} PCl_5\cdot py + SbCl_5 py$$

This reaction may not be energetically favourable with very low basicity pyridines. This explanation does not, however, show the difference in reactivity between pyrazine

and 3,5-dichloropyridine. As a $PCl_4py_2^+SbCl_6^-$ adduct is produced with the former base it would perhaps be expected that the dissociation reaction would be less worthwhile.

Despite the lack of formation in solution, solid PCl_4 (3,5-diCl pyridine)$_2^+$ $SbCl_6^-$ is isolable from nitrobenzene solutions containing an excess of 3,5-dichloropyridine (Chapter 3 section 2(ii)b).

Although 3,5-dichloropyridine is a very slightly stronger base than pyrazine [144,145], pyrazine is found to co-ordinate to $PCl_4^+SbCl_6^-$ in solution, whereas 3,5-dichloropyridine does not. This reversal of the co-ordination properties from the order expected from the basicities is also found with the phosphorus pentachloride adducts. The limiting point of co-ordination, however, in the absence of steric hindrance, appears to be around this pKa.

2-X pyridine (X = Cl, Br, I, CN)

The 2-halopyridines all show no detectable adduct formation in solutions containing a 2:1 molar ratio of the pyridine to $PCl_4^+SbCl_6^-$. This is similar to the co-ordination properties of phosphorus pentachloride where 1:1 solutions of phosphorus pentachloride and the 2-halopyridine have little tendency to form complexes. Phosphorus pentachloride dissolved in neat 2-halopyridine does, however, show some complex formation. It was not possible to simulate these conditions with $PCl_4^+SbCl_6^-$, since the ionic adducts $PCl_4py_2^+SbCl_6^-$ were found to be insoluble in the neat pyridine. No six co-ordinate ^{31}P n.m.r. peaks were visible after accumulation when

attempts were made to dissolve $PCl_4^+SbCl_6^-$ in 2-chloropyridine. When $PCl_4^+SbCl_6^-$ was dissolved in pyridine or 3-bromopyridine peaks were observed at +227.8 and +228.4 ppm respectively, attributable to the molecular PCl_5.py adduct. No six co-ordinate peaks were found with $PCl_4^+SbCl_6^-$ in neat 3-chloropyridine. The non-formation of the molecular complex with 2-chloropyridine may be due to the non formation of PCl_4 $(2\text{-Clpyr})_2^+SbCl_6^-$. A similar explanation cannot be used for the 3-chloropyridine solution as co-ordination of 3-chloropyridine to $PCl_4^+SbCl_6^-$ has been previously shown to be possible in nitrobenzene solution. Perhaps in this case the solution has not been mixed sufficiently for the solid state/solution reaction to proceed.

$$PCl_4^+SbCl_6^-\ (\text{insol}) + 2\ \text{py} \longrightarrow PCl_4py_2^+SbCl_6^-\ (\text{insol}) \downarrow PCl_5.\text{py(sol)} + SbCl_5.\text{py}$$

The 2:1 2-cyanopyridine and $PCl_4^+SbCl_6^-$ solution in nitrobenzene shows three peaks above 0 ppm at +18.0, +107.3, and +173.4 ppm. The resonance at highest field is in the same position as in the analogous phosphorus pentachloride system. As previously shown (Chapter 3 section 1(ii)a) possible assignments of these peaks are $PCl_4(\leftarrow N \equiv C\ \text{pyr})^+$, $PCl_4(\leftarrow N \equiv C\ \text{pyr})_2^+$, and PCl_5. $\leftarrow N \equiv C$ pyr respectively, by analogy with the relative order of chemical shifts in other $PCl_4^+SbCl_6^-$ / pyridine systems. This assignment explains the two lower field peaks being found only with the $PCl_4^+SbCl_6^-$ system. Much more evidence would, however, be needed to confirm this hypothesis.

Methyl pyridines

Similarly to phosphorus pentachloride (Chapter 3 section 1(ii)a) $PCl_4^+SbCl_6^-$ does not form stable adducts with the hindered 2-substituted methyl pyridines, 2,4,6-collidine and 2-picoline, but reacts forming phosphorus trichloride. (δ^{31} P found -218.5, -218.1 ppm respectively). The reaction product from the hexachloroantimonate anion was not determined. Unfortunately both the unhindered methyl pyridines used, namely 3,5-lutidine and 3-picoline, formed adducts insoluble in nitrobenzene. The solution from which the 3-picoline complex precipitates slowly turns dark brown, which may indicate reaction of the small amount of complex left in solution.

Possibility of PCl_4py^+ species

Beattie and Webster [10] found no evidence for the presence of five co-ordinate species in $PCl_4^+SbCl_6^-$ /pyridine systems. The i.r. spectrum of a solution containing $PCl_4^+SbCl_6^-$ and pyridine in a 1:2 molar ratio showed [10] no trace of a free pyridine band at 403 cm^{-1}. The presence of five co-ordinate PCl_4py^+ species would be difficult to determine unambiguously using ^{31} P n.m.r. techniques. The shift of PCl_4py^+ would be expected to be between PCl_4^+ (-85.8 ppm) and PCl_5 (+82 ppm) and probably in the region of 0 ppm. Unfortunately this is also the hydrolysis product region (Appendix 2). With the 1:2 solutions in nitrobenzene of $PCl_4^+SbCl_6^-$ and various pyridines one or more small peaks were generally found in the region of 0 ppm.

Examples are

	$PCl_4^+SbCl_6^-$ in 3-bromopyridine	-1.6, +12.0
	$PCl_4^+SbCl_6^-$ in 3-chloropyridine	-4.9, +5.2, +9.0
	$PCl_4^+SbCl_6^-$ in pyridine	+9.3
1:2	$PCl_4^+SbCl_6^-$ /3-Br pyridine in $PhNO_2$	-2.3
1:1	$PCl_4^+SbCl_6^-$ /dipyridyl in $PhNO_2$	-2.5

It is not possible to determine whether all the peaks are due to hydrolysis or whether PCl_4py^+ species are present in some of the systems.

An equimolar solution of $PCl_4^+SbCl_6^-$ and 3-iodopyridine in nitrobenzene gave no observable ^{31}P n.m.r. peak even after 150 scans whilst the 1:2 solution showed peaks clearly visible after about 30 scans. The lack of signal in the 1:1 solution probably indicates that the peaks present (PCl_4^+, $PCl_4(3\text{-Ipy})_2^+$, PCl_6. 3-Ipy and perhaps $PCl_4(3\text{-Ipy})^+$) were broadened beyond detection by mutual exchange. The possibility of formation of PCl_4py^+ in the $PCl_4^+SbCl_6^-$ /3-cyanopyridine system has been discussed previously.

Stereochemistry

Octahedral co-ordination of phosphorus is expected in $PCl_4py_2^+$. The pyridines can then occupy cis or trans positions relative to each other (Chapter 1 section 3(iii)). Little, however, can be deduced about the configuration of the complexes from the ^{31}P n.m.r. solution spectra alone. In some systems discussed later distinct signals from the isomeric forms can be found. (See Chapter 4 section 1(iv). Here only one signal attributable to $PCl_4py_2^+$ is found. This signal may be due

either to one isomeric form in solution, or to a rapid equilibrium between two isomeric forms. PCl_4phen^+ and PCl_4dipy^+ must have cis configurations. The shifts of these species are at least 5 ppm higher than are found for the monodentate pyridines (with the exception of 3-iodopyridine). This shift difference could be due to a difference in configuration, the majority of monodentate pyridines then being trans in solution, but the difference may just reflect the spread in n.m.r. shifts for the different $PCl_4X_2^+$ species. Stereochemical evidence from other physical techniques is given in Chapter 3 section 2(ii)b,

b) Solid Investigations

Over a period of days solutions of $PCl_4py_2^+SbCl_6^-$ equilibrate with PCl_5.py and $SbCl_5$.py. By choice of a solvent so that crystallisation is very rapid, however, the adducts may be separated. The complexes isolated were $PCl_4L_2^+SbCl_6^-$ where L = 3-picoline; 3,5-lutidine; pyridine; 3(hal)pyridine (hal = Cl, Br, I); 4-cyanopyridine; 3,5-dichloropyridine and $PCl_4(L\text{-}L)^+ SbCl_6^-$ where L-L = 1,10-phenanthroline or 2,2'-dipyridyl. The adduct with 4-cyanopyridine was also isolated as its bisnitrobenzene solvate, $PCl_4(4\text{-}CNpyr)_2^+ SbCl_6^-$. $2PhNO_2$. In addition the complex $PCl_4py_2^+AlCl_4$ was prepared, and there were indications that $PCl_4py_2^+BPh_4^-$ could be isolated. One sample of $PCl_4(3,5\text{-}diClpyr)_2^+ SbCl_6^-$ was prepared by J. Lincoln.

Properties

All complexes of monodentate pyridines analysed (Chapter 3 section 2(ii)c) as 1:1:2 $PCl_5/SbCl_5$/pyridine, whereas those with bidentate pyridines analysed as 1:1:1 $PCl_5/SbCl_5$/pyr. Spectroscopic data described later indicate the structures to be $PCl_4L_2^+SbCl_6^-$ and $PCl_4(L\text{-}L)^+SbCl_6^-$.

A lack of change in the i.r. spectrum of $PCl_4py_2^+SbCl_6^-$ after 11 months shows that no equilibration with PCl_5.py and $SbCl_5$.py takes place in the solid state. With the exception of the 4-cyanopyridine and 3-iodopyridine complexes, the other complexes appear also to be stable. Although the 4-cyano, 3-chloro and 3-bromopyridine complexes change colour over a period of months the i.r. spectrum of the latter two remained unchanged. Presumably their colour change is due to slight changes in the crystal lattice which did not have time to form ideally during the rapid crystallisation.

The solids are markedly stable to moist air. The pyridine, phenanthroline, and 3-bromopyridine complexes were exposed to the atmosphere overnight and showed no change in their i.r. spectra, apart from a change in intensity of two minor peaks at 1534 and 1418 cm^{-1} with the phenanthroline complex. Indeed the pyridine and phenanthroline complexes showed no signs of decomposition after several weeks exposure or after addition of water. The particles of the phenanthroline complex coalesced into loose globules indicating its strongly hydrophobic

nature. Although co-ordination saturation may be partly responsible for the resistance to hydrolysis the insolubility of the salt-like structure must contribute greatly. c.f. the ease of hydrolysis of solid PCl_5.pyridine. The resistance is also dependent on the stability of the anion. $PCl_4phen^+PCl_6^-$ rapidly hydrolyses with at least slight attack on the cation. No such change occurs with $PCl_4phen^+SbCl_6^-$.

$PCl_4py_2^+SbCl_6^-$ and $PCl_4phen^+SbCl_6^-$ are white crystalline solids, the latter only slighty soluble in nitrobenzene. $PCl_4phen^+SbCl_6^-$ has been previously described as a pale yellow solid when isolated from acetonitrile solution, not readily hydrolysable in the solid state [10]. The reported i.r. spectrum [10] agrees only approximately with this work.

TABLE 19

i.r. SPECTRUM OF $PCl_4phen^+SbCl_6^-$

Ref.10	564vw, 534s, 506s, 468sbr, 445m, 334m, 277m
Present Work	572w, 539s, 528m, 512s, 481s, 474sh, 452m, 358sh, 342s, 332s, 302w, 278w
c.f. $PCl_4phen^+PCl_6^-$	572w, 539s, 525sh, 508s, 482s, (452sh, 438s, 422sh) 338w, 302w, 282w

( ) Mainly PCl_6^-

$PCl_4dipy^+SbCl_6^-$ is a pale yellow solid which is very soluble in nitrobenzene, nitromethane and nitroethane. With the exception of bands attributable to the anions present the i.r. spectra of $PCl_4dipy^+SbCl_6^-$ and $PCl_4dipy^+PCl_6^-$ were identical, showing the presence of identical cations.

TABLE 20

I.r. SPECTRA OF PCl_4dipy^+ SALTS 660-250 cm^{-1}

$PCl_4dipy^+SbCl_6^-$	658m,	512s,	502s,	461s,	417w,	398w,
	342s,*	306w,	280w,	258m,		
$PCl_4dipy^+PCl_6^-$	653m,	620w, 590w,	517s,	510s,	460sh,*	438s,*
	428sh,*	354w,	298w,	288w,	270m,	

* Mainly PCl_6^- or $SbCl_6^-$

$PCl_4(3,5\text{-lutidine})_2^+ SbCl_6^-$ and $PCl_4(3\text{-picoline})_2^+ SbCl_6^-$ are both stable white solids. Their stability compares with that of solid PCl_5. 3,5-lutidine. The 3-picoline complex seems slightly soluble, and the 3,5-lutidine complex insoluble in nitrobenzene.

The 3-halopyridine complexes $PCl_4(3\text{-halpyr})_2^+SbCl_6^-$ (hal = Cl, Br, I) are soluble in nitrobenzene. The white 3-chloro and 3-bromopyridine complexes turn fawn coloured over several weeks. The yellow 3-iodopyridine complex undergoes no colour change. As the i.r. spectrum of $PCl_4(3\text{-Ipyr})_2^+SbCl_6^-$ after several months showed a peak which may be attributed to phosphoryl chloride, it could not be determined whether changes in other parts of the spectrum were due to hydrolysis or to solid state reaction.

$PCl_4(4\text{-CNpyr})_2^+ SbCl_6^-$ and its bisnitrobenzene solvate are white solids. Both turn brown over a period of weeks at room temperature. Their i.r. spectra after this period showed distinct differences which may be attributed to formation of PCl_5.(4-CN pyridine) and presumably also $SbCl_5$.(4-CN pyridine). Although the PCl_5 adduct has not

been previously isolated, the new i.r. lines are in very similar positions to those found with other PCl_5.pyridine complexes. Even after 8 months at 35°C however, the solid state reaction had not proceeded to completion. $PCl_4(4\text{-CNpyr})_2^+ SbCl_6^-$. $2PhNO_2$ seems indefinitely stable at -15°C.

TABLE 21

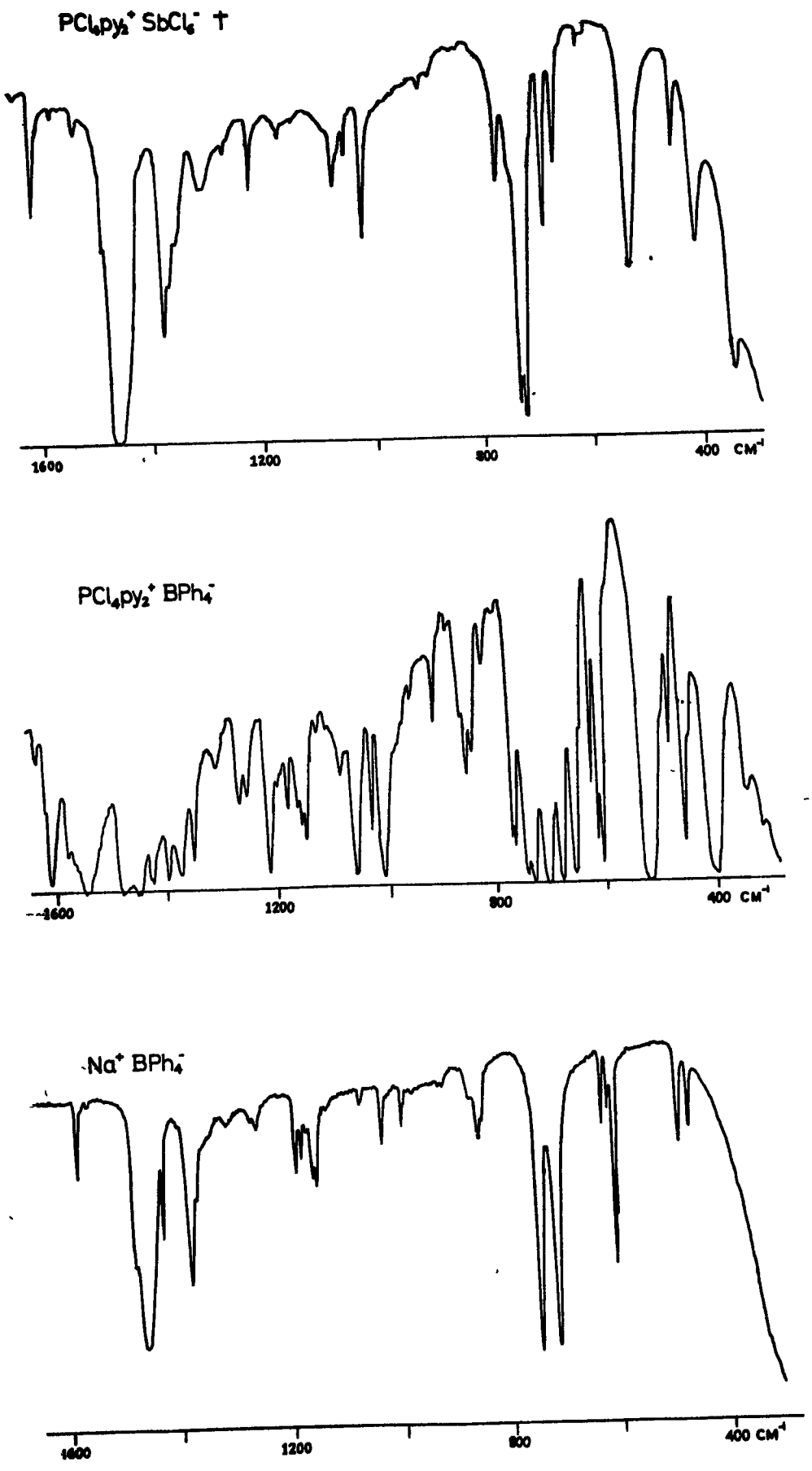
i.r. SPECTRUM $PCl_4(4\text{-CNpyr})_2^+SbCl_6^-$
650-250 cm^{-1}

New			570s,	552m,		522m,
	507s,		420w,	390s,	360s,	340s,
8 months	630s,	588s,	572sh,	554m,	537w,	524w,
	508m,	470m,	445m,	392m,		343s,
	330sh,	274w				

Unfortunately co-ordination decreased the intensity of the - C ≡ N stretching vibration to below detection, so the effect of co-ordination on the frequency of this line could not be observed. The nitrobenzene in the lattice was detected by elemental analyses and by its characteristic infra red frequencies, particularly at 1521, 1347 and 852 cm^{-1}. The 676 cm^{-1} nitrobenzene line appears to split into two lines at 676 cm^{-1} and 683 cm^{-1}, similar to its behaviour in transition metal complexes [176]. No splitting is detectable in solvates of the other adducts studied in this work.

$PCl_4(3,5\text{-dichloropyridine})_2^+ SbCl_6^-$ is a white, stable solid. No evidence has been found for its existence in solution.

Fig15 Ir spectra 1650-300 cm^{-1}



KBr plates † with polythene discs

$PCl_4py_2^+ AlCl_4^-$ is a white solid. Its i.r. spectrum, with the exception of the anion bands, corresponded to that of $PCl_4py_2^+SbCl_6^-$.

TABLE 22

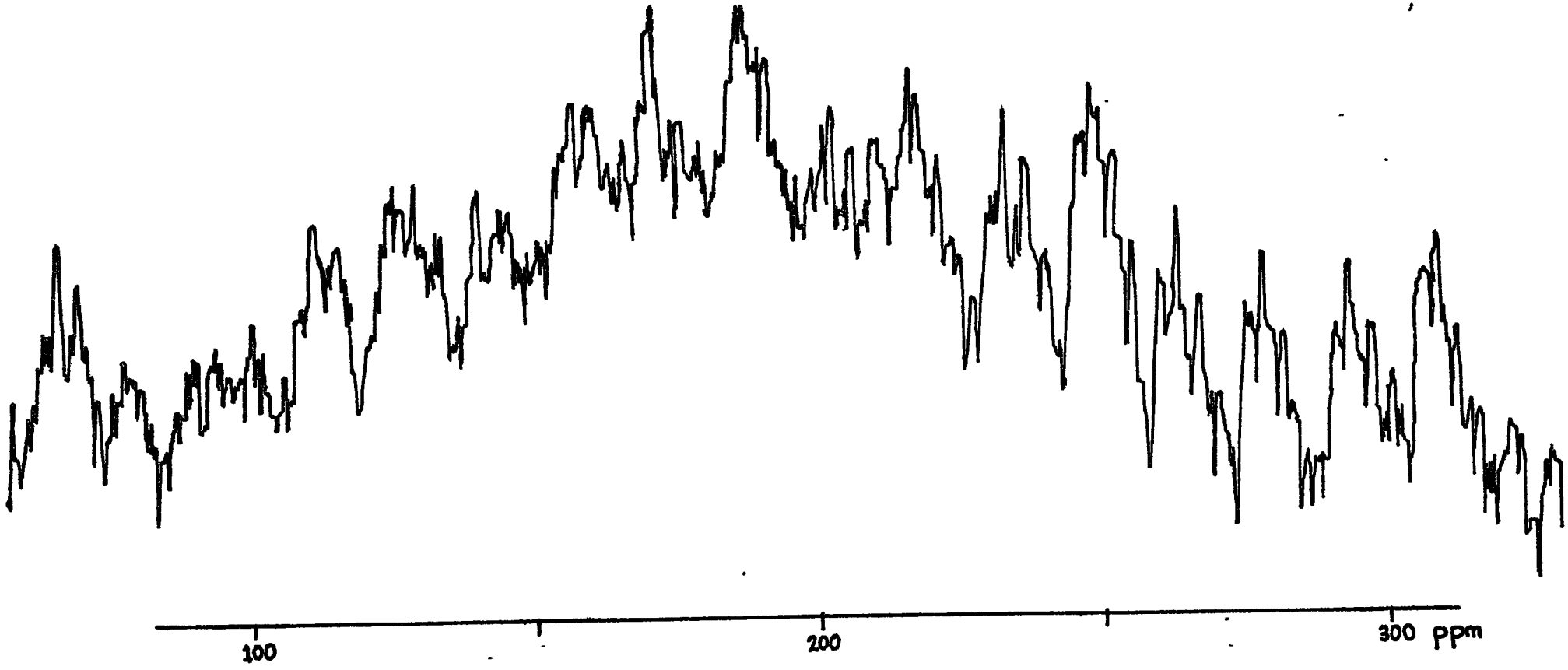
i.r. SPECTRA OF $PCl_4py_2^+$ SALTS 660-340 cm^{-1}

$PCl_4py_2^+SbCl_6^-$	612w,	536s,	447s,	410s,	340*s
$AlCl_4^-$	610w,	535sh,	528s,	496*s,	450m,
	410m,				
BPh_4^-	658s,	627*m,	616*m,	608*m,	527s,
	487*w,	458m,	408s,	348w	

*Bands due to anion

When freshly made up nitromethane solutions of $PCl_4py_2^+SbCl_6^-$ and $Na^+BPh_4^-$ were mixed, a yellow precipitate immediately appeared. The i.r. spectrum of this solid did not show the large band expected for $SbCl_6^-$ (the weak 348 cm^{-1} peak may be due to this in very small amounts) but showed peaks attributable to both $PCl_4py_2^+$ and BPh_4^- (Fig.15). Presumably the antimony remained in solution as $Na^+SbCl_6^-$ [192] or as $SbCl_5$, precipitating sodium chloride. The analysis of the compound (see Chapter 3 section 2(ii)c) did not fit the above formulation, but no extra peaks were found in the i.r. spectrum of the material. The solid decomposed quickly at 35°C and over periods of days at room temperature. One sample showed the presence of $PCl_4py_2^+$ in the i.r. spectrum even after one year. The BPh_4^- frequencies had altered, however.

Fig16 ^{31}P n.m.r. solid state spectrum of $PCl_4py_2^+ SbCl_6^-$
908 scans



The possibility of isolation of the tetraphenylborate shows the marked lowering of the reactivity of PCl_4^+ by co-ordination. An attempt was made to produce $PCl_4^+BPh_4^-$ from PCl_5 and $Na^+BPh_4^-$ by evaporating a nitromethane solution of the components under reduced pressure. Although PCl_4^+ was shown to be present in the infra red spectrum of the remaining brown solid, the other lines did not correspond to those of the tetraphenylborate anion. Indeed very few salts of the tetrachlorophosphonium ion are known, except with halide or complex halide anions [1]. These include $PCl_4^+ClO_4^-$ [126], $PCl_4^+SO_3F^-$ [193], and $PCl_4^+SO_3Cl^-$ [194-6]. The latter salt was unstable at room temperature. Other attempts to produce the perchlorate, nitrate [10], difluoroborate and fluorosulphate [197,198] salts have failed. However the $PCl_4py_2^+$ cation can be isolated with as potentially reactive an anion as tetraphenylborate. By protecting the PCl_4^+ cation a whole range of salts may in future be formed.

^{31}P n.m.r. spectra

The complexes gave broad but well-defined resonances at about +190 ppm, indicative of the six co-ordinate cationic species. The bis nitrobenzene 4-cyanopyridine complex did not stabilise in the spectrometer, presumably due to its slow dissociation. One sample showed a liquid peak in the solid at +232.3 ppm, confirming the dissociation to PCl_5. 4-CNpyr and $SbCl_5$. 4-CNpyr.

TABLE 23

^{31}P n.m.r. SOLID SHIFTS OF $PCl_4(pyr)_2^+$ $SbCl_6^-$ COMPLEXES

Complex	δ^{31}P
$PCl_4py_2^+SbCl_6^-$	188.2 ± 3.8
$PCl_4phen^+SbCl_6^-$	184.6 ± 2.2
$PCl_4dipy^+SbCl_6^-$	191.2 ± 3.3
$PCl_4(3,5\text{-lutidine})_2^+SbCl_6^-$	176.4 ± 3.6
$PCl_4(3\text{-picoline})_2^+SbCl_6^-$	187.3 ± 5.7
$PCl_4(3\text{-Clpyr})_2^+SbCl_6^-$	184.0 ± 6.5
$PCl_4(3\text{-Brpyr})_2^+SbCl_6^-$	-
$PCl_4(3\text{-Ipyr})_2^+SbCl_6^-$	189.5 ± 12
$PCl_4(3,5\text{-diClpyr})_2^+SbCl_6^-$	-
$PCl_4(4\text{-CNpyr})_2^+SbCl_6^-$	182.9 ± 2.2

The shifts are within experimental error of the solution values, and distant from those of the molecular complexes, PCl_5.pyr. Spectrometer drift, leading to sloping baselines is reflected in the large error spread with $PCl_4(3\text{-Ipyr})_2^+SbCl_6^-$ and the inability to determine a reproducible shift for the 3-bromopyridine complex.

No signal could be found from $PCl_4(3,5\text{-diClpyr})_2^+SbCl_6^-$.

Infra red spectra

The complexes show a number of intense bands below 660 cm^{-1} which are not present in the starting materials, and the line at 654 cm^{-1} expected for PCl_4^+ is absent. Each complex has an intense band between 335 and 350 cm^{-1} which may be attributed [11] to $SbCl_6^-$. For monodentate pyridine complexes the line positions below 660 cm^{-1} are

different from those found in the corresponding PCl_5/pyridine complex (Chapter 3 section 1(ii)b) whilst for bidentate pyridines the lines in this region (apart from those attributable to PCl_6^- or $SbCl_6^-$) are very similar (Tables 19 and 20). The partial hydrolysis product, pyridinium hexachloroantimonate (see Chapter 3 section 2(ii)c) is expected to have no intense lines below 660 cm^{-1}, except for $SbCl_6^-$. In addition to a peak at about 449 cm^{-1} due to PCl_6^-, a complex of the alternative formulation $SbCl_4py_2^+$ PCl_6^- would be expected to have intense bands only in the region [11,12] below about 370 cm^{-1}. Thus the i.r. spectra are entirely consistent with the formulation of the complexes as $PCl_4L_2^+SbCl_6^-$ for L = monodentate pyridine, or $PCl_4(L\text{-}L)^+SbCl_6^-$ for L-L = bidentate pyridine. The spectra of the solid complexes below 660 cm^{-1} are given in Table 24.

I.r. SPECTRA OF $PCl_4py_2^+$ COMPLEXES AND FREE LIGANDS 650–250 cm^{-1}

Pyridine	a	612w			536s				447s	410s			340s*		265w	
	b	605m								412m						
3,5-lutidine	a				542s	538sh		468s	438s	412s	365sh	348s*	340sh*	302w		
	b	618w				537w										
3,5-diCl pyridine	a			588w	545s	508w		478s	456w	424m	388s		342s*	302w		
	b	618w							452m		393m					
4-CN pyridine	a			570s	554m	521m	507s			420w	390s	360m	340s*			
	a*	610w		572s	556m	520m	508s	472w		424w	398s		348s*	330w		
	b	614w		563s				467w				377m				
3-Cl pyridine	a			590w	545s	527s		472s	434m		400s	366s	358m	338s*		248w
	b	617s						463w	430m		407m					
3-Br pyridine	a			590w	547s	527s		472s			403s	372m	360m	338s*		
	b	637s	614m					452w			402m					
3-I pyridine	a	618w		579w	541s	518s		463s			398s		358m	341s*	331sh	278w
	b	614m						443w			396m					
3-picoline	a			581w	530s			469s			396s			346s*	302w	276w
	b	631m			538w			468w			403w					

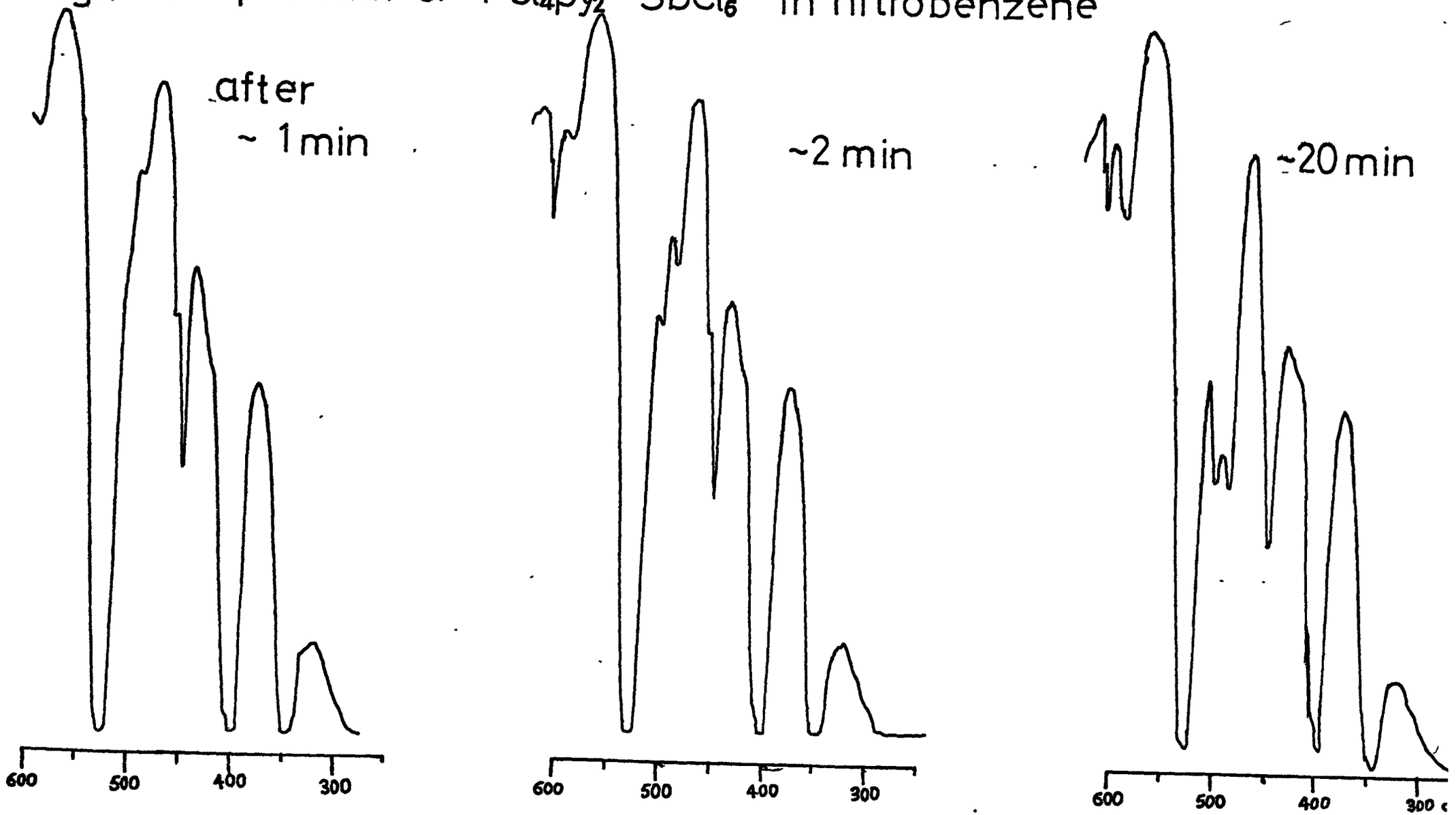
a. $PCl_4pyr_2^+ SbCl_6^-$

b. free ligand

* $SbCl_6^-$

* $PCl_4(4\text{-CNpyr})_2^+ SbCl_6^- . 2PhNO_2$

Fig17 I.r. spectrum of $PCl_4py_2^+ SbCl_6^-$ in nitrobenzene



Beattie et al [10] reported the spectrum of $PCl_4py_2^+SbCl_6^-$ in acetonitrile. Their results bear little resemblence to the spectrum of the solid reported here. In order to clarify the situation $PCl_4py_2^+SbCl_6^-$ was dissolved in acetonitrile and the i.r. spectrum run immediately after dissolution. The spectrum (Table 25) was very similar to that of the solid. The spectrum was also investigated in nitrobenzene. Nitrobenzene, which has been shown not to be attacked by the complex (Chapter 3 section 2(ii)a) is not too suitable for i.r. investigations since it has absorptions at 612 (w), 536 (s), 426 (w), and 398 (s) cm^{-1}. This leaves an effective window only between 400 and 525 cm^{-1}. The initial spectrum in this region is a single peak at 449 cm^{-1} with very weak shoulders at ~500 and 489 cm^{-1}. The peak in the region of 530 cm^{-1} is far more intense than found with neat nitrobenzene, suggesting the presence of a strong peak from the complex (c.f. acetonitrile solution and solid state spectra). The lines between 500 and 450 cm^{-1} rapidly increase in intensity (Fig.17), slowing down after about 20 minutes. These lines (at 502 and 489 cm^{-1}) are in the same position as those found with PCl_5.pyridine in nitrobenzene solution (502 and 488 cm^{-1} : c.f. 495 and 483 cm^{-1} in benzene ref.29). Both PCl_5.py and $PCl_4py_2^+SbCl_6^-$ have absorptions at 448 cm^{-1}, hence the lack of change in this line. The shoulder at 458 cm^{-1} in the initial spectrum may be due to the resolution of the line into its two components. Alternatively the absorption of $PCl_4py_2^+$ in this region may itself consist of two components. Thus the solution data are entirely consistent with the ^{31}P n.m.r. results, the complex rapidly equilibrating with PCl_5.py and $SbCl_5$.py

TABLE 25

INFRA RED SPECTRUM OF $PCl_4py_2^+SbCl_6^-$ 660-300 cm^{-1}

Mull or Solvent										
Nujol Mull	612w		536s				447s	410s		340*s
Acetonitrile Ref 10	621m	568m		517w[a]	499s	488s	445s		(372s)[b]	340*s
Acetonitrile present work		598s[c]	532s			489w[c]	458sh	452w	408m (371m)[b]	347*m
Nitrobenzene Initially e		595w[c]	(527s)[d]		~500sh	489sh	457sh	449m	(400s)[d]	345*s
+ 20 mins	(612w)[d]	594w[c]	(528s)[d]		502m	489m		448m	(398s)[d]	344*s
c.f. PCl_5.py in $PhNO_2$			(534m)[f]		502s	488s		448s	(398s)[f]	
Neat acetonitrile									370m	
Neat nitrobenzene	612w		536s					426w	398s	

a. Impurity
b. Acetonitrile
c. $POCl_3$
d. Partly nitrobenzene
e. Fast sweep rate
f. Nitrobenzene
* $SbCl_6^-$

$$PCl_4py_2^+SbCl_6^- \rightleftharpoons PCl_5.py + SbCl_5.py$$

It would also appear that the bands at 499(s) and 488(s) cm^{-1} reported by Beattie et al [10] are due to PCl_5.pyridine. The assignment of the 568 cm^{-1} line is not clear, however.

In principle, from the i.r. spectrum, it should be possible to determine the configuration of the $PCl_4py_2^+$ species, a trans substituted cation showing only one major P-Cl absorption at high frequencies [10], whilst a cis substituted species would show three [10]. If the P-N force constant has a particular value [29c.f. 199], however, the three lines of the cis complex will occur at the same frequency. Other complications may arise because of an additional band in the P-Cl region due to a P-N stretch, and also because of possible splitting of the P-Cl stretching vibration. These have been discussed by Beattie, Gilson and Ozin [29] for the isoelectronic $SiCl_4.py_2$ complex. Even with a full normal co-ordinate analysis from complete i.r. and Raman data they were unable to distinguish whether the complex was cis or trans. Beattie, Livingston, and Webster [10] had originally suggested a cis configuration for $PCl_4py_2^+$ in solution, from their i.r. spectra. Beattie later acknowledged that their evidence was inconclusive [29]. This conclusion is not altered by correcting the positions of the lines to those found in this work.

Due to the equilibration in solution, the complexes with monodentate pyridines could not be purified by recrystallisation, in order to obtain definitive solid state spectra. Furthermore, complete solution spectra without interference from the other species present could not be recorded. An assignment of the

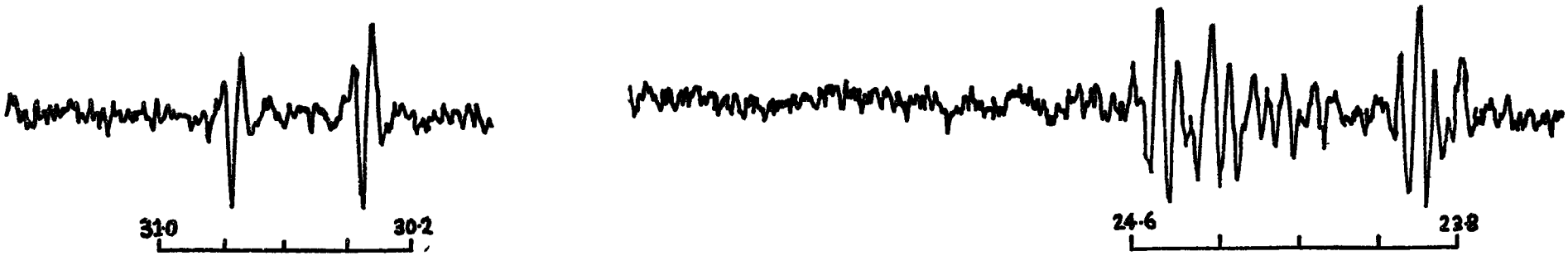
stereochemistry of the complexes on the basis of i.r. (together with Raman) data was thus not attempted.

The i.r. spectrum of the bispyridine adduct below 650 cm^{-1}, excluding the line from $SbCl_6^-$ at 340 cm^{-1}, consists of lines at 612(w), 536(s br), 447(s sharp), and 410(s) cm^{-1}. The spectrum of $PCl_4py_2^+AlCl_4^-$ shows an additional weak line at 325 cm^{-1} which would be hidden underneath the $SbCl_6^-$ line in $PCl_4py_2^+SbCl_6^-$. The 612 cm^{-1} line is equivalent to the 605 cm^{-1} line in pyridine which has moved to higher field on co-ordination, as is generally found [130,172]. The sharp absorption at 447 cm^{-1} is probably due to the pyridine ligand, having moved from 412 cm^{-1}. This leaves two strong lines in the i.r. spectrum below 650 cm^{-1}, attributable to P-Cl stretches, fewer than the three lines expected for cis co-ordination [10]. The spectrum may be deceptively simple, however, as shown by that of $PCl_4dipy^+SbCl_6^-$, where the bidentate ligand must occupy cis positions. Its i.r. spectrum includes two strong lines at 517-510 cm^{-1} and 461 cm^{-1}, the higher field line being slightly split into two peaks. The two weak bands between 390 and 420 cm^{-1} can be attributed to ligand modes. The width of the combined 517-510 cm^{-1} line is approximately the same width as the 536 cm^{-1} line in the pyridine adduct. (In acetonitrile solution of $PCl_4py_2^+SbCl_6^-$ this line is considerably narrowed but still shows no sign of resolution). Other lines below 350 cm^{-1} may easily be lost if of slightly lower intensity. Thus the situation arises where, although the spectrum of $PCl_4py_2^+$ is very simple, analogous cis adducts give almost identical spectra.

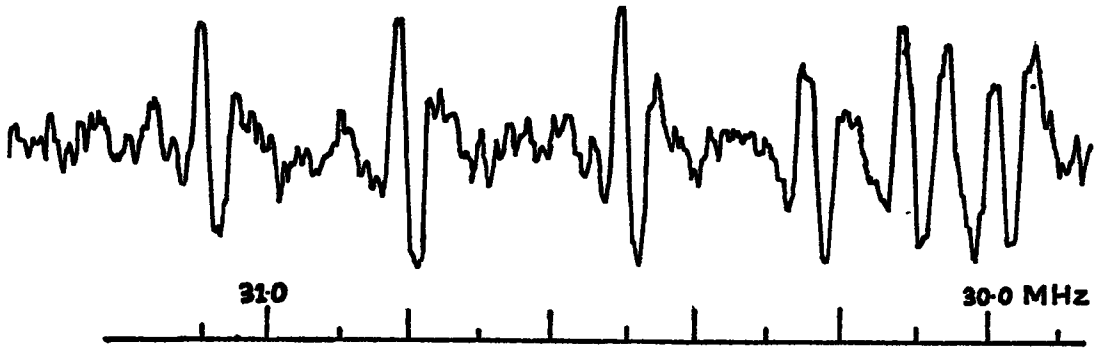
The n.q.r. results discussed in the next section are consistent with a trans configuration for the pyridine complex

Fig18 N.q.r. spectra

a) $PCl_4py_2^+ SbCl_6^-$



b) $PCl_4phen^+ SbCl_6^-$



and a cis configuration for those of the other pyridines, although it is difficult to see why the pyridine case would be exceptional. The i.r. spectra of the substituted pyridine complexes are even more difficult to interpret in this region since a number of extra ligand modes are generally present (Table 24). The spectrum of the pyridine complex in this region does, however, appear to be simpler than those of complexes with ligands of the same ring symmetry.

The spectra of the complexes of the 3-halopyridines are very similar. This is not unexpected since they differ only by a change of the relatively distant 3-halogen, and the basicities of the ligands are very similar.

N.Q.R. spectra

As discussed in Chapter 1 section 3(iii), in the absence of crystal effects, a trans $PCl_4py_2^+$ species would have a single line n.q.r. spectrum, whilst a cis $PCl_4py_2^+$ species would show two lines of equal intensity.

The spectra of the complexes are shown in Table 26.

TABLE 26

N.Q.R. RESULTS FOR $PCl_4X_2^+SbCl_6^-$ SPECIES

X	ν^{35} (Cl) MHz	Signal/noise	Other lines
Pyridine	30.35	6:1	23.90 (^{37}Cl?)
	30.79	5:1	23.93 (^{37}Cl?)
			24.19 multiplet
			24.38
			24.50
3-Brpyridine	29.98	2:1	23.1
	30.20	2:1	23.65 (^{37}Cl?)
	30.92	2:1	24.7 (^{37}Cl?)
	31.22	3:1	25.5
3-Clpyridine	30.045	4:1	37.18 4.5:1 1
	31.13	4.5:1	29.30 2:1 (^{37}Cl) 1
			23.34
			23.73_5
			24.16
			24.83
			24.6(?)
4-CNpyridine. $2PhNO_2$	31.11	2:1	
3-picoline	30.15	4:1	
	30.80	3.5:1	
½ 1,10-phenanthroline	29.97	2:1	24.07 (S/N all 1.5:1)
	30.09	3:1	24.36
	30.22	3.5:1	24.47 (^{37}Cl?)
	30.48	3.5:1	24.70
	30.80	4:1	24.98
	31.07	3:1	25.30

Fig 19 ^{35}Cl n.q.r. frequency vs. basicity of pyridine for PCl_4^+ adducts

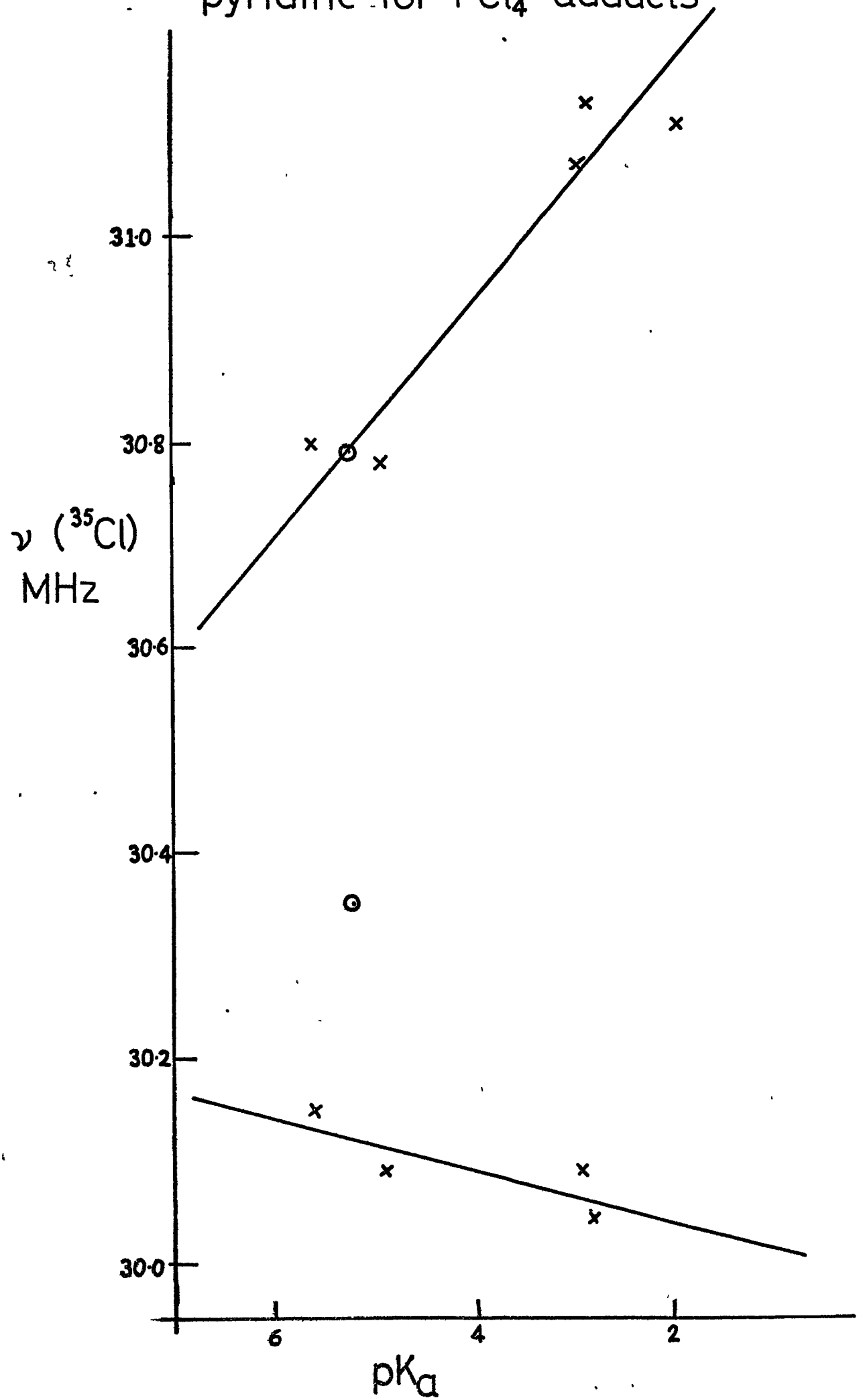


Table 26 cont.

No signals were found when

X = 3,5 dichloropyridine; ½ 2,2'-bipyridyl; 3,5-lutidine

or with $PCl_4py_2^+$ BPh_4^-

Except where stated all the other frequencies are attributable to the ^{35} Cl resonances of $SbCl_6^-$.

1. Line dueto chlorine from pyridine ring.

In all cases where absorptions are found, except for $PCl_4(4\text{-}CNpyr)_2^+Sb\ Cl_6^-$. $2PhNO_2$, two or more lines are found in the spectrum attributable to $PCl_4X_2^+$ species. Where more than two lines are found, e.g. PCl_4phen^+, they can usually be separated into two distinct groups. The frequency difference between the two groups of lines ranges between 0.45 and 1.1 MHz. In the lower part of this range the difference is only of the order of crystallographic splitting. If the group average line frequencies are plotted against basicity of the pyridine a linear variation of the frequencies is found, with the exception of the frequencies of $PCl_4py_2^+$ (Fig.19). Included in this plot are the results for PCl_4phen^+, which must have a cis configuration but gives a splitting of only 0.69 MHz between the two types of chlorine (the spectrum wasrun over the range 23-45 MHz to detect any distant frequencies). A smooth change in the line position with change in donor strength of the pyridine is reasonable, since this will affect the ionic character of the P-Cl bond.

It would thus not be unreasonable to deduce that the pyridines which obey this linear relationship have a similar (i.e. cis) configuration.

With $PCl_4py_2^+$ the higher frequency line lies along the plot, but the lower frequency line is about 0.2 MHz above the plot. A tentative explanation is that $PCl_4py_2^+$ has a trans configuration in the solid state, the two lines being caused by crystal splitting. A splitting of 0.43 MHz is within the range quite generally found for crystal splittings (up to about 0.5 MHz). The reason for the apparent difference between $PCl_4py_2^+$ and the substituted pyridine complexes is not clear. $PCl_4(4\text{-}CNpyr)_2^+$ gave only one n.q.r. line in this region. The intensity of this spectrum was so weak (signal/noise 2:1), however, that a second line could easily have been missed.

A second method of interpreting n.q.r. spectra does not show any clear difference between the data for $PCl_4py_2^+$ and those of the other pyridine species. Maksyutin et al [179] suggested that for tin tetrachloride adducts the average ^{35}Cl frequencies for cis and trans isomers should be different. Thus, if the average frequencies for the supposed cis isomers lay on a straight line, then, if $PCl_4py_2^+$ were cis, its frequency would be expected to lie on the line, whereas if it were trans, the frequency would lie off the line. When the average values are calculated, the PCl_4phen^+ value lies as far off the best straight line as that of $PCl_4py_2^+$.

From Fig.19 it is seen that a change in the basicity of the pyridine has a greater effect on the high frequency than on the low frequency line. As the two sets of lines

are of equal intensity the definite assignments of the lines to chlorines trans to pyridines, or trans to chlorines cannot be made in the absence of crystallographic data. With tin tetrachloride [179] complexes the high frequency line was assigned to chlorines trans to the ligand. If this holds for the PCl_4^+ complexes the chlorines trans to pyridine undergo the greatest change in frequency, whereas in the PCl_5.py complexes the mutually trans chlorines show the greatest change. With both PCl_5.py and PCl_4py_2 species, however, a change in the basicity of the ligand has a large effect on only one of the types of chlorine present. The frequency of the remaining chlorines is only slightly removed from that of PCl_6^-. The lower the basicity of the pyridine in $PCl_4py_2^+$, the more the high frequency chlorines become like those in unco-ordinated PCl_4^+.

Both ^{35}Cl signals of $SbCl_6^-$ [59] and ^{37}Cl signals of $PCl_4X_2^+$ occur in the region of 24-25 MHz. $SbCl_6^-$ at 77K often gives a complex multiplet of lines [59,115]. Due to the multiplicity, the individual line intensities are not very high and so $SbCl_6^-$ is sometimes very difficult to detect.

The average frequency for PCl_4^+ in $PCl_4^+SbCl_6^-$ is 32.43 MHz, whilst the frequency for an isolated chlorine atom is 54.87 MHz. Using the formula described in Chapter 1 section 3(iii), assuming no chlorine sp hybridisation and no π character of the P-Cl bond, the charge residing on the chlorine atoms in PCl_4^+ is calculated as 0.409e. If a similar treatment is applied to the n.q.r. frequencies

in PCl_4 (3-Cl pyridine)$_2^+$ $SbCl_6^-$ 30.045 MHz ≡ 0.452e and 31.13 MHz ≡ 0.433 e. The total charge on the chlorines in $PCl_4X_2^+$ is then (2 x 0.452 + 2 x 0.433)e = 1.770e, compared with 4 x 0.409e = 1.636e in PCl_4^+. The net transfer of charge to the chlorines on co-ordination is then 0.134e. When the same treatment is used for the chlorine in the pyridine ring, which drops from 37.18 [200] to 35.24 MHz on co-ordination, the decrease in charge on complex formation is found to be 0.0353. i.e. about $\frac{1}{4}$ of the electron charge transfer to the chlorines attached to phosphorus has come from each of the ring chlorines by inductive effects. This agrees with the concept of acceptor-donor complexes, where charge is transferred from the acceptor to the donor molecule. The assumption that there is no change in the π interaction between the ring chlorine and the ring is reasonable, since the only change in bonding at this site is through inductive effects. The neglect of π bonding in PCl_4^+ is not justified [59], and will tend to underestimate the charge transfer on complexing.

c) Experimental

Preparation of n.m.r. solution samples

A saturated solution of $PCl_4^+SbCl_6^-$ in nitrobenzene was prepared and two equivalents of the liquid pyridines were then directly added. For solid pyridines, two equivalents (one equivalent for bidentate pyridines) were either dissolved in the minimum quantity of nitrobenzene, and the solution added, or else dissolved directly in the nitrobenzene containing the $PCl_4^+SbCl_6^-$. 2-cyanopyridine was melted, then added as a liquid. The solutions were generally yellow. Solutions containing

2-cyanopyridine, 2,4,6-collidine and 2-picoline slowly turned dark red.

The molar ratios of pyridine to $PCl_4^+SbCl_6^-$ used are shown below. In a number of cases the adducts partially crystallised from solution, however. The solutions were either decanted off, or more nitrobenzene was added to redissolve the solid.

TABLE 27

MOLAR RATIOS PYRIDINE/$PCl_4^+SbCl_6^-$ USED

2,4,6-collidine	2.04:1	3-chloropyridine		2.06:1
2-picoline	2.04:1	3-cyanopyridine	(i)	2.00:1
			(ii)	2.02:1
Pyridine	1.97:1	Pyrazine		2.05:1
1,10-phenanthroline	1.01:1	3,5-dichloropyridine		2.12:1
2,2'-dipyridyl	0.997:1	2-bromopyridine		2.03:1
3-Iodopyridine	2.00:1	2-chloropyridine		2.00:1
3-fluoropyridine	1.92:1	2-cyanopyridine		2.26:1
3-bromopyridine	2:1	2-fluoropyridine		2.02:1

The initial hydrolysis product (besides $POCl_3$ which was often detected) is pyridinium hexachloroantimonate.

$$PCl_4^+SbCl_6^- + H_2O + 2py \longrightarrow pyH^+SbCl_6^- + POCl_3 + pyH^+Cl^-$$

The spectra were scanned from about -10 to +360 ppm to determine the species present, then over a shorter range for accurate shift determination. With low basicity pyridines the spectra were initially scanned from about -100 to +267 ppm. Where reaction was seen to occur or where no four or six co-ordinate peaks could be found, additional scans were made over the low field region from about -300 to +50 ppm to detect any three co-ordinate products.

Preparation of Solids

The complexes were synthesised by direct addition of the pyridine, or a solution of the pyridine, to $PCl_4^+SbCl_6^-$ in solution. By suitable choice of solvent the solids crystallised as soon as the components were mixed. Absence of contamination by PCl_5.py or $SbCl_5$.py species was confirmed by the lack of characteristic absorptions of the PCl_5.py complexes in the i.r. spectrum. Only solutions of pure $PCl_4^+SbCl_6^-$ were used, as shown by its solution in redistilled nitrobenzene being golden-yellow. Slightly decomposed samples gave brownish solutions. In general, absolutely saturated solutions of the starting materials were necessary because many of the complexes are only slightly less soluble than their components. PCl_4dipy$^+SbCl_6^-$ could not be isolated by mixing the components in any solvent tried and was isolated by evaporating a nitrobenzene solution at elevated temperatures under reduced pressure. This method is possible because of the resistance of nitrobenzene to attack and the lack of equilibration of bidentate pyridine complexes in solution.

$PCl_4py_2^+SbCl_6^-$

In the glove box apparatus (Chapter 2 section 1(ii)) 15.438g (30.252 mmole) $PCl_4^+SbCl_6^-$ were dissolved in the minimum quantity of nitroethane forming a clear solution. 4.89 ml (4.80g 60.7 mmole) pyridine were slowly dripped into the stirred solution under reduced pressure. There was an immediate white precipitate. After five minutes the solid was filtered, washed with methylene chloride then dried at the pump and finally on the vacuum line.

The solvent used rapidly darkened.

Yield = 7.20g = 35.5% based on $PCl_4py_2^+SbCl_6^-$

Analyses: Found C,17.27; H,1.19; N,5.08; P,4.35; Cl,53.38

$PCl_4py_2^+SbCl_6^-$ requires C,18.04; H,1.52; N,4.21; P,4.66; Cl,53.28

PCl_4(3,5-lutidine)$_2^+SbCl_6^-$

In the glove box apparatus 7.135g (14.06 mmole) $PCl_4^+SbCl_6^-$ were dissolved in the minimum quantity of nitrobenzene. 1.602ml (14.04 mmole) 3,5-lutidine were slowly dripped into the stirred solution under reduced pressure. A white precipitate was formed in a yellow solution. This solution did not appear to darken. Stirring was continued for a few minutes. The solid was then filtered off, washed with methylene chloride and 30/40 pet ether, and dried at the pump.

Yield = 4.30g = 84.9% based on PCl_4 (3,5-lutidine)$_2^+$ $SbCl_6^-$

Analyses: Found C,23.59; H,2.84; N,3.76; P,4.08; Cl,48.94

PCl_4 (3,5-lutidine)$_2^+$ $SbCl_6^-$ requires C,23.30; H,2.52; N,3.88; P,4.29; Cl,49.14

PCl_4 (3-picoline)$_2^+SbCl_6^-$

In the glove box apparatus 7.946g (15.66 mmole) $PCl_4^+SbCl_6^-$ were dissolved in the minimum quantity of nitrobenzene. 3.3ml (3.2g 34 mmole) 3-picoline were slowly dripped into the stirred solution under reduced pressure. Too rapid addition led to a red colour in the solution. On slow addition the solution remained yellow. The thick yellowish precipitate was filtered from the warm solution after stirring for one minute, (the reaction being exothermic).

On washing with methylene chloride and 30/40 pet ether, and then drying at the pump a pure-white solid was produced.
Yield = 5.99g = 55.2% based on PCl_4 (3-picoline)$_2^+$ $SbCl_6^-$
Analyses Found C,19.96; H,2.66; N,4.48; P,4.33; Cl,50.85
PCl_4 (3-picoline)$_2^+$ $SbCl_6^-$ requires C,20.78; H,2.04; N,4.04; P,4.47; Cl,51.12.

PCl_4 (3-Clpyr)$_2^+$ $SbCl_6^-$

Inside the glove box 3.754g (7.399 mmole) PCl_4^+ $SbCl_6^-$ were dissolved in the minimum amount of nitroethane. With stirring, 1.685g (16.93 mmole) 3-chloropyridine were slowly dripped into the solution. A thick white crystalline precipitate formed in a yellow solution. Stirring was continued for one to two minutes. The crystals were filtered, washed with methylene chloride, then 30/40 petroleum ether, and dried at the pump.
Yield = 3.644g = 69.7% based on PCl_4(3-Clpyr)$_2^+$ $SbCl_6^-$
Analyses: Found C,16.35; H,1.09; N,4.13; P,4.05; Cl,58.8
PCl_4 (3-Clpyr)$_2^+$ $SbCl_6^-$ required C,16.35; H,1.10; N,3.82; P,4.22; Cl,57.94.

PCl_4 (3-Brpyr)$_2^+$ $SbCl_6^-$

In the glove box apparatus 5.833g (11.50 mmole) PCl_4^+ $SbCl_6^-$ were dissolved in the minimum amount of nitroethane. 2.4ml (3.9g 24 mmole) 3-bromopyridine were dripped into the solution. This produced a white precipitate in a bright yellow solution. After leaving for five minutes, during which time the solvent showed little sign of darkening, the solid was filtered, washed with methylene chloride, 30/40 pet ether and dried at the pump, then on the vacuum line.

Yield = 5.52g = 58.3% based on $PCl_4\ (3\text{-Brpyr})_2^+\ SbCl_6^-$
Analyses: Found C,14.38; H,1.18; N,3.42; P,3.77; Cl,42.66 Br,19.72. $PCl_4\ (3\text{-Brpyr})_2^+\ SbCl_6^-$ requires C,14.59; H,0.98; N,3.40; P,3.76; Cl,43.07; Br,19.41.

$PCl_4\ (3\text{-Ipyr})_2^+\ SbCl_6^-$

1.958g (3.859 mmole) $PCl_4^+SbCl_6^-$ and 1.580g (8.282 mmole) 3-iodopyridine were each separately dissolved in the minimum quantity of nitromethane. The two solutions were then mixed with stirring. There was an immediate precipitate. This precipitate was filtered, washed, and dried at the pump to produce a fine light yellow powder.
Yield = 0.901g = 26.3% based on $PCl_4\ (3\text{-Ipyr})_2^+\ SbCl_6^-$
Analyses: Found C,13.14; H,0.92; N,3.41; P,3.14; Cl,37.77; I,35.31. $PCl_4\ (3\text{-Ipyr})_2^+\ SbCl_6^-$ requires C,13.09; H,0.88; N,3.05; P,3.38; Cl,38.65; I,27.67.
The high iodine analysis is unlikely to be due to interference from the chlorine present [204]. It is difficult to explain, however, as the other elemental analyses are in very good agreement with the theoretical values.

$PCl_4\ (4\text{-CNpyr})_2^+\ SbCl_6^-.\ 2PhNO_2$

3.656g (7.206 mmole) $PCl_4^+\ SbCl_6^-$ and 1.506g (7.232 mmole) 4-cyanopyridine were each separately dissolved in the minimum quantity of nitrobenzene. The 4-cyanopyridine solution was slowly dripped into the $PCl_4^+SbCl_6^-$ solution. A thick precipitate quickly formed. After stirring for two minutes the precipitate was filtered at the pump, and, after leaving

until the solid was almost dry, washed with 30/40 pet ether and dried at the pump. This produced a white powder.

Yield = 4.964g = 71.7% based on PCl_4 $(4\text{-CNpyr})_2^+$ $SbCl_6 . 2PhNO_2$.

Analyses: Found C,28.21; H,1.83; N,8.52; P,3.07; Cl,37.2.

PCl_4 $(4\text{-CNpyr})_2^+$ $SbCl_6^-$. $2PhNO_2$ requires C,29.95; H,1.89; N,8.74; P,3.22; Cl,36.9.

PCl_4 $(4\text{-CNpyr})_2^+$ $SbCl_6^-$

3.911g (7.709 mmole) PCl_4^+ $SbCl_6^-$ and 1.600g (7.683 mmole) 4-cyanopyridine were each separately dissolved in the minimum quantity of nitroethane. The two solutions were then mixed with stirring. A white precipitate immediately formed in a yellow solution. The precipitate was filtered, washed with methylene chloride, then dried at the pump to give an extremely fine off-white powder.

Yield = 2.72g = 49.3% based on PCl_4 $(4\text{-CNpyr})_2^+$ $SbCl_6^-$.

Analyses: Found C,16.11; H,0.97; N,7.62; P,4.62; Cl,52.36.

PCl_4 $(4\text{-CNpyr})_2^+$ $SbCl_6^-$ requires C,20.61; H,1.18; N,4.09; P,4.53; Cl,51.80. The reason for the low carbon and high nitrogen analyses is not clear.

PCl_4 $(3,5\text{-diClpyr})_2^+$ $SbCl_6^-$

A saturated solution of 3,5-dichloropyridine was made up in nitrobenzene. Small amounts of PCl_4^+ $SbCl_6^-$ were added to the solution with stirring until there was a sudden thickening of the solid remaining. The product was then filtered, washed and dried at the pump, to produce a white solid.

Analyses: C,15.75; H,1.10; N,4.89; P,3.5; Cl,60.4

PCl_4 $(3,5\text{-diClpyr})_2^+$ $SbCl_6^-$ requires C,14.95; H,0.75; N,3.49; P,3.86; Cl,61.8.

$PCl_4phen^+ SbCl_6^-$

6.169g (12.12 mmole) $PCl_4^+SbCl_6^-$ and 2.200g (12.21 mmole) phenanthroline were each separately dissolved in the minimum quantity of nitrobenzene. With stirring the phenanthroline solution was added to the $PCl_4^+ SbCl_6^-$ solution. A white precipitate was formed in the bright yellow solution in an exothermic reaction. After leaving for 5-10 minutes the precipitate was filtered, washed with methylene chloride and 30/40 pet ether and dried at the pump, and then on the vacuum line. This gave a very fine slightly off-white powder.
Yield = 4.70g = 56.1% based on $PCl_4phen^+ SbCl_6^-$.
Analyses: Found C,20.67; H,1.28; N,3.92; P,4.43; Cl,51.74
$PCl_4phen^+ SbCl_6^-$ requires C,20.96; H,1.18; N,4.08; P,4.51; Cl,51.57.

$PCl_4dipy^+ SbCl_6^-$

Inside the glove box 6.260g (12.34 mmole) $PCl_4^+SbCl_6^-$ and 1.923g (12.31 mmole) dipyridyl were each separately dissolved in nitrobenzene and the solutions were mixed in a round bottomed flask. The stoppered flask was removed from the glove box, and, with continuous flushing of dry nitrogen over the solution, connected to a vacuum distillation apparatus. Nitrobenzene was rapidly distilled from the solution at 110°C or below until the solution contained a large amount of solid. The flask was then allowed to cool and was retransferred into the glove box. The solid was filtered, washed with 30/40 pet ether, and dried at the pump to produce pale yellow crystals.

Yield = 5.391g = 66.0% based on $PCl_4dipy^+ SbCl_6^-$.

Analyses: C,18.00; H,1.21; N,4.16; P,4.32; Cl,53.00

$PCl_4dipy^+ SbCl_6^-$ requires C,18.10; H,1.22; N,4.22; P,4.67; Cl,53.44.

$PCl_4py_2^+ AlCl_4^-$

0.519g (1.52 mmole) $PCl_4^+ AlCl_4^-$ was dissolved in a small quantity of nitrobenzene producing an extremely viscous solution. Approx. 0.25ml (0.25g 3.1 mmole) pyridine was then added, with stirring, into the solution together with a little extra nitrobenzene. After a few moments there was a thick white precipitate. This was filtered, washed and dried at the pump with 30/40 pet ether.

Yield = 0.41g = 54% based on $PCl_4py_2^+ AlCl_4^-$.

Analyses: Found C,23.62; H,1.87; N,6.58; P,5.79; Cl,55.5.

$PCl_4py_2^+ AlCl_4^-$ requires C,24.03; H,2.02; N,5.61; P,6.20; Cl,56.75.

$PCl_4py_2^+BPh_4^-$

1.392g (2.091 mmole) $PCl_4py_2^+ SbCl_6^-$ and 0.716g (2.07 mmole) $Na^+ BPh_4^-$ were each separately dissolved in the minimum quantity of nitromethane. Immediately afterwards, to prevent the equilibration of $PCl_4py_2^+ SbCl_6^-$ being established (see Chapter 3 section 2(ii)a), the $PCl_4py_2^+SbCl_6^-$ solution was slowly dripped into the $Na^+ BPh_4^-$ solution. A yellow precipitate immediately appeared. After stirring for a few minutes the precipitate was filtered, left to dry, then washed with 30/40 pet ether, and dried at the pump (the compound appeared to be slightly soluble in methylene chloride).

Yield = 1.351g = 99.8% based on $PCl_4py_2^+ BPh_4^-$ (see, however, analyses below).

Analyses: Found C,53.74; H,3.85; N,8.13. $PCl_4py_2^+ BPh_4^-$ requires C,64.60; H,1.92; N,4.43.

The compound had decomposed before the P and Cl analyses could be attempted. Despite the poor analyses the infra red spectrum was entirely consistent with the formula $PCl_4py_2^+ BPh_4^-$.

3. The Hexachlorophosphate Ion

(i) Phosphorus pentachloride as a chlorinating agent

(a) Introduction

Phosphorus pentachloride was investigated as a reagent for the one step synthesis of pentavalent phosphorus compounds, and their hexachlorophosphate salts from organic phosphines. Although phosphorus pentachloride has been widely used [77,202,203] for reactions of the type

$$R_3PO + PCl_5 \longrightarrow R_3PCl_2 + POCl_3$$

and, in a few instances, with the further reaction[204-206],

$$R_3PCl_2 + PCl_5 \longrightarrow R_3PCl^+ PCl_6^-$$

there is only one report of the chlorination of tertiary phosphines [61].

$$Ph_3P + 2PCl_5 \longrightarrow Ph_3PCl^+ PCl_6^- + PCl_3$$

The reaction was investigated in this work to discover its scope, and to determine whether the reaction could be stopped before addition of the second molecule of phosphorus pentachloride to form the hexachlorophosphate. Phosphorus pentachloride could then be used as an alternative chlorinating agent to chlorine. The analogous reactions with antimony pentachloride [127] cannot, however, be stopped at the intermediate stage.

Chlorination of the phenylchlorophosphines, Ph_xPCl_{3-x} ($x = 1-3$), was studied in particular. The known compounds $PhPCl_3^+ PCl_6^-$ [119,204] and $Ph_2PCl_2^+ PCl_6^-$ [205] are formed by the abstraction of a chloride ion by phosphorus pentachloride from mainly covalent molecules [23,59,60] (See also Chapter 4).

Phosphorus pentachloride is a very weak chloride ion acceptor [19,207,208]. With the exception of $Ph_3C^+ PCl_6^-$ [19] and $(C_7H_7^+)_2 Cl^- PCl_6^-$ [18], all known hexachlorophosphates are derived from salts containing free chloride ions. Even $Ph_3C Cl$ [209] and C_7H_7Cl [51] are unionised only in certain circumstances.

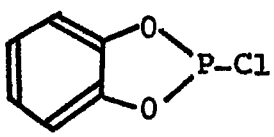
$Ph_3PCl^+ PCl_6^-$ has been previously prepared by the above route [61] as well as from triphenylphosphine oxide [33]. It has been used as a source of PCl_6^- ions [33], being very soluble even in methylene chloride. $Ph_2PCl_2^+ PCl_6^-$ [205] and $PhPCl_3^+ PCl_6^-$ [204] have been prepared from Ph_2POCl and $PhPOCl_2$ respectively, and also by direct reaction of the parent phosphoranes with phosphorus pentachloride [31,119].

Some doubt has been expressed recently about the existence of hexachlorophosphate salts of the above type [207], due to the apparent instability of the hexachlorophosphate ion. The complete characterisation of the salts would then confirm their existence.

b) Present Work

Solution Investigations

Phosphorus pentachloride was investigated as a reagent for the oxidative chlorination of the chlorophenylphosphines Ph_xPCl_{3-x} (x = 1-3), tributylphosphine, Bu_3P, dimethyloctadecylphosphine, $Me_2PC_{18}H_{37}$, and σ-phenylenephosphorochloridite

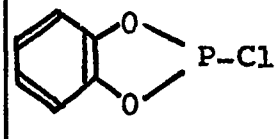
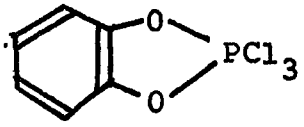


In a number of instances the use of $PCl_4^+SbCl_6^-$ as a reagent was also investigated.

The chemical shifts of the starting materials and possible products are given in Table 28. Reactions were, in general, carried out in methylene chloride solution, all starting materials and products, with the exception of Ph_2PCl_3, $Ph_2PCl_2^+$ PCl_6^- and $PhPCl_3^+PCl_6^-$ being very soluble in this solvent.

TABLE 28

STRUCTURE AND ^{31}P n.m.r. SHIFTS OF VARIOUS R_3PCl_2 SPECIES AND THEIR DERIVATIVES

Phosphine R_3P	Structure of R_3PCl_2 in solution	Solvent	δ^{31}P R_3PCl_2	δ^{31}P R_3PCl^+	δ^{31}P R_3P ppm
Ph_3P	Ph_3PCl^+ Cl^-	CH_2Cl_2	-	-65.0*[a]	+6 [d]
$PhPCl_2$	$PhPCl_4$	CH_2Cl_2	+44.3[c]	-103*[a]	-163 [d]
Bu_3P	Bu_3PCl^+ Cl^-	$PhNO_2$	-	-104 [b]	+33 [d]
		MeCN	-	-106 [b]	
$Me_2PC_{18}H_{37}$					+53.1 [c]
		CH_2Cl_2	+26.3 [c]	-77.1*[c]	-173.0 [e]

* measured as the hexachloroantimonate salt

a. Ref.126

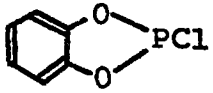
b. Ref. 58

c. Present work

d. Ref.89

e. Ref.210

^{31}P n.m.r. RESULTS FROM ADDITION OF PCl_5 AND PCl_4^+ $SbCl_6^-$ TO VARIOUS PHOSPHINES

Phosphine	Reactant	Mole ratio Phosphine/ Reactant	^{31}P Shifts Found					
			PCl_3	R_3PCl_2 R_3PCl^+	PCl_6^-	Other Small peaks	Solvent	
Ph_3P	PCl_5	1:1	-216.0	-54.9	-	+6.2(Ph_3P)	CH_2Cl_2	
		1:2	-217.9	-63.6	+297.5		CH_2Cl_2	c.f. ref.61 $Ph_3PCl^+PCl_6^-$ was also isolated
	$PCl_4^+SbCl_6^-$		-217.2	-63.3	-	-2.2($POCl_3$)	CH_2Cl_2	
Bu_3P	PCl_5	1:1	-209.0	-102.7	-		CH_2Cl_2	
		1:2	-218.8	-100.7	+297.4	-36.5(Ph_3PO?)	CH_2Cl_2	
	$PCl_4^+SbCl_6^-$	-	-216.6	-103.9	-			
$Me_2PC_{18}H_{37}$	PCl_5	1:2	-219.1	-94.7	+283.1 (v.broad)		CH_2Cl_2	
	$PCl_4^+SbCl_6^-$	1:1	-218.9	-92.5	-	-3.8, -9.4, +10.3	CH_2Cl_2	
$PhPCl_2$	PCl_5	Neat $PhPCl_2$	-218.1	+46.7	-	-32.8($PhPOCl_2$)	$PhPCl_2$	
		1:1	-219.0	+19.7	+295.5 (v.weak)		$PhNO_2$	
		1:1	$PhPCl_3^+PCl_6^-$ isolated				CH_2Cl_2	
		1:2						
Ph_2PCl	PCl_5	1:1	Ph_2PCl_3 isolated				CH_2Cl_2	
		1:2	$Ph_2PCl_2^+PCl_6^-$ isolated				CH_2Cl_2	
	PCl_5	1:1	-219.4	+26.4	-		CH_2Cl_2	
		1:2	No reaction between PCl_3 and PCl_5 Ref 210					

The results are given in Table 29. All phosphines investigated were oxidised to the corresponding phosphorus(v) species with the concomitant reduction of PCl_5 to PCl_3. With the exception of o-phenylene phosphorochloridite reported in Ref.210 hexachlorophosphate salts are formed with excess phosphorus pentachloride. With the exception of $PhPCl_4$ the phosphine dichlorides R_3PCl_2 were obtained directly from equimolar quantities of the phosphine and phosphorus pentachloride.

Although several side reactions are theoretically possible, all reactions appeared to proceed quantitatively, within minutes, and with little or no sign of the interference (no large unassigned n.m.r. solution peaks or highly insoluble precipitates). Phosphorus trichloride and tertiary phosphines react [211,212] according to

$$3R_3P + 2PCl_3 \longrightarrow 3R_3PCl_2 + 2\ \text{"P"}$$

The "phosphorus" forms as an orange solid but is found to be only 80-90% pure. It is thought [212] to consist of a three dimensional framework of phosphorus atoms terminated by alkyl groups and chlorine atoms. Challenger and Prichard [213] reported the formation of a yellow flocculent precipitate on mixing triphenyl phosphine and phosphorus trichloride. They attribute this to a "decomposition product of phosphorus subchloride, P_2Cl_4". Ali [214] found evidence for species of the type $(Ph_3P)Cl^+Cl^-$ from a 1:2 molar ratio of triphenyl phosphine to chlorine. Various addition products between two phosphines have also been found[215] which decompose, on warming, to cyclopolyphosphines

$$\text{e.g. } PhPCl_2 + PEt_3 \longrightarrow PhPCl_2 \cdot PEt_3$$

$$5PhPCl_2 \cdot PEt_3 \longrightarrow (C_6H_5P)_5 + 5Et_3PCl_2$$

This type of reaction has not, however, been reported with phosphorus trichloride as one of the components.

The reactions of individual phosphines are discussed below. The isolation and characterisation of $Ph_xPCl_{4-x}^+ PCl_6^-$ (x = 1-3) salts is described in Chapter 3 section 3(ii) whereas the preparation of Ph_2PCl_3 and catechyl phosphorus trichloride by this route is described in Chapter 2 section 1.

Triphenylphosphine

The reaction described by Rozinov, Grechkin and Kalabina [61] was repeated, using various molar ratios of phosphorus pentachloride to phosphine. With equimolar quantities two peaks were found in the ^{31}P n.m.r. spectrum, at -216.0 ppm and -54.9 ppm, corresponding to PCl_3 and Ph_3PCl^+. When two equivalents of phosphorus pentachloride were used, peaks corresponding to PCl_3, Ph_3PCl^+ and PCl_6^- were found (δ^{31}P -217.9, -63.6, +297.5 ppm). Thus this reaction proceeds in a stepwise manner.

$$Ph_3P + PCl_5 \longrightarrow Ph_3PCl^+ Cl^- + PCl_3$$

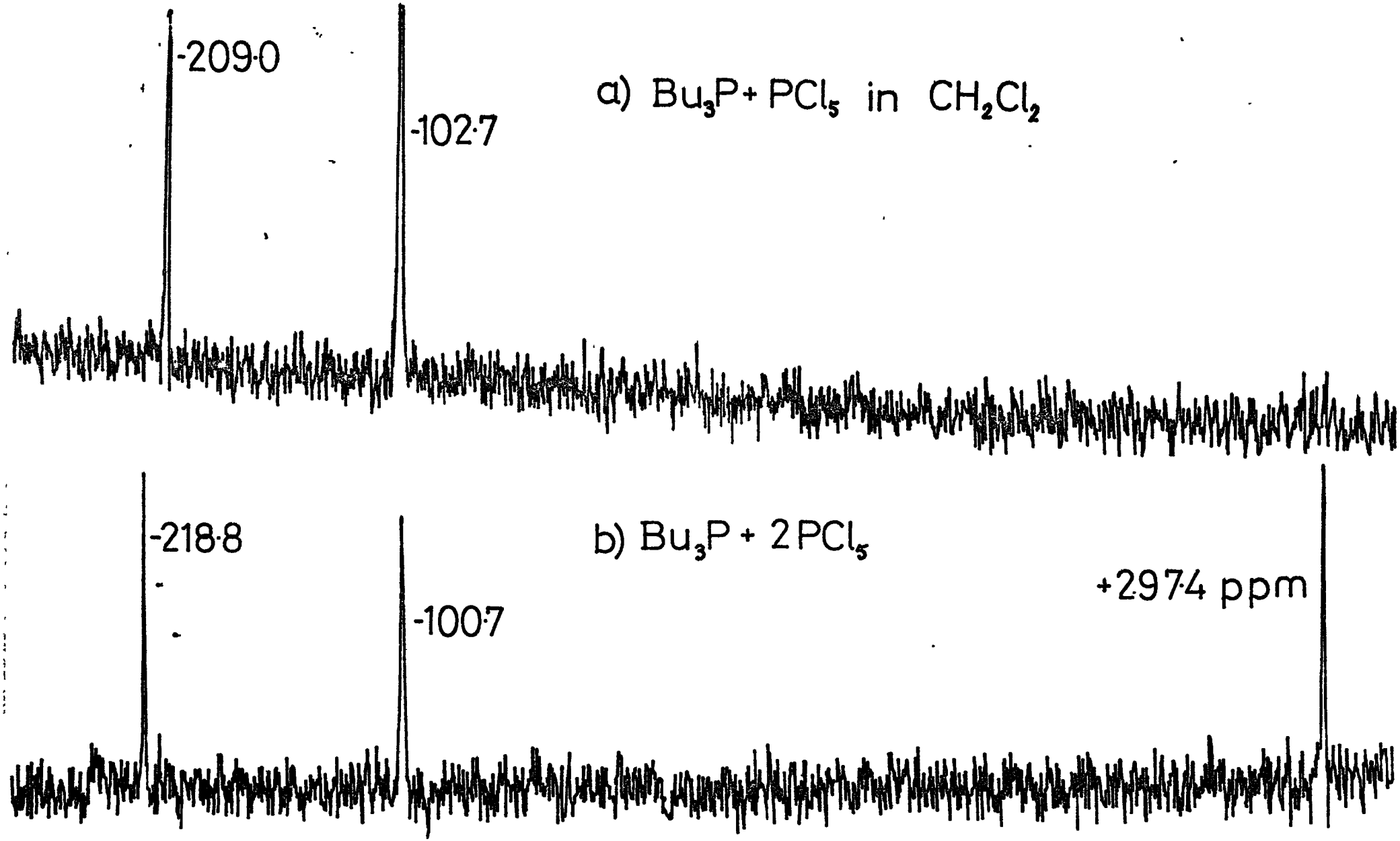
$$Ph_3PCl^+ Cl^- + PCl_5 \longrightarrow Ph_3PCl^+ PCl_6^-$$

The shift of $Ph_3PCl^+ Cl^-$ in the 1:1 solution is a little higher than is found with the free ion and corresponds to the ionic species in equilibrium with a small amount of the covalent form Ph_3PCl_2.

To extend the scope of the reaction, $PCl_4^+ SbCl_6^-$ was reacted with triphenylphosphine. ^{31}P n.m.r. peaks corresponding to PCl_3 and Ph_3PCl^+ (δ^{31}P -217.2, -63.3 ppm) were found, showing the reaction to be

$$Ph_3P + PCl_4^+ SbCl_6^- \longrightarrow Ph_3PCl^+ SbCl_6^- + PCl_3$$

Fig 20 ^{31}P n.m.r. solution spectra (single scans)



Tributylphosphine

From equimolar quantities of tributylphosphine and phosphorus pentachloride in methylene chloride, peaks of approximately equal intensity were found at -209.0 (PCl_3) and -102.7 (Bu_3PCl^+) (Fig.20). Bu_3PCl_2 thus appears to be ionic as has also been found in nitrobenzene and acetonitrile solutions [58]. When two moles of phosphorus pentachloride were added, peaks were found at -218.8 (PCl_3), -100.7 (Bu_3PCl^+), +297.4 (PCl_6^-), the last two being of equal intensity and the PCl_3 being slightly less intense. A third, much smaller peak was observed at -36.5 ppm after accumulation of the spectrum, presumably due to Bu_3PO. The shift, however, is slightly removed from the literature values of -43.2 and-45.8 [89]. The PCl_6^- signal in this solution was very sharp with a linewidth at half peak height of about 0.7 ppm. In the 1:1 solution the shift of PCl_3 was about 10 ppm higher than is normal (-215 to -220 ppm [89]) and appeared to be reproducible. Such a high shift was not observed with any other phosphine solutions. The shift cannot be accounted for by co-ordination of any excess tributylphosphine with phosphorus trichloride since these are known to react under similar conditions [212]. Indeed the slightly low intensity of the PCl_3 peak in the 2:1 solution may indicate a small amount of reaction according to

$$Bu_3P + PCl_3 \longrightarrow Bu_3PCl_2 + P$$

although no phosphorus was precipitated.

Tributylphosphine reacted with $PCl_4^+ SbCl_6^-$ in methylene chloride to give the expected peaks at -216.6 ppm (PCl_3) and 103.9 ppm (Bu_3PCl^+) showing the formation of $Bu_3PCl^+ SbCl_6^-$.

$$Bu_3P + PCl_4^+ SbCl_6^- \longrightarrow Bu_3PCl^+ SbCl_6^- + PCl_3$$

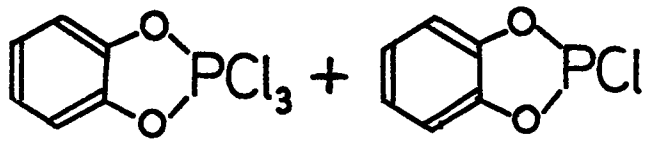
Dimethyloctadecylphosphine

$Me_2PC_{18}H_{37}$ appears only once in the literature [216]. A sample was kindly donated by Dr. A. F. Childs of Messrs. Albright and Wilson Limited. Two equivalents of phosphorus pentachloride chlorinated the phosphine, leaving no residual starting material. The ^{31}P n.m.r. spectrum appeared to indicate only $Me_2PC_{18}H_{37}Cl^+$ and phosphorus trichloride ($\delta^{31}P$ -94.7, -219.1), however. On spectrum accumulation a very broad hexachlorophosphate peak was found at +283.1 ppm, slightly lower than usual. The peak width at half height was ~6 ppm (c.f. PCl_6^- in $Bu_3PCl^+ PCl_6^-$). The low shift and broadness of the signal are characteristic of an exchanging system in which PCl_6^- is incompletely formed. The hexachlorophosphate ion thus appears to be relatively unstable towards dissociation in this system. The ^{31}P n.m.r. spectrum of the reaction solution of the phosphine and $PCl_4^+ SbCl_6^-$ ($\delta^{31}P$ -218.9, -92.5 ppm) shows the reaction to be

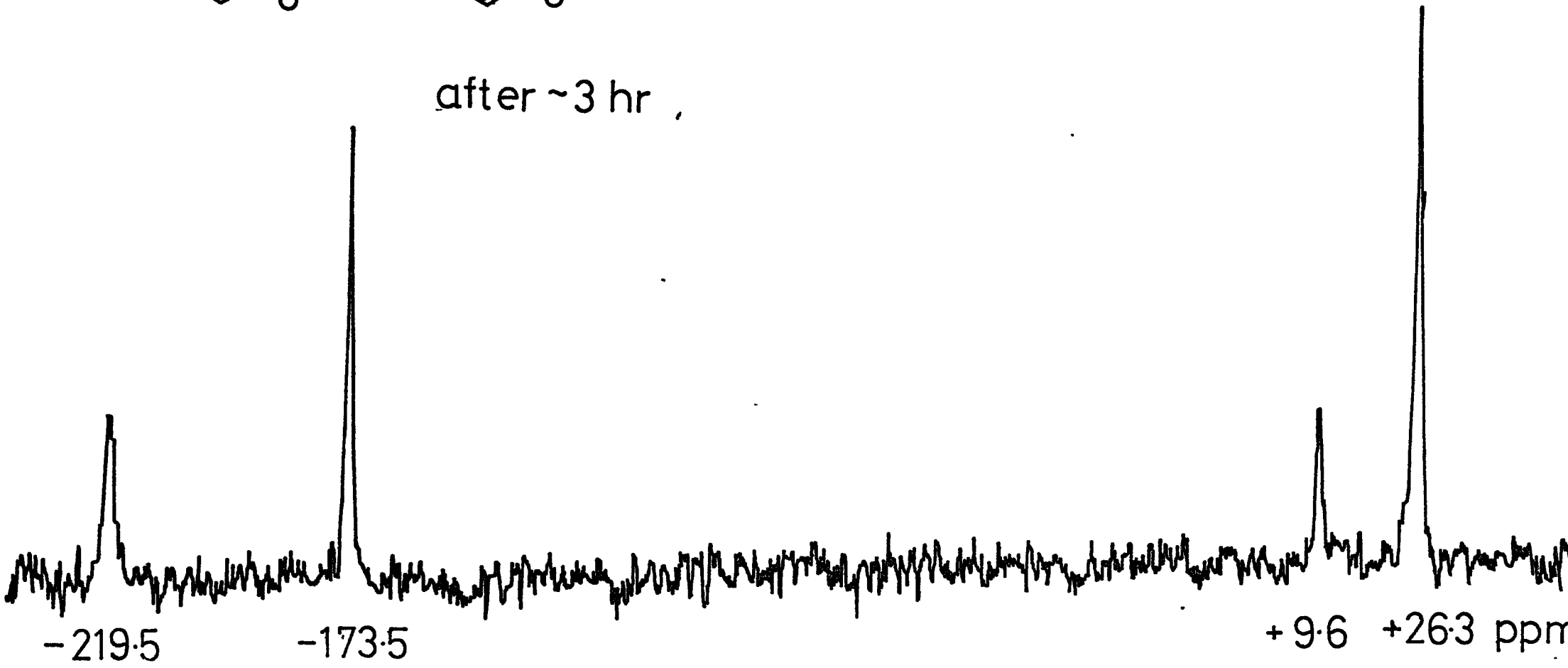
$$Me_2P(C_{18}H_{37}) + PCl_4^+ SbCl_6^- \longrightarrow Me_2P(C_{18}H_{37})Cl^+ SbCl_6^- + PCl_3$$

Unfortunately the sample of the phosphine oxidised before the solution containing equimolar quantities of the phosphine and phosphorus pentachloride was made up. Two peaks of approximately equal intensity were found in this solution at -95.2 and +0.2 ppm, as expected for the reaction

$$Me_2P(O)C_{18}H_{37} + PCl_5 \longrightarrow Me_2P(C_{18}H_{37})Cl^+Cl^- + POCl_3$$

Fig 21  in methylene chloride

after ~3 hr

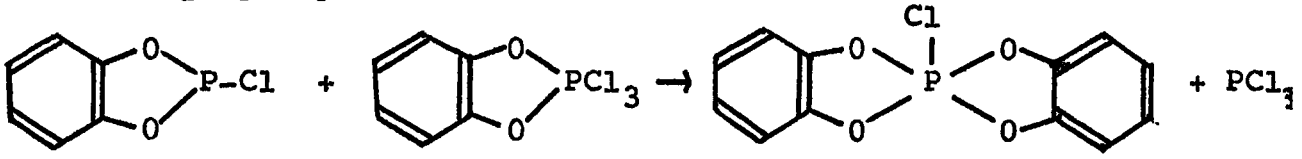


$Me_2PC_{18}H_{37}Cl_2$ thus appears to be ionic in methylene chloride solution, as expected for a species containing three electron-donating aliphatic groups (c.f. $Bu_3PCl^+Cl^-$).

o-phenylene phosphorochloridite (catechylphosphorus monochloride)

Catechyl phosphorus trichloride ($catPCl_3$) is molecular in methylene chloride solution (see Chapter 5). It has been reported not to react with excess phosphorus pentachloride [210], comparing with the instability of the hexachloroantimonate salt (Chapter 5 section 2).

When approximately equimolar amounts of the monochloride and phosphorus pentachloride were mixed peaks of equal intensity were found in the ^{31}P n.m.r. spectrum at -219.4 (PCl_3) and +26.4 ppm (cat PCl_3) together with a small peak corresponding to the slight excess of monochloride reactant. Over a period of hours this latter signal disappeared whilst a peak at +9.5 ppm appeared. The new peak may be attributed to biscatechyl phosphorus monochloride [210].



This deduction was confirmed by studying the behaviour of an equimolar mixture of catechyl phosphorus monochloride and trichloride. A smooth reaction took place. Over a period of hours signals of approximately equal intensity appeared at -219.5 ppm (PCl_3) and +9.6 ppm (biscatechylphosphorus monochloride) (Fig.21). This presents a novel method of preparing pure biscatechyl phosphorus monochloride, which slowly crystallises out of solution. A similar reaction

has been shown to occur between catechyl phosphorus monobromide and catechyl phosphorus tribromide [217]. Using substituted catechyl phosphorus(III) compounds this type of reaction may be useful as a route to new phosphorus(v) compounds.

Phenyldichlorophosphine

Phenyltetrachlorophosphorane has a molecular structure both in the solid state, and in solution (Chapter 4 section 1(ii)). When phosphorus pentachloride was dissolved in neat phenyldichlorophosphine, peaks of equal intensity were found at -218.1 ppm and +46.7 ppm (together with the solvent peak at -159.4 ppm), showing the formation of $PhPCl_4$ and PCl_3. A small peak was also present at -32.8 ppm due to $PhPOCl_2$, the oxidation product of the solvent.

When two equivalents of phosphorus pentachloride were added to phenyldichlorophosphine in methylene chloride, the salt $PhPCl_3^+ PCl_6^-$ immediately crystallised from solution. When equimolar amounts of the starting materials were used, however, $PhPCl_3^+PCl_6^-$ was still the product, not the expected phosphorane. In order to observe the reaction in solution the reaction was repeated in nitrobenzene. When equimolar amounts of the reagents were mixed a white solid precipitated. A sample of the remaining solution did not stabilise in the n.m.r. machine for several hours, indicative of the reaction still proceeding. After 20 minutes, peaks of approximately equal intensity corresponding to phosphorus trichloride and phenyldichlorophosphine were found, together with a peak of about half the intensity at +28.4 ppm. After about 50 minutes the phosphorus trichloride peak had doubled in intensity whilst the $PhPCl_2$ peak had decreased

to half. The third peak had doubled in intensity and moved to +35.9 ppm. After about 2 hours the PCl_3 had become more intense and the $PhPCl_2$ peak diminished with the third peak moving to +39.6 ppm. The initial reaction produces the hexachlorophosphate, $PhPCl_3^+PCl_6^-$, giving a solution which contains equimolar amounts of $PhPCl_2$ and PCl_3 plus a much smaller low field peak due to $PhPCl_3^+$ from $PhPCl_3^+PCl_6^-$ saturated in nitrobenzene, the majority of this precipitating. The hexachlorophosphate immediately starts to react with $PhPCl_2$ to produce $PhPCl_4$ and PCl_3. The $PhPCl_4$ and $PhPCl_3^+$ form a rapidly exchanging system, giving a single peak [60]. Even when a small amount of the $PhPCl_3^+PCl_6^-$ has reacted the exchange peak is well over to the side of $PhPCl_4$ because of the much lower solubility of $PhPCl_3^+PCl_6^-$.

$$2PhPCl_2 + 2PCl_5 \longrightarrow PhPCl_3^+PCl_6^- + PhPCl_2 + PCl_3$$

$$\downarrow$$

$$2PhPCl_4 + PCl_3$$

This is the situation after 20 minutes. The reaction proceeds further, increasing the concentration of PCl_3 whilst decreasing the concentration of $PhPCl_2$. The $PhPCl_3^+/PhPCl_4$ peak moves to higher field due to the increasing amount of $PhPCl_4$ present.

The sample was then returned to the bulk of the solution which was then shaken for several days. The great majority of the solid redissolved. The ^{31}P n.m.r. spectrum of the stable solution contained lines of approximately equal

intensity at -219.0 (PCl_3) and +19.8 ppm ($PhPCl_3^+ \leftrightarrow PhPCl_4$) plus much smaller ones due to $PhPOCl_2$ and PCl_6^- (+295.4 ppm). The reaction has now proceeded as far as possible to form $PhPCl_4$. It cannot go to completion because of a small amount of oxidation of $PhPCl_2$ to $PhPOCl_2$ which lowered the relative amount of $PhPCl_2$. $PhPOCl_2$ does not react further with $PhPCl_3^+PCl_6^-$ under these conditions although reactions of this type are known at elevated temperatures [202,205].

The results are thus explained by the rapid precipitation of $PhPCl_3^+PCl_6^-$ which then slowly redissolves and reacts. This does not occur with the other systems studied since the hexachlorophosphate salts are more soluble and any formed would remain in solution and immediately react.

Analogous reaction systems using antimony pentachloride instead of phosphorus pentachloride have been studied by Ruff [127]. He was unable to isolate free phosphoranes from the systems, always obtaining the hexachloroantimonate salt. In order to confirm these results, the reaction between equimolar amounts of antimony pentachloride and phenyldichlorophosphine was investigated in nitrobenzene. A white precipitate of the hexachloroantimonate salt immediately formed. The ^{31}P n.m.r. spectrum of the solution containing a little of the solid showed a large peak due to unreacted $PhPCl_2$ together with a smaller peak due to a saturated solution of $PhPCl_3^+ SbCl_6^-$ in nitrobenzene. The solution was stable in the n.m.r. machine, showing that no further reaction was taking place. Moreover the shift of $PhPCl_3^+$ (-99.7 ppm) suggests that almost no $PhPCl_4$ is present. Thus, at room temperature, $PhPCl_3^+ SbCl_6^-$ is stable to attack by $PhPCl_2$. The difference in reaction

between antimony pentachloride and phosphorus pentachloride can be attributed to this stability.

$PhPCl_3^+PCl_6^-$ was used in investigations of the $PhPCl_3^+$ ion. As two phosphorus-containing species were present the salt was ideal for ^{31}P n.m.r. solution studies. The anion peak was, however, a possible source of interference with the cation peak in solid state n.m.r. and n.q.r. studies.

Diphenylchlorophosphine

By reacting diphenylchlorophosphine with an equimolar amount of phosphorus pentachloride, diphenyltrichlorophosphorane could be isolated. When 1 mole excess phosphorus pentachloride was used, diphenyldichlorophosphonium hexachlorophosphate was obtained. Unlike the reaction with $PhPCl_2$ there was no difficulty in isolating the phosphorane.

Phosphorus Tribromide

The reaction between phosphorus pentachloride and phosphorus tribromide was investigated to determine whether mixed chlorobromophosphonium ions, as found by Dillon, Gates et al, and by Grimmer [100,103,218,219,101] could be stabilised by hexachlorophosphate as counter ion. A solid complex of composition PCl_3Br_4 had been previously isolated [220] from PCl_5/PBr_3 mixtures. Other workers could isolate only $PCl_3Br_7 . 2CCl_4$ from the system [221]. The preparation was repeated, and a solid of composition $PCl_{2.59}Br_{4.22}$ obtained. Unfortunately the compound did not stabilise in the n.m.r. spectrometer, and so no solid state spectrum could be obtained. The Raman spectrum (run by P. Gates), however, showed large signals attributable to PBr_4^+. A very weak

signal was also found at 267 cm^{-1}. This is very similar to the position found for the trichloride ion in tetraalkylammonium salts [222] (268 cm^{-1}). The ideal structure of the complex would seem to be $PBr_4^+ Cl_3^-$. The deviation from this formulation is then probably due to free chloride and bromide ions in the lattice.

Phosphorus pentachloride was then dissolved in phosphorus tribromide. No large peaks were observed in the 4,5 or 6 co-ordinate region. Peaks, of decreasing relative intensity were found at -227.1, -226.1,-223.0, and -217.8 ppm corresponding to PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 respectively [223].

Experimental

Preparation of n.m.r. samples

For liquid phosphines, the phosphine was mixed with an approximately equal volume of methylene chloride and the required amount of solid phosphorus pentachloride added. Vigorous reactions took place during which the phosphorus pentachloride dissolved. Only with tributylphosphine and two equivalents of phosphorus pentachloride did any precipitate form. This redissolved on doubling the amount of methylene chloride. For solid phosphines, the phosphine was dissolved in the minimum amount of methylene chloride and the phosphorus pentachloride then added.

With $PCl_4^+ SbCl_6^-$ and dimethyloctadecylphosphine equimolar quantities of the materials were reacted. In other cases $PCl_4^+ SbCl_6^-$ was added to a methylene chloride solution of the phosphine until excess $PCl_4^+ SbCl_6^-$ remained undissolved.

Large peaks appeared on a single scan of the n.m.r. spectrum for many of the solutions, but the spectra were in some cases accummulated to clarify the peak positions and detect any minor peaks. The molar ratios of PCl_5 to PR_3 used were (1.00 ± 0.01):1 and (2.000 ± 0.003):1 except with catechyl phosphorus monochloride where a ratio of 0.850:1 was used.

For the phenyldichlorophosphine - antimony pentachloride reaction in nitrobenzene the reactants (1:1.06 $PhPCl_2$:$SbCl_5$) were each mixed with a little nitrobenzene, the antimony pentachloride producing a yellow adduct [1]. The two solutions were then mixed and more nitrobenzene added. The yellow solid reacted and was replaced by the white solid $PhPCl_3^+$ $SbCl_6^-$.

$PCl_{2.59}$ $Br_{4.2}$

The method used by Kuz'menko to produce PCl_3Br_4 [220] was followed. 3.02g (14.5 mmole) PCl_5 were slowly added to 2.1ml (6.0g 22.1 mmole) PBr_3 in 15ml carbon tetrachloride. The precipitate formed was filtered and dried at the pump.

Yield = 2.19g

Analyses: Found P,6.92; Cl,20.5; Br,75.2, equivalent to an empirical formula $PCl_{2.59}$ $Br_{4.2}$.

The Raman spectrum of the compound was run by Dr. P. Gates.

Possible Applications of Phosphorus Pentachloride as a chlorinating agent

The reactions

$$R_3P + PCl_5 \longrightarrow R_3PCl_2 + PCl_3$$

$$R_3PCl_2 + PCl_5 \longrightarrow R_3PCl^+ PCl_6^-$$

proceeded quickly and quantitatively, having finished within minutes in concentrated solutions. The preparation of the

hexachlorophosphate salts may be achieved directly, in one stage from the phosphines. The use of phosphorus pentachloride instead of chlorine to produce the chlorophosphoranes has in many circumstances, also distinct advantages. The addition of exact amounts of chlorine is sometimes difficult to monitor, and excess chlorine is frequently used. This will sometimes contaminate the product by forming adducts with the phosphorus(v) compound [60,23,119]. Phosphorus pentachloride may be easily added in weighed amounts. It may also chlorinate phosphine oxide impurities which otherwise may be difficult to remove.

$$R_3PO(\text{traces}) + PCl_5 \longrightarrow R_3PCl_2 + POCl_3$$

Several disadvantages in using phosphorus pentachloride are, however, found. If an excess is used, the compound may be contaminated with the hexachlorophosphate salt, whereas if too little is used, the compound may be contaminated with the phosphine. The reactions involve the weighing of exact amounts of two air or water-sensitive materials. Reactions may be carried out entirely inside a glove box, however. Although chlorination using phosphorous pentachloride seems general for the phosphines investigated the reaction with trimethylphosphine is reported to proceed in a different manner. No reaction occurs at $0^{\circ}C$. A slow reaction occurs at $100^{\circ}C$ forming $2Me_3P.PCl_5$ [43].

The method was found particularly useful in the preparation of diphenyltrichlorophosphorane, and catechyl phosphorus trichloride. The large difference in solubility between Ph_2PCl_3 and its hexachlorophosphate salt permitted

its isolation without contamination by the latter. A pure-white sample was obtained without recrystallisation. The compound remained unchanged under an atmosphere of nitrogen for at least one year. A similar sample prepared from diphenylchlorophosphine and chlorine was yellow-tinged and gave signs of decomposition after several months, becoming bright yellow in patches. In the preparation of catechyl phosphorus trichloride there is no chance of contamination by the hexachlorophosphate salt [210]. Reaction between catechyl phosphorus monochloride (giving a single ^{31}P n.m.r. line) and chlorine produced a yellow semi liquid. The ^{31}P n.m.r. showed two lines at +25.5 and +27.5 ppm [23] instead of the reported literature single line at +26 ppm [210,224]. The use of phosphorus pentachloride with the same catechyl phosphorus monochloride produced a white solid with a yellowish tinge, giving a single ^{31}P n.m.r. peak at +26.3 ppm in methylene chloride.

The reactions of $PCl_4^+ SbCl_6^-$ with phosphines to form hexachloroantimonate salts have the advantage over using antimony pentachloride directly that the inorganic reaction product, phosphorus trichloride, is a liquid, whereas antimony trichloride is a solid and thus liable to contaminate the product. Since reaction solutions using $PCl_4^+ SbCl_6^-$ may then be pumped to dryness, yields of the desired product may also be significantly higher.

(ii) Solid State investigations of the Hexachlorophosphate ion

Introduction

As well as the hexachlorophosphates prepared using phosphorus pentachloride as a chlorinating agent, various

other hexachlorophosphates were synthesised to confirm their structure. The known [18] salt $(C_7H_7)PCl_7$ was prepared for which the possible structures $C_7H_7^+Cl^-.C_7H_7^+PCl_6^-$ and $(C_7H_7^+)_2\ PCl_7^{2-}$ have been suggested [18]. Its formulation as a hexachlorophosphate was supported by i.r. evidence [11] and by the number of bonding orbitals available to phosphorus. Co-ordination numbers of greater than six are not found in row three elements. $C_7H_7^+PCl_6^-$, bis (2,4,6-collindium) chloride hexachlorophosphate (Chapter 3 section 1(ii)b), and the known [16] salt $Et_4N^+PCl_6^-$ were also prepared.

Other hexachlorophosphates investigated include salts of the type $PCl_4(L\text{-}L)^+\ PCl_6^-$, $PCl_4(L\text{-}L)^+(PCl_6^-)_{1-x}\ Cl_x^-$ (Chapter 3 section 1(ii)), and $PhPCl_3(L\text{-}L)^+\ PCl_6^-$, (Chapter 4 section 2) (L-L = 1,10-phenanthroline or 2,2'-dipyridyl). These are described in other sections as indicated.

Properties

All hexachlorophosphates investigated were moisture-sensitive, the tropylium salts exceptionally so, fuming in moist air. The tropylium salts, bis (2,4,6-collidinium) chloride hexachlorophosphate, and tetraethylammonium hexachlorophosphate are white solids soluble in nitrobenzene. $Ph_3PCl^+\ PCl_6^-$ is a white solid very soluble in methylene chloride and nitrobenzene. $Ph_2PCl_2^+PCl_6^-$ and $PhPCl_3^+PCl_6^-$ are slightly yellowish white solids. The former is soluble in nitrobenzene and slightly soluble in methylene chloride whereas the latter is slightly soluble in nitrobenzene and insoluble in methylene chloride. Thus the solubility of

the chlorophenylphosphonium salts increases with the number of phenyl groups and with the cation size.

No reaction took place between pyridine and a nitrobenzene solution of $Ph_3PCl^+PCl_6^-$. With $PhPCl_3^+PCl_6^-$ a white solid was immediately precipitated and PCl_5.pyridine remained in solution. With $Ph_2PCl_2^+PCl_6^-$ peaks were found attributable to PCl_5.pyridine and PCl_6^-, but since no other peak was found (except $Ph_2P(O)Cl$) the salt had probably been hydrolysed by traces of water.

As is shown in the following chapter $PhPCl_4$ forms an insoluble complex with pyridine. If pyridine displaces a chloride ion from PCl_6^- in $PhPCl_3^+$ PCl_6^-, this may then combine with $PhPCl_3^+$ to form $PhPCl_4$. Both PCl_5 and $PhPCl_4$ can then also co-ordinate to the pyridine. Ph_3PCl^+ PCl_6^- is stable to attack by pyridine since Ph_3PCl^+ Cl^- does not co-ordinate to pyridine, and there is thus no added driving force to the reaction

$$PhPCl_3^+\ PCl_6^- + py \longrightarrow PhPCl_4 + PCl_5.py$$

$$PhPCl_4 \xrightarrow{py} PhPCl_4.py$$

$$Ph_3PCl^+\ PCl_6^- + 2py \not\longrightarrow Ph_3PCl^+\ Cl^- + PCl_5.py$$

N.m.r. spectra

The solid state and solution ^{31}P n.m.r. spectra of the salts all gave signals in the range +295 - +305 ppm confirming the presence of PCl_6^-. The values are in excellent agreement with known solution [225-7,31,142]

(δ^{31}P 290-305 ppm) and solid state [99] high resolution (δ^{31}P 299.7 ppm) data. The solid state lines are the narrowest six co-ordinate lines found in this work, which can be attributed to the symmetry of the species and the absence of neighboring quadrupoles (contrast PCl_5.pyridine). The line width varies with the salt studied, as expected from the different interdipolar distances in each salt, together with different nuclei being present in the counter ions. No large variation of the solid state shift with the counter ion was observed.

TABLE 30

^{31}P n.m.r. SHIFTS OF HEXACHLOROPHOSPHATE SALTS

Compound	Solvent	δ^{31}P (soln)	δ^{31}P (solid)
$Ph_3PCl^+ PCl_6^-$	CH_2Cl_2	-66.3*	-64.3
		+296.0	+305.0
	$PhNO_2$	-64.7*	
		+298.7	
$Ph_2PCl_2^+PCl_6^-$	$PhNO_2$	-90.5*	-89.7
		+298.0	+294.8
$PhPCl_3^+PCl_6^-$	$PhNO_2$	-93.6*	-96.9
		+298.6	+296.4
$PCl_4phen^+PCl_6^-$	$PhNO_2$	+192.7*	
		+299.1	
$C_{14}H_{14}PCl_7$	$PhNO_2$	+299.2	+295.7
$C_7H_7PCl_6$	$PhNO_2$	+297.3	+296.1
$[C_8H_{12}N]_2 PCl_7$	$PhNO_2$	+297.5	+298.7
$Et_4N^+PCl_6^-$	$PhNO_2$	+297.9	+298.5

* attributable to cation

Fig 22 ^{31}P n.m.r. solid state spectrum in $PhPCl_3^+PCl_6^-$ in the 4-coordinate shift region

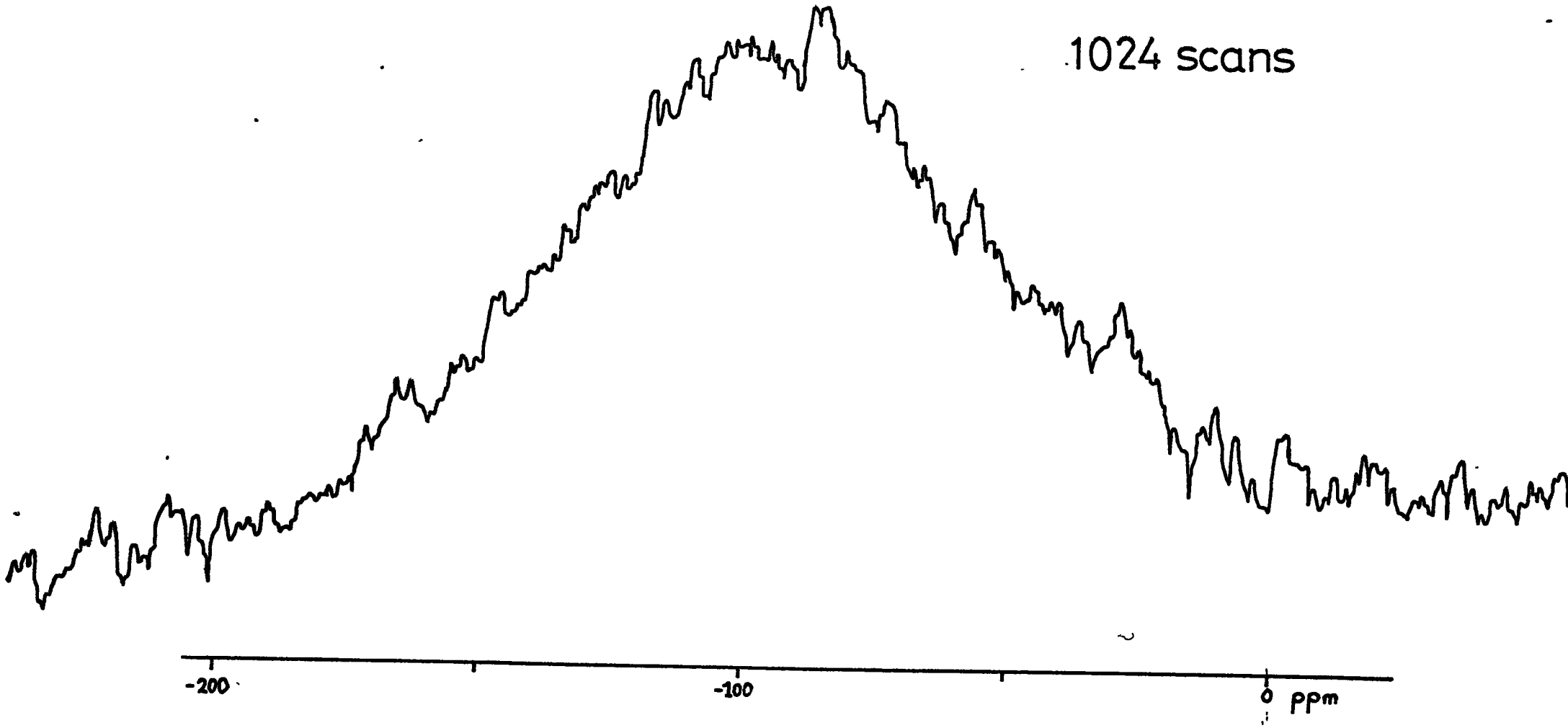
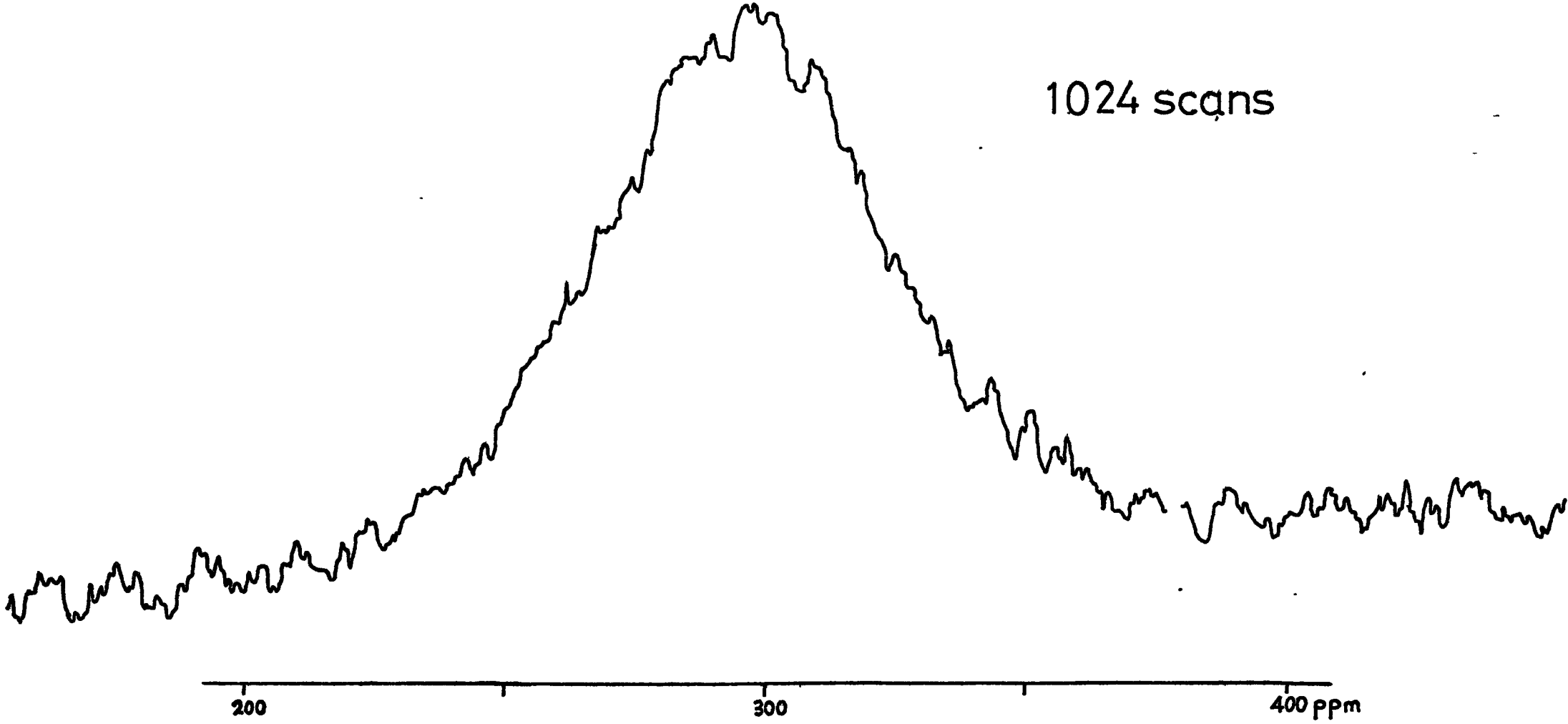


Fig23 ^{31}P n.m.r. solid state spectrum of $PhPCl_3^+ PCl_6^-$ in the 6-coordinate shift region



Despite changes in diamagnetic susceptibility and crystal packing effects, there are only minor differences between the solid state and solution shifts of the complexes, and these are within the limits of experimental error. The solid lines were reproducible to within ± 2 ppm and the solution data to within ± 0.2 ppm.

The solid state lines of the cations are broader than that of PCl_4^+ in $PCl_4^+PCl_6^-$ [99] but are sharper than those of the six co-ordinate species (other than PCl_6^-) found in this work. The broadening compared with PCl_4^+ can be attributed to the lowering of symmetry of the species and also to the proximity of large organic groups. Complete resolution of the cation and anion solid state lines was in all cases found (c.f. Figs.22,23). The shifts of the cations both in the solid state and in solution are close to the literature solution shifts [126]. The rather high value for $PhPCl_3^+$ in solution (-93.6 c.f. $PhPCl_3^+SbCl_6^-$ -102.9 ppm, $PhPCl_3^+$ ClO_4^- -103.0 [126], $PhPCl_3^+$ $AlCl_4^-$ -100.5 [60]) can be attributed to exchange [60] with a small amount of $PhPCl_4$ impurity. Weak lines of intensity varying with the sample were present in the i.r. spectrum at 590 and 568 cm^{-1}. These are not found in $PhPCl_3^+$ $SbCl_6^-$ but are found in $PhPCl_4$. This small amount of impurity will not affect the solid ^{31}P n.m.r. spectrum of the salt as $PhPCl_4$ gives a peak which is so broad as to be undetectable by high resolution techniques [23].

N.q.r. spectra

The n.q.r. spectra recorded by Dr. R. J. Lynch similarly gave results (Table 31) in agreement with previous data for PCl_6^- 115-7,228.

TABLE 31

^{35}Cl n.q.r. FREQUENCIES (MHz) OF SOME HEXACHLOROPHOSPHATES

Compound	ν(MHz) and assignment
$Ph_3PCl^+ PCl_6^-$	29.33, 29.53, 29.59, 29.76, 29.93, 30.44 (PCl_6^-); 31.15 (Ph_3PCl^+) - see below
$Ph_2PCl_2^+PCl_6^-$	29.49, 29.58 (Av 29.53 PCl_6^-); 30.23 (Broad Multiplet $Ph_2PCl_2^+$)
$PhPCl_3^+PCl_6^-$	30.1 (Broad Multiplet PCl_6^-); 30.62, 30.68, 30.79, 30.90 ($PhPCl_3^+$ Av 30.75)
$C_{14}H_{14}PCl_7$	29.40, multiplet centred at 29.77 (Av 29.7 PCl_6^-)
$C_7H_7^+PCl_6^-$	29.32, multiplet centred at 29.80 (Av 29.65 PCl_6^-)
$[C_8H_{12}N]_2 PCl_7$	28.78, 29.31, 29.65, 30.15, 30.55, 30.67 (Av 29.85 PCl_6^-)
$Et_4N^+PCl_6^-$	29.37, 30.025, (Av 29.81 PCl_6^-)
c.f. PCl_6^-(in $PCl_4^+PCl_6^-$)[117]	28.405, 29.720, 30.040, 30.075, 30.470, 30.580 (Av 29.88 PCl_6^-)

Each of the salts gave lines attributable to PCl_6^-. The lines of the chlorine-containing cations although close to those from PCl_6^-, could be assigned by comparison with the spectra of other salts containing the cations [59].

Only the Ph_3PCl^+ assignment had a slight uncertainty. The frequency for Ph_3PCl^+ in $Ph_3PCl^+BCl_4^-$ is 30.08 MHz [59], in $Ph_3PCl^+Cl^-$ 30.12 MHz [59] and in Ph_3PCl^+ $AlCl_4^-$ 30.15 MHz. The line in Ph_3PCl^+ PCl_6^- at 31.15 MHz seems too high to be included in the PCl_6^- multiplet, however. If the 31.15 MHz line is ascribed to Ph_3PCl^+ the average frequency of the remaining signals (29.76 MHz) is in good agreement with the average PCl_6^- frequencies of the other salts.

The lines in the other salts attributable to PCl_6^- lie within the range found for PCl_6^- in PCl_4^+ PCl_6^- [115-7] and in Et_4N^+ PCl_6^- [155,228]. Up to six lines are found, as is observed in the most recent work on ionic PCl_4^+ PCl_6^- [117]. The crystal structures are not known, so that it is not possible to correlate the number of n.q.r. lines with the structure. Six lines attributable to PCl_6^- would, however, suggest a comparatively low crystal symmetry, or else a considerable distortion of the PCl_6^- octahedra at this temperature. Previous studies of Et_4N^+ PCl_6^- have shown three lines at 77K, at 29.32 ± 0.03, 30.06 ± 0.02, 30.34 ± 0.02 (intensity ratio 1:2:1)[115] and at 29.374 ± 0.005, 30.024 ± 0.005 and 30.365 ± 0.005 MHz in the same intensity ratio [228]. In this work only two lines were found, at 29.37 and 30.025 MHz in a 1:2 intensity ratio. The reason for the non-observance of the third line is not clear.

The average n.q.r. frequencies of the cations in PCl_4^+ PCl_6^-, $PhPCl_3^+$ PCl_6^-, $Ph_2PCl_2^+$ PCl_6^-, and Ph_3PCl^+ $AlCl_4^-$ (the latter compound being chosen as there is no ambiguity in line assignments) fall in the order

$$PCl_4^+ > PhPCl_3^+ > Ph_2PCl_2^+ > Ph_3PCl^+$$

As chlorines are successively replaced by phenyl groups, the remaining phosphorus-chlorine bonds becomes more ionic, and this causes a drop in n.q.r. frequency. This drop is, however, not linear. Lynch and Waddington [59] using the data above and results from salts with different counter ions, compared the lowering of frequency in the silicon and carbon analogues. In the carbon series Ph_nCCl_{4-n} the substitution of phenyl for chlorine shows a linear drop in frequency. The n.q.r. frequency is sensitive only to the inductive influence of substituents as there are no low lying d orbitals on the carbon to transmit the conjugative effects to chlorine. Where data are available the drop in frequency along the silane series is non-linear. With the phosphonium and silane compounds d orbitals are available for conjugation with the chlorine π orbitals. Their behaviour along the series is attributable to a changing degree of P-Cl or Si-Cl π character. Evidence for Ph-P-Cl conjugation has been previously found by n.q.r. in the phosphoryl series [180].

I.r. spectra

All the salts showed a strong, broad absorption in the region 440-450 cm^{-1}, as expected for the PCl_6^- ion[11,182]. In other regions the spectrum of $Et_4N^+PCl_6^-$ was very similar to that of $Et_4N^+Cl^-$. The similarity of the spectra of $Ph_3PCl^+PCl_6^-$ and Ph_3PCl_2 (apart from a strong absorption at 490 cm^{-1}) and the dissimilarity of the spectra of $PhPCl_3^+PCl_6^-$ and $Ph_2PCl_2^+PCl_6^-$ to that of $PhPCl_4$ and Ph_2PCl_3 respectively (Tables 33,51), especially below 650 cm^{-1}, indicates molecular structures for $PhPCl_4$ and Ph_2PCl_3, and an ionic structure for Ph_3PCl_2 in the solid

state, as has been suggested by other techniques [23,59].

TABLE 32

I.r. SPECTRA OF Ph_3PCl_2 AND ITS SALTS 650-340 cm^{-1}

PCl_2 [23]	616w, 588m,	539s, 517m,	497s,	458m, 448sh,	398m
$PCl^+PCl_6^-$	621m, 591s,	543w, 520s,		445sbr*	
$PCl^+AlCl_4^-$	623m, 597s,	543m, 521s,	491s,*	468w, 452w, 438w,	388w,
$PCl^+BCl_4^-$ [23]	620m, 597s,	540m, 519s,		468w, 454w, 434w,	
$PCl^+SbCl_6^-$ [23]	621m, 594s/589s,	535w, 517s,		469w, 449w, 362w,	346s,*

*bands attributable mainly to counter ion

Preparation of Solids

$(C_7H_7)_2PCl_6,Cl$

This was prepared by method (b) of Bryce-Smith and Perkins [18].

Under an atmosphere of nitrogen 3.63g (39.4 mmole) cycloheptatriene in 40ml carbon tetrachloride were slowly added to 15.78g (75.8 mmole) PCl_5 stirred in 40ml carbon tetrachloride. Stirring was continued for 1¾ hr during which time the solution became a white gelatinous mass and hydrogen chloride was liberated. The mixture was then refluxed for 15 minutes, the solid filtered, washed with carbon tetrachloride and low boiling pet ether and dried overnight under vacuum at room temperature.

Yield = 8.23g = 90.4% as $C_{14}H_{14}PCl_7$

Analyses: Found C,31.17; H,3.04; P,7.18; Cl,56.98.

$C_{14}H_{14}PCl_7$ requires C,36.4; H,3.03; P,6.72; Cl,53.8.

The low carbon, and high phosphorus and chlorine analyses suggest that the compound contained tropylium hexachlorophosphate, $C_7H_7PCl_6$, as impurity.

$(C_7H_7)PCl_6$

This was prepared by a modification of method (a) used by Bryce Smith and Perkins [18] to prepare $(C_7H_7)_2PCl_6,Cl$.

Under an atmosphere of nitrogen 4.38g (47.5 mmole) cycloheptatriene in 49ml carbon tetrachloride were added to 19.78g (95.0 mmole) PCl_5 stirred into 195ml carbon tetrachloride. After stirring for several hours the white solid was filtered at the pump in the dry box and washed with carbon tetrachloride, then 30/40 pet ether. The white solid was dried under vacuum for several hours.

Yield = 13.59g = 84.9% as $C_7H_7PCl_6$

Analyses: Found C,26.67; H,2.71; P,9.08; Cl,60.94

$C_7H_7PCl_6$ requires: c,25.1; H,2.11; P,9.25; Cl,63.53

$Et_4N^+PCl_6^-$

This was prepared by the method of Gutman and Mairinger [16]. Inside the glove box 6.06g (36.6 mmole) $Et_4N^+Cl^-$ were slowly added to 7.54g (36.2 mmole)PCl_5 each dissolved in phosphoryl chloride. A white precipitate in a yellow solution immediately formed. The precipitate was filtered at the pump, washed with a small amount of phosphoryl chloride and then with 30/40 pet ether, and finally dried under vacuum.

Yield = 8.72g = 64.3% as $Et_4N^+PCl_6^-$

Analyses: Found C,25.40; H,5.05; N,3.60; P,8.39; Cl,56.1

$Et_4N^+PCl_6^-$ requires C,25.69; H,5.40; N,3.75; P,8.28; Cl,56.89

$Ph_3PCl^+PCl_6^-$

This was prepared by the method of Rozinov et al [61].

6.41g (24.4 mmole) triphenylphosphine were dissolved in 17.2ml methylene chloride. With stirring under an atmosphere of nitrogen 10.15g (48.73 mmole) PCl_5 were added. There was a vigorous exothermic reaction during which all the PCl_5 dissolved. On cooling a solid crystallised. This was filtered at the pump, washed with 30/40 pet ether and dried, producing a light yellow solid.

Yield = 9.22g = 68.9% as $Ph_3PCl^+PCl_6^-$

The compound was dissolved in a 50/50 mixture of carbon tetrachloride and 1,2-dichloroethane, and was then precipitated as pure-white flakes by addition of more carbon tetrachloride. Analyses: Found C(by wet oxidation) 39.5; H,3.08; P,11.00; Cl,46.0; $Ph_3PCl^+PCl_6^-$ requires C,39.9; H,2.79; P,11.44; Cl,45.8. Rozinov et al [61] analysed for chlorine only, and their calculated value is incorrect. Despite many attempts, satisfactory carbon analyses could not be obtained by use of the automatic analyser. The reason for this is not clear.

$Ph_2PCl_2^+PCl_6^-$

3ml (3.69g 16.72 mmole) diphenylchlorophosphine were mixed with 30ml methylene chloride, inside the dry box. 6.87g (32.98 mmole) PCl_5 were slowly added in portions, dissolving each portion before addition of the next. At the end of the addition a white precipitate formed. After stirring for a few minutes to complete the reaction the methylene chloride was evaporated at room temperature on the vacuum line until only a few mls were left. The solution was then retransferred

to the glove box and the solid filtered, washed with 30/40 pet ether, then dried at the pump.

Yield = 6.25g = 75.8% as $Ph_2PCl_2^+PCl_6^-$

Analyses: Found C,25.12; H,2.60; P,12.64; Cl,54.02;

$Ph_2PCl_2^+PCl_6^-$ requires C,28.83; H,2.02; P,12.40; Cl,56.75

$PhPCl_3^+PCl_6^-$

Inside the glove box, with stirring, 8.63g (41.4 mmole) finely powdered PCl_5 were dissolved in 100ml methylene chloride. 2.6ml (3.4g 19.2 mmole) phenyldichlorophosphine in 15ml methylene chloride were slowly added to the PCl_5 solution. A precipitate slowly formed. After stirring for several minutes the solid was filtered, washed with 30/40 pet ether, and dried at the pump.

Yield = 6.76g = 64.2% as $PhPCl_3^+PCl_6^-$

Analyses: Found C = 16.05; H = 1.39; P = 13.78; Cl = 69.5

$PhPCl_3^+PCl_6^-$ requires C = 15.73; H = 1.10; P = 13.52; Cl = 69.65

The preparation of bis 2,4,6-collidinium chloride hexachlorophosphate has been described in Chapter 3 section 1(ii)c

$Ph_3PCl^+AlCl_4^-$

This salt has previously been prepared by an indirect route [229].

5.990g (17.98 mmole) Ph_3PCl_2, and 2.452 (18.39 mmole) $AlCl_3$ were separately dissolved in very small quantities of nitrobenzene. The $AlCl_3$ solution was slowly added, with stirring, to the Ph_3PCl_2 solution. Approximately 1 litre diethyl ether was mixed in the solution to precipitate the complex.

The white crystals were filtered at the pump and dried.

Yield = 4.00g = 47.7% as $Ph_3PCl^+AlCl_4^-$.

Analyses: Found C,42.48; H,3.62; P,6.23; Cl,34.9

$Ph_3PCl^+AlCl_4^-$ requires C,46.33; H,3.25; P,6.64; Cl,38.00.

CHAPTER 4

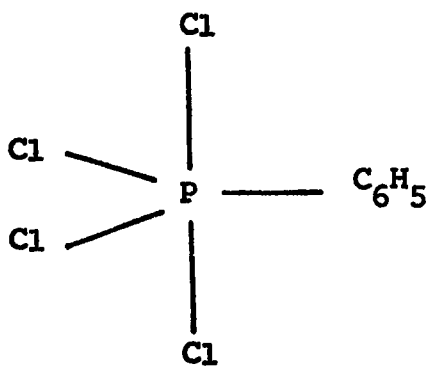
PHENYLTETRACHLOROPHOSPHORANE AND RELATED SPECIES

1. Acceptor Properties of Phenyltetrachlorophosphorane

(i) Introduction

Phenyltetrachlorophosphorane was first prepared by Michaelis [118,230]. It is the first member of a series of compounds Ph_xPCl_{5-x} (x = 1-3) previously studied in this laboratory [23,59] to determine their structure in the solid state. $PhPCl_4$ itself is molecular, both in the solid [59] and in solution. As the compound differs from molecular PCl_5 only in the substitution of a single weakly electronegative phenyl group for chlorine, and retains a 5 co-ordinate structure, it was thought that $PhPCl_4$ might possess acceptor properties towards suitable bases. Such properties, however, have not previously been described. Steric difficulties from the bulky phenyl group were thought to be relatively small, since pentaphenylphosphorane [231], in which the phosphorus is surrounded by five phenyl groups, is quite stable.

The ^{35}Cl n.q.r. spectrum [232] of the compound is consistent with a trigonal bipyramidal structure with the phenyl group occupying an equatorial position. This follows the general rule that the more electronegative groups occupy axial positions [233].



Lines at 24.61 and 25.51 MHz are attibuted to the axial chlorines and those at 33.59 and 33.74 MHz to the equatorial chlorines. Other investigations [234] incorrectly suggested an ionic structure because the low frequency lines were not located. Trichlorophenylphosphonium derivatives give a single set of cation lines between 30.6 and 31.2 MHz [59].

Unfortunately the solid state ^{31}P n.m.r. spectrum [23] contains no detectable signal, probably due to line broadening caused by asymmetric shielding of the phenyl group. This contrasts with the ease of detection of the phenyltrichlorophosphonium cation (Ref.23 and Chapter 3 section 3(ii)). The i.r. spectra also confirms that $PhPCl_4$ does not have an ionic structure. The spectra of $PhPCl_3^+$ in its salts are very similar whilst the spectrum of $PhPCl_4$ is somewhat different.

TABLE 33

I.r. SPECTRA OF $PhPCl_4$ AND $PhPCl_3^+$ SALTS 800-350 cm^{-1}

$PhPCl_4$	747(s), 721(s), 712(s), 617(s), 592(s), 567(s) 542(s), 520(s), 492(s), 421(w), 380(sbr)
$PhPCl_3^+SbCl_6^-$	742(s), 732(m), 722(sh), 704(w), 672(s), (644, 630)(sbr), 608(m), 546(s), 460(m) 373(sh), 340(s-$SbCl_6^-$)
$PhPCl_3^+PCl_6^-$	752(s), 732(s), 722(sh), 704(w), 688(sh)* 678(s) 654(s), 638(sh), 631(s), 609(m), 590(w)*, 568(w)*, 548(s), 436(sbr - PCl_6^-)

* Small amount of $PhPCl_4$ impurity

The ^{31}P n.m.r. spectrum in a variety of solvents consists of a single peak at about +44 ppm.

TABLE 34

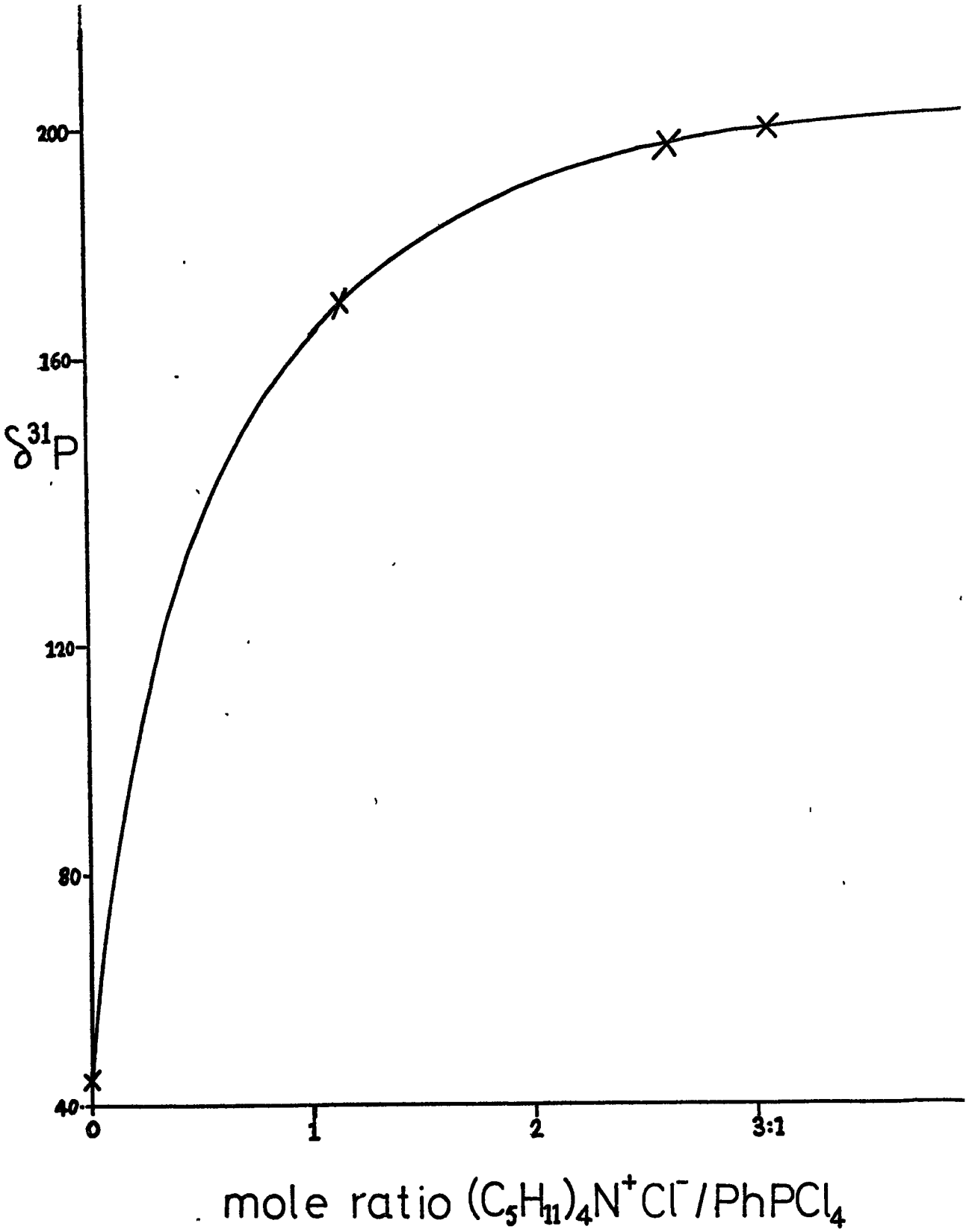
SHIFTS OF $PhPCl_4$ IN VARIOUS SOLVENTS

Solvent	Shift	Ref.
sym-$C_2H_2Cl_4$	+39.3	31
$PhNO_2$	+41	60
$PhNO_2$	+44.2	Present work
C_6H_6	+44.2	" "
CH_2Cl_2	+44.3	" "

The lack of variation of the shifts suggests a single molecular species present and not an equilibrium between $PhPCl_3^+$ and $PhPCl_5^-$ (average shift +50 ppm). Although $PhPCl_4$ has been shown to give a single equilibrium peak with both $PhPCl_3^+$ (as $PhPCl_3^+Cl_3^-$) [60] and $PhPCl_5^-$ (as $(C_5H_{11})_4N^+PhPCl_5^-$) (Chapter 4 section 1(ii)) such equilibria with solely $PhPCl_4$ in solution are expected to be highly solvent dependent (c.f. phosphorus pentachloride). This in turn would make the chemical shift solvent dependent.

Phenyltetrachlorophosphorane was prepared by J. Lincoln as described in Chapter 2 section 1(ii)b. It is very soluble in methylene chloride, 1,2-dichloroethane, benzene, and nitrobenzene. $PhPCl_4$ has previously found use in the synthesis of phenyl substituted phosphonitrilic compounds [235,236] and as a phosphorylating agent [237,238].

Fig24 ^{31}P chemical shift of $(C_5H_{11})_4N^+Cl^-/PhPCl$ solutions in nitrobenzene



(ii) Adduct with the Chloride Ion. The Phenylpentachlorophosphate Ion

Solutions containing approximately 1:1, 2.5:1 and 3:1 molar ratios of tetra-n-pentylammonium chloride to phenyltetrachlorophosphorane were made up in nitrobenzene. As the relative amount of chloride ion increased, the chemical shift of the single peak moved upfield (Table 35). On extrapolation the limiting shift was approximately +203 ppm (Fig.24) and within the range +200 - +210 ppm. This is unambiguously in the six co-ordinate region of the spectrum when considering chloro-species, and may be assigned to the phenylpentachlorophosphate ion. When stoichiometric amounts of $PhPCl_4$ and Cl^- are present, $PhPCl_5^-$ is incompletely formed and exchanges rapidly with free $PhPCl_4$.

$$PhPCl_4 + (C_5H_{11})_4N^+ Cl^- \rightleftharpoons (C_5H_{11})_4N^+ PhPCl_5^-$$

From Fig. 24, and assuming the shifts of $PhPCl_4$ and $PhPCl_5^-$ to be +44.2 and +203 ppm, 75.2% association occurs in this solution.

TABLE 35

SHIFTS FOUND IN $PhPCl_4/(C_5H_{11})_4N^+Cl^-$ SYSTEMS IN NITROBENZENE

Molar ratio (a) $PhPCl_4/(C_5H_{11})_4N^+ Cl^-$	$\delta^{31}P$	% association of $PhPCl_5^-$ (b)
1:1.16	+170.3	79.4
1:2.63	+195.1	95.0
1:3.09	+200.3	98.3

(a) From weighed quantities after taking into account the small amount of hydrolysis of $PhPCl_4$ determined by the relative areas of the $PhPCl_4/PhPCl_5^-$ and $PhPOCl_2$ peaks

(b) Assuming $\delta^{31}P$ $PhPCl_4$ +44.2 ppm
$PhPCl_5^-$ +203 ppm

Adduct formation was also found in other solvents (Table 36). The association depended greatly on the solvent polarity, being smaller for less polar solvents.

TABLE 36

SOLVENT DEPENDENCE OF $PhPCl_4 + Cl^- \rightleftharpoons PhPCl_5^-$ EQUILIBRIUM

Molar ratio $PhPCl_4/(C_5H_{11})_4N^+ Cl^-$	Solvent	$\delta^{31}P$	% association of $PhPCl_5^-$ at 34.2°C
1:1.16	$PhNO_2$	+170.3	79.4
1:1.20	CH_2Cl_2	+117.5	46.2
1:1.07	CCl_4	+81.7	23.6
1:1.43	$MeNO_2$	+129.2	53.5

The nitromethane solution showed extensive hydrolysis. Although this has been accounted for in the mole ratio the degree of association is still only approximate. Hydrolysis adversely affects $PhPCl_5^-$ formation by the equilibria

$$PhPCl_5^- + HCl \rightleftharpoons PhPCl_4 + HCl_2^-$$

$$PhPCl_4 + HCl \rightleftharpoons PhPCl_3^+ + HCl_2^-$$

In low polarity solvents salts exist as ionic aggregates. Thus $(C_5H_{11})_4N^+ Cl^-$ in benzene consists of ion pairs [239]. In order to form $PhPCl_5^-$, $(C_5H_{11})_4N^+$ and the anionic centre will have to be separated somewhat to accommodate the larger anion. This charge separation will require energy, which must be provided by the rather weak complex formation (the chloride ion interaction with carbon tetrachloride [240,241] was considered to be only an extremely weak hindering effect in comparison). The solvent dependence of $PhPCl_5^-$ formation may be compared with a similar dependence of the formation of $SiCl_5^-$ [241,242].

Several other chlorides were investigated to determine any relationship between adduct formation and the counter ion. A nitrobenzene solution of tetra-n-propyl ammonium chloride and phenyltetrachlorophosphorane (molar ratio 1.05:1) did not stabilise in the n.m.r. machine and showed extensive hydrolysis (increasing the molar ratio to 3.61:1) but nonetheless showed a peak at +163.4 ppm. Ph_3PCl_2 was investigated as a chloride ion donor in 1,2-dichloroethane. Ph_3PCl_2 synthesised in this laboratory appeared to be mainly ionic, at least in nitrobenzene. Indeed the low field phosphorus peak showed very little movement on complexation. The higher field line again moved upfield with increasing chloride ion concentration consistent with the equilibrium

$$Ph_3PCl^+ Cl^- + PhPCl_4 \rightleftharpoons Ph_3PCl^+ PhPCl_5^-$$

The results are given in Table 37.

TABLE 37

δ^{31} P FOR $PhPCl_4$/$Ph_3PCl^+ Cl^-$ SYSTEMS

Ph_3PCl^+	Ph_3PO	$PhPCl_5^-$	Mole ratio $PhPCl_4/Ph_3PCl^+ Cl^-$ *	% association **
-57.4	-32.8	+73.2	1:0.375	18.3
-59.0	-37.0	+101.5	1:0.946	36.1

* from relative peak areas .

** assuming δ^{31} P $PhPCl_4$ =+44.2 ppm

$PhPCl_5^-$ =+203 ppm

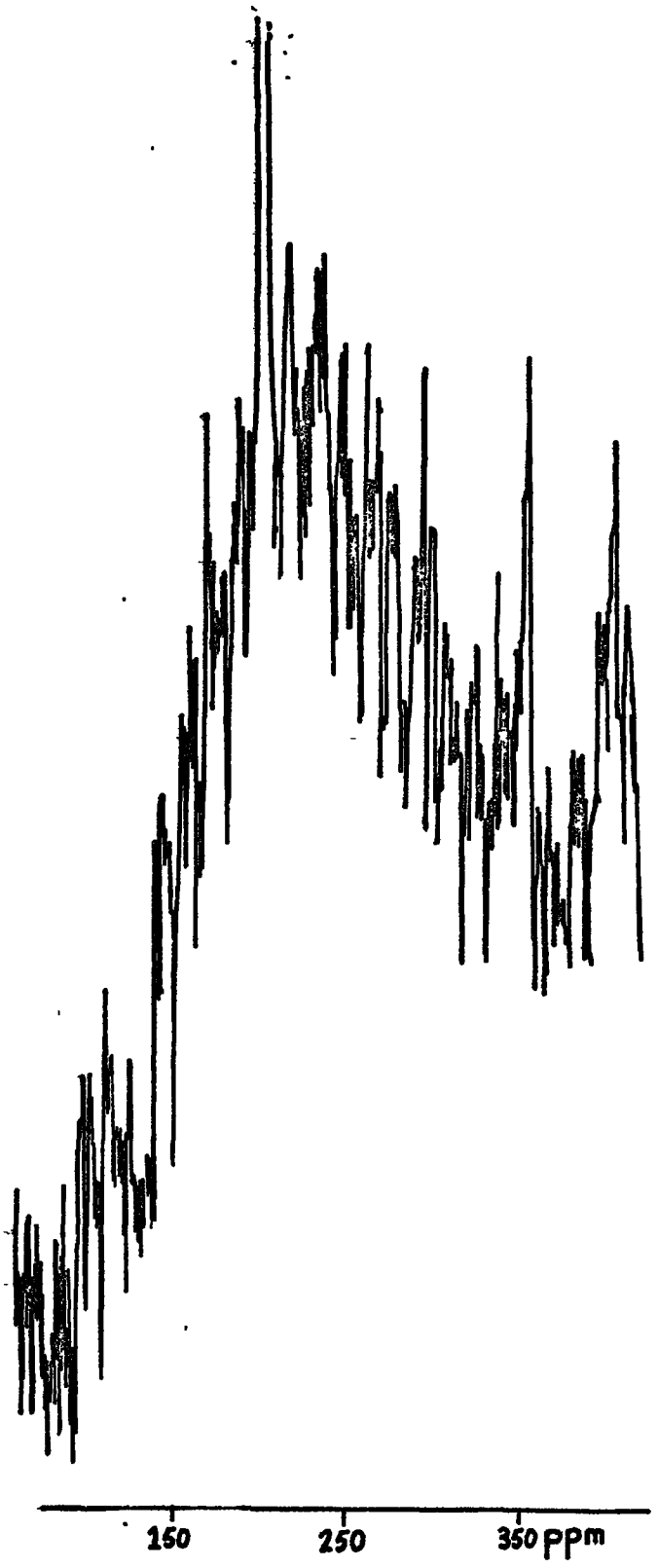


Fig25 ^{31}P n.m.r. solid state spectrum of

$(C_5H_{11})_4N^+ \; PhPCl_5^-$

An extrapolation of these values to a molar ratio 1:1.20 gives an association of ~42%, very similar to that found with $(C_5H_{11})_4N^+ Cl^-$ in methylene chloride (Table 36).

When sym-tetrachloroethane solutions of $PhPCl_4$ and Ph_2PCl_3 were mixed there was little change in the ^{31}P n.m.r. peak positions ($\delta^{31}P$ found -63.4, +47.4 ppm) from those found for the components individually ($\delta^{31}P$ Ph_2PCl_3 in $C_2H_2Cl_4$ -67.4 ppm). This is indicative of no complex formation even though Ph_2PCl_3 is partially ionised in this solvent (Chapter 4 section 3(ii)). Even in carbon tetrachloride solutions of $PhPCl_4$ and $(C_5H_{11})_4N^+ Cl^-$ a significant amount of complex formation occurred. The lack of formation of the $PhPCl_5^-$ ion in sym-tetrachloroethane may be explained by strong hydrogen bonding between chloride ions and the solvent. Indeed, where no hydrogen bonding is possible Ph_2PCl_3 is mainly covalent in solution (e.g. in nitrobenzene). This is discussed further in Chapter 4 section 3(i). It would be interesting in future to determine whether $PhPCl_4$ is a strong enough acceptor to abstract a chloride ion from molecular Ph_2PCl_3 in solution.

The system $PhPCl_3phen^+ Cl^-/PhPCl_4$ will be discussed in Chapter 4 section 1(iv).

The tetrapropylammonium and tetrapentylammonium salts were isolated as very moisture-sensitive solids. $(C_5H_{11})_4N^+ PhPCl_5^-$ was prepared by two methods. The ^{31}P n.m.r. solid state spectrum of the complex from method 1 (Chapter 4 section 1(v)) produced a narrow signal at +223.3 ± 5.7 ppm (Fig.25), 20 ppm higher than the extrapolated solution shift.

The discrepancy may be due to a conservative extrapolation, or to error caused by the sloping baseline on the solid state spectrum, but could also be due to a genuine solid state effect. The solid shift is, however, still in reasonable agreement with the solution data, and is the highest anionic shift found except for PCl_6^-. Superposed is a very sharp peak at +203.4 ± 1.7 ppm. This may be due to $PhPCl_5^-$ dissolved either in unremoved solvent or in $PhPOCl_2$ hydrolysis impurity, or may be due to self diffusion of the ion through the solid lattice. The latter explanation is the most likely. Self diffusion has been previously found in a number of solids [243]. The melting point of the salt is below 95° (the complex being prepared from a melt at this temperature) and so at 34.2°C the lattice may not be too rigid. Although free rotation of a molecule in the lattice would produce a narrowing of the solid state line the effect would be unable to narrow the line to the observed degree [244].

The sample of $(C_5H_{11})_4N^+ PhPCl_5^-$ prepared by the second method, although giving a solid state peak in this region, produced a less well defined spectrum. An insufficient quantity of $(C_3H_7)_4N^+ PhPCl_5^-$ was prepared to run a solid state ^{31}P n.m.r. spectrum.

The i.r. spectra of the salts show new bands in the region 500-400 cm^{-1} and a lowering of the intensity of many of those between 500 and 650 cm^{-1} (Table 38). Although it would be difficult to distinguish between the P-Ph [113] and P-Cl vibrations occurring in this region the generally lower line frequencies can be attributed to the lowering of the P-Cl bond strength by co-ordination (c.f. the change in frequencies $PCl_4^+ \rightarrow PCl_5 \rightarrow PCl_6^-$).

TABLE 38

I.r. SPECTRA $PhPCl_5^-$ SALTS 650-250 cm^{-1}

$(C_5H_{11})_4N^+$ $PhPCl_5^-$	
Method 1	618w, 596sh, 568s, 544s, 512s, ~480sh, 461s, 428s, 393s, 328w, 299m, 266w.
Method 2	618m, 596w, 569s, 544s, 512s, 495w, 462s, 427s, 394s, 352w, 330w, 300w, 268w,
$(C_3H_7)_4N^+$ $PhPCl_5^-$	618m, 590sh, 568s, 544s, 512s, ~485sh, 452s, 430s, 422s, 400s, 328w, 299w, 264w.
c.f. $PhPCl_4$ (to 350 cm^{-1})	617s, 592s, 567s, 542s, 520s, 492s, 421w, 380sbr.

$(C_5H_{11})_4N^+$ Cl^- is transparent in this region whereas $(C_3H_7)_4N^+$ Cl^- has weak absorptions at 578 and 356 cm^{-1}

The region from 650-1200 cm^{-1} is obscured by a very broad absorption, presumably due to the cations.

The ^{35}Cl n.q.r. spectrum of $(C_5H_{11})_4N^+$ $PhPCl_5^-$ showed lines at 30.575 and 31.07 MHz (S/N 2.5:1, 4:1 respectively). A third line at 32.3 MHz was not reproducible. The two lines may be attributed to chlorines cis and trans to the phenyl group, but the separation seems very small compared with the splittings found in $PhPCl_3dipy^+$ (Chapter 4 section 2(i)). The frequencies are, however, similar to those found in isoelectronic PCl_5.pyridine (Chapter 3 section 1(ii)b).

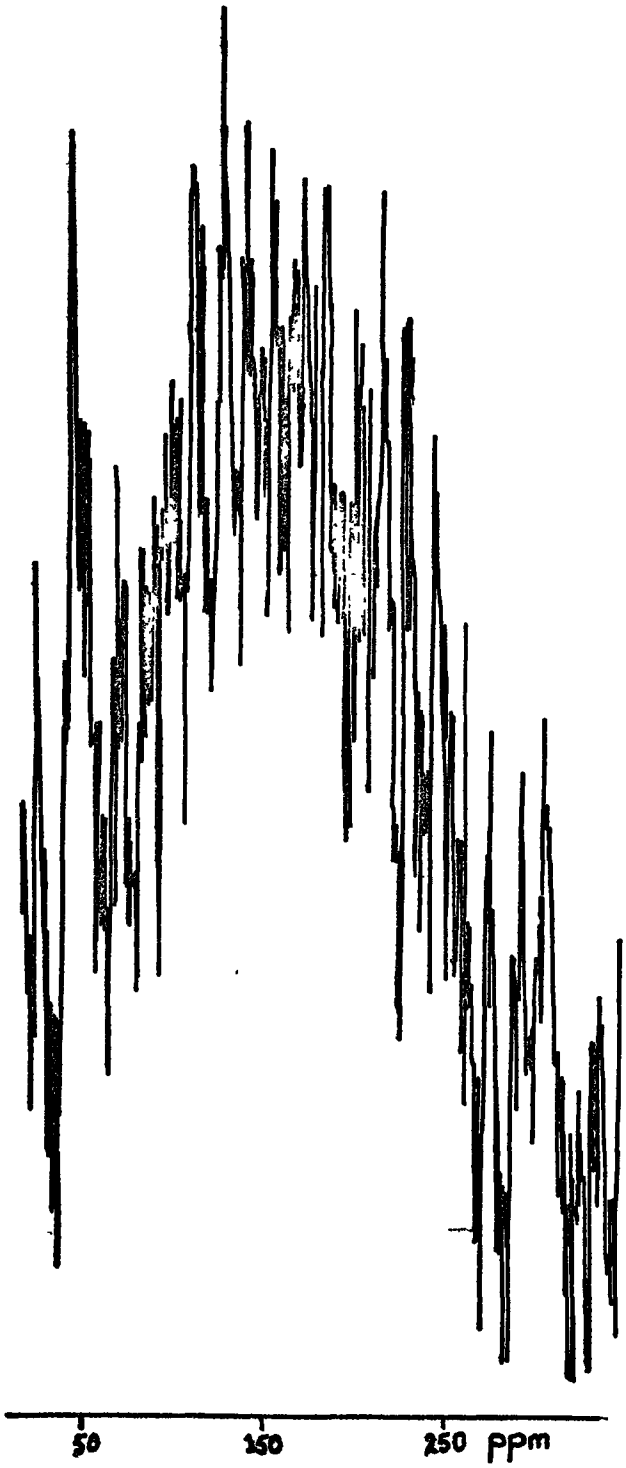
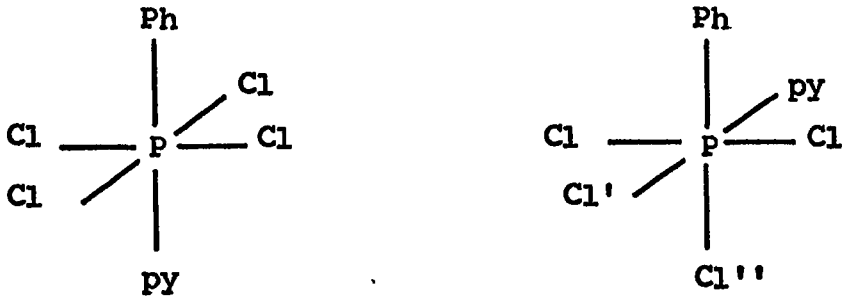


Fig26. ^{31}P n.m.r. solid state spectrum of $PhPCl_4.py$

(iii) Adducts with Monodentate pyridines

When nitrobenzene or methylene chloride solutions of phenyltetrachlorophosphorane and nitrogen bases with a lower basicity than pyridine were mixed, no observable reaction occurred. When pyridine was added in these solvents, however, a thick white precipitate immediately formed, which analysed as $PhPCl_4$.pyridine. The ^{35} Cl n.q.r. spectrum is quite distinct from that of $PhPCl_4$, consisting of a single line at 27.26 MHz (signal/noise 5:1). (The hydrolysis product $PhPOCl_2$ would give a signal at 25.357 MHz [180]). The single peak is consistent with the pyridine being trans to the phenyl group. If the pyridine were cis, then three lines would be present with an intensity ratio 2:1:1. The lower intensity peaks should still be clearly visible above the noise level.



Possible isomers of $PhPCl_4$.py

The solid state ^{31} P n.m.r. spectrum shows a very broad line in the six co-ordinate region of the spectrum at +161.7 ± 2.7 ppm. (Fig.26). The line is broader than that of $PhPCl_5^-$. This may be due to the proximity of the nitrogen quadrupole.

Because of the very low solubility of the moisture-sensitive complex in nitrobenzene, chloroform and sym-tetrachloroethane it is difficult to establish whether the shifts found in these solvents (+53.4, +47.3, +44.5 ppm respectively) are due to only weak association of the complex

$$PhPCl_4.py \rightleftharpoons PhPCl_4 + py \qquad 1.$$

or to complete dissociation with the shift from $PhPCl_4$ being due to partial hydrolysis (See Chapter 2 section 1(iv)a)

$$PhPCl_4 + H_2O \longrightarrow PhPOCl_2 + 2HCl$$

$$py + HCl \longrightarrow PyH^+ Cl^-$$

$$PhPCl_4 + pyH^+ Cl^- \rightleftharpoons pyH^+ PhPCl_5^- \qquad 2.$$

If pyridine is added to a sym-tetrachloroethane solution the peak moves upfield with partial precipitation of the complex. Although this may be explained by the precipitation increasing the relative chloride ion concentration (equilibrium 2) the solvent is extremely poor for the formation of $PhPCl_5^-$ (see last section). The upfield movement is better explained by the displacement of equilibrium 1 to the left by the excess pyridine. The largest shift observed before solubility became too low for detection was +68.2 ppm, corresponding to ~22% complex formation (assuming the shift of $PhPCl_4.py$ to be +163.2 ppm).

Complexes were also synthesised with 3-picoline and 3,5-lutidine by a similar reaction. Both donors are more basic than pyridine itself. Complex formation does not occur with 2-picoline, or 2,4,6-collidine, presumably due to steric hindrance from the 2-substituent.

The ^{35}Cl n.q.r. spectrum of $PhPCl_4$. 3,5-lutidine shows intense lines at 27.10 (signal/noise 5.6:1) and 27.585 MHz (signal/noise 3.6:1) plus a much weaker line at 32.4 MHz (signal/noise 1.6:1). Although the number of lines is consistent with cis co-ordination, the high frequency is so weak that it is probably due to impurities (The frequency is however different from those of the most likely impurities $PhPCl_4$, $PhPOCl_2$, and $PhPCl_5^-$). The low frequency lines are of slightly different width, so the signal/noise ratios cannot be taken as a precise measure of their relative intensities. Their average value is 27.35 MHz, only 0.09 MHz different from the single line in trans-$PhPCl_4$.pyridine. This suggests that the 3,5-lutidine complex is also trans. No n.q.r. signals were detected from $PhPCl_4$. 3-picoline.

The infra red spectra of the complexes are given below.

TABLE 39

INFRA RED SPECTRA OF $PhPCl_4$.PYRIDINE COMPLEXES 600-350 cm^{-1}

$PhPCl_4$.py	619w, 596w, 569m, 546m, 510s, 477s, 446s, 398s
$PhPCl_4$. 3,5-lut	617w, 593w, 568s, 544s, 525s, 499s, 440s, 430s, 401sbr
$PhPCl_4$. 3-pic	634w,* 617w, 592w, 568s, 547s, 522s, 502w, 492m, 467w,* 443s, 432s, 398s
$prop_4N^+$ $PhPCl_5^-$	618m, 590sh, 568s, 544s, 512s, 485sh, 452s, 430s, 400s
$PhPCl_4$	617s, 592s, 567s, 542s, 520s, 492s, 421w, 380sbr

* = ligand bands

There was some resemblance to the spectrum of $prop_4N^+$ $PhPCl_5^-$ in the region below 490 cm^{-1}. Because of the weak co-ordination the complexes may have partially hydrolysed to pyH^+ $PhPCl_5^-$. There is a suggestion of very weak N-H stretch at about 2600 cm^{-1} in the spectrum of $PhPCl_4$.py and at 2440 cm^{-1} with $PhPCl_4$. 3,5-lutidine. Hydrolysis may be caused by traces of water remaining even in sodium-dried nujol [11]. The spectra of the complexes may, however, be coincidentally similar to those of $PhPCl_5^-$. Co-ordination in both cases would be expected to lower the P-Cl stretching frequencies. P-Ph frequencies will be similar in the two complexes. Further work is thus necessary before the spectra can be unambiguously ascribed to the non-hydrolysed complexes.

The solid state ^{31}P n.m.r. shifts of the 2-picoline and 3,5-lutidine complexes seemed higher than that of the pyridine complex. It was, however, difficult to obtain accurate shift data. The effect, if genuine, may be due to the increasing bulk and donor ability of the pyridine having a large effect on such weakly bound complexes.

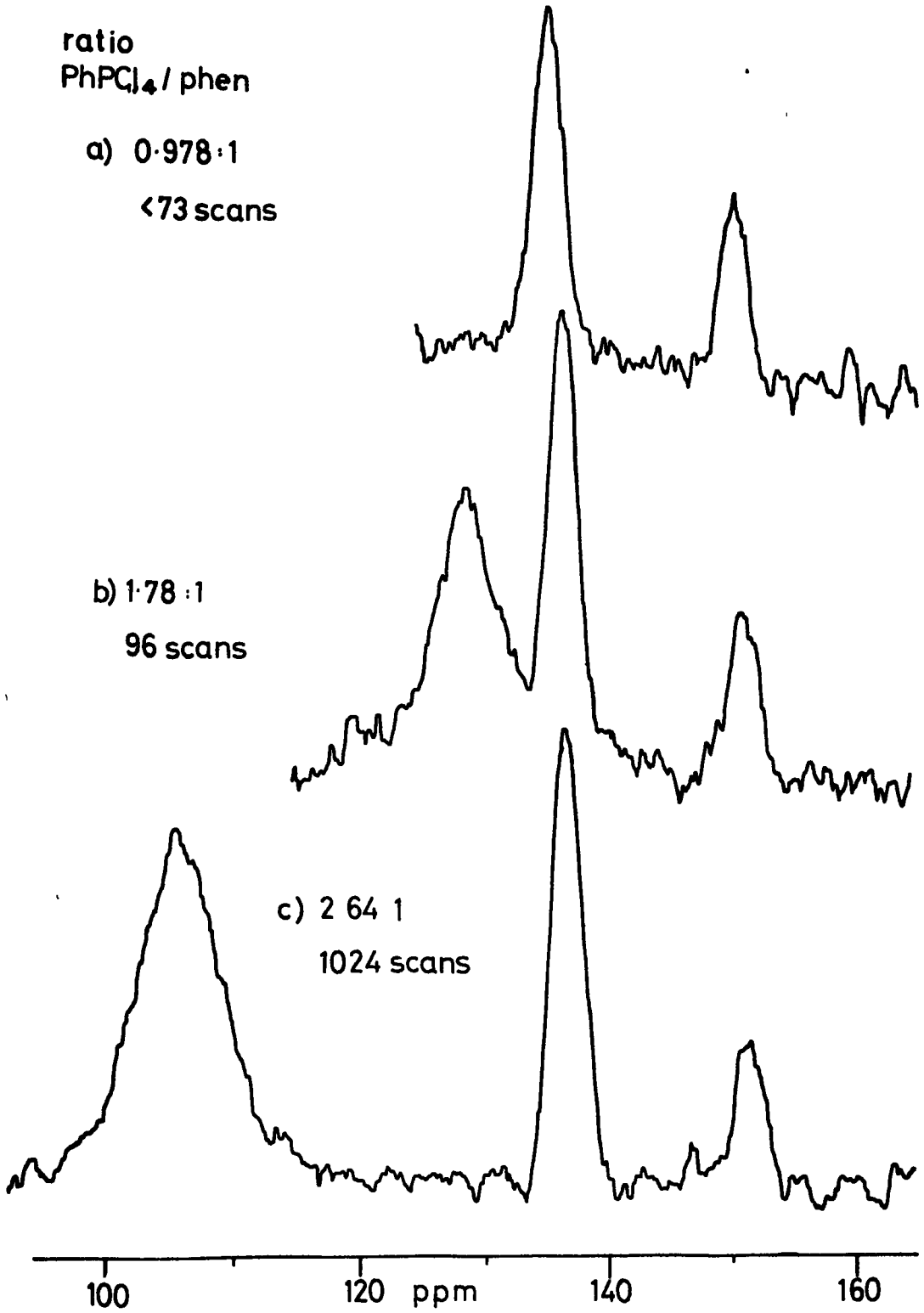
TABLE 40

^{31}P SOLID STATE n.m.r. SHIFTS

$PhPCl_4$.pyridine	+161.2 ± 2.7 ppm
$PhPCl_4$.3-picoline	+178.3 ± 7.7 ppm
$PhPCl_4$.3,5-lutidine	+182.6 ± 11.6 ppm

In each of these solid state spectra sharp lines were visible corresponding to freely diffusing, almost completely uncomplexed $PhPCl_4$. Shifts found were +45.9 ± 0.4 ($PhPCl_4$.py), +58.3 ± 0.5 ($PhPCl_4$.3-pic), and +48.0 ± 0.4 ($PhPCl_4$.3,5-lut).

Fig 27 ^{31}P n.m.r. spectra of $PhPCl_4$ / phenanthroline solutions in nitrobenzene

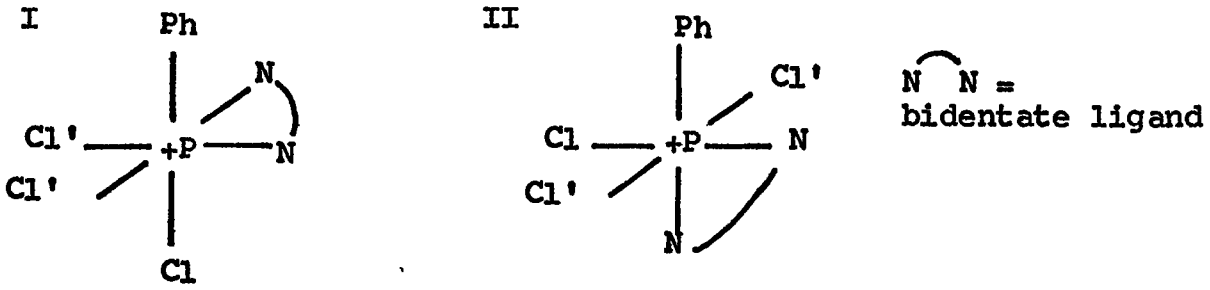


The shifts reflect the dissociation of the complex when not fixed in a crystal lattice.

(iv) Adducts with bidentate pyridines

1,10-phenanthroline

With a nitrobenzene solution containing equimolar amounts of $PhPCl_4$ and 1,10-phenanthroline, peaks are present in the ^{31}P n.m.r. spectrum at +135.4 ppm and +150.6 ppm (Fig.27). Similar peaks are found in nitrobenzene solutions containing equimolar amounts of $PhPCl_3^+$ $SbCl_6^-$ and 1,10-phenanthroline. These solutions are stable. The peaks are in the 6 co-ordinate region of the spectrum. Because of the rigid nature of phenanthroline, monodentate or bridging behaviour of this ligand is unlikely. The complexes are then expected to be $PhPCl_3phen^+$ derivatives. $PhPCl_3phen^+$ may, however, exist in two isomeric forms.



Possible isomeric forms of $PhPCl_3(L\text{-}L)^+$

We may assign the two peaks to these species. Isomerism in six co-ordinate phosphorus chemistry has previously been found only with fluorine present [245]. No ^{31}P n.m.r. spectra were reported, hence there is no comparison available for the 15 ppm isomer shift found here. Few nuclei which can act as a 6 co-ordinate central atom are amenable to n.m.r. investigation.

Isomer shifts are, however, found in ^{59}Co and ^{195}Pt n.m.r. [246,247].

Although isomerism in solution is often found in co-ordination chemistry it is by no means universal. Labile complexes tend to form the most stable configuration in solution and only when two configurations are of approximately equal stability do the species coexist. Rapid interconversion of isomers, giving a single n.m.r. peak, often hinders their detection. The present system seems ideal for detection of isomers. In order for the species to interconvert rapidly by a dissociative mechanism, there must be rapid exchange of either chlorines or ligands. Phenanthroline, being a bidentate ligand, would not be expected to dissociate easily from the complex. Since the phosphorus already bears a positive charge a P-Cl bond is unlikely to break easily.

No attempt was made to assign the n.m.r. peaks to specific configurations. Configurations may sometimes be assigned by analysis of the proton n.m.r. spectrum of the phenanthroline [248,249]. The 2 and 2' proton signals generally separate from the rest of the spectrum [249,248]. In $PhPCl_3phen^+$ one isomer would give equivalent 2 and 2' protons, whilst in the other they would be inequivalent. However both isomers would give spectra in the same region (although of different intensity, as the isomers are present in unequal amounts - Table 41) with the phenyl signals superposed, hence interpretation would be most difficult.

If less than one equivalent of 1,10-phenanthroline is added to $PhPCl_4$ in nitrobenzene a third n.m.r. peak is found (Fig.27). This increases in intensity relative to the combined

areas of the other two peaks and moves to lower field as the excess of $PhPCl_4$ is increased. The peak is due to $PhPCl_4$ co-ordinating Cl^- ions, as previously found.

$$PhPCl_3phen^+ Cl^- + PhPCl_4 \rightleftharpoons PhPCl_3phen^+ PhPCl_5^-$$

The cation peak shifts remain constant. Thus, although $PhPCl_5^-$ equilibrates on the n.m.r. time scale with free $PhPCl_4$, $PhPCl_3phen^+$ does not. A 1:1 solution of $PhPCl_4$ and phenanthroline shows no sign of free $PhPCl_4$, hence the complex is totally associated in solution. The stability of $PhPCl_3phen^+$ contrasts sharply with that of $PhPCl_4$.py and $PhPCl_5^-$, and may be attributed to the chelation of the phenanthroline.

TABLE 41

N.m.r. SHIFTS IN $PhPCl_4$/PHENANTHROLINE SOLUTIONS

Ratio $PhPCl_4$/phen approx	δ^{31} P($PhPCl_3phen^+$) A	B	$PhPCl_4 \rightleftharpoons PhPCl_5^-$ C	Relative area A : B
0.978:1	+135.4	+150.5	-	100:43
1.78 :1	+136.4	+150.9	+128.5	100:39.2
2.64:1	+136.8	+151.5	+105.8	100:25.0
c.f. $PhPCl_3phen^+SbCl_6^-$	+135.1	+149.5		100:30

The concentration of $PhPCl_5^-$ at a given ratio of $PhPCl_4$ and $PhPCl_3phen^+ Cl^-$ is much lower than found with a similar ratio of $PhPCl_4$ and $(C_5H_{11})_4N^+ Cl^-$ in nitrobenzene (Table 42). $PhPCl_3phen^+ Cl^-$ is thus not as favourable as $(C_5H_{11})_4N^+ Cl^-$ for the formation of $PhPCl_5^-$. The reason for this behaviour is not clear, especially as the possible competing reaction

$$PhPCl_4 + phen \longrightarrow PhPCl_3phen^+ Cl^-$$

appears to go to completion.

TABLE 42

RELATIVE AREAS OF $PhPCl_3phen^+/PhPCl_4 \leftrightarrow PhPCl_5^-$ PEAKS

$PhPCl_4$/phen approx	$\frac{PhPCl_3phen^+ Cl^-}{PhPCl_4}$		δ^{31} P(C)	δ^{31} P as found in $Pent_4N^+ Cl^-/PhPCl_4$ system at same ratio
	rel. areas (B + C) : A	By wt. components 1.		
2.64:1	0.54:1	0.61:1	105.8	142.0
1.78:1	1.11:1	1.28:1	128.5	168.2

1. After taking into account observed partial hydrolysis of $PhPCl_4$. The phenanthroline will, however, still form a cationic species capable of stabilising $PhPCl_5^-$

$$PhPCl_3phen^+ Cl^- + H_2O \longrightarrow PhPOCl_2 + phen\ H^+ Cl^- + HCl$$

When an excess of $PhPCl_4$ is present, the intensity of the +150 ppm peak decreases with respect to that of the +135 ppm peak. The intensity ratio is, however, generally higher than found with $PhPCl_3phen^+ SbCl_6^-$ (Chapter 4 section 2(i)).

$PhPCl_3phen^+ Cl^-$ is extremely soluble in methylene chloride and nitrobenzene. Insufficient solid was isolated for solid state n.m.r. or n.q.r. investigation. The i.r. spectrum showed a number of new bands between 500 and 400 cm^{-1}.

TABLE 43

I.r. SPECTRUM $PhPCl_3phen^+ Cl^-$ 650-250 cm^{-1}

617m, 568m, 541s, 534s, 516m, 502s, 486s, 466s, 452m, 438s, 428m, 342w, 318w, 287w, 273w

The complex was found to hydrolyse slowly in moist air. This contrasts with the stability of the hexachloroantimonate salt under similar conditions (Chapter 4 section 2(i)) and demonstrates the effect of the counter-ion on the stability of $PhPCl_3phen^+$.

2,2'-dipyridyl

When nitrobenzene solutions of phenyltetrachlorophosphorane and 2,2'-dipyridyl were mixed, a bright yellow viscous solution was formed. Within a few minutes this became a solid white mass. The isolated complex analysed as $PhPCl_4.dipy.PhNO_2$. The presence of free nitrobenzene was also indicated by i.r. absorptions at 1525(s), 1345(s), 852(s), and 702(s) cm^{-1}.

Solutions behaved similarly in nitroethane, methylene chloride, and acetonitrile. When benzene was used as solvent precipitation occurred over several hours. A solvate seems to be formed from the nitroethane solution, as shown by the lines at 1547 and 876 cm^{-1} in the i.r. spectrum (c.f. 1553, 876 cm^{-1} in free nitroethane) but elemental analyses were more consistent with the unsolvated species. The complexes from the other solvents were unsolvated. Few of the samples gave satisfactory analyses, however, apart from that isolated from acetonitrile solution. Somedifficulty was found in the analyses, as described in Chapter 2 section (vi), which may

partially account for the discrepancies.

An equimolar solution of $PhPCl_4$ and dipyridyl in benzene was investigated by ^{31}P n.m.r. as it slowly precipitated the complex. Only free $PhPCl_4$ ($\delta^{31}P$ + 47.5) was detactable. The signal decreased in intensity but did not vary in shift as the precipitation proceeded. The precipitation would then seem to be controlled by the rate of formation of the complex. Co-ordination of a bidentate ligand to a covalent molecule by displacement of a chloride ion appears sometimes to be very slow, and monitorable by ^{31}P n.m.r. techniques (see Chapter 5).

The complexes gave identical i.r. spectra above 850 cm^{-1}, showing no signs of impurities. There were, however, differences in the spectra between 850 and 640 cm^{-1} (Table 44).

I.r. SPECTRA OF $PhPCl_4$.dipy COMPLEXES 850–640 cm^{-1}

$PhPCl_4$.dipy $PhNO_2$	808s, 696sh,	797m, 694s,	792s, 688w,	682s,	770m, 667m,	758m, 652m,	746w, 642m,	721/718s,	708sh,	706sh,	702s,*
$PhPCl_4$.dipy from CH_2Cl_2	812w,	797m, 694s,	786sh,	782m,	772m, 667m,	751m, 654m,	733s, 642w,	719s,			
from MeCN	836w,	798m, 690s,	~683s,	778s,	773m, 668w,	768sh,	750s,	739w, 642m,	717sh,	713s,	
from benzene	836w, 812w,	797m, 694s,	782m, 687m,	678s,	773s, 668m,	760w, 656m,	750s,	643w,	720s,	718s,	
from Et NO_2	810w, 695s,	797m, 690sh,	786sh, 684sh,	782m,	772s, 667m,	753m, 656m,	736w, 642w,	719s,			

* Nitrobenzene

C-H vibrations from both phenyl [250,251] and dipyridyl [250] groups occur in this region. The differences appeared to be mainly due to the splitting of lines at 780 and 690 cm^{-1} into two or more components for certain of the samples, and to the appearance of a line at 632 cm^{-1} in others.

Lines between 550 and 400 cm^{-1} (Table 45) are ascribed to P-Cl and P-Ph [113] vibrations. In this region the samples show similar spectra with variations in intensity and position.

The differences in the i.r. spectra of the compounds contrast with the close similarity of the spectra of $PhPCl_3dipy^+ SbCl_6^-$ and $PhPCl_3dipy^+ PCl_6^-$. 0.25 $PhNO_2$ and are discussed in Chapter 4 section 2(i).

TABLE 45

I.r. SPECTRA OF $PhPCl_3dipy^+ Cl^-$ SAMPLES 650-350 cm^{-1}

From MeCN	642m, 618m, 568m, 533s, 515s, 490s, 483m, 470m, 453s, 447s, 431s, 392m,
From CH_2Cl_2	642w, 618m, 570sh, 532s, 516s, 496s, 487m, 472s, 464sh, 453s, 440s, 427s, 384m,

Solid state ^{31}P n.m.r. shifts of the $PhPCl_4$/dipy complexes were very difficult to obtain. The peaks were very weak and broad and in some instances highly distorted. The shift of $PhPCl_3dipy^+ Cl^-$ isolated from methylene chloride was +158.5 ± 10.7 ppm whilst that of the nitrobenzene solvate was +157.3 ± 13.6 ppm. The agreement between the two values is largely fortuitous in view of the large estimated errors. No reliable shift could be determined for $PhPCl_3dipy^+ Cl^-$ isolated from benzene solution.

Very weak signals were found in the n.q.r. spectrum of $PhPCl_4$.dipy.$PhNO_2$ at 28.27 MHz (signal/noise 14/8, 8/6 on two different scans), and at 27.34 MHz (signal/noise 12/8, 8/6). A third line once appeared at 26.42 MHz but was not reproducible. The two reproducible signals are in similar positions to the higher intensity lines of $PhPCl_3dipy^+$ $SbCl_6^-$ (27.49 .27.96 MHz) suggesting that the complexes have similar structures. However this is not suggested by the differences in their i.r. spectra (Chapter 4 section 2(ii)). Due to the insolubility of the $PhPCl_4$.dipy complex there is little physical evidence on its structure.

No n.q.r. signals could be detected from $PhPCl_4$.dipy isolated from benzene solution.

(v) Preparation of Complexes

$(C_5H_{11})_4N^+$ $PhPCl_5^-$

Method 1.

An intimate mixture of 3.586g (14.35 mmole) $PhPCl_4$ and 4.772g (14.28 mmole) $(C_5H_{11})_4N^+$ Cl^- was heated to produce a yellow oil at 95°C. This was quickly cooled to produce a pale yellow-brown solid which became a liquid over a period of months. The compound was not analysed, but gave an identical i.r. spectrum between 4000-250 cm^{-1} to the sample produced by method 2.

Method 2.

1.747g (6.990 mmole) $PhPCl_4$ and 2.339g (7.000 mmole) $(C_5H_{11})_4N^+$ Cl^- were separately dissolved in small amounts of methylene chloride. These were mixed producing a bright yellow solution. The solution was allowed to stand in

ice-water for a few minutes and the solvent then slowly pumped away under vacuum. When almost all the solvent had been removed, the flask was removed from the bath to complete the drying. This produced a slightly yellowish white solid which was stable under an atmosphere of nitrogen.

Yield = 3.270g = 80.1% based on $(C_5H_{11})_4N^+ PhPCl_5^-$

Analyses: Found C,53.77; H,5.83; N,2.25; P,5.48; Cl,31.48.

$(C_5H_{11})_4N^+ PhPCl_5^-$ requires: C,53.47; H,8.47; N,2.40; P,5.30; Cl,30.36.

$(C_3H_7)_4N^+ PhPCl_5^-$

$(C_3H_7)_4N^+Cl^-$ and $PhPCl_4$ were individually saturated in methylene chloride. The $PhPCl_4$ solution was slowly added to the $(C_3H_7)_4N^+ Cl^-$ solution, producing a yellowish solution and yellowish white crystals. The moisture-sensitive crystals were filtered, washed with 30/40 pet ether, and dried at the pump.

Analyses: Found C,46.33; H,5.14; N,3.65; P,6.44; Cl,37.43

$(C_3H_7)_4N^+ PhPCl_5^-$ requires C,45.82; H,7.06; N,2.97; P,6.57; Cl,37.58.

$PhPCl_4$·pyridine

4.91g (19.6 mmole) $PhPCl_4$ were dissolved in the minimum quantity of methylene chloride. With stirring, 1.58ml (15.5g 18.96 mmole) pyridine were slowly dripped in. A thick white precipitate was immediately produced in an exothermic reaction. After leaving for an hour the solid was filtered, washed with 30/40 pet ether, and dried at the pump, producing a fine white solid.

Yield = 5.20g = 80.6% as $PhPCl_4$.py

Analyses: Found C,36.72; H,3.40; N,4.22; P,9.12; Cl,43.88

$PhPCl_4$.py requires C,40.12; H,3.04; N,4.26; P,9.42; Cl,43.16

The reason for the consistently low carbon analyses was not clear.

The method was repeated, using nitrobenzene as solvent to give an identical adduct as shown by its i.r. spectrum between 4000 and 250 cm^{-1}. 3.085g (12.34 mmole) $PhPCl_4$ and 1.02ml (1.00g, 12.6 mmole) pyridine gave 3.39g adduct.

Yield = 84.3%

$PhPCl_4$.3,5-lutidine

3.263g (13.06 mmole) $PhPCl_4$ were dissolved in the minimum amount of nitrobenzene to give a clear solution. 1.510g (14.11 mole) 3,5-lutidine were slowly dripped into the solution. There was an immediate yellow precipitate. The solution was stirred for a few minutes. The precipitate was then filtered, washed with 30/40 pet ether and dried at the pump to give a yellowish solid. On further drying under vacuum the colour became very pale cream.

Yield = 3.82g = 80.4% as $PhPCl_4$.3,5-lutidine

Analyses: Found C,43.47; H,3.63; N,4.32; P,8.34; Cl,40.23

$PhPCl_4$.3,5-lutidine requires C,43.72; H,3.96; N,3.92; P,8.68; Cl,39.72.

$PhPCl_4$.3-picoline

2.618g (10.47 mmole) $PhPCl_4$ were dissolved in the minimum quantity of nitrobenzene to produce a clear solution. 1.1ml (1.1g 11 mmole) 3-picoline were slowly added. There was an immediate extremely thick yellow precipitate. After several minutes the precipitate was filtered, washed with nitrobenzene, then 30/40 pet ether and dried at the pump.

Yield = 2.52g = 70.8% as $PhPCl_4$.3-picoline. The complex was finally dried for 30 minutes under vacuum to produce an off-white powder.

Analyses: Found C,43.64; H,3.53; N,4.20; P,9.04; Cl,41.36; $PhPCl_4$.3-picoline requires C,42.01; H,3.53; N,4.08; P,9.03; Cl,41.34.

$PhPCl_3phen^+ Cl^-$

An 8.5mm n.m.r. tube was made up containing 0.342g (1.36 mmole) $PhPCl_4$ and 0.251g (1.39 mmole) 1,10-phenanthroline in nitrobenzene. Additional $PhPCl_4$ was then added. After several hours a thick precipitate came out of solution. This was filtered, washed with 30/40 pet ether, and dried at the pump, producing a light yellow solid.

Yield = 0.390g = 66.2% as $PhPCl_3phen^+ Cl^-$

Analyses: Found C,50.01; H,3.02; N,7.87; Cl,32.38

$PhPCl_3phen^+ Cl^-$ requires C,50.26; H,3.05; N,6.51; Cl,32.97

Decomposed solutions for the spectrophotometric determination of phosphorus were pink, and thus the analysis could not be carried out.

$PhPCl_3dipy^+ Cl^-$

Preparations were attempted with methylene chloride, nitrobenzene, nitroethane, benzene, and acetonitrile as solvents. In each case equimolar quantities of $PhPCl_4$ and 2,2'-dipyridyl were separately dissolved in the minimum quantity of solvent. The dipyridyl solution was added to the $PhPCl_4$ solution, producing a viscous bright yellow solution. After about one minute the solutions generally produced a very thick precipitate. After leaving a few minutes the precipitate was filtered, washed with 30/40 pet ether and dried at the pump.

The benzene solution only slowly precipitated and was left for three days before isolation of the complex.

TABLE 46

$PhPCl_3dipy^+ Cl^-$ PREPARATIONS

Solvent	$PhPCl_4$ used		2,2'-dipyridyl used		Yield	
	gm	mmole	gm	mmole	g	% (assuming $PhPCl_3.dipy^+ Cl^-$)
CH_2Cl_2	2.335	9.343	1.470	9.411	2.977	78.5
$EtNO_2$.	0.726	2.90	0.466	2.983	0.598	50.8
MeCN	3.948	15.80	2.309	14.78	3.257	54.3
C_6H_6	3.222	12.89	2.008	12.85	3.439	65.9
$PhNO_2$	1.654	6.618	1.030	6.594	2.601	74.5 as $PhPCl_4.dipy.PhNO_2$

The analyses are given in Table 47.

TABLE 47

ANALYSES

$PhPCl_3dipy^+ Cl^-. PhNO_2$

Theoretical	C 49.92	H 3.43	N 7.94	P 5.85	Cl 26.80
Found	48.83	3.23	7.64	5.50	26.79
$PhPCl_3dipy^+ Cl^-$ Theoretical	C 47.30	H 3.23	N 6.90	P 7.63	Cl 34.92
Found from CH_2Cl_2	46.4	5.63	6.71	6.65	40.2 39.5 - by oxygen flask method
MeCN	47.14	3.31	9.20	7.55	33.8
Benzene	49.72	4.05	7.02	6.92	32.5
$EtNO_2$*	47.89	3.05	7.10		

* shows free nitroethane in solid by its i.r. absorption at 1547 cm^{-1}. No P or Cl analyses were performed on the sample

2. Acceptor Properties of Phenyltrichlorophosphonium Salts

The phenyltrichlorophosphonium cation can be synthesised by addition of a number of chloride ion acceptors to phenyltetrachlorophosphorane [23,59]. The hexachloroantimonate and hexachlorophosphate salts were studied to provide a comparison with the acceptor properties of the parent phosphorane.

(i) Phenyltrichlorophosphonium Hexachloroantimonate

This salt was first prepared by Köhler [253]. It has since been prepared by Schmidtpeter and Brecht [126], by Ruff [127], and by Dillon [23]. Antimony pentachloride is reacted with either one equivalent of phenyltetrachlorophosphorane [126],

$$PhPCl_4 + SbCl_5 \longrightarrow PhPCl_3^+ SbCl_6^-$$

or with half an equivalent of phenyldichlorophosphine [23,127,253]

$$PhPCl_2 + 2SbCl_5 \longrightarrow PhPCl_3^+ SbCl_6^- + SbCl_3$$

The second method was used in this work.

The ionic constitution of the adduct is shown by its solid state ^{31}P n.m.r. shift of -88 ppm [23]. The shift in nitrobenzene solution was found to be -100.5 ppm (c.f. -102.9 ppm [126]). The ^{35}Cl n.q.r. spectrum [59] shows signals at 31.03 MHz ($PhPCl_3^+$) and 24.95 MHz ($SbCl_6^-$).

The salt exists as white, moisture-sensitive crystals, insoluble in methylene chloride and non-polar solvents, but soluble in nitrobenzene, nitroethane, and nitromethane. It is stable in the absence of moisture at room temperature. Saturated solutions in nitrobenzene gave a ^{31}P n.m.r. signal just visible on a single scan of the spectrum.

When two equivalents of pyridine were added to the nitrobenzene solution a white precipitate formed and the $PhPCl_3^+$ signal disappeared from the solution ^{31}P n.m.r. spectrum. No consistent new signal could be found on a single scan. The solution was too unstable for spectrum accumulation, presumably due to reaction. By analogy with $PCl_4py_2^+ SbCl_6^-$, and also with $PhPCl_3^+ PCl_6^-$ + pyridine, the reaction is probably,

$$PhPCl_3^+ SbCl_6^- + 2py \longrightarrow \left[PhPCl_3py_2^+ SbCl_6^-\right]$$

$$\downarrow \text{rapid}$$

$$PhPCl_4.py + SbCl_5.py$$

the $PhPCl_4.py$ precipitating from solution, thereby giving no large ^{31}P n.m.r. signal.

When a solution was made up containing equimolar amounts of 1,10-phenanthroline and $PhPCl_3^+ SbCl_6^-$ in nitrobenzene, ^{31}P n.m.r. peaks were observed at +135.1 ppm and +149.7 ppm, in completely analogous positions to those found in the $PhPCl_4$/phenanthroline system. The similarity of the spectra from $PhPCl_3^+$ and $PhPCl_4$ systems confirms the presence of similar species. The signals may be attributed to the two isomers of $PhPCl_3phen^+$. The solution remained stable over a period of months. The high field peak is of much lower relative intensity (26:100) than in the corresponding $PhPCl_4$ system (43:100).

Attempts were made to isolate the solid complex. When equimolar solutions of $PhPCl_3^+ SbCl_6^-$ and phenanthroline in nitromethane were mixed, a yellow solid was produced.

Analysis (see experimental section) showed the compound to contain no phosphorus. The analyses, however, did not correspond to any simple adduct of phenanthroline with antimony pentachloride, nor to any simple partial hydrolysis product of hexachloroantimonate salts. The i.r. spectrum showed no band attributable to N^+-H and only one band attributable to a Sb-Cl vibration, at 338 cm^{-1}. This is in a similar position to the single absorption found in $SbCl_4phen^+ SbCl_6^-$ [22]. The complex was not further investigated.

A second method of preparation is available. On addition of antimony pentachloride to $PhPCl_3phen^+ Cl^-$ in methylene chloride $PhPCl_3phen^+ SbCl_6^-$ was precipitated as a fawn coloured solid.

$$PhPCl_4 + phen \rightarrow PhPCl_3phen^+ Cl^- \xrightarrow{SbCl_5} PhPCl_3phen^+ SbCl_6^- \downarrow$$

There are a number of disadvantages to the method. If any free $PhPCl_4$ remains in solution, $PhPCl_3^+ SbCl_6^-$ may precipitate. Similarly if there is any free phenanthroline $SbCl_4phen^+ SbCl_6^-$ [22] may precipitate. Phenanthrolinium salts are also liable to precipitate if any moisture is present. The $PhPCl_3phen^+ SbCl_6^-$ precipitates, rather than crystallises out of solution and so may also bring down any material formed by side reactions, hence the fawn colour of the compound.

This route was not generally applicable to the other phosphorus acceptors studied, since 1:1 phosphorane/ phenanthroline adducts were unstable in solution with respect to the 2:1 adducts.

$PhPCl_3phen^+ SbCl_6^-$ was characterised by elemental analyses, by a broad solid state ^{31}P n.m.r. peak at

+165.9 ± 6.2 ppm, and by the similarity of its infra red spectrum to that of $PhPCl_3phen^+ Cl^-$, with the addition of an absorption at 343 cm^{-1} attributable to $SbCl_6^-$. As with the similar dipyridyl adducts discussed later there are a number of differences in the spectra between 800 and 650 cm^{-1}, but there is closer agreement below this value.

TABLE 48

I.r. SPECTRA OF $PhPCl_3phen^+ Cl^-$ AND $PhPCl_3phen^+ SbCl_6^-$ 800-250 cm^{-1}

$PhPCl_3phen^+ SbCl_6^-$

775w, 770sh, 752sh, 748s, 736s, 722s, 717w, 704s, 689sh, 687sh, 684s, 653w, 617w, 567w, 551s, 542w, 517s, 485s, 476s, 450s, 446s, 428sh, 343vs, 316w, 281w

$PhPCl_3phen^+ Cl^-$

793w, 773s, 753s, 721s, 702s, 697s, 683m, 657w, 617m, 568m, 541s, 534s, 516m, 502s, 486s, 466s, 452m, 438s, 428m, 342w, 318w, 287w, 273w

No n.q.r. signals could, however, be detected from the sample.

The complex shows a similar lack of reaction towards water as $PCl_4phen^+ SbCl_6^-$, presumably again due to its complete insolubility in this medium, and also to the stability and size of the counter ion (c.f. $PhPCl_3phen^+ Cl^-$ Chapter 4 section 1(iv)). $PhPCl_3phen^+ SbCl_6^-$ underwent no change on exposure to air overnight, as shown by the lack of change in its i.r. spectrum, and did not react on addition

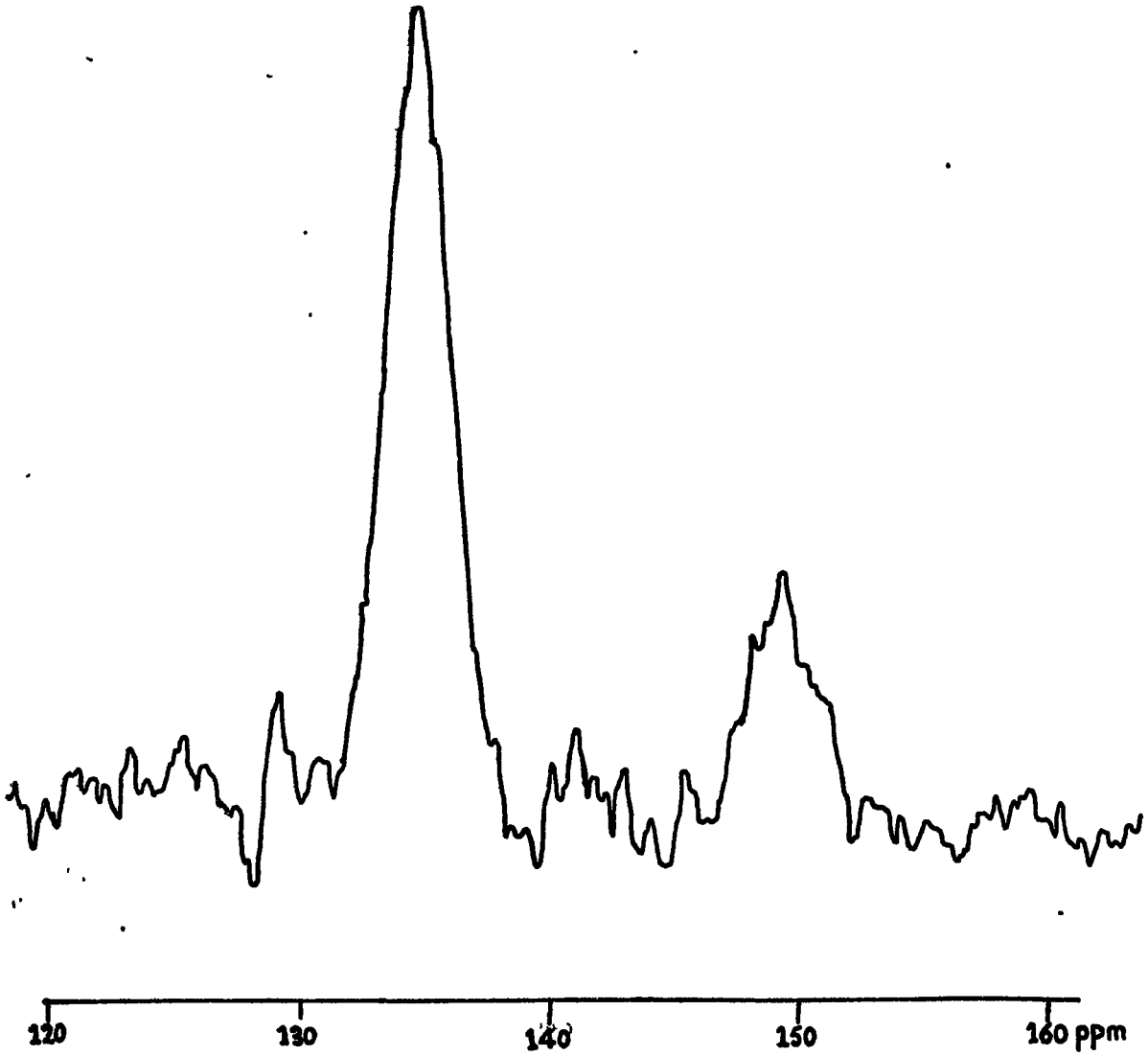


Fig 28 ^{31}P n.m.r. spectrum of $PhPCl_3phen^+SbCl_6^-$ in nitrobenzene 155 scans

of water, remaining completely unchanged.

On dissolution of the complex in nitrobenzene, peaks occurred in the ^{31}P n.m.r. spectrum at +135.1 and +149.5 ppm (Relative intensities 100:30. Fig.28). There was no change in the spectrum after three weeks. The complex formed in nitromethane is thus difficult to explain. In one nitrobenzene solution, however, a third peak was visible at +108.6 ppm. The solution later precipitated a large amount of solid. The i.r. spectrum of this solid was identical with the complex crystallising from nitromethane solution. One explanation would be the equilibrium

$$PhPCl_3phen^+\ SbCl_6^- \rightleftharpoons SbCl_4phen^+\ Cl^- + PhPCl_4$$
$$\Downarrow\Uparrow$$
$$PhPCl_5^-$$

which would be pushed to the right by precipitation of the antimony complex. Further work would be necessary to substantiate this hypothesis.

2,2'-dipyridyl similarly forms a 1:1 complex with $PhPCl_3^+\ SbCl_6^-$. In a nitrobenzene solution containing equimolar amounts of the reactants a peak was found on spectrum accumulation at +137.9 ppm. There was, on some accumulations an indication of a second peak at +153.2 ppm but the signal was hardly above the noise level even after 1024 scans. The relative intensity of this peak is $\leqslant$25:100.

$PhPCl_3dipy^+\ SbCl_6^-$ may be prepared from nitroethane solution without difficulty. The solid state ^{31}P n.m.r. spectrum showed a broad line at +162.6 ppm. The solid

state shift of this and other $PhPCl_4$ and $PhPCl_3^+$ $SbCl_6^-$ complexes of phenanthroline and dipyridyl lie in the range 157-166 ppm. This value is to higher field of the solution peaks and corresponds more closely to the solution resonance at $\sim$+153 ppm. The solid state lines were, however, too broad to distinguish conclusively between the two isomers.

The i.r. spectrum of $PhPCl_3dipy^+$ $SbCl_6^-$ was identical over the range 1650-250 cm^{-1} with that of the complex $PhPCl_3dipy^+$ PCl_6^-. $0.25PhNO_2$ discussed in the next section (except for the lines attributable to $SbCl_6^-$, PCl_6^- and $PhNO_2$) and differed considerably from those of the various $PhPCl_4dipy^+$ Cl^- samples discussed previously (Chapter 4 section 1(iv)). In the range 1650-800 cm^{-1} there are differences in the intensities and splittings of many of the lines. The spectrum in the region 800-650 cm^{-1} is somewhat simplified. Although many bands lie in the region 600-400 cm^{-1}, in the hexachlorophosphate and hexachloroantimonate salts there is a noticeable gap between 475 and 510 cm^{-1}. In the spectra of the $PhPCl_3dipy^+$ Cl^- samples there is a strong band at 490-495 cm^{-1} with a medium intensity band between 483 and 488 cm^{-1}.

TABLE 49

INFRA RED SPECTRA IN THE RANGE 650-250 cm^{-1}

$PhPCl_3dipy^+$	647w,	620w,	592w,	535s,	514s,	
PCl_6^-. 0.25 $PhNO_2$	474s,	440sbr (PCl_6^-),		377m,	258m,	
$PhPCl_3dipy^+$	534s,	513s,	469s,	459m,	452m,	438s,
$SbCl_6^-$	418s,	377m,	345s ($SbCl_6^-$),		258m	
$PhPCl_3dipy^+$ Cl^-	618w,	570sh,	532s,	516s,	496s,	487m,
from CH_2Cl_2	472s,	464s,	453s,	440s,	427m,	384m,
	330w,	313w,	287w,	254s.		

The n.q.r. spectrum of $PhPCl_3dipy^+$ $SbCl_6^-$ is given in Table 50.

TABLE 50

N.q.r. SPECTRUM OF $PhPCl_3dipy^+$ $SbCl_6^-$

77K 32.7 - 22.4 MHz

Frequency MHz	Signal/Noise	Assignment
29.82	2.0:1	^{35}Cl $PhPCl_3dipy^+$
27.96	4.0:1	
27.49	2.5:1	
25.09	2.5:1	^{35}Cl $SbCl_6^-$
24.66	2:1	
24.53 (may be multiplet)	1.5:1	
24.20	2:1	
23.99	1.75:1	
23.80	2:1	

The spectrum is consistent with the presence of one isomeric form. Each of the possible isomers would give spectra consisting of two lines in a 2:1 intensity ratio. The higher intensity line is in fact found to be split into two, giving lines at 27.49 and 27.96 MHz. As each isomer gives a similar spectrum it is not possible to decide which is present on the basis of line intensities.

In transition metal chemistry complexes of the type [117] cis-L_2MCl_4 and L_3MCl_3 (L = pyridyl, PEt_3, $AsEt_3$, and M = Re, Os, Ir, Pt) chlorine atoms trans to another chlorine are generally found at higher n.q.r. frequency than chlorines which are trans to the ligand L [273,274]. The ligand, L, has a trans effect which lower the n.q.r. frequency of a chlorine atom trans to itself and a cis effect which raises the n.q.r. frequency of a cis located chlorine atom. If this applies to phosphorus complexes, as may be suggested by the results of PCl_5.pyridine, then for isomer II (Chapter 4 section 1(iv)) we should expect the signals from the two equivalent chlorines to be at a higher frequency than the single chlorine. Any cis effect from the phenyl group should equally effect all the three chlorine atoms. The expected spectrum is opposite to that observed.

The alternative structure I has two chlorines trans to a pyridine ring and one chlorine trans to the phenyl ring. The splittings between the signals from the two chlorines will therefore depend upon the relative magnitudes of the trans effect of the pyridine and phenyl groups. If the pyridine ring has a greater trans effect then the two

chlorines would be at lower frequency than the single chlorine, as observed.

The average frequency of the 27.49 and 27.96 MHz lines is 27.78 MHz. This is very similar to the average frequency of the lines found in $PhPCl_4.dipy.PhNO_2$ (27.81 MHz). This suggests that similar isomers are present in each case (The low intensity of the $PhPCl_4.dipy.PhNO_2$ signal would make the expected line at 29.8 MHz undetectable). The difference in the i.r. spectra of $PhPCl_4.dipy$ and $PhPCl_3dipy^+$ $SbCl_6^-$ (and PCl_6^-) below 640 cm^{-1} would, however, suggest that different species were present. A possible explanation is that the $PhPCl_4.dipy$ complex is in fact a mixture of isomers, the second isomer being undetectable in the n.q.r. spectrum due to the low signal level. The variation of the composition with preparation would explain the varying i.r. spectrum of $PhPCl_4.dipy$.

(ii)Phenyltrichlorophosphonium Hexachlorophosphate

The synthesis and properties of this salt, and its reaction towards pyridine have been described in Chapter 3 section 3.

When equimolar quantities of $PhPCl_3^+$ PCl_6^- and 1,10-phenanthroline were dissolved in nitrobenzene, three peaks appeared in the spectrum, at +136.1, +151.1, (relative intensities 100:39) and +297.9 ppm. The first two peaks are attributable to $PhPCl_3phen^+$, whilst the third peak is assigned to PCl_6^-. The combined areas of the $PhPCl_3phen^+$ peaks were approximately equal to that of the PCl_6^- peak. Thus, unlike the pyridine complex

$PhPCl_3phen^+ PCl_6^-$ is stable in solution.

When $PhPCl_3^+ PCl_6^-$ and dipyridyl were mixed in an equimolar ratio in nitrobenzene solution a white crystalline moisture-sensitive precipitate immediately formed. Although many of the nitrobenzene absorptions are in the region of absorptions from the complex itself, comparison of the i.r. spectrum with that of $PhPCl_3.dipy^+ SbCl_6^-$ showed nitrobenzene to be present in the hexachlorophosphate salt, giving absorptions at 1527 cm^{-1} and also probably at 1348 cm^{-1} and 852 cm^{-1}. The elemental analysis showed that only a small amount of nitrobenzene was present, corresponding to the formula $PhPCl_3dipy^+ PCl_6^-.0.25\ PhNO_2$. The i.r. spectrum of this complex, and its similarity to that of $PhPCl_3dipy^+ SbCl_6^-$, has already been discussed. An insufficient quantity of the complex was prepared to investigate the complex by solid state n.m.r. or n.q.r. techniques.

(iii) Experimental

$PhPCl_3phen^+ SbCl_6^-$

3.032g (12.13 mmole) $PhPCl_4$ and 2.180g (12.10 mmole) 1,10-phenanthroline were each separately dissolved in the minimum quantity of methylene chloride. The two solutions were then mixed to give a bright yellow, slightly cloudy solution. 1.6ml (3.7g 12 mmole) $SbCl_5$ were mixed with a little methylene chloride and dripped into the solution with stirring. A bright red solution was formed in a very exothermic reaction and a brownish precipitate formed. After stirring

the solution until it had become cooler, the precipitate was filtered, washed with a little methylene chloride, then with 30/40 pet ether, and dried at the pump to produce a fawn powder.

Yield = 8.274g = 93.8% as $PhPCl_3phen^+ SbCl_6^-$

Analyses: Found C,26.70; H,1.98; N,3.79; P,3.94; Cl,45.18. $PhPCl_3phen^+ SbCl_6^-$ requires C,29.65; H,1.80; N,4.25; P,3.84; Cl,43.77.

$PhPCl_3dipy^+ SbCl_6^-$

3.832g (6.980 mmole) $PhPCl_3^+ SbCl_6^-$ and 1.144g (7.324 mmole) 2,2'-dipyridyl were each separately dissolved in the minimum quantity of nitroethane. The dipyridyl solution was slowly dripped into the $PhPCl_3^+ SbCl_6^-$ solution with stirring. This produced a bright yellow solution. After a few seconds white crystals formed. The solution was allowed to stand for a few minutes. The white crystals were then filtered, washed with methylene chloride, then 30/40 pet ether, and dried at the pump.

Yield = 1.144g = 23.2% as $PhPCl_3dipy^+ SbCl_6^-$

Analyses: Found C,25.61; H,1.98; N,4.36; P,4.19; Cl,45.24. $PhPCl_3dipy^+ SbCl_6^-$ requires C,27.25; H,1.86; N,3.97; P,4.39; Cl,45.26.

$SbCl_5$/phenanthroline complex

5.924g (10.79 mmole) $PhPCl_3^+ SbCl_6^-$ and 1.471g (8.162 mmole) 1,10-phenanthroline were each separately dissolved in the minimum quantity of nitromethane. The phenanthroline solution was slowly dripped into the $PhPCl_3^+ SbCl_6^-$ solution with stirring, forming at first a yellow solution and, in the

later stages, a precipitate. The reaction was very exothermic. The yellow precipitate only slowly came out of solution. After about ½ hour the precipitate was filtered, washed with a small amount of methylene chloride, then 30/40 pet ether and dried at the pump producing an extremely fine yellow powder.

Yield = 1.471g

Analyses: Found C,31.72; H,3.05; N,5.44; P, — ; Cl,39.35

$SbCl_4phen^+ Cl^-$ requires C,30.07; H,1.69; N,5.85; P, — ; Cl,36.99 $phenH^+ SbCl_6^-$ requires C,27.94; H,1.76; N,5.43; P, — ; Cl,41.25.

$PhPCl_3dipy^+ PCl_6^- 0.25PhNO_2$

0.438g (0.956 mmole) $PhPCl_3^+ PCl_6^-$ and 0.151g (0.967 mmole) 2,2'-dipyridyl were mixed in nitrobenzene. There was an immediate precipitate. The solid was filtered, washed with 30/40 pet ether and dried at the pump.

Yield = 0.339g = 54.9% as $PhPCl_3dipy^+ PCl_6^-$. 0.25 $PhNO_2$.

Analyses: Found C,29.93; H,2.30; N,4.73; P,9.59; Cl,49.8

$PhPCl_3dipy^+ PCl_6^-.0.25PhNO_2$ requires C,32.64; H,2.23; N,4.83; P,9.60; Cl,49.42.

3. Related Species

(i) Diphenyltrichlorophosphorane

The second member in the series $Ph_x PCl_{5-x}$, diphenyltrichlorophosphorane, has been found to retain a 5-co-ordinate structure in the solid state [59], and also in certain solvents [60]. The n.q.r. spectrum [232] of the solid is consistent with a trigonal bipyramidal structure, with both phenyl groups occupying equatorial positions, and is clearly distinguishable from the spectrum of the related $Ph_2PCl_2^+$ cation [59]. The infra red spectrum below 650 cm^{-1} also shows major differences between the parent compound and its salts.

TABLE 51

INFRA RED SPECTRUM OF Ph_2PCl_3 AND ITS SALTS 650-250 cm^{-1}

Ph_2PCl_3	618m, 571s, 568s, 527m, 497s, 489s,	
$Ph_2PCl_2^+ SbCl_6^-$	628s, 606m, 577s, 526m, ~496s, 472m, 451m, ~340sbr*	23
$Ph_2PCl_2^+ BCl_4^-$	760-620vs* 606m, 575-555s, 526m, 493s, 472m 461m, ~400w, 348w	23
$Ph_2PCl_2^+ PCl_6^-$	631s, 606m, 576s, 558m, 526m, 497s, ~440sbr* 347w.	

* absorptions mainly attributable to counter ion

The solid state ^{31}P n.m.r. spectrum could not be found using high resolution techniques [23], although spectra from its salts are easily detected [23]. The ^{31}P n.m.r. shifts of the compound in solution are given in Table 52.

TABLE 52

CHEMICAL SHIFTS OF Ph_2PCl_3 IN VARIOUS SOLVENTS

		$\delta^{31}P$	ref.	Species present
Ph_2PCl_3	sym-$C_2H_2Cl_4$	-73	31	$Ph_2PCl_2^+ \rightleftharpoons Ph_2PCl_3$
	sym-$C_2H_2Cl_4$	-67.4	a	" "
	$CHCl_3$	-77.2	a	" "
	CH_2Cl_2	+12.6	a	Predominantly Ph_2PCl_3 *
	$PhNO_2$	+17.2	a	" *
$Ph_2PCl+Cl_2$ 1:0.98	$PhNO_2$	+25	60	" *
c.f. $Ph_2PCl_2^+ SbCl_6^-$		-93.2	126	$Ph_2PCl_2^+$

a Present work

1. Technical grade

2. Reagent grade containing ~1% ethanol

* The variation of shift with solvent suggests the presence of small amounts of $Ph_2PCl_2^+$

Ph_2PCl_3 is only slightly soluble in methylene chloride and nitrobenzene. From the ^{31}P n.m.r. shifts the compound is predominantly, if not completely, molecular in these solvents. The compound is far more soluble in sym-tetrachloroethane and chloroform, but partially ionises in these solvents.

Ph_2PCl_3 dissolved as a molecular species when no interaction with the solvent is possible. The covalent bonding, however, is very weak and the compound may become partially ionised by the addition of weak chloride ion acceptors e.g. hydrogen chloride and chlorine [60]. Chloroform is capable of producing adducts with chloride ions [254-6] both in the solid state and solution, by hydrogen-bonding[255]. Although no investigations have been made with sym-tetrachloroethane, the similarity of the species would suggest that similar adducts would be possible. The adduct formation would promote solubility and would also suppress formation of adducts of the chloride ion with other weak acceptors. Thus there is no adduct formation when $PhPCl_4$ is added to the solution (Chapter 4 section 1(ii)), the $PhPCl_4$ being too weak an acceptor to abstract the chloride ion from the solvate species.

The slightly lower shift for Ph_2PCl_3 in this work, compared with that of Denney et al [60], may be due to small amounts of hydrogen chloride, formed by partial hydrolysis of Ph_2PCl_3 promoting ionisation.

Thus, under many conditions, Ph_2PCl_3 exists as a molecular species, albeit very weakly bonded. Attempts were therefore made to determine the acceptor properties of the molecule. Tetrapentyl ammonium chloride was dissolved in a saturated solution of Ph_2PCl_3 in nitrobenzene. A small upfield shift occurred with an approximately 2.8:1 excess of tetrapentyl ammonium chloride, from +17.2 ppm to +31.4 ppm, but this is only 6.4 ppm higher than the shift found by Denney et al [60] for the phosphorane. Although this value

may indicate some co-ordination, according to

$$Ph_2PCl_3 + Cl^- \rightleftharpoons PhPCl_4^-$$

it may equally be explained by the equilibrium

$$Ph_2PCl_2^+ + Cl^- \rightleftharpoons Ph_2PCl_3$$

being pushed to the right by the excess chloride ions present. Without knowing the shift of the un-ionised phosphorane (the solution of Denney [60] may still contain a small amount of $Ph_2PCl_2^+$) it is difficult to determine which equilibrium is operative. Due to the low solubility of Ph_2PCl_3 in nitrobenzene, making hydrolysis by small amounts of residual water appreciable, further chloride ions could not be added without extreme precautions to prevent hydrolysis, which would favour ionisation [60] to the cation.

Several of the solid substituted chlorophosphate salts have been prepared in this work by fusing the chloride and parent phosphorane. Equimolar amounts of tetrapentyl ammonium chloride and diphenyltrichlorophosphorane were then fused. The i.r. spectrum of the solid product, however, showed the presence of unchanged Ph_2PCl_3 and $(C_5H_{11})_4N^+ Cl^-$.

Attempts were then made to detect an adduct with a bidentate pyridine ligand. As Ph_2PCl_3 never appears to be completely ionic in solution, the acceptor properties of $Ph_2PCl_2^+ PCl_6^-$ were examined. There was no extra peak or shift in the $Ph_2PCl_2^+$ peak position on the addition of 2,2'-dipyridyl, showing no co-ordination to have taken place. Peaks were found at -89.0 ($Ph_2PCl_2^+$) and +299.3 (PCl_6^-) of approximately equal intensity. Similarly there was no change in shift when phenanthroline was added to Ph_2PCl_3 in sym-tetrachloroethane (δ^{31} P found -69.7 ppm).

Ph_2PCl_3 thus appears to have very weak, if any, acceptor properties towards chloride or pyridine ligands. The co-ordination properties of phosphorus pentachloride seem to have been completely removed by the substitution of two chlorines by phenyl groups. When only one group has been substituted, extensive acceptor properties still remain (Chapter 4 sections 1 and 2).

Due to the lack of detectable acceptor properties found with Ph_2PCl_3, Ph_3PCl_2 was not examined. Although the compound synthesised in this laboratory is ionic in nitrobenzene, Denney et al [60], and also Wiley and Stein [58], found it to be partly covalent in this solvent. Thus under completely anhydrous conditions it may be possible to obtain molecular Ph_3PCl_2. This compound has the possibility of acceptor properties towards, say, chloride ions, but the extent of co-ordination is expected to be very small.

(ii) Methyltetrachlorophosphorane

Beattie et al [78] showed that the solid state infra red spectrum of $MePCl_4$ was consistent with an ionic formulation, $MePCl_3^+ Cl^-$. This was confirmed by the solid state ^{31}P n.m.r. shift [23] of -119 ppm, being in the four co-ordinate region of the spectrum, and similar to the shift of $MePCl_3^+ AlCl_4^-$ (-117 ppm). The n.q.r. spectrum was also consistent with an ionic structure in the solid state, giving signals at 30.82 and 31.31 MHz.

In carbon disulphide, methylene chloride and benzene $MePCl_4$ is molecular with probable C_{2v} symmetry [78]. The ^{31}P n.m.r. spectrum of the complex in methylene chloride

indeed gave a peak at +39.7 ppm, attributable to a mainly, but not necessarily completely molecular formulation. The shift in nitrobenzene solution was slightly lower (+34.1 ppm) perhaps showing some ionisation.

The compound was prepared by J. Lincoln as described in Chapter 2 section 1(ii)f. The white powder was only slightly soluble in nitrobenzene but a little more soluble in methylene chloride. Due to the strong solvent dependence on acceptor properties of $PhPCl_4$ towards chloride ions, nitrobenzene was chosen as the solvent for the investigations.

On addition of tetrapentyl ammonium chloride to a nitrobenzene solution of $MePCl_4$, the ^{31}P n.m.r. shift became more positive. The maximum shift observed was +197.1 ppm, although this may not be the limiting shift of the species. An insufficient quantity of $MePCl_4$ was available for a complete investigation of its properties, but the shift would suggest that $MePCl_5^-$ is formed with relative ease. As the methyl group is electron donating, $MePCl_4$ is expected to be a poorer acceptor than $PhPCl_4$. The methyl group is far smaller than a phenyl group, however, so will not provide as much steric hindrance to adduct formation.

The acceptor properties towards bidentate pyridines were studied using $MePCl_3^+ AlCl_4^-$. This complex is a white solid, extremely soluble in nitrobenzene and methylene chloride, giving a ^{31}P n.m.r. shift in the former solvent of -119.1 ppm. No shift of the n.m.r. signal occurred on addition of dipyridyl in nitrobenzene solution ($\delta^{31}P$ -119.1 ppm before addition, -119.4 after addition). On

addition of 1,10-phenanthroline, however, a large amount of white precipitate formed. The remaining solution showed a weak line at +147.1 ppm, indicative of the formation of $MePCl_3phen^+$. The solution was too weak to observe any peaks of lower intensity from other possible isomers. Another line, of greater intensity, was found at -78.5 ppm. This is in the correct region of the spectrum to be due to a complex of the partial hydrolysis product $MeP(O)Cl_2$ with the then liberated $AlCl_3$ (c.f. δ^{31} P $EtP(O)Cl_2.AlCl_3$ -77 ppm [89]).

The white solid, although containing a significant amount of phosphorus (2.61%) did not analyse as $MePCl_3phen^+$ $AlCl_4^-$, or as its nitrobenzene solvate. Furthermore there was no strong band at 495 cm^{-1} attributable to $AlCl_4^-$. The i.r. spectrum showed only weak or medium intensity bands between 650 and 470 cm^{-1}, but many intense bands below 470 cm^{-1}. This region seems very low for P-Cl stretches if no bands are found above this figure. The i.r. spectrum contained a strong absorption at 1522 cm^{-1} suggesting the presence of nitrobenzene.

Analyses: Found C,39.53; H,3.59; N,8.50; P,2.61, Cl,33.35; Al,5.52 Total = 92.9% $MePCl_3phen^+$ $AlCl_4^-$. $PhNO_2$ requires C,36.56; H,2.59; N,6.73; P,4.96; Cl,39.77; Al,4.32; Total = 94.93% $MePOCl_2.AlCl_3.$ $2PhNO_2$ requires C,30.46; H,2.56; N,5.47; P,6.04; Cl,34.59; Al,5.26; Total = 84.38%.

TABLE 53

INFRA RED SPECTRUM OF $MePCl_3^+ AlCl_4^-$/PHENANTHROLINE COMPLEX 660-250 cm^{-1}

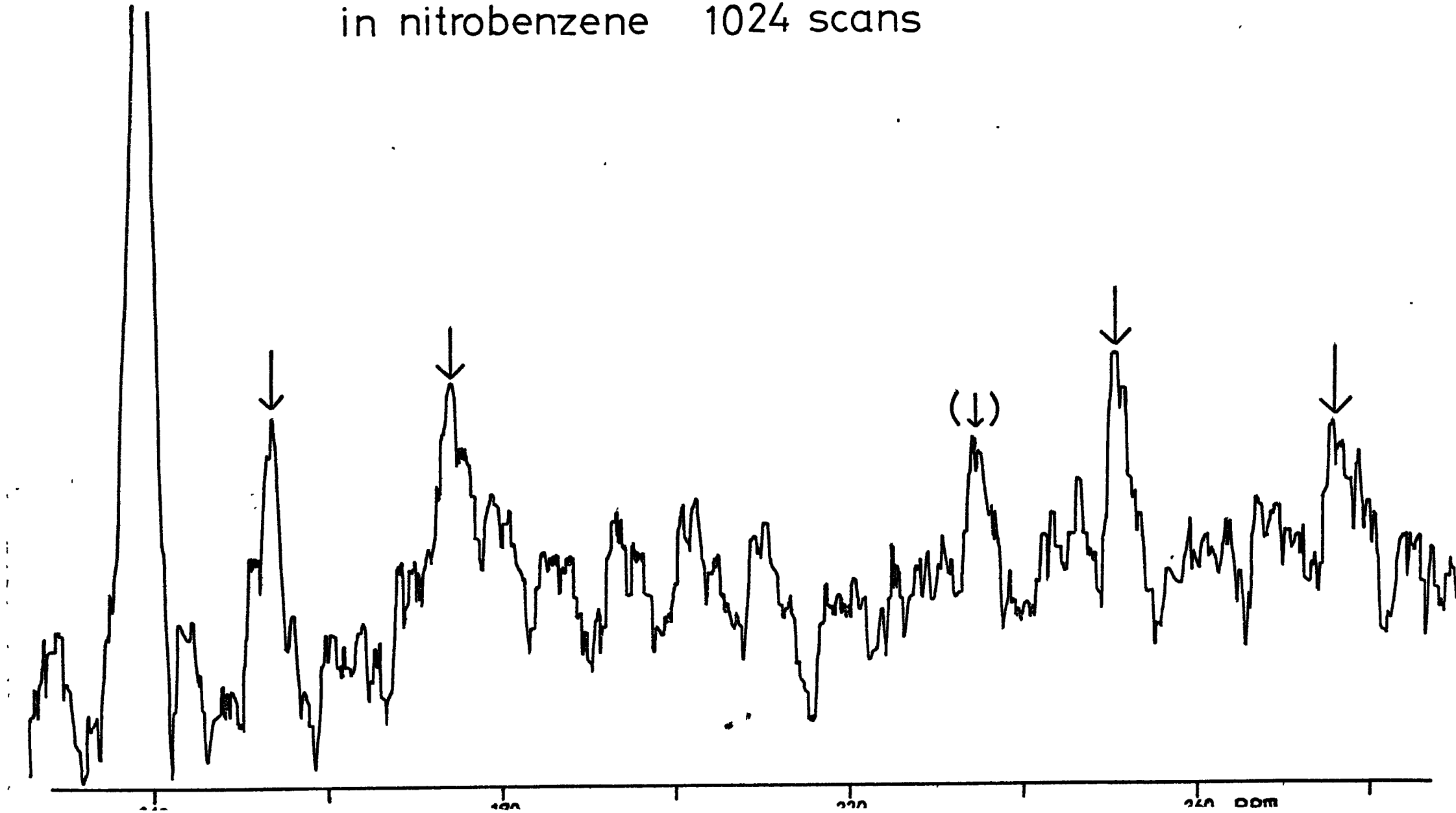
652s, 618w, 567w, 536w, 508w, 468s,
453s, 437s, 422sh, 418w, 392s, 362sh,
320s, 308s, ~295sh, ~285sh

Pyridine has been suggested to attack $MePCl_3^+ AlCl_4^-$ to produce $MePCl_4$ and $AlCl_3$.pyr [257]. A similar reaction may occur with bidentate pyridines and the product may be contaminated with aluminium trichloride complexes.

Much further work is necessary for a complete understanding of this system, and for a more extensive comparison with the acceptor properties of phenyltetrachlorophosphorane. A simpler route to the formation of $MePCl_4$ would seem desirable to produce enough material for a more thorough investigation. One possible route, in view of the great solubility of $MePCl_3^+ AlCl_4^-$ in methylene chloride, would be to add a solution of a large tetraalkyl ammonium chloride in methylene chloride to a solution of $MePCl_3^+ AlCl_4^-$ in the same solvent. This would lead to crystallisation of the only moderately soluble $MePCl_3^+ Cl^-$.

The second member of the methylchlorophosphorus(v) series, Me_2PCl_3, is ionic in the solid state. It was found to be highly insoluble in all common solvents tried, and would not even dissolve when 1,10-phenanthroline, or tetrapentylammonium chloride were present. The properties of the compound were not investigated further.

Fig 29 ^{31}P n.m.r. spectrum of $PhPCl_2Br_4$ + dipyridyl in nitrobenzene 1024 scans



(iii) Phenyldichlorotetrabromophosphorus(v) $PhPCl_2Br_4$

An attempt was made to produce $PhPCl_2Br_2$ by the method of Meisenheimer [125]. The yellow solid produced analysed as $PhPCl_2Br_4$. Michaelis has previously isolated this complex by the addition of bromine to $PhPCl_2Br_2$ prepared by a second method [118].

The compound gave a solid state ^{31}P n.m.r. line at -66.6 ± 1.5 ppm. The shift compares with the solid state shifts of $PhPCl_3^+ SbCl_6^-$ (-88 ppm), $PhPCl_3^+ BCl_4^-$ (-101 ppm), and $PhPBr_3^+ Br^-$ (+4 ppm). Assuming a linear relationship between the shifts of $PhPBr_{3-x}Cl_x^+$, as found with $PBr_{4-x}Cl_x^+$ salts [100,101], the predicted shifts for $PhPBrCl_2^+$ and $PhPBr_2Cl^+$ are -61.7 ± 6.5 ppm and -28.9 ± 6.5 ppm respectively. The solid state ^{31}P n.m.r. spectrum is then consistent with the structure $PhPCl_2Br^+Br_3^-$.

This conclusion is unaltered if the solution shift of $PhPCl_3^+ SbCl_6^-$ (-100.5 ppm) is used. The predicted shift is then -70.3 ppm for $PhPCl_2Br^+$ and -35.1 ppm for $PhPClBr_2^+$.

Although the compound was insoluble in nitrobenzene it was soluble in nitrobenzene saturated with 2,2'-dipyridyl (but not with 1,10-phenanthroline). On spectrum accumulation the ^{31}P n.m.r. spectrum showed peaks at 137.6 ppm and 151.9 ppm attributable to $PhPCl_3dipy^+$. In the lower field region peaks were found at -154.0 ppm and -30.7 ppm, assignable to $PhPBr_2$ ($\delta^{31}P$ -152.4 ppm [89]) and a hydrolysis product ($\delta^{31}P$ $PhPOCl_2$ -34 ppm [89]). There were also a number of small but reproducible lines to the high field of $PhPCl_3dipy^+$ (see Table 54 and Fig.29). These peaks, if genuine, may indicate the existence of $PhPCl_xBr_{3-x}dipy^+$ species.

TABLE 54

HIGH FIELD ^{31}P n.m.r. SIGNALS FROM $PhPCl_2Br_4$/DIPYRIDYL IN NITROBENZENE

Accumulation						
(a)	+136.5	+150.7	+170.5		+248.9	+276.5
(b)	+138.0	+153.2	+173.6	(+237.3?)	+250.7	+277.7
(c)	+138.4					

As substitution of bromine for chlorine usually causes an upfield shift[210,100,101] the resonances of the $PhPCl_xBr_{3-x}dipy^+$ cations would indeed be expected to occur to higher field of the $PhPCl_3dipy^+$ signal. The exact assignment of the peaks is very difficult since each species may exist in two or more isomeric forms. Each isomer may be present and give separate ^{31}P n.m.r. signals.

The probable existence of the chloro-bromo-adducts suggests the possibility of other six co-ordinate bromo-complexes. Because of the insolubility of the starting compound, and weak acceptor properties of even the parent chloride, $PhPCl_2Br_4$ is probably not the best compound for future investigations. A catechyl derivative would be far better. The mixed catechyl chlorobromides are soluble in methylene chloride and the parent chloride, $catPCl_3$, is an excellent acceptor (Chapter 5). Although stoichiometric compounds $catPCl_{3-x}Br_x$ (x = 1-3) can be isolated in the solid state [23], on dissolution the mixed compounds undergo halide scrambling reactions, similar to those found with phosphorus(III) compounds. There would, however, probably be sufficient difference between the shifts of the various species to analyse the spectra.

CHAPTER 5

CATECHYL DERIVATIVES OF PHOSPHORUS PENTACHLORIDE

1. Acceptor Properties of Catechyl Phosphorus Trichloride (2,2,2-trichloro-1,3,2-benzodioxaphosphole)

(i) Introduction

Catechylphosphorus trichloride was first prepared by Anschütz [134,258]. His work has been recently reinvestigated by Ramirez et al [62]. The compound has been intensively studied by Gross [210,259-64] as a chlorinating agent with superior physical properties to phosphorus pentachloride. No acceptor properties of the molecule have, however, been recorded. The compound was studied in this work as an example of a bis substituted PCl_5 derivative with fairly electronegative substituents. It is extremely soluble in nitrobenzene, methylene chloride, hexane and diethyl ether. ^{31}P n.m.r. indicates a five co-ordinate molecular structure in solution. Chemical shifts found are +26 [224] (unspecified solvent), +26.4 in chloroform [210], +25.7 in hexane [62], +26.4 in benzene, +26.2 [62] (+26.3[a]) in methylene chloride, +26.1 in diethyl ether [62], +26.9 in acetonitrile and +27.2[a] in nitrobenzene (a-determined in this work).

The n.q.r. spectrum of the solid shows signals [234] of equal intensity at 27.841, 31.233 and 31.761 MHz, consistent with a trigonal bipyramidal structure, with the catechyl group occupying one axial and one equatorial position.

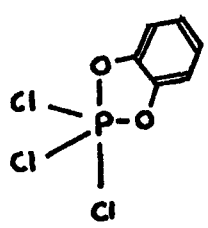
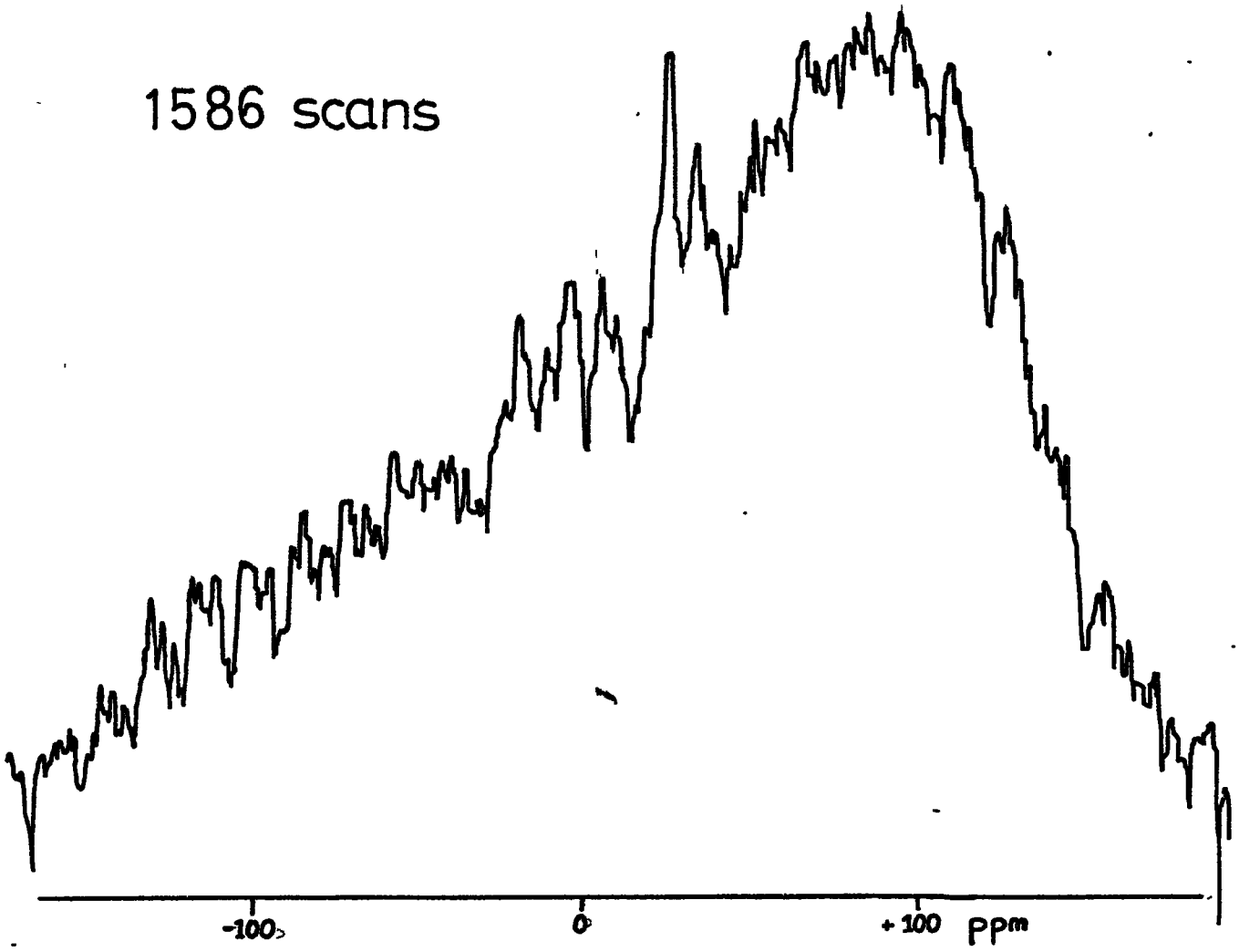


Fig30 ^{31}P n.m.r. solid state spectrum of $(C_6H_4O_2)PCl_3$



The solid state ^{31}P n.m.r. spectrum is, however, difficult to interpret. With both a commercial sample, and a laboratory-synthesised sample (Fig.30), a narrow peak was found at +93.0 ± 1.3 ppm with a shoulder on the low field side. On deconvolution the shoulder corresponded to a peak maximum at -11.4 ± 6.4 ppm with the two peaks of approximately equal area. The peak maxima do not seem to correspond to any reasonable structure. $CatPCl_2^+$ $catPCl_4^-$, for example, would have peaks at approximately -70 and +160 ppm (Chapter 5 sections 2(ii) and 1(ii)a). A shift of +93.0 ppm is consistent with phosphorus co-ordinated by six oxygens (Appendix 1) but it is difficult to suggest a structure giving a peak at -11.4 ppm.

If the compound did consist of two, presumably ionic, species there is a change of structure between solid and solution. Confirmation of this is difficult. The compound is probably soluble in nujol (c.f. hexane) and a mull will then show a solution i.r. spectrum. The spectra as a nujol mull and as a hexane solution were indeed identical. A thin solid film on KBr plates showed a spectrum differing from these but it was not certain that the film had not hydrolysed.

An alternative explanation of the spectrum is that the compound is five co-ordinate and has an anisotropic n.m.r. shift. The structure would then agree with that suggested by n.q.r. at 77K (although there may be a change of phase between 77K and n.m.r. temperature a change of structure is unlikely). Biscatechyl phosphorus monochloride (Chapter 5 section 3) is the only other five co-ordinate phosphorus

compound to have given a detectable solid state peak. The inability to detect spectra of $PhPCl_4$ and Ph_2PCl_3 has been possibly attributed to signal broadening by the anisotropic environment of the phosphorus [23]. The detection of solid spectra of catechyl derivatives is probably due to the relative distance of the aromatic rings from phosphorus.

Several observations mitigate against shift anisotropy. The spectrum resembles theoretical lineshapes for compounds with axial shift symmetry [108]. The ratio of the deconvoluted peak areas should be 2:1 with the most pronounced peak (+93 ppm) having the largest area. The ratio is within experimental error to that found. The weighted average shift should be equal to the solution shift, however. This is not found, the weighted average being $+65.8 \pm 3.0$ ppm.

Superposed on the solid spectrum of the commercial product were narrow "solution" peaks at +82.3 ppm, -0.1 ppm and +27.8 ppm (the laboratory-prepared compound gave a single "solution" peak at +26.5 ppm). It would be difficult to explain several "solution" peaks by the self-diffusion mechanism in the five co-ordinate solid unless the molecule remains orientated in the crystal. This seems unlikely.

Before a definite assignment of a spectrum is made much more information is needed on anisotropic spectra and on catechyl phosphorus trichloride from other physical techniques.

Catechyl phosphorus trichloride (prepared as in Chapter 2 section 1(ii)c) is violently hydrolysed by water, producing ultimately phosphoric acid [259]. No hydrolysis was observed in solution in this work, presumably due to its high solubility making hydrolysis by small amounts of residual moisture negligible.

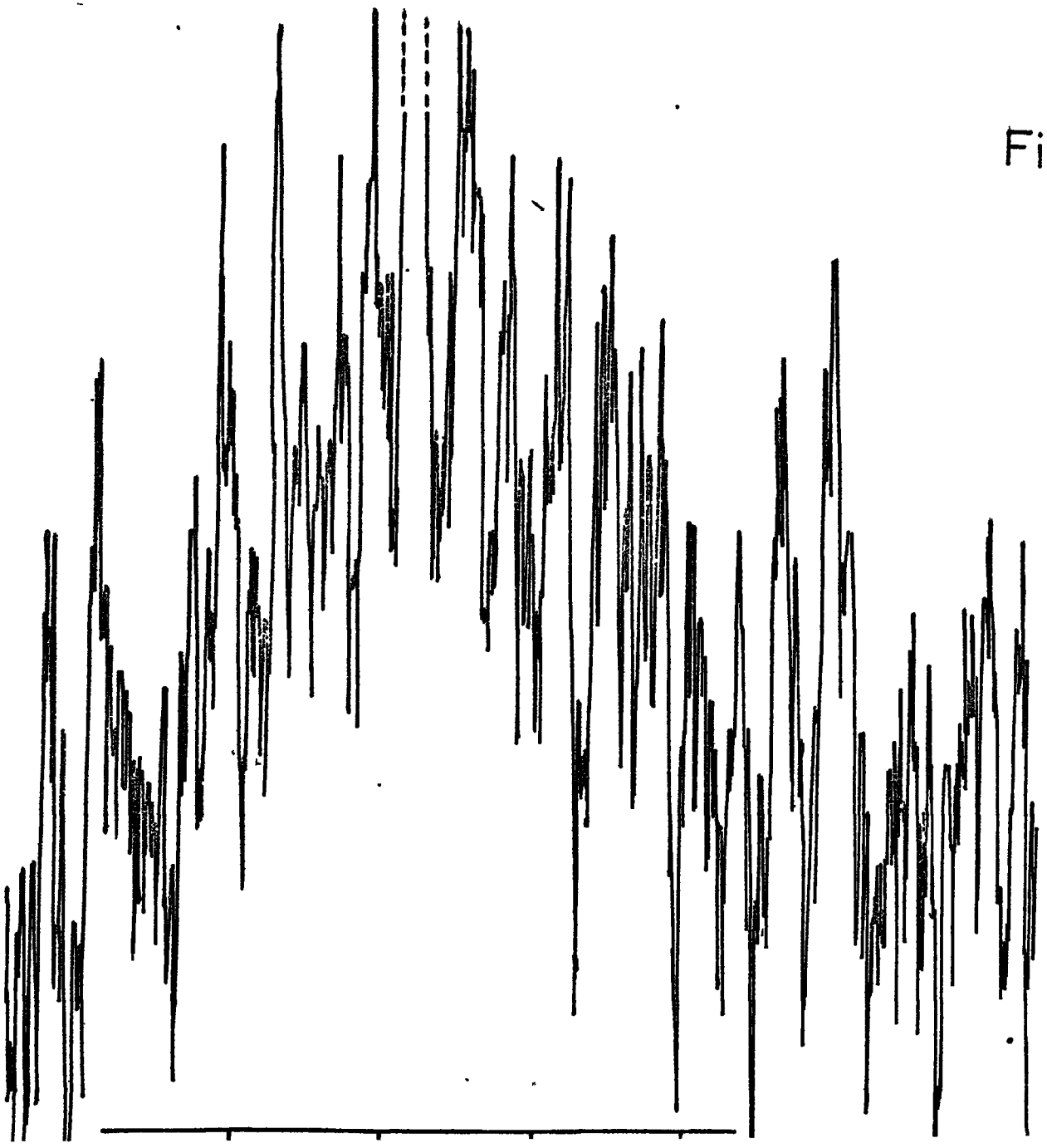
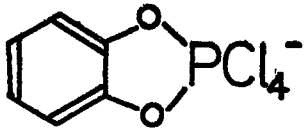


Fig31 ^{31}P n.m.r. solid state spectrum of

$(C_5H_{11})_4N^+$ 

952 scans

(ii) Present Work

(a) Acceptor Properties towards Chloride Ions

A 1:1 solution of tetrapentyl ammonium chloride and catechyl phosphorus trichloride in nitrobenzene produced a sharp peak at +150.7 ppm. This is indicative of at least partial adduct formation to give $(C_6H_4O_2)PCl_4^-$. As the maximum shift obtained by adding excess tetrapentyl ammonium chloride was +157.3 ppm, the ion is 95% associated in the 1:1 molar ratio solution. A 1:1 molar ratio in methylene chloride gave a shift of +157.3 ppm, showing complete association in this solvent. Catechyl phosphorus trichloride thus appears to be an excellent acceptor towards chloride ions, $catPCl_4^-$ being far more associated than $PhPCl_5^-$ under similar conditions (Chapter 4 section 1(ii)).

When solutions of tetrapentyl ammonium chloride and catechyl phosphorus trichloride in carbon tetrachloride were mixed a bright yellow liquid upper layer formed. The ^{31}P n.m.r. spectrum of this layer contained a very sharp line at +159.1 ppm, showing the formation of completely associated $(C_5H_{11})_4N^+$ $catPCl_4^-$. When the yellow liquid was placed under vacuum, a small amount of evaporation produced a pale yellow solid, which analysed as $(C_5H_{11})_4N^+$ $catPCl_4^-$.

$(C_5H_{11})_4N^+$ $catPCl_4^-$ showed a narrow ^{31}P solid state line at +162.0 $\pm$ 1.7 ppm (Fig.31), thereby confirming the limiting shift found by solution data. The shift falls between those found for $PhPCl_5^-$ and cat_3P^- (+82 ppm [265]). A sharp liquid line was observed on the top of the broad solid line at +158.7 ppm.

The i.r. spectrum of the complex showed a lowering of frequency of lines attributable to P-Cl stretches compared with $catPCl_3$ and a great simplification of the spectrum in this region. As found with the $PhPCl_5^-$ salts the spectrum between ~1600-800 cm^{-1} is obscured by a very broad band due to the tetraalkylammonium cation.

$(C_3H_7)_4N^+$ $catPCl_4^-$ was isolated by mixing equimolar amounts of the reactants in methylene chloride solution. This produced a yellow solid, the i.r. spectrum of which was identical below 650 cm^{-1} to that of $(C_5H_{11})_4N^+$ $catPCl_4^-$. The solid, however, did not stabilise in the n.m.r. machine and so no solid state line could be observed.

TABLE 55

INFRA RED SPECTRA OF $catPCl_4^-$ SALTS 650-250 cm^{-1}

$(C_5H_{11})_4N^+$	620s,	596m,	586m,	552w,	522s,	473s,
$catPCl_4^-$	448s,	425s,	361s,	342w,	298w	
$(C_3H_7)_4N^+$	622s,	598w,	586w,	552w,	522s,	468s,
$catPCl_4^-$	447s,	424s,	352s,		300w,	286w
c.f. $catPCl_3$	644m,	622w,	588s,	537s,	500w,	458s,
	430w,	403w,	376w,	317w,	264m	

Both solids are very moisture-sensitive, but are completely stable under an atmosphere of nitrogen. The n.q.r. spectrum of neither of these compounds could be observed.

When methylene chloride solutions containing equimolar quantities of $PhPCl_4$ and $catPCl_3$ were mixed, a bright yellow solid immediately crystallised out of solution. The analysis

corresponds to a 1:1 adduct of the two compounds, whilst the solid state ^{31}P n.m.r. spectrum gave signals at -101.6 ppm ($PhPCl_3^+$) and +163.2 ± 5.5 ppm ($catPCl_4^-$) corresponding to the structure $PhPCl_3^+$ $catPCl_4^-$. The i.r. spectrum could also be interpreted in terms of this structure.

TABLE 56

I.r. SPECTRUM $PhPCl_3^+$ $catPCl_4^-$ 650-340 cm^{-1}

647s', 618s'', 608 sharp m', 590m'', 568m, 543s', 517s'', 496w, 472s'', 458w', 443s'', 439s'', 400m, 362s'', 340w''

' attributable to $PhPCl_3^+$ see Table 33

'' attributable to $catPCl_4^-$ see Table 55

Unlike the tetraalkyl ammonium salts of $catPCl_4^-$ the spectrum remained sharp over the range 4000-250 cm^{-1}, and lines corresponding to the cation and anion were clearly distinguished.

A broad multiplet at 31.01, 31.16, 31.28 MHz (S/N 5.5:1, 10:1, 9:1 respectively) was found in the n.q.r. spectrum of the highly crystalline salt. Although the absorptions may all be assigned to $PhPCl_3^+$ (c.f. Ref.59) there may be an overlap of lines attributable to the cation and anion. No other lines were found attributable to the anion.

Catechyl phosphorus trichloride is thus a strong enough chloride ion acceptor to abstract a chloride ion from phenyltetrachlorophosphorane, which may itself act as a chloride ion acceptor. The complex is the first example of an organophosphorus(v) salt which is formed by chloride ion transfer from a molecular organophosphorus(v) donor to an organophosphorus(v) acceptor. The possibility of

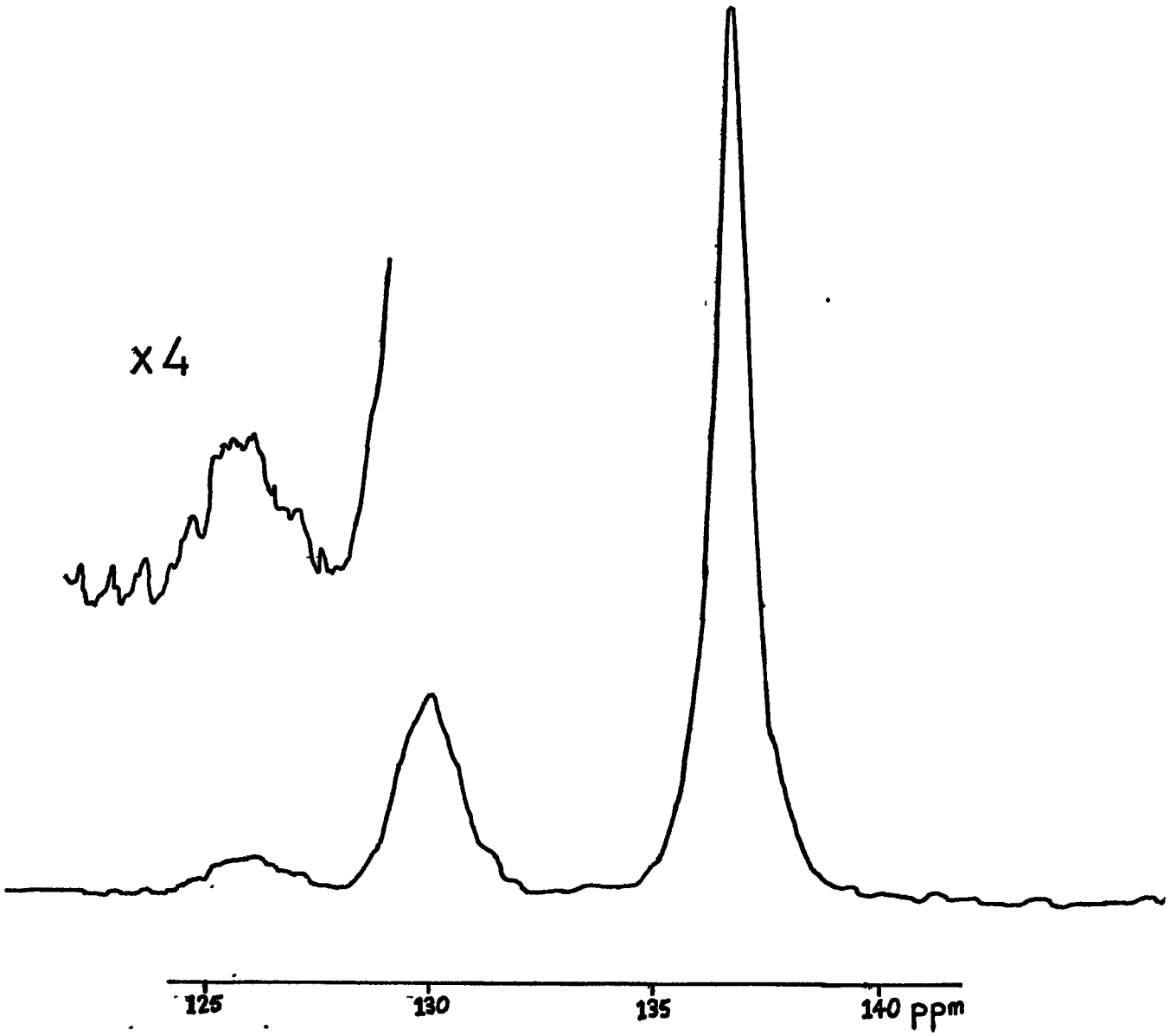


Fig32. ^{31}P n.m.r. spectrum of $(C_6H_4O_2)PCl_3$ + pyridine (1:2 molar ratio) in nitrobenzene. 81 scans

existence of such a species will depend on the relative donor and acceptor properties of the two components. $PhPCl_4$ is a weak chloride donor and weak chloride acceptor. Catechyl phosphorus trichloride is a very poor chloride donor but very good acceptor. Thus $PhPCl_3^+$ $catPCl_4^-$ is formed. Phosphorus pentachloride and catechyl phosphorus trichloride do not interact in solution [210]. PCl_5 is a slightly better acceptor than $catPCl_3$ as shown by the lack of dissociation of hexachlorophosphate salts in nitrobenzene. $CatPCl_3$ is a very poor chloride donor (see Chapter 5 section 2(i)), however, hence a salt is not formed.

It should be possible to prepare many salts of the above type if suitable donors and acceptors are used. This will be discussed further in Chapter 6.

(b) Acceptor Properties towards Pyridine

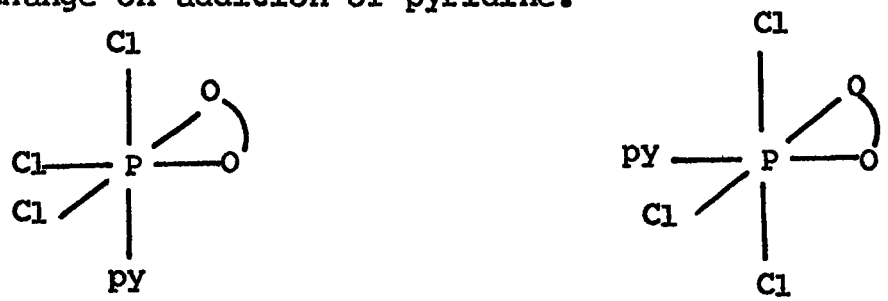
When equimolar amounts of catechyl phosphorus trichloride and pyridine were mixed in nitrobenzene solution peaks were found at +136.7 and +129.9 ppm, together with a much smaller peak at +125.9 ppm. The intensity ratios of these three peaks were 100:36.4:6.5. The peaks all correspond to six co-ordinate species. As the amount of pyridine was increased relative to catechyl phosphorus trichloride the smaller peak increased slightly in intensity. The relative intensity of the other two peaks remained constant (Table 57).

TABLE 57

^{31}P n.m.r. SHIFTS OF $(C_6H_4O_2)PCl_3$/PYRIDINE IN NITROBENZENE

Ratio $catPCl_3$/pyridine	δ^{31}P			Relative intensities	
	a	b	c	a:b:c	a:b+c
1:1	+125.9	+129.9	+136.7	6.5:36.4:100	4.7:100
2:1	+125.9	+130.1	+136.9	7.2:29.9:100	5.5:100
5:1	+125.2	+129.7	+137.1	9.3:32.2:100	7.1:100

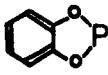
$CatPCl_3$.pyr can exist in two isomeric forms. As was shown for $PhPCl_3phen^+$, isomers may be detectable in the ^{31}P n.m.r. spectrum in favourable circumstances. This would only account for the two high field peaks whose relative intensity does not change on addition of pyridine.



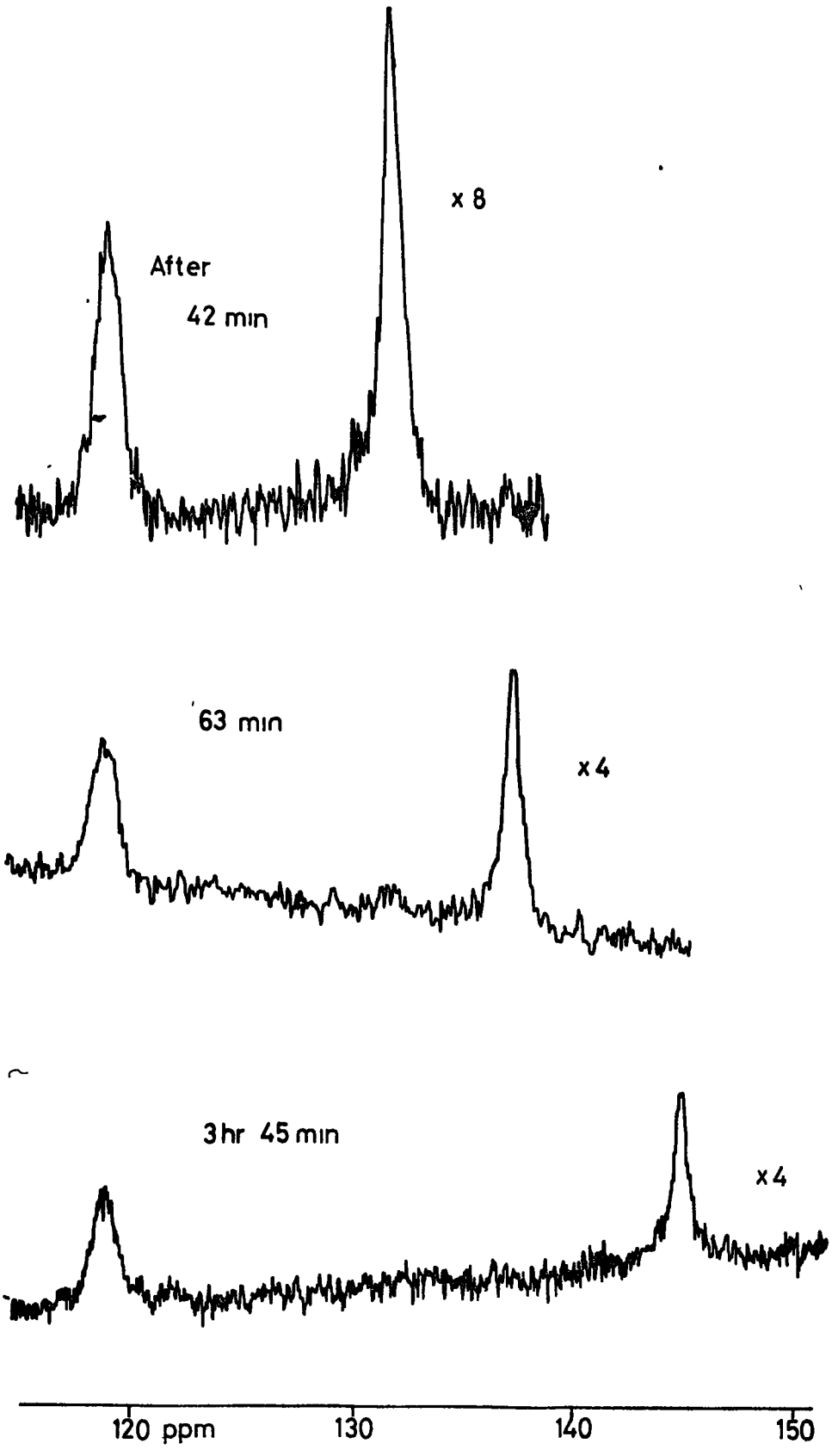
Isomers of $catPCl_3$.pyridine

The difference of shift between the two isomers is less than found with $PhPCl_3phen^+$ (Chapter 3 sections 1 and 2) but the whole range of shifts in catechyl phosphorus trichloride complexes is smaller than in phenyltetrachlorophosphorane complexes (c.f. shifts of $PhPCl_5^-$, $PhPCl_4$.py; $catPCl_4^-$, $catPCl_4$.py).

Fig33 ^{31}P n mr spectrum of



PCl_3 + dipyridyl (2 1 molar ratio) in CH_2Cl_2



The increase in intensity of the low field peak indicates that the species is more favoured in higher relative concentrations of pyridine. The peak may be assigned to the cationic species $catPCl_2py_2^+$, formed by displacement of chlorine by pyridine,

$$2py + catPCl_3 \longrightarrow catPCl_3.py + py \rightleftharpoons catPCl_2py_2^+ Cl^-$$

The assignment of the peak is confirmed by the similarity of the shift of $catPCl_2py_2^+ SbCl_6$ (δ^{31} P + 124.8 ppm Chapter 5 section 2(ii)). Each spectrum shows only one peak assignable to the cation although the cation has several possible isomers.

(c) Acceptor Properties towards Bidentate Pyridines

When a 1:1 molar solution of 2,2'-dipyridyl and catechyl phosphorus trichloride was made up in nitrobenzene, two strong n.m.r. peaks were observed, one at about +119 ppm and the other peak further upfield. Over several hours the higher field peak moved upfield to +154.7 ppm. The two peaks were then of approximately equal area. The solution simultaneously deposited a yellow solid. The reaction proceeded similarly in methylene chloride with the molar ratio $catPCl_3$/pyridine 1:1 and 2:1 (Fig.33), the results of these being given below.

TABLE 58

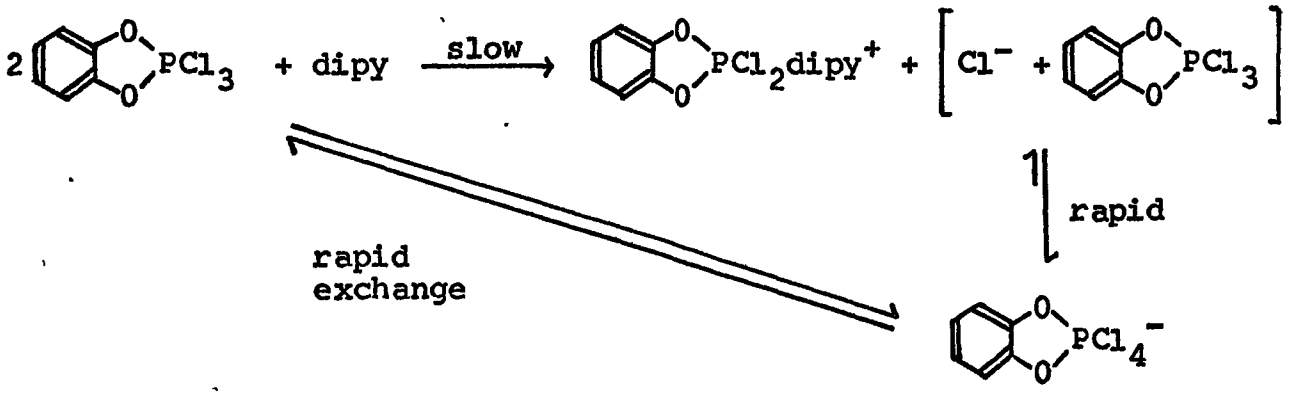
^{31}P n.m.r. SHIFTS OF $(C_6H_4O_2)PCl_3$/DIPYRIDYL SOLUTIONS IN METHYLENE CHLORIDE

1:1 $(C_6H_4O_2)PCl_3$/dipy				2:1 $(C_6H_4O_2)PCl_3$/dipy			
Time	δ^{31}P		Relative area	Time	δ^{31}P		Relative area
1 hr 28 min	+118.3	+133.9	36:64	~30 min	+118.7	+124.3	
2 hr 06 min	+118.6	+141.8		~33 min	+118.9	+127.1	42:58
2 hr 48 min	+118.8	+145.5	51.5:49.5	~42 min	+118.9	+131.8	41:59
3 hr 48 min	+118.0	+147.5		~61 min	+119.0	+137.1	
5 hr 20 min	+119.2	+150.0	59.5:43.5	63 min	+118.8	+137.3	
6 hr 45 min	+119.4	+150.8		2 hr 13 min	+118.7	+143.1	47:52
Av	+118.7			3 hr 43 min	+118.8	+145	
				4 hr 48 min	+118.9	+145.4	47:53
				Av	+118.8		

The peaks at 150.8/154.7 ppm may be attributed to slightly dissociated $catPCl_4^-$, and the peak at ~118 ppm to $catPCl_2dipy^+$. This shift is slightly different from that assigned to $catPCl_2py_2^+$. This may be due to the latter ion being predominantly or entirely in the isomeric form containing trans pyridines, this isomer being precluded from the dipyridyl complex because the ligand is bidentate. Alternatively the shift may be due to the slightly different ligand nature of pyridine and dipyridyl.

Possible isomers of $catPCl_2phen^+$ and $cat_2PCl_2dipy^+$

The movement of the anion peak may be explained in terms of a slow attack of dipyridyl on catechyl phosphorus trichloride and rapid equilibration of $catPCl_3$ with $catPCl_4^-$ as previously found.



Consider a time before reaction has gone to completion with the 1:2 molar solution in methylene chloride. Unchanged

$catPCl_3$ will be present together with the product $catPCl_2dipy^+$ $catPCl_4^-$. N.m.r. peaks will then be observed for $catPCl_2dipy^+$ and for $catPCl_3/catPCl_4^-$ in rapid exchange. $CatPCl_4^-$ is in equal concentration to $catPCl_2dipy^+$. The anion/neutral peak will be greater in intensity than the cation peak. As the reaction proceeds the $catPCl_2dipy^+$ peak will grow in absolute intensity and remain at a constant shift, whilst the $catPCl_3/catPCl_4^-$ peak will decrease in absolute intensity and slowly move to the shift position for $catPCl_4^-$. Unfortunately absolute intensity measurements could not be used reliably since the solid complex slowly precipitated. As the $catPCl_3/catPCl_4^-$ peak moves upfield, however, it does decrease in relative intensity to the cation peak. After about 33 min the mobile peak is at +127.1 ppm. If the shift for $catPCl_3$ is taken as +26.3 ppm, and $catPCl_4^-$ as +157.3 ppm the mobile peak is due to 76.9% $catPCl_4^-$ and 23.1% $catPCl_3$. Since there must be equimolar proportions of $catPCl_2dipy^+$ and $catPCl_4^-$ present (assuming the latter ion does not dissociate appreciably in this system) the intensity ratio $catPCl_2dipy^+$ to $catPCl_3 \rightleftharpoons catPCl_4^-$ will be 76.9:100 $\equiv$ 43.3:56.3. This is an excellent agreement with that observed.

The relative intensities of the 1:1 mixture are not so amenable to discussion since precipitation of a 1:2 complex will increase the ratio of dipy:$catPCl_3$ remaining in solution. The excess dipyridyl present may also make the solution formulation $catPCl_2dipy^+Cl^-$ more favourable than $catPCl_2dipy^+$ $catPCl_4^-$ + dipy.

During one run with $catPCl_3$/dipyridyl in nitrobenzene a small but definite peak was found at +133.0 ppm. This could not be detected in methylene chloride solution, but is close to the position of a probable peak in the 1:1 $catPCl_3$/phenanthroline solution in nitrobenzene. Confirmation of the small peak was very difficult because of the instability of concentrated solutions made in situ, caused by slow precipitation of the complex (the hexachloroantimonate salt was similarly insoluble in nitrobenzene). If the peak is genuine it may be attributed to the second isomeric form of $catPCl_3dipy^+$. Confirmation would only be possible by isolation of a more soluble salt, perhaps $catPCl_3dipy^+ AlCl_4^-$.

$CatPCl_2dipy^+ catPCl_4^-$ was isolated as an orange powder from the n.m.r. tube containing stoichiometric quantities of reactants in methylene chloride. The i.r. spectrum below 650 cm^{-1} showed lines attributable to $catPCl_4^-$ as well as lines assignable to $catPCl_2dipy^+$. With the reaction in nitrobenzene $catPCl_2dipy^+ catPCl_4^-$. $PhNO_2$ was isolated. The compound hydrolysed slowly in moist air and instantly on addition of water. The i.r. spectrum was identical with the unsolvated complex except for lines at 1531(s), 1348(s), and 398(w) cm^{-1} attributable to nitrobenzene.

TABLE 59

I.r. SPECTRA 650-250 cm^{-1} $catPCl_2dipy^+ catPCl_4^-$

$catPCl_2dipy^+ catPCl_4^-$

624m, 542sh, 536sh, 526s, 517s, 504s, 474s, 458m, 450m, 424s, 383m, 363m, 302w

$catPCl_2dipy^+ catPCl_4^-$. $PhNO_2$

647w, 626s, 602w, 547s, 537sh, 524s(br), 503m, 474s, 465s, 460s, 448m, 423s, 398w*, 383m, 360sh, 352sh, 303w, 287w, 267w

* $PhNO_2$

The solid state ^{31}P n.m.r. spectrum of $catPCl_2dipy^+$ $catPCl_4^-$. $PhNO_2$ showed a single broad peak at +144.8 ± 3.0 ppm with no resolution apparent (c.f. average shift of $catPCl_2dipy^+$ and $catPCl_4^-$, +138.2 ppm).

A 1:1 solution of catechyl phosphorus trichloride and 1,10-phenanthroline behaved slightly differently. Initially only one peak was present, due to the cation. $CatPCl_2phen^+$ $catPCl_4^-$ was, however, completely formed after less than 2 hours. After two hours the shifts found were +118.8 and +156.6 ppm. As the cation peak did not decrease in intensity with growth of the anion peak, as would occur if the reaction was

$$2catPCl_3 + 2phen \rightarrow 2catPCl_2phen^+ Cl^- \rightarrow catPCl_2phen^+ catPCl_4^- + phen$$

it was thought that the anion peak was not initially visible because of broadening by the reaction.

After several hours the spectrum was accumulated to detect any minor peaks. Peaks were found at +118.7, +129.9, +157.2 and +194.4 ppm, the +157.2 peak being the most intense. The peaks at +118.7 and +157.2 can be attributed to $catPCl_2phen^+$ and $catPCl_4^-$ respectively. The peak at +129.9 was only slightly above noise level. If genuine it may be from the second isomer of $catPCl_2phen^+$.

The peak at +194.4 ppm must be cationic to make the sum of the areas of the cationic species equal to that of the anion. It is assigned to PCl_4phen^+ produced either by disproportionation of $catPCl_2phen^+$ or from phosphorus pentachloride impurity in the commercial sample used.

$CatPCl_2phen^+$ $catPCl_4^-$ was isolated from a methylene chloride solution of the stoichiometric amounts of reactants,

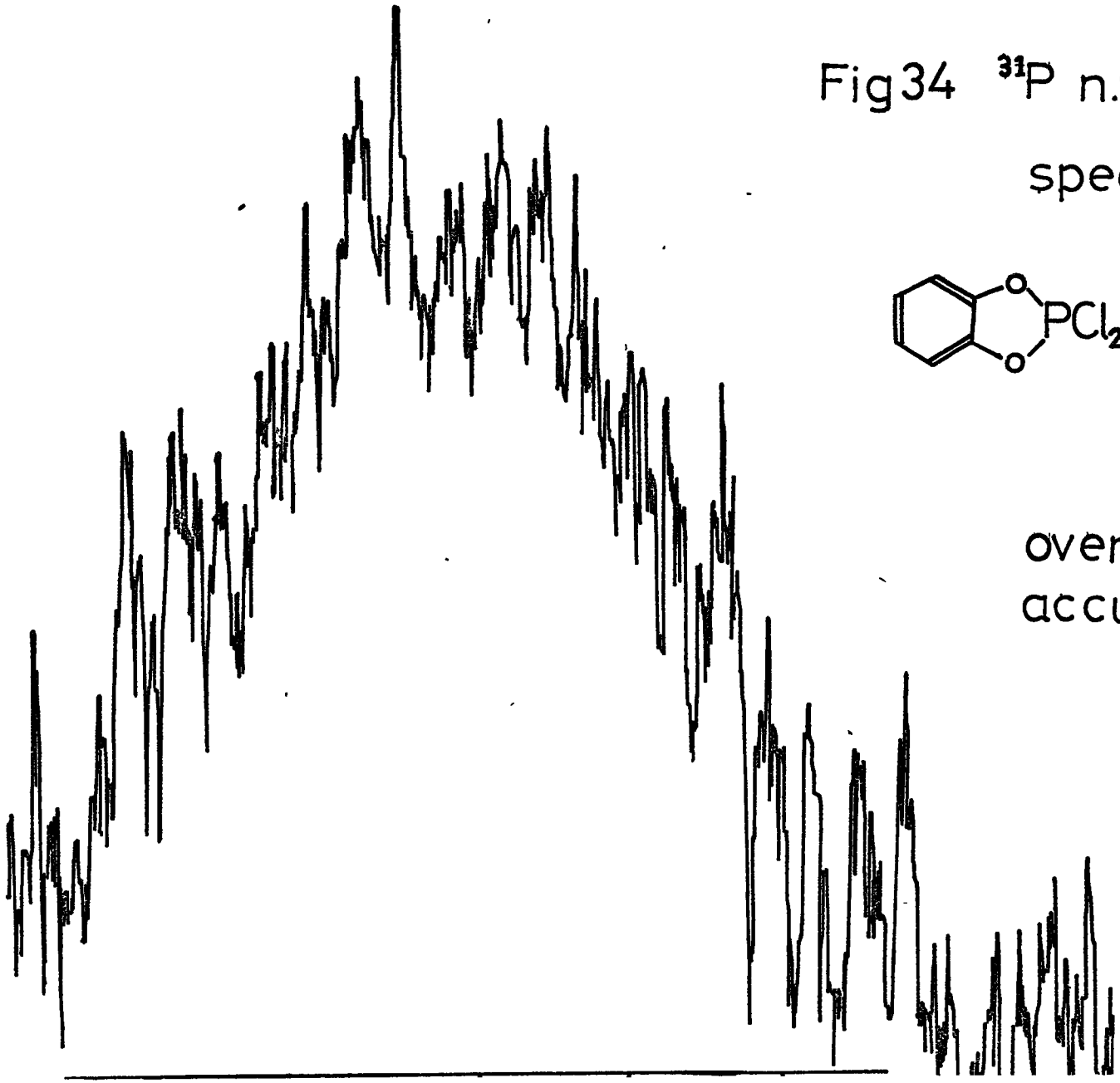
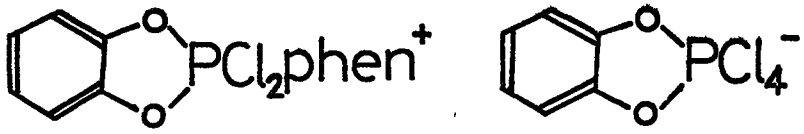


Fig 34 ^{31}P n.m.r. solid state spectrum of



overnight accumulation

after leaving the solution stirring overnight. This produced a very fine orange moisture-sensitive powder. The i.r. lines ascribed to $catPCl_4^-$ seem slightly displaced compared with other salts of this ion.

TABLE 60

I.r. SPECTRUM $catPCl_2phen^+$ $catPCl_4^-$ 650-250 cm^{-1}

634m, 621s, 613w, 596w, 570sh, 568m, 547s, 513s, 492s, 478s, 468m, 456m, 447s, 438s, 426s, 376m, 358w, 343w, 298w

The solid ^{31}P n.m.r. spectrum showed a single symmetrical line centred at +146.6 ppm with perhaps slight resolution of the two constituent peaks (Fig.34).

A number of n.m.r. tubes which precipitated solids produced a lower layer of orange crystals and an upper layer of smaller light yellow crystals. It was hoped that these might be due to selective crystallisation of different isomers. For 1:1 $catPCl_3$/dipyridyl in methylene chloride each layer was separately isolated. Both layers turned bright yellow in a nujol mull, however, and gave i.r. spectra identical to that of the previously isolated $catPCl_2dipy^+$ $catPCl_4^-$.

(d) Other Work

Catechyl phosphorus trichloride, being very soluble in common solvents, and also having strong co-ordination characteristics, is ideally suited for the investigation of co-ordination of ligands to phosphorus(v). The shifts of the unco-ordinated phosphorane in hexane and benzene are +25.7 and +26.4 ppm respectively [62]. Any large positive

shift from these values on addition of a ligand would be indicative of co-ordination.

The phosphorane was dissolved separately in the potential donor solvents diethyl ether, tetrahydrofuran, and tetrahydrothiophene. The phosphorane was extremely soluble in each solvent. To distinguish possible small shifts from co-ordination the solutions were diluted and rerun. If co-ordination occurs the peak will move to higher field with the larger excess of donor molecules. The results are shown in Table 61.

TABLE 61

δ^{31} P $catPCl_3$ IN POTENTIAL DONORS

Solvent			
Et_2O	+26.7 (~ sat)		
Tetrahydrofuran	+27.9 (~ sat)	+28.3 (~ $\frac{sat}{4}$)	+27.9 (~ $\frac{sat}{8}$)
Tetrahydrothiophene	+30.2 (~ sat)	+31.7 (~ $\frac{sat}{2}$)	+33.1 (~ $\frac{sat}{8}$)

Approximate concentration in brackets

All the solutions contained a single peak. The diethyl ether and THF solutions have very similar shifts throughout to those found with non co-ordinating solvents, so that no co-ordination seems to occur. With tetrahydrothiophene, however, an upfield shift does occur which increases with increasing dilution. Some co-ordination would then seem to be occurring.

$catPCl_3$ + ⟵⟶ $catPCl_3$·

The co-ordination of sulphur but not oxygen is indicative of class b behaviour, as found with arsenic and antimony(v) species [266] and as indicated by phosphorus pentafluoride in its preferential co-ordination of trimethylphosphine to trimethylamine [267]. It has, however, been suggested that phosphorus(v) is a non-b acceptor [266].

The solutions were not investigated over long periods to see whether slow attack on the ligand takes place (Tetrahydrothiophene reacts with PCl_5 to produce PCl_3 as is shown by the single n.m.r. peak in neat tetrahydrothiophene at -213.5 ppm. The ligand also immediately reacts with $PCl_4^+ SbCl_6^-$ in nitrobenzene to produce a yellow solid containing no phosphorus. This decomposes at room temperature but is stable at -15^oC. Its n.q.r. spectrum of a single line at 24.44 MHz, S/N 2.25:1, suggests the structure $SbCl_5$. tetrahydrothiophene, the other line expected being below noise level, but the analyses C,17.69; H,3.49; Cl,46.4; S,17.53 do not correspond to any simple formula). Attack would perhaps take place more slowly than with PCl_5 and $PCl_4^+ SbCl_6^-$ due to the lower chlorinating power of catPCl_3, shown by PCl_5 quickly and quantitatively oxidising catPCl to catPCl_3 with the concomitant reduction of PCl_5 to PCl_3. The large solubility of catPCl_3 enables ^{31}P n.m.r. signals to be obtained on a single scan of the spectrum so that spectra could be obtained even with unstable solutions. This is a further advantage over PCl_5 which is relatively sparingly soluble in most solvents. Detection is also hindered with PCl_5 since more than one species may be present in solution.

The use of $catPCl_3$ to study co-ordination properties seems very favourable. Systems which may be usefully studied in future would be $catPCl_3$ in, for example, trimethylamine, dimethylformamide, and tetramethylurea.

(e) Experimental

$(C_5H_{11})_4N^+ catPCl_4^-$

Saturated solutions of 1.929g (7.859 mmole) $catPCl_3$ and 2.627g (7.863 mmole) tetrapentylammonium chloride in carbon tetrachloride were mixed with stirring. After leaving to settle, a viscous yellow layer formed on the top of the clear liquid. The top layer was pipetted off and pumped down under vacuum to produce a pale yellow solid.

Yield = 2.607g = 57.2% as $(C_5H_{11})_4N^+ catPCl_4^-$

Analyses: Found C,53.62; H,7.83; N,3.27; P,5.74; Cl,24.82. $(C_5H_{11})_4N^+ catPCl_4^-$ requires C,53.88; H,8.36; N,2.42; P,5.34; Cl,24.47.

$(C_3H_7)_4N^+ catPCl_4^-$

2.133g (8.690 mmole) $catPCl_3$ and 1.994g (8.987 mmole) tetrapropyl ammonium chloride were individually dissolved in approximately the minimum quantity of methylene chloride. The $catPCl_3$ solution was added to the $(C_3H_7)_4N^+ Cl^-$ solution. The resulting solution turned dark red, then orange in a very exothermic reaction. As the solution cooled a bright yellow solid separated. The solution was left for 1½ hours and the solid then filtered, washed with 30/40 pet ether, and dried at the pump (the pet ether was, however, found to make the solid cake together).

Yield = 1.087g = 26.8% as $prop_4N^+$ $catPCl_4^-$

Analyses: Found C,47.10; H,6.81; N,3.03; P,6.53; Cl,29.73.

$Prop_4N^+$ $catPCl_4^-$ requires C,46.26; H,6.92; N,3.00; P,6.63; Cl,30.35

The solid did not mull very well until it had also been dried under vacuum.

$PhPCl_3^+$ $catPCl_4^-$

3.371g (13.47 mmole) $PhPCl_4$ and 3.258g (13.27 mmole) $catPCl_3$ were each separately dissolved in the minimum quantity of methylene chloride. The $catPCl_3$ solution was dripped into the $PhPCl_4$ solution with stirring. A bright yellow precipitate formed with a slight evolution of heat. The solution was left for a few minutes and then the solid was filtered, washed with 30/40 pet ether and dried at the pump to give a bright yellow fine powder.

Yield = 4.424g = 67.3% as $PhPCl_3^+$ $catPCl_4^-$

Analyses: Found C,27.96; H,1.84; P,11.66; Cl,51.52.

$PhPCl_3^+$ $catPCl_4^-$ requires C,29.09; H,1.83; P,12.51; Cl,50.11.

$CatPCl_2dipy^+$ $catPCl_4^-$. $PhNO_2$

1.095g (7.010 mmole) dipyridyl and 3.441g (14.02 mmole) $catPCl_3$ were dissolved together in the minimum quantity of nitrobenzene to produce a clear yellow solution. The solution was stirred overnight and then left a further day, by which time it had become a solid mass. The solid was filtered, washed with a little nitrobenzene and methylene chloride and dried at the pump giving a bright yellow dry powder with a reddish tinge. Each time the solid was mixed with solvent the tinge disappeared only to reappear on drying.

Yield = 3.632g = 67.3% as $catPCl_2dipy^+$ $catPCl_4^-$. $PhNO_2$

Analyses: Found C,43.92; H,3.98; N,5.34; P,8.3; Cl,29.32; dipyridyl, 19.6.

$CatPCl_2dipy^+$ $catPCl_4^-$. $PhNO_2$ requires C,43.66; H,2.76; N,5.46; P,8.04; Cl,27.62; dipyridyl, 20.28

$CatPCl_2dipy^+$ $catPCl_4^-$

0.283g (1.81 mmole) dipyridyl and 0.891g (3.63 mmole) $catPCl_3$ were dissolved together in the minimum quantity of methylene chloride. The solution was kept at n.m.r. temperature (34.2°C) for several hours, by which time the solution had become a solid bright orange mass. The solid was separated, washed with 30/40 pet ether and dried at the pump.

Yield = 0.829g = 70.8% as $catPCl_2dipy^+$ $catPCl_4^-$

Analyses: Found C,41.00; H,3.33; N,4.35; P,9.09; Cl,33.83.

$CatPCl_2dipy^+$ $catPCl_4^-$ requires C,40.83; H,2.50; N,4.33; P,9.58; Cl,32.88.

$CatPCl_2phen^+$ $catPCl_4^-$

3.236g (13.18 mmole) $catPCl_3$ and 1.123g (6.231 mmole) 1,10'-phenanthroline were each dissolved in small quantities of methylene chloride. The two solutions were mixed. On stirring the resulting solution overnight an orange precipitate formed. The solid was then filtered, washed with 30/40 pet ether and dried at the pump producing a fine orange powder.

Yield = 3.871g = 99.2% as $catPCl_2^{phen+}$ $catPCl_4^-$.

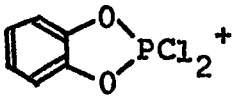
Analyses: Found C,42.31; H,2.20; N,4.23; P,9.06; Cl,31.80.

$CatPCl_2phen^+$ $catPCl_4^-$ requires C,42.95; H,2.41; N,4.17; P,9.23; Cl,31.70.

2. Acceptor Properties of the Catechyl Bischlorophosphonium Cation

(i) Introduction

Salts containing the catechyl bischlorophosphonium ion,



have not previously been synthesised. The hexachloroantimonate was prepared by addition of antimony pentachloride to catechyl phosphorus trichloride in methylene chloride (Chapter 2 section 1 (ii)h). Its extreme sensitivity to moisture has been described in Chapter 2 section 1(ii)h, the compound hydrolysing within seconds when exposed to the glove box atmosphere, and within days even in a stoppered container. With the complete exclusion of moisture the compound is probably stable.

The extreme sensitivity of catPCl_2^+ $SbCl_6^-$ to moisture may be explained by the phosphorus bearing a positive charge and being co-ordinatively unsaturated , thereby being very open to nucleophilic attack. The phosphorus is further exposed by the benzene ring holding back the two oxygen atoms. This is shown by the even greater sensitivity of the biscatechyl phosphonium cation $(C_6H_4O_2)_2P^+$, and the relative insensitivity of PCl_4^+ $SbCl_6^-$ which may be handled by conventional glove box techniques without difficulty.

The solid state ^{31}P n.m.r. of the compound showed a sharp peak at -71.7 ppm, confirming the four co-ordinate nature of the phosphorus. The sharpness of the peak once again shows the narrowness and ease of detection of four co-ordinate phosphonium species. The salt was readily soluble in nitrobenzene. An unstable solution was formed, presumably due to slow attack on the solvent. A ^{31}P n.m.r. peak was found at -77.1 ppm, however. The solution in phosphoryl chloride was more stable

and produced a ^{31}P n.m.r. peak at -77.8 ppm. Over a period of days the solution became dark purple. After a fortnight peaks of equal intensity were found at -77.0 and -66.3 ppm. The assignment of the last peak is not known. From its shift the species would appear to be four-co-ordinate.

The ^{35}Cl n.q.r. spectrum of the solid showed intense lines at 30.047 and 31.725 MHz attributable to $catPCl_2^+$.

TABLE 62

^{35}Cl n.q.r. SPECTRUM OF $(C_6H_4O_2)PCl_2^+$ $SbCl_6^-$

ν (Cl) MHz	S/N	Assignment
18.98	2:1	^{37}Cl
19.96	2:1	^{37}Cl
24.07	12.5:1	^{35}Cl $SbCl_6^-$
24.20	7:1	^{35}Cl $SbCl_6^-$
24.42_5	3.5:1	^{35}Cl $SbCl_6^-$
25.02_5	3.5:1	^{37}Cl
25.36	7:1	^{35}Cl $SbCl_6^-$
30.047	12:1	^{35}Cl $catPCl_2^+$
31.725	11:1	^{35}Cl $catPCl_2^+$

The two lines for $catPCl_2^+$ are separated by 1.678 MHz, which is surprising in view of the expected C_{2v} symmetry of cation. The highest frequency line attributable to $SbCl_6^-$ is also much higher than normal for this ion. Thus interaction of one of the antimony chlorines with the phosphorus cation may be occurring, thereby distorting the structure and making the cation chlorines inequivalent.

The i.r. spectrum of the compound is given below. Since the compound turned bright yellow on addition of nujol, it may have already reacted.

TABLE 63

I.r. SPECTRUM $catPCl_2^+ SbCl_6^-$ 650-300 cm^{-1} Fast Run

636s, 593w, 566m, 423s, 417w, 397w, ~360sh, ~330sbr

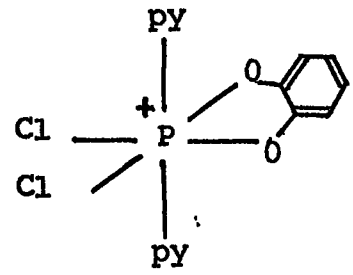
The line at ~330 cm^{-1} is attributable to $SbCl_6^-$. The strong 636 cm^{-1} P-Cl absorption is at higher frequency than those found in $catPCl_3$ (Table 55) as would be expected from cation formation.

All reactions involving the salt were performed as quickly as possible. Ligands were initially mixed with nitrobenzene and the $catPCl_2^+ SbCl_6^-$ dissolved in this so that co-ordination would occur before $catPCl_2^+ SbCl_6^-$ had time to decompose. The adducts formed were found to possess no exceptional sensitivity to moisture.

(ii) Acceptor Properties

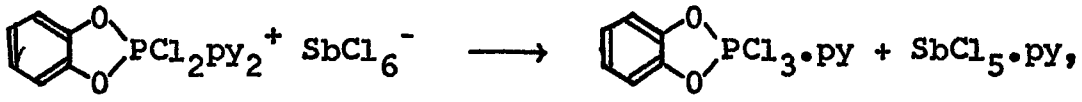
A 1:2 molar ratio solution of $catPCl_2^+ SbCl_6^-$ and pyridine made up in nitrobenzene produced a clear yellow stable solution. A single peak was found at +124.8 ppm, attributable to $catPCl_2py_2^+$. This is very close to the +125.5 ppm signal found in $catPCl_3$/pyridine systems. The single peak may be due either to a rapid equilibrium between the possible isomers, or to a single isomer being present in solution. If the latter explanation holds the shift would perhaps suggest a trans configuration for the two pyridines, the shift being somewhat different from that found with bidentate

pyridines (Chapter 5 section 1(ii)c).



Trans co-ordination is precluded with these ligands because of their bidentates nature.

After two months a small peak was visible at +134.8 ppm, while the major peak had moved slightly to +125.4 ppm. The probable assignment of the small peak is to catPCl_3.py, indicating a slow reaction



although the peak is slightly removed from the position of catPCl_3py in nitrobenzene. Further work would thus seem necessary to confirm the assignment.

On dissolving 2,2'-dipyridyl or 1,10-phenanthroline in nitrobenzene and adding catechyl bischlorophosphonium hexachloroantimonate, bright yellow precipitates were immediately formed. A yellow solid was isolated from a 1:1 catPCl_2^+ $SbCl_6^-$/dipyridyl solution. A second sample was similarly isolated except that before isolation, the solution was kept at n.m.r. temperature for several hours. The i.r. spectra from the two samples were identical. On storing under nitrogen green spots appeared in the first sample, and the bulk of the powder slowly turned yellow-green. This colour change did not, however, occur with the second sample.

The i.r. spectra of the samples showed lines at ~1531(sh) and 1347(s) cm^{-1} (but not at 852 cm^{-1}) indicative of a nitrobenzene solvate, as well as a line attributable to the hexachloroantimonate ion. The analyses corresponded approximately with the formula $catPCl_2dipy^+ SbCl_6^-$. $3/4PhNO_2$ although the amount of nitrobenzene could not be determined exactly. Many of the lines in the i.r. spectrum below 660 cm^{-1} were in similar positions to those found in $catPCl_2dipy^+ catPCl_4^-$. The similarity of the positions would suggest that the same isomer of $catPCl_2dipy^+$ is present in the two salts.

TABLE 64

I.r. SPECTRUM

$catPCl_2dipy^+ SbCl_6^-$. $3/4PhNO_2$

(Second Sample) 650-250 cm^{-1}

627m, 543m, 532w, 509s, 457m, 452m, 420s, 383m, 342w

On exposure of the second sample to air little change occurred, the solid gradually becoming paler, but not becoming a viscous liquid. On addition of water the compound did not dissolve, but once again there was a slight colour change. This is in contrast to $catPCl_2dipy^+ catPCl_4^-$. $PhNO_2$, which slowly hydrolyses in moist air, and again illustrates the stability of the hexachloroantimonate salts produced in this work.

(iii) Experimental

$CatPCl_2dipy^+ SbCl_6^-$. $3/4PhNO_2$

First method

1.070g (6.850 mmole) 2,2'-dipyridyl were dissolved in a small amount of nitrobenzene and this was added to 3.708g (6.810 mmole)

white $catPCl_2^+ SbCl_6^-$, with stirring. There was an immediate yellow colouration and a very exothermic reaction. A little more nitrobenzene was added and the mixture stirred for a few minutes. The solid was filtered, washed with methylene chloride and 30/40 pet ether, dried at the pump, and then under vacuum.

Yield = 4.814g = 89.1% as $catPCl_2dipy^+ SbCl_6^-$. $3/4PhNO_2$

Analyses: Found (whilst still yellow) P,5.1; Cl,34.73

Second method

The method was similar to that above, using 0.166g (1.06 mmole) dipyridyl, and 0.575g (1.06 mmole) $catPCl_2^+ SbCl_6^-$, but the solution was kept for several hours at n.m.r. temperature, then at room temperature for several days, before isolation of the complex.

Analyses: Found C,30.04; H,2.42; N,4.61; P,4.11; Cl,34.6

$catPCl_2dipy^+ SbCl_6^-$. $3/4PhNO_2$ requires C,31.05; H,2.01; N,4.86; P,3.91; Cl,35.77.

3. Acceptor Properties of Biscatechylphosphorus monochloride (2-chloro-2,2'-spirobi-[1,3,2-benzodioxaphosphole])

(i) Introduction

Biscatechyl phosphorus monochloride was first prepared by Anschütz [258]. This work was reinvestigated by Ramirez [62], but the compound has otherwise been little studied. It is formed by reaction of catechyl phosphorus trichloride with boron trifluoride [268] or catechol [134] and by reaction of phosphorus

pentachloride with 2-ethoxy-4,5-benzodioxolane [259] or catechol [62], the latter route being the most convenient preparation of the compound. Anschütz also isolated a dimeric form of the compound [258] but this could not be repeated by Ramirez [62].

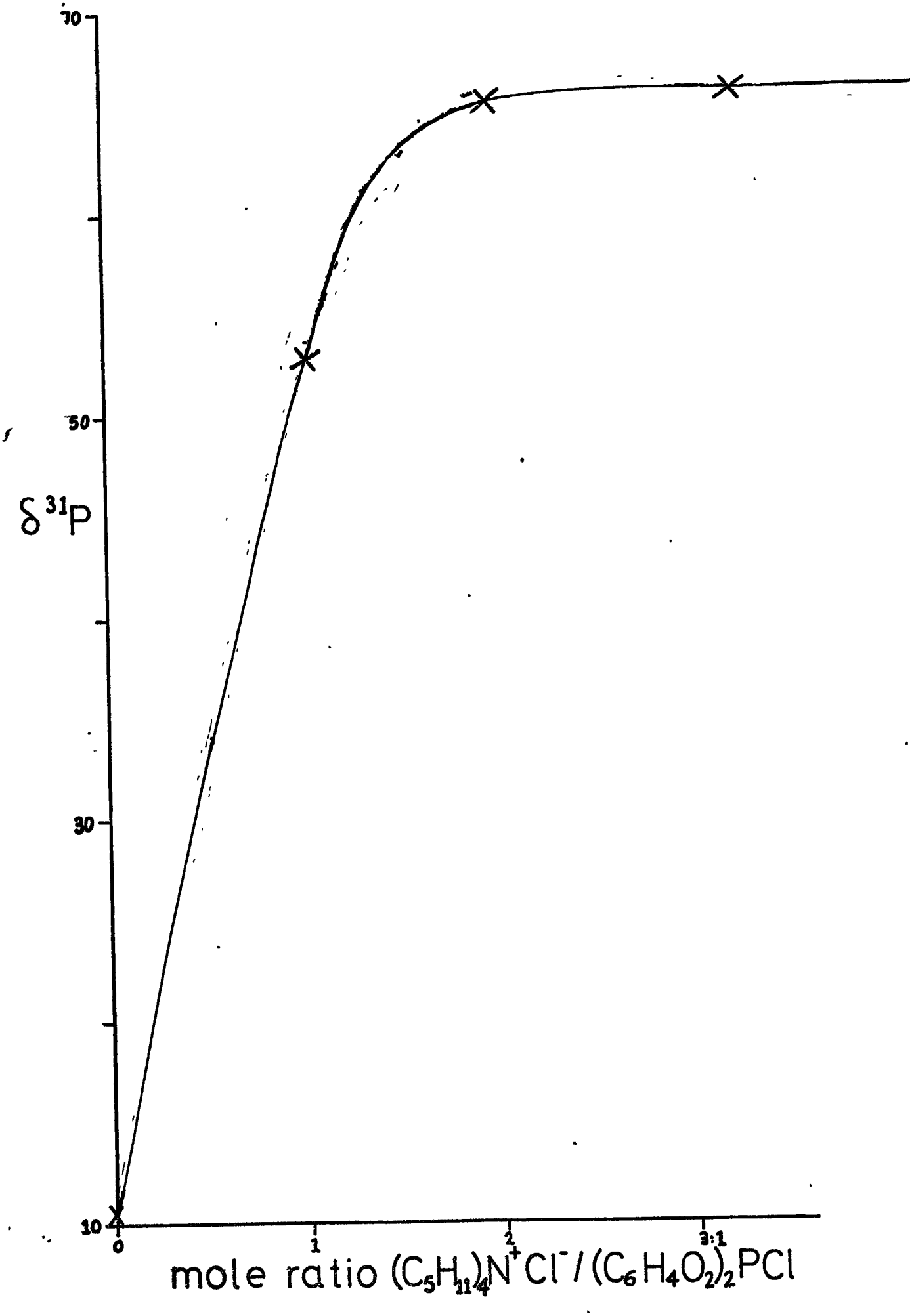
Although no adducts of biscatechyl phosphorus monochloride have been previously reported, a number of 6 co-ordinate anionic species are known, of the general formula $cat_2PR_1R_2^-$, where R_1 = organic group and R_2 = organic group, or H (Appendix 1). The cat_2P^+ framework is thus useful for building up six co-ordinate species.

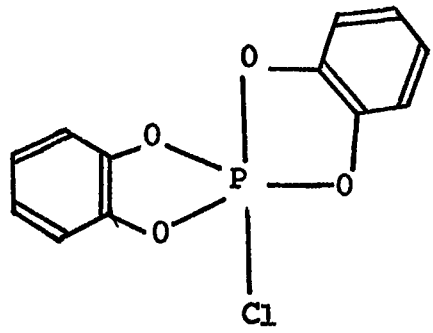
Biscatechyl phosphorus monochloride has a ^{31}P n.m.r. shift of +9.7 ppm in chloroform [210], +10.5 ppm in benzene [268], and +9.4 ppm in methylene chloride [62].

In this work shifts were determined as +10.0 ± 0.3 ppm in methylene chloride and + 10.5 ± 0.3 ppm in nitrobenzene. The compound is moderately soluble in these solvents, producing ^{31}P n.m.r. peaks clearly visible on a single scan.

The compound gave a single solid state ^{31}P n.m.r. peak at +2.9 ± 12 ppm, in reasonable agreement with the solution values. It gave a single line in the n.q.r. spectrum at 27.25 MHz. Comparison with the spectrum of catechyl phosphorus trichloride (27.841 ax, 31.233, 31.761 eq) suggests a trigonal bipyramidal structure with one axial chlorine. Although it has been suggested that 5 membered rings containing O-P-O bonds are less strained with O-P-O angles of 90° than with 120° angles [269,270] the second catechyl group occupies an equatorial-equatorial position.

Fig 35 ^{31}P chemical shift of $(C_5H_{11})_4N^+Cl^-$ / $(C_6H_4O_2)_2PCl$ solutions in nitrobenzene





Complete hydrolysis of biscatechyl phosphorus monochloride produces catechol and phosphoric acid [259]. Partial hydrolysis likely to occur from traces of moisture in solution has not been studied. Small peaks in the ^{31}P n.m.r. spectra of the crude material were found at +31.4 ppm in nitrobenzene solution and +31.1 ppm in methylene chloride solution. These shifts are very similar to those obtained from cat_2POH isolated by Nisbet [217] (δ^{31}P = +31.8 ppm). Because the partial hydrolysis product is itself five co-ordinate and a possible acceptor the starting material was usually recrystallised from dry benzene/hexane (c.f. Ref.62). The concentration of hydrolysis impurity was considerably lowered by this process.

Biscatechyl phosphorus monochloride was prepared by the optimum method of Ramirez et al [62] (Chapter 2 section 1(ii)d).

(ii) Present Work

(a) Acceptor Properties towards Chloride Ions

The addition of chloride ions moved the ^{31}P n.m.r. peak of the phosphorane upfield, showing formation of a six co-ordinate species in rapid equilibrium with the parent compound. The results for various molar ratios are given below and are plotted on Fig.35.

TABLE 65

δ^{31} P FOR $cat_2PCl/(C_5H_{11})_4N^+$ Cl^- SOLUTIONS IN NITROBENZENE

Molar Ratio $cat_2PCl/(C_5H_{11})_4N^+$ Cl^-	Shift	% adduct formation
1:1.03	+52.9	76.0
1:1.973	+65.6	98.7
1:3.242	+66.1	99.7

From Fig.35 a limiting shift of approximately +66.3 ppm may be derived with a probable extrapolation error of less than 1 ppm. A solution containing equimolar quantities of reactants would then be 74.3% associated. This is very similar to the degree of association of $PhPCl_5^-$ under similar conditions (Chapter 4 section 1(ii)), reflecting very similar acceptor properties of $PhPCl_4$ and cat_2PCl towards chloride ions. The degree of association is, however, somewhat less than that of $catPCl_4^-$ under similar conditions showing a lowering of the acceptor properties towards chloride ions by the substitution of a second catechyl group into phosphorus pentachloride.

Although no hydrolysis peaks were visible in the spectra, the spectrum of the parent cat_2PCl in nitrobenzene showed a hydrolysis peak 10.4% of the intensity of the unhydrolysed peak. This has not been taken into account in the above calculations.

Although the limiting shift is more positive than that of the parent compound it is very low for a six co-ordinate species.

The substitution of only two chlorines of PCl_6^- by a catechyl group lowers the shift from +296 to +159 ppm, however, and the shift of the triscatechyl phosphate anion is +82 ppm [265]. The reliability of the limiting shift is supported by the ^{31}P shift of the solid adduct (+69.3 $\pm$ 2.3 ppm). The shifts of the pyridine, dipyridyl and phenanthroline adducts are also of the same order of magnitude (Chapter 5 sections 3(ii)b and c). $Cat_2PCl_2^-$ has the lowest six co-ordinate shift yet found and reflects the constriction of the range of ^{31}P co-ordination shifts caused by substitution of catechyl groups (cat_2P^+ has a high shift for a 4 co-ordinate cation). The constriction of shift ranges of compounds containing P-O bonds is supported by protonation studies of P=O compounds [271,272]. These compounds protonate on the oxygen producing a downfield shift, ascribed to a reduction of the electron density around the phosphorus. This shift is progressively reduced as the number of oxygens increase.

e.g. $\delta^{31}P$ Ph_3PO $\sim$ -27 ppm Ph_3POH^+ $\sim$ -60 Δ 33 ppm

H_3PO_4 0 $P(OH)_4^+$ - 2 Δ 2 ppm

The oxygen seems able to delocalise charge from phosphorus. It is difficult to see how this occurs with a six co-ordinate species, however.

Tetrapentylammonium biscatechylbischlorophosphate, $(C_5H_{11})_4N^+$ $cat_2PCl_2^-$, was prepared by fusing the components together at 140°C then quickly cooling the melt. This produced a fawn moisture-sensitive solid, the i.r. spectrum of which showed no peaks attributable to free cat_2PCl. A

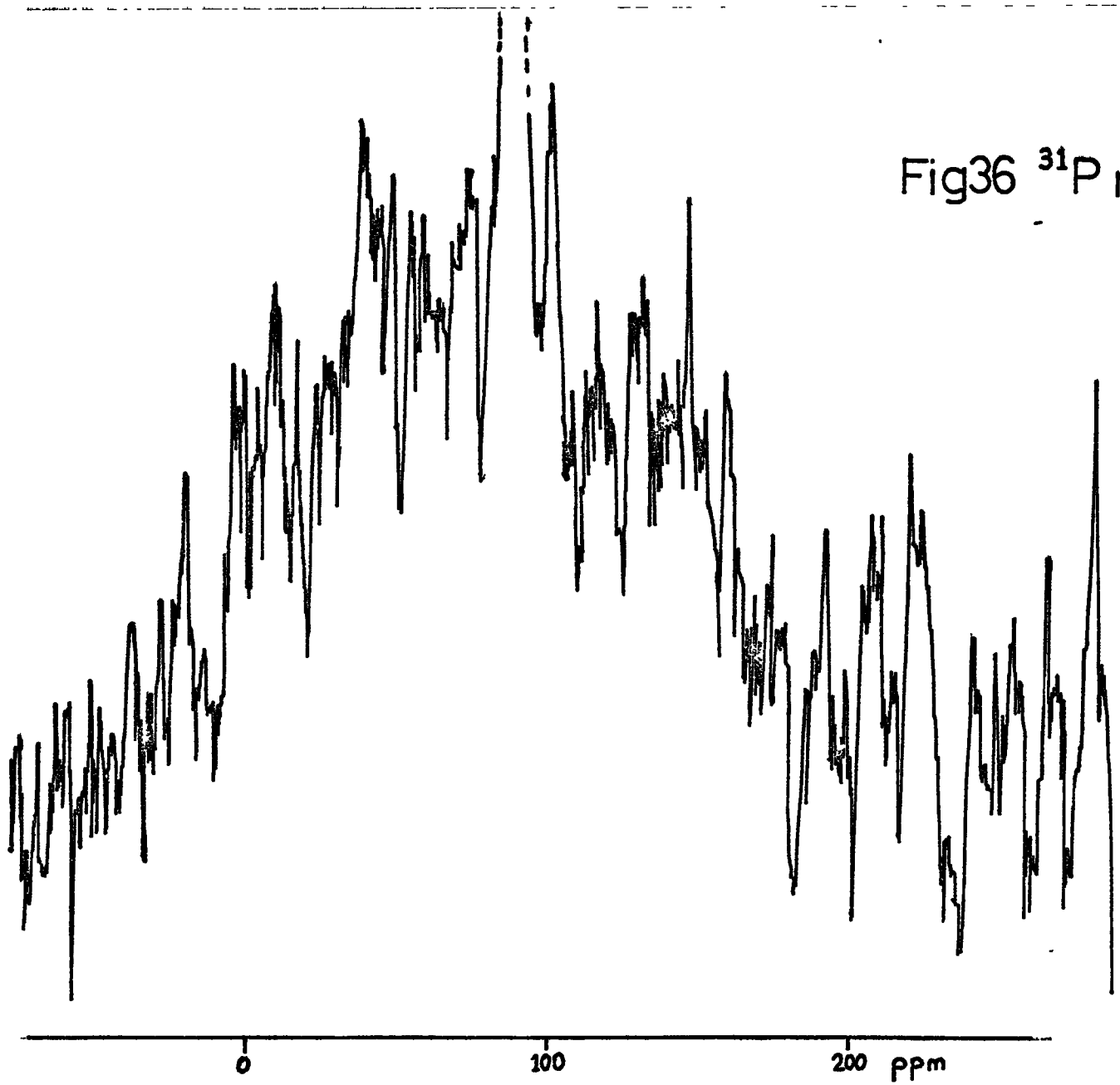
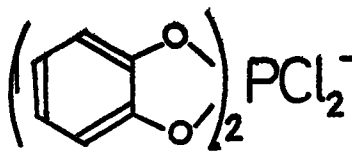


Fig36 ^{31}P n.m.r. solid state spectrum of

$(C_5H_{11})_4N^+$ 

broadish ^{31}P solid state n.m.r. line was found at +69.3 ± 2.3 ppm (Fig.36). There was also a narrow "solution" peak at +83.6 ppm. This is presumably due to the anion although the shift is somewhat higher than predicted here. Unfortunately no lines could be found in the n.q.r. spectrum. The number of lines might have given an indication of the stereochemistry of $cat_2PCl_2^-$ in the solid state. The i.r. spectrum of the solid gave absorptions below 650 cm^{-1} as shown below.

TABLE 66

I.r. SPECTRUM $(C_5H_{11})_4N^+$ $cat_2PCl_2^-$ 650-350 cm^{-1}

639s, 636s, 617w, 546sh, 539s, 494s, 470s, 426s,

c.f. cat_2PCl

624m, 587s, 576s, 563sh, 550sh, 540w, 530s, 507w,

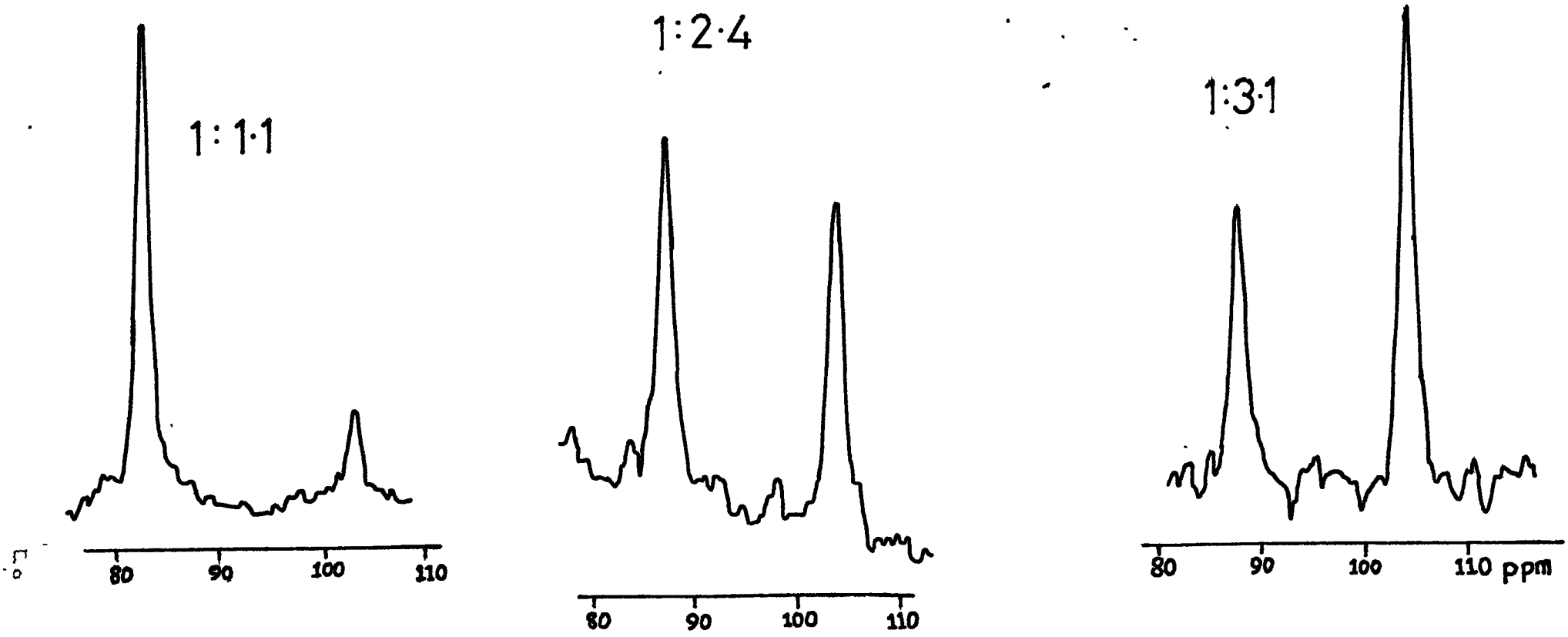
483w, 468s, 432s, 423sh, 397w, 360m

The preparation of $(C_5H_{11})_4N^+$ $cat_2PCl_2^-$ was also attempted by slow evaporation of methylene chloride solvent under vacuum at -20 to -30°C. This produced a white solid, but extra lines were visible in its i.r. spectrum at 627m, 588m, 576m, 563m, 470w cm^{-1} attributable to unreacted cat_2PCl. Presumably, in order to produce purer samples by this method, lower temperatures and a slower rate of evaporation of the solvent will be needed.

(b) Acceptor Properties towards Pyridine

When a methylene chloride solution of biscatechyl phosphorus monochloride and pyridine was prepared containing a very slight excess of pyridine the ^{31}P n.m.r. spectrum showed a large peak at +80.7 ppm, and a much smaller one at +101.0 ppm. When the

Fig37 ^{31}P n.m.r. spectra of $(C_6H_4O_2)_2PCl$/pyridine solutions in nitrobenzene



solution was made up with a 1:2 molar ratio of cat_2PCl:pyridine the lines were of approximately equal intensity. With a 1:3 molar ratio the high field line had about twice the intensity of the low field line. (Fig.37).

TABLE 67

δ^{31} P FOR cat_2PCl/PYRIDINE SOLUTIONS IN NITROBENZENE

Molar ratio cat_2PCl/py	δ^{31} P		Relative area
1:1.1	80.7	101.0	100:17.0
1:2.4	84.7	100.9	100:106.7
1:3.1	85.4	101.3	100:174.3

$Cat_2PCl.py$ can exist in two isomeric forms, but the two signals would not seem to be due to this. Although a shift difference of about 20 ppm would not be unreasonable for two isomeric forms, such a large difference in the relative amounts of the isomers with change of the relative amounts of constituents would not be expected. Moreover, from studies of $cat_2Ppy_2^+ SbCl_6^-$ the chemical shift of $cat_2Ppy_2^+$ was found to be +101.7 ppm (Chapter 5 section 4(ii)). It thus appears that both 1:1 (neutral) and 2:1 (ionic) adducts are formed in the system.

$$cat_2PCl \quad +py \longrightarrow cat_2PCl.py \quad +85 \text{ ppm}$$

$$\Big\| \text{ excess py}$$

$$cat_2Ppy_2^+Cl^- \quad +100 \text{ ppm}$$

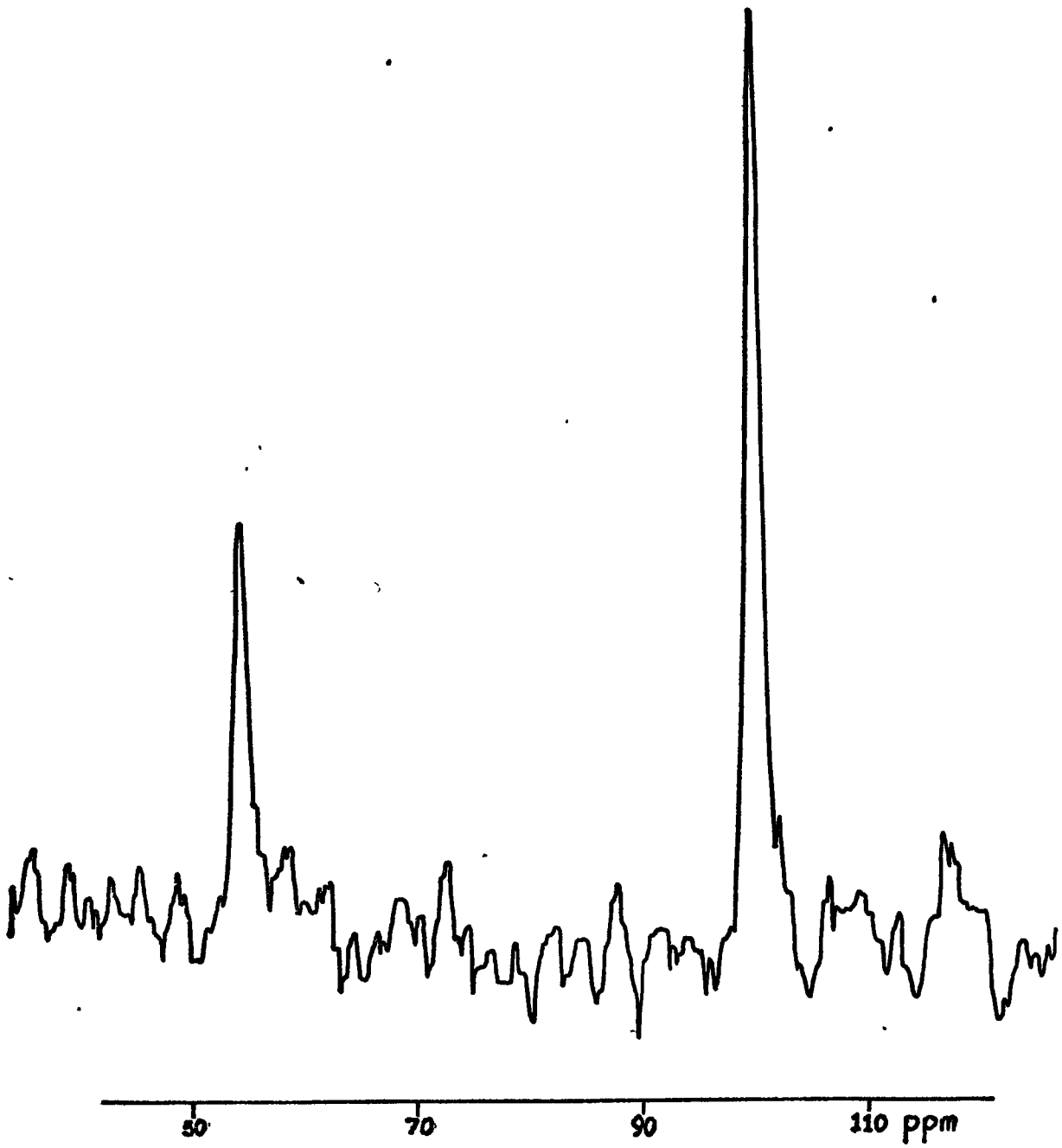


Fig38 ^{31}P n.m.r. spectrum of $(C_6H_4O_2)_2PCl$ + dipyridyl (1:1 molar ratio) in nitrobenzene after four days. 94 scans

The relative shift positions of the species are opposite to those found in previous systems, the cationic species usually having a lower shift than the related neutral species. This is discussed in Chapter 6 section 2.

Only single lines were visible for each of the two species present. Thus either only single isomers for each species occur in solution, or there is rapid exchange between the various isomers.

This system provides the first unequivocal example of a pyridine being a strong enough ligand to displace a chloride ion when excess of the pyridine is added. It occurs to a very minor extent with catechyl phosphorus trichloride. When phosphorus pentachloride is dissolved even in neat pyridine the 1:1 adduct is the sole product.

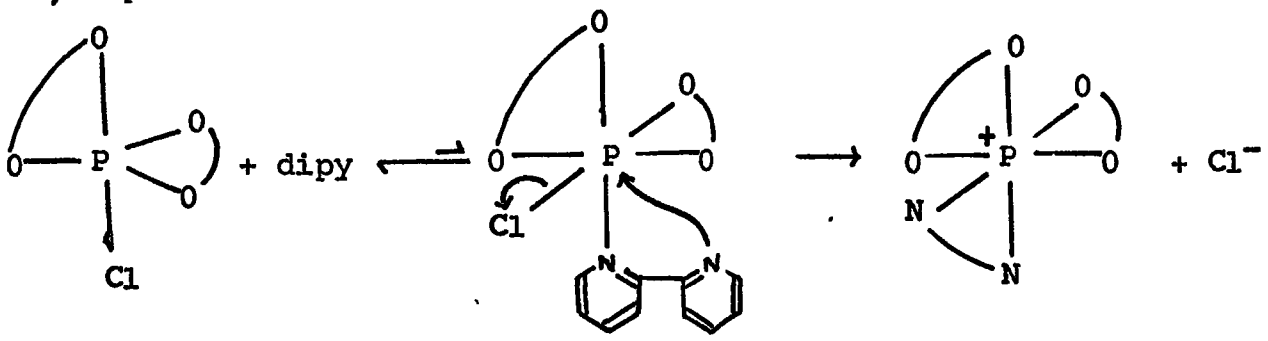
(c) Acceptor Properties towards Bidentate Pyridines

When first prepared, 1:1 solutions of dipyridyl or phenanthroline with biscatechyl phosphorus monochloride in nitrobenzene gave lines only slightly displaced from that of the parent phosphorane (δ^{31} P +16.7 ppm for dipyridyl, +14.9 ppm for phenanthroline after ~6 hours). After four days, the spectrum of the cat_2PCl/dipyridyl system had changed, showing peaks at +52.0 and +95.4 ppm in the approximate intensity ratio 43.4:100 (Fig.38). After 6 days, however, the phenanthroline solution still gave a single line, now at +17.7 ppm.

From solution studies of the hexachloroantimonate salts the shifts of cat_2P^+dipy and cat_2P^+ phen are +93.4 and +89.9 ppm respectively. The high field peak in the cat_2PCl/dipy solution is thus ascribed to cat_2P^+dipy. It is then reasonable to assume that the low field peak is due to $cat_2PCl + Cl^- \rightleftharpoons cat_2PCl_2^-$.

As this peak is somewhat lower in intensity than that due to the cation, the adduct in solution when equimolar quantities of reagents are present appears to lie between $cat_2Pdipy^+ Cl^-$ and $cat_2Pdipy^+ cat_2PCl_2^-$. Presumably when there is a 1:2 molar ratio of cat_2PCl:dipyridyl $cat_2Pdipy^+ cat_2PCl_2^-$ will be preferred to a greater extent.

The solution data is once again consistent with only slow displacement of a chloride ion by a bidentate pyridine (c.f. Chapter 4 section 1(iv), Chapter 5 section 1(ii)c). The slightly higher than normal shift of cat_2PCl in the initial solutions may suggest that the reaction proceeds via very weak monodentate co-ordination of the ligand. Because of the more flexible nature of 2,2'-dipyridyl the intermediate would be less sterically hindered than with the completely rigid 1,10-phenanthroline.



When there is no steric barrier to formation of the neutral complex, with pyridine, displacement of a chloride ion takes place within minutes. Dipyridyl and phenanthroline complexes prepared directly from the hexachloroantimonate salt, where no chloride ion displacement is necessary, were formed immediately.

When a 2:1 molar ratio of cat_2PCl:dipyridyl was mixed in methylene chloride, a yellow powder precipitated after several days. It gave a solid state ^{31}P n.m.r. signal at +100.6 ± 5 ppm, suggestive of the 1:1 adduct. The compound is air stable and does not react on addition of water suggesting the absence of $cat_2PCl_2^-$. Elemental analyses did not, however, clearly distinguish between the 1:1 and 1:2 adducts.

Unless the reaction between biscatechyl phosphorus monochloride and phenanthroline can be speeded up by heating without decomposing the complex the best possible route to its future isolation may be by a metathetical reaction between its readily formed hexachloroantimonate and a tetraalkyl ammonium chloride.

(d) Experimental

$(C_5H_{11})_4N^+$ $cat_2PCl_2^-$

1. Free from starting materials

2.448g (8.661 mmole) cat_2PCl and 2.897g (8.671 mmole) $(C_5H_{11})_4N^+$ Cl^- were intimately mixed in the solid state. The mixture was then rapidly heated to 140°C to produce a yellow-brown viscous melt. With continuous swirling the liquid was then allowed to cool to produce a dirty yellow wax-like solid.

Yield = 4.923g = 92.1% as $(C_5H_{11})_4N^+$ $cat_2PCl_2^-$

Analyses: Found C,19.96; H,2.66; N,4.48; P,4.33; Cl,50.85.

$(C_5H_{11})_4N^+$ $cat_2PCl_2^-$ requires C,20.78; H,2.04; N,4.04; P,4.47; Cl,51.12.

2. By low temperature evaporation

2.062g (7.295 mmole) cat_2PCl and 2.447g (7.324 mmole) $(C_5H_{11})_4N^+$ Cl^- were dissolved in sufficient methylene chloride so that the solution could be cooled to -30°C without producing

crystallisation. The solution was kept at -30°C for a few minutes. The solvent was then removed under vacuum, keeping the temperature between -20 and -30°C, to produce a white solid. The i.r. spectrum (Chapter 5 section 1(ii)a) showed, however, that the product was contaminated with starting material.

$Cat_2Pdipy^+ Cl^-$

2.510g (8.880 mmole) recrystallised cat_2PCl were dissolved in the minimum quantity of 1,2-dichloroethane. 0.694g (4.44 mole) dipyridyl was then dissolved in this to produce a yellow solution, which after one hour had become golden. The solution was stirred for several days. The stirring kept the solution temperature slightly above room temperature. After one day the solution had a reddish tinge, and after two days a precipitate had formed. The solution was allowed to cool, the precipitate filtered, washed with 30/40 pet ether, and dried at the pump to produce a canary yellow powder.

Yield = 1.047g

The analytical data was poor and did not distinguish between the formulations $cat_2Pdipy^+ Cl^-$ and $cat_2Pdipy^+ cat_2PCl_2^-$. In addition the chlorine analyses were far higher than either formula indicated. Dipyridyl group analysis was also unsuccessful. The complex did not dissolve in cold water. After heating, on addition of the ferrous salt no deep colour formed presumably because of decomposition of the ligand. Although the solid dissolved in acetone, neither this, nor the dipyridyl standard produced a measurable colour in this solvent.

Analyses: Found C,53.39; H,5.38; N,5.54; P,7.08; Cl,16.02. $Cat_2Pdipy^+ Cl^-$ requires C,60.21; H,3.68; N,6.39; P,7.06; Cl,8.08. $Cat_2Pdipy^+ cat_2PCl_2^-$ requires C,56.60; H,3.36; N,3.88; P,8.59; Cl,9.83.

4. Co-ordination Chemistry of the Biscatechyl phosphonium ion

(i) Introduction

Salts containing the biscatechyl phosphonium cation have not been previously prepared. The hexachloroantimonate was prepared from biscatechyl phosphorus monochloride and antimony pentachloride in methylene chloride. The compound is extremely moisture-sensitive, as has been discussed in Chapter 2 section 1(ii) It appears to be even less stable than $catPCl_2^+ SbCl_6^-$, being more readily attacked in stoppered containers.

The salt gave a narrow solid state ^{31}P n.m.r. signal at -44.0 ppm. It is readily soluble in nitrobenzene. Fresh solutions gave a solution n.m.r. signal at -42.4 ppm in good agreement with the solid, but the spectrum also contained a peak at +19.6 ppm. The solution rapidly turned black. After three days peaks were visible, of equal intensity at +0.3 ppm and +37.2 ppm, probably due to H_3PO_4 and cat_2POH hydrolysis products. Because of great reactivity of the salt, solutions of the adducts were made by dissolving the potential ligand in nitrobenzene, then dissolving the salt in this solution. Solutions of the adducts were far more stable and showed no signs of dissociation in the ^{31}P n.m.r. spectrum.

The great sensitivity of the salt to water can be attributed to its tetrahedral co-ordination while carrying a positive charge, and also to the chelate nature of the catechyl ligands which further open the phosphorus to attack.

As with $catPCl_2^+ SbCl_6^-$, the solid turned yellow on addition of nujol. The resulting i.r. spectrum is given below.

TABLE 68

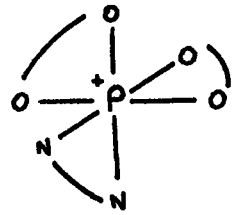
I.r. SPECTRUM 660-300 cm^{-1} $cat_2P^+ SbCl_6^-$ Fast Run

657s, 597w, 528w, 468s, 416s, ~335sbr

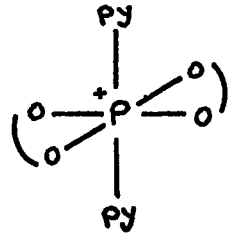
(ii) Acceptor Properties

A 1:2 molar ratio solution of biscatechyl phosphonium hexachloroantimonate to pyridine showed a single peak at +101.7 ppm. This is in a very similar position to the high field peak in biscatechyl phosphorus monochloride/pyridine systems and may be ascribed to the $cat_2Ppy_2^+$ cation. The single peak may again indicate either one isomer present in solution or rapid exchange between the isomers present. $Cat_2Ppy_2^+$ seems quite stable as the hexachloroantimonate salt. After five days no change had occurred in the spectrum, the peak being at +101.8 ppm. The colour of the solution now had a brown tinge, probably indicating a small amount of decomposition. A very small peak compared with the +101.8 ppm peak was found at +83.0 ppm after a large number of scans. The peak may be caused by a minor reaction to form cat_2PCl.pyridine. The extent of reaction is not expected to be large in view of the cat_2PCl/pyridine system which forms the cation with excess pyridine present.

1:1 molar ratio solutions of the salt and 2,2'-dipyridyl in nitrobenzene gave a single peak at +93.4 ppm. Similarly with 1,10-phenanthroline a single line was found at +89.9 ppm. In both systems only one isomer can be present because of the chelate nature of the ligands:



The shift of $cat_2Ppy_2^+$ is somewhat higher than found for the bidentate pyridine complexes. This may just reflect the slightly different nature of the ligand (c.f. difference in shift between the dipyridyl and phenanthroline complexes) but may also be due to a predominance of the trans isomer in the pyridine complex which cannot be formed with bidentate pyridines



After several weeks the phenanthroline solution was brownish yellow with a dark green precipitate on the sides of the container. The dipyridyl solution was dark green and had a dark green precipitate. The signals from the complexes, however, were the only ^{31}P n.m.r. signals found (scan range -10 to +190 ppm). The shifts found after two months were +92.5 ppm for cat_2P^+phen and +96.0 ppm for cat_2P^+dipy. The deepening in colour parallels change in colour of solid $cat_2Pphen^+ SbCl_6^-$.

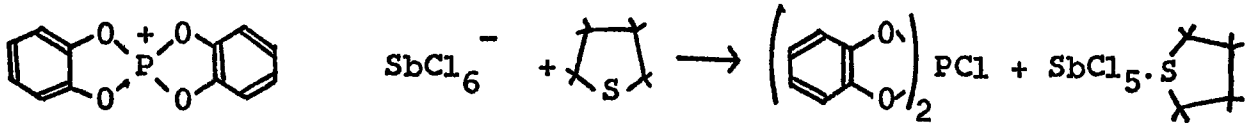
When 1,10-phenanthroline was saturated in nitrobenzene and the stoichiometric amount of biscatechylphosphonium hexachloroantimonate added with stirring a thick orange precipitate formed. On isolation this was characterised as the adduct $cat_2P^+phen\ SbCl_6^-$. The solid gave a peak in the solid state ^{31}P n.m.r. spectrum at approximately +72 ppm. Over a period of weeks the colour of the solid slowly changed to green. This change in colour was not paralleled by any change in the i.r. spectrum, so is probably due to crystal effects.

TABLE 69

I.r. SPECTRUM $cat_2Pphen^+\ SbCl_6^-$ (green) 650-250 cm^{-1}

645w, 638w, 612w, 576w, 545s, 514w, 499w, 476w, 456w, 446w, 429w, 400w, 339s

As the phosphorus in this system seems unwilling to remain four co-ordinate, other potential ligands were then tried. Tetrahydrothiophene was added to a solution of the salt in nitrobenzene, producing a brown-orange opaque solution containing a black deposit. A peak at +10.7 ppm clearly showed on a single scan. The most probable product is thus biscatechyl phosphorus monochloride, presumably formed by the reaction



The antimony pentachloride - tetrahydrothiophene adduct produced from $PCl_4^+ SbCl_6^-$ and the ligand seemed very unstable at room temperature, producing a black solid (See Chapter 5 section 1(ii)d). Decomposition of the complex would then explain the production of the black deposit. After three weeks the solution was clear. Two peaks were found in the ^{31}P n.m.r. spectrum, at +11.2ppm and +32.3 ppm. The second peak may be attributed to a small amount of hydrolysis producing cat_2POH.

Triphenylphosphine was also tried as a potential ligand. As there is only no chlorine in cat_2P^+ oxidative chlorination of the ligand was not expected to take place. A 1:2 molar ratio mixture of triphenylphosphine and biscatechylphosphonium hexachloroantimonate was made up in nitrobenzene. Peaks were found in the ^{31}P n.m.r. spectrum at -64.8, +6.2, and +10.8 ppm of approximately equal intensity, ascribable to to Ph_3PCl^+ ($\delta^{31}P$ = -65 ppm [126]), Ph_3P ($\delta^{31}P$ = +6 ppm [89]) and cat_2PCl respectively. The hexachloroantimonate ion thus appears to have been reduced.

$$2Ph_3P + \left(\text{C}_6\text{H}_4\text{O}_2\right)_2 P^+ SbCl_6^- \longrightarrow Ph_3PCl^+ Cl^- + \left(\text{C}_6\text{H}_4\text{O}_2\right)_2 PCl + SbCl_3 + Ph_3P$$

This was confirmed by repeating the reaction using equimolar quantities of Ph_3P and $cat_2P^+ SbCl_6^-$. The signal attributed to Ph_3P was now absent, leaving peaks at -64.8 ppm and +10.9 ppm in approximately equal intensities. It would be interesting to see in future if an adduct can be produced

using a non-reducible anion, e.g. BCl_4^- or $AlCl_4^-$, assuming that BCl_3 or $AlCl_3$ are strong enough chloride acceptors to abstract a chloride ion from biscatechyl phosphorus monochloride.

(iii) Experimental

$Cat_2Pphen^+ SbCl_6^-$

0.695g (3.86 mmole) 1,10-phenanthroline was dissolved in the minimum quantity of nitrobenzene. This solution was then added to 2.223g (3.820 mmole) solid $cat_2P^+ SbCl_6^-$. On stirring, the solid dissolved to give an immediate dark solution. After a few seconds the solution solidified with formation of an orange precipitate. The precipitate was filtered, washed with 30/40 pet ether and dried to give an orange powder.

Yield = 2.570g = 88.3% as $cat_2Pphen^+ SbCl_6^-$

Analyses: Found C,37.40; H,2.28; N,4.04; P,3.49; Cl,27.51.

$Cat_2Pphen^+ SbCl_6^-$ requires C,37.84; H,2.12; N,3.68; P,4.07; Cl,27.92.

CHAPTER 6

DISCUSSION

1. Comparison of Acceptor Properties

Phosphorus pentachloride, phenyltetrachlorophosphorane, catechyl phosphorus trichloride and biscatechyl phosphorus monochloride have all been shown to possess strong acceptor properties towards pyridine and chloride ligands. With the exception of PCl_6^-, all chloride adducts are partially dissociated in solution. The acceptor strength of the molecules, as measured by the association of 1:1 solutions of the acceptor and $(C_5H_{11})_4N^+ Cl^-$ in nitrobenzene, decreases in the order

$$PCl_5 > catPCl_3 > cat_2PCl = PhPCl_4 \gg Ph_2PCl_3$$

As expected from the relative electronegativities of a phenyl group and a chloride ion, the acceptor properties of $PhPCl_4$ are much less pronounced than those of PCl_5. The effect of substitution is so large that Ph_2PCl_3 shows little, if any, affinity for chloride. Although the precise degree of association of chloride ions with $MePCl_4$ was not investigated, adduct formation was unequivocably detected, contrasting with Ph_2PCl_3. Thus the partial series of acceptor strengths of alkyl and aryl chlorophosphoranes towards chloride ions is

$$PCl_5 > PhPCl_4, \quad MePCl_4 \gg Ph_2PCl_3 .$$

The relative order is identical to that found with the analogous fluorophosphoranes [57]. As expected from the greater electronegativity of fluorine, the acceptor strength of a

particular fluoro-species is greater than that of its chloro-analogue, as shown by the complete association of $Ph_2PF_4^-$ in solution [70]. Fluorine atoms are also far smaller than chlorines and thus may be easier to accommodate around phosphorus.

The relative effects of size and electronegativity in hindering complex formation by chloro-species may in future be indirectly studied by a more complete comparison of the acceptor properties of $MePCl_4$ and $PhPCl_4$. Electronegativity considerations alone would suggest $MePCl_4$ to be a far weaker acceptor than $PhPCl_4$, because of the electron-donating capacity of the methyl group. Phenyl groups have a greater bulk than methyl groups, however, so if steric effects are important the difference in properties may be reduced or even reversed.

The substitution of catechyl groups for chlorines has a far smaller effect than phenyl substitution (Table 70).

TABLE 70

ASSOCIATION OF CHLORO-IONS IN NITROBENZENE

PCl_6^-	100%*
$catPCl_4^-$	95%
$cat_2PCl_2^-$	74%
$PhPCl_5^-$	75%

* as $(C_2H_5)_4N^+$ salt others as $(C_5H_{11})_4N^+$ salt

Even after the replacement of four chlorines by two catechyl groups, the phosphorus(v) compound still retains a covalent structure and has strong acceptor properties. The oxygens of the catechyl group will have a greater electron-withdrawing effect than aryl groups. In addition the chelating group is held firmly in position, minimising any steric hindrance from

the aromatic ring. The greater stability of 5 co-ordinate aryloxyphosphoranes containing five membered chelate rings over those without rings has previously been attributed [275] to a similar cause.

A further effect in certain cases may be the preferred O-P-O bond angle, an extension of the arguments of Turnbloom, Katz [79-81] and others [269,270,276]. An O-P-O bond angle of 90° in a five membered ring is probably less strained than angles of 109° 28' and 120°. This is implied by the lack of deviation of the O-P-O bond angles from 90° in Et_4N^+ cat_3P^- [277], and also in the 5 membered ring of 2,2,2-triisopropoxy-4,5-(2',2''-biphenyleno)-1,3,2-dioxaphosphole [278]. On the other hand the O-P-O bond angles are distorted greatly from the tetrahedral angle in tris (o-phenylenedioxy) phosphonitrile trimer [279], (contrast the Cl-P-Cl angles in trimeric phosphonitrilic chloride [280]). Thus not only are 5 co-ordinate structures sterically favoured over 4 co-ordinate ones (c.f. the completely molecular structures of $catPCl_3$, cat_2PCl and even $catPBr_3$ [210]), but in some cases adduct-formation may also be facilitated. Cat_2PCl, in the solid state, has imposed O-P-O bond angles of 90° and 120° (Chapter 5 section 3), and $cat_2PCl_2^+$ and cat_2P^+ have imposed tetrahedral geometry. By co-ordination of ligands the imposed angles are lowered to 90°. The stability of the adducts of the cations, compared with the cations themselves, may also be partially explained by lack of ring strain, together with protection of the phosphorus from nucleophilic attack.

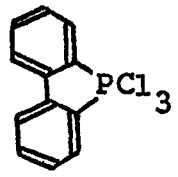
If $catPCl_3$ has a similar conformation in solution to that suggested by n.q.r. measurements in the solid state [234], normal ring strain cannot influence the acceptor properties of the compound since the imposed bond angle in the five co-ordinate structure is already 90°. $CatPCl_3$ may, however, still have a non-ideal structure. Without the steric imposition of a five-membered ring both the catechol oxygens would probably occupy equatorial positions, chlorine having a greater tendency to occupy axial positions than R-O- groups [281]. The strain from the non-ideality of the structure would then be relieved by six co-ordinate adduct formation.

The relative ring strains have been used previously to explain the formation of cat_3P^- when catechol and base is reacted with $(PNCl_2)_4$. Similar reactions with diols where 6- or 7- membered rings would result preferentially form $[PN(O_2Z)]_4$ spiro-compounds [276].

The favouring of acceptor properties where ring strain is relieved is illustrated by the compound cat_2Si, isoelectronic with cat_2P^+. This compound forms stable adducts [282] with pyridine and triethylamine although analogous compounds containing 6-or 7- membered O-Si-O rings (where no ring strain would be expected) do not. In addition the six- and seven-membered heterocycles are not so susceptible to hydrolysis or polymerisation as cat_2Si.

In order to investigate further the effect of restraining large groups, so lessening steric effects and imposing relatively fixed bond angles, a system must be considered where possible electronegativity effects are much lower. A suitable species

would be 2,2'-biphenylylene trichlorophosphorane,



Diphenyltrichlorophosphorane, identical with the species above except that the two phenyl groups are not bound to each other, lies on the borderline between having a covalent or ionic structure in solution (in non interacting solvents it appears to be mainly covalent but abstraction of a chloride ion is extremely easy) (Chapter 4 section 3(i)). It is also the first member of the phenylchlorophosphorus(v) series in which acceptor properties towards pyridine and chloride ions have been almost completely lost. Thus if any effect from joining the two aromatic rings occurs, the biphenylylene compound is expected to have a completely covalent structure, with a far smaller tendency to ionise, and also to possess increased acceptor properties towards chloride ions.

If this effect is found to be significant it may explain the predominance of six co-ordinate phosphorus species containing two or more five-membered rings (see Appendix 1).

Each of the phosphorus(v) species mentioned above forms a 1:1 adduct with pyridine. With the exception of $PhPCl_4$ all the species appear to be 100% associated in solution. Acceptor properties towards pyridine then decrease in the order

$$PCl_5,\ catPCl_3,\ cat_2PCl > PhPCl_4$$

The partial association of $PhPCl_4$.pyridine in solution is similar to the behaviour of $PhPF_4$.pyridine [57]. The difference in acceptor properties of cat_2PCl and $PhPCl_4$ towards pyridine,

in contrast with their similar behaviour towards chloride ions, probably reflects the increased steric hindrance in the $PhPCl_4$ case. Although the catechyl groups are bulkier than the chlorine and phenyl groups the aromatic rings are held firmly in position away from the phosphorus.

In order to determine a more comprehensive order of acceptor strengths towards pyridine-type donors a much weaker base than pyridine would need to be used. 3,5-dichloropyridine would seem to be suitable. Its PCl_5 complex is 60% associated in nitrobenzene. Variation of the degree of association of adducts under similar conditions would give an indication of the acceptor strength of the phosphorane.

The stoichiometry of the solution-stable adducts of the acceptors with an equimolar amount of bidentate pyridine varies between 1:1 and 2:1 (Table 71).

TABLE 71

SOLUTION-STABLE SPECIES IN 1:1 SOLUTION OF PHOSPHORANE AND BIDENTATE PYRIDINE

Phosphorane	Structure	% formation anion
PCl_5	$PCl_4phen^+ PCl_6^-$ + phen	100%
$catPCl_3$	$catPCl_2phen^+ catPCl_4^-$ + phen	100%
	$catPCl_2dipy^+ catPCl_4^-$ + dipy	98%
cat_2PCl	$(cat_2Pdipy^+) (cat_2PCl_2^-)_{0.321}(Cl^-)_{0.679}$	74% *
	$+0.113\ cat_2PCl + 1.434dipy$	
$PhPCl_4$	$PhPCl_3phen^+ Cl^-$	-

* from $cat_2PCl_2^-/cat_2PCl$ peak shift and area relative to cat_2Pphen^+

With PCl_5 and $catPCl_3$ which are strong chloride ion acceptors the 2:1 complex is formed. With $PhPCl_4$, which is a weak chloride ion acceptor, all of the phenanthroline is complexed and $PhPCl_5^-$ is not found in solution. Although cat_2PCl appears to have approximately the same chloride ion acceptor strength as $PhPCl_4$ (Table 70), however, $cat_2PCl_2^-$ is found in solution. As the reaction in this system is very slow and both cat_2PCl and dipyridyl are present in solution the reaction even after four days may not have reached equilibrium. The true equilibrium position may then very well lie further to the side of $cat_2Pdipy^+ Cl^-$.

The adducts of bidentate pyridines with hexachloroantimonate salts were stable, having no tendency for any reaction of the type.

$$Z_4P(L\text{-}L)^+ MCl_6^- \rightleftharpoons MCl_4(L\text{-}L)^+ \quad Z_4PCl_2^-.$$

Comparisons of the stability of adducts of the cations with monodentate pyridines was hampered by the tendency for the adducts to rearrange to the neutral forms

$$\text{e.g. } PCl_4py_2^+ SbCl_6^- \rightleftharpoons PCl_5py + SbCl_5.py$$

Such rearrangements took place with $PCl_4py_2^+ SbCl_6^-$ and to a small extent with $cat_2Ppy_2^+ SbCl_6^-$ but no reaction was apparent with $catPCl_2py_2^+ SbCl_6^-$. $PhPCl_3^+ SbCl_6^-$ did not form a stable adduct with pyridine presumably forming $PhPCl_4.py$ and $SbCl_5.py$. The equilibration has also been shown to be anion-dependent (Chapter 3 section 2). In view of the slowness of the equilibrations involving $PCl_4L_2^+ MCl_6^-$ it would be interesting to see whether $PCl_4py_2^+ PCl_6^-$, produced by adding PCl_6^- ions to a fresh solution of $PCl_4py_2^+ SbCl_6^-$, has more than a transient existence.

Attempts to displace chloride ions by pyridine from the neutral complex similarly differed. PCl_5.py was stable even in neat pyridine solution. $CatPCl_3$.py in the presence of excess pyridine showed a slight tendency to form $catPCl_2py_2^+ Cl^-$, but this effect was much more pronounced with cat_2PCl.

Except for PCl_4^+/PCl_5, the relative acceptor strengths of the phosphorane and its corresponding cation were not studied. With the weaker acceptors cat_2PCl and $PhPCl_4$, however, the acceptor properties were not prevented by formation of the cation, presumably because the positive charge on phosphorus compensated for the lack of an additional electronegative group attached to it. Future work to determine whether cat_2P^+ possesses greater acceptor powers than cat_2PCl, as may perhaps be expected from the relief of the far greater ring strain in the cation, would be interesting.

Many of the reactions between phosphoranes and bidentate ligands proceed very slowly at room temperature. This has been attributed to the difficulty of ionisation of the P-Cl bond in cases where 5 co-ordinate structures are greatly favoured over 4 co-ordinate ones (e.g. catechyl compounds). A second effect with the catechyl compounds may be the steric rigidity imposed by the five-membered rings, thus making any transition state which increases the O-P-O bond angles very unfavourable. This latter argument has been used to explain the difference in reaction of $P_3N_3Cl_6$ and $P_4N_4Cl_8$ with catechol [276].

The slow reactions of $PCl_4py_2^+$ species can be interpreted in terms of the co-ordinative saturation of the reactants. Slow

reactions of 6 co-ordinate species together with the detection of isomers in some systems, suggest the possibility of resolution of optical isomers in favourable systems where three bidentate ligands are present, such as cat_2Pphen^+, c.f. the resolution of P (2,2'-biphenylylene)$_3^-$ [283].

The stability of the adducts of the hexachloroantimonates towards air and moisture has been noted. The stability of the isolated adducts was not investigated in solution, except in the case of $PCl_4py_2^+ SbCl_6^-$. Rapid hydrolysis occurred but the adduct was also in equilibrium with the easily hydrolysed PCl_5.py. The solid state stability of the complexes cannot be attributed solely to the stability of the cation since $PhPCl_3phen^+ Cl^-$ rapidly hydrolyses. Perhaps the large anion $SbCl_6^-$ forms a more regular crystal lattice than chloride ions, preventing attack by moisture.

No conclusive evidence was found for the existence of five co-ordinate adducts of the type MX_4L^+ or $MX_3L_2^{2+}$. Such adducts are generally not found [1] with P(V), As(V), or Sb(V), but silicon(IV) and other members of group (IV) show a marked tendency to do so. Thus $SiCl_4.NMe_3$ [284], $Ph_3Sidipy^+$ [285], and $Me_3SnCl.py$ [286] are known. In addition six co-ordinate species formed by displacement of halide ions are known e.g. $Sidipy_3^{4+}(Br^-)_4$ [287]. Although the displaced ions are usually bromide or iodide, examples are known with chloride ions e.g. $Si(OCH_3)_2dipy_2^{2+} (Cl^-)_2$ [288]. The addition of pyridine to $SiCl_4$ produces $SiCl_4py_2$ [284] (decomposing in nitrobenzene). With $SiCl_xI_{4-x}$ as the starting material, however, $SiCl_3py_3^+$ (x=3)

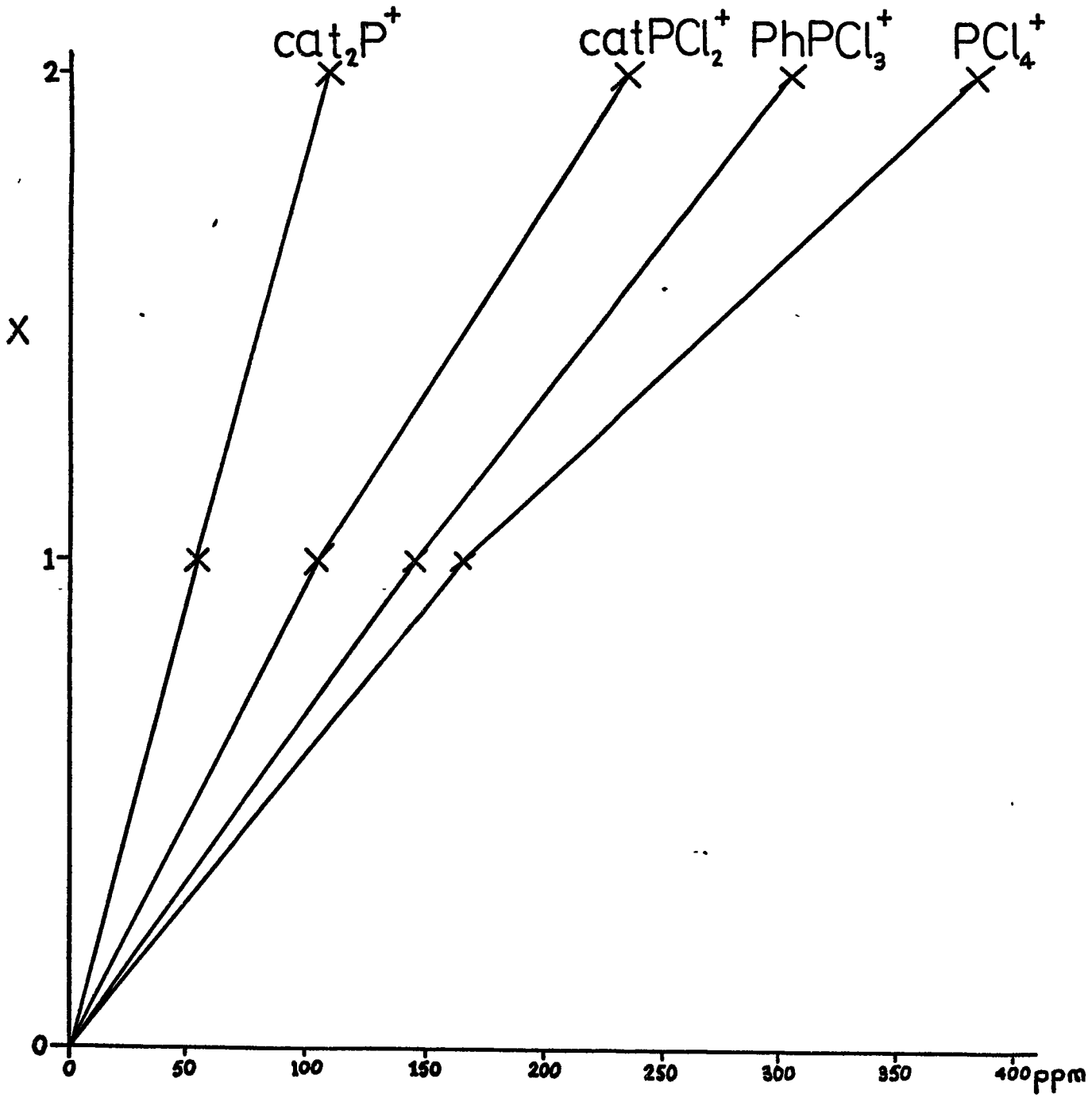
and $SiCl_2py_4^{2+}$ (x=2) are produced [29]. Reaction of dipyridyl and $SiCl_4$ gives $SiCl_4$.dipy as the sole product [284]. No evidence whatsoever was found in the phosphorus systems for the displacement of more than one chloride ion by co-ordination. Displacements analogous to those in the silicon system will be more difficult with phosphorus because of its additional positive charge. The compound cat_2Si forms a 1:1 adduct with pyridine [282], rather than a 1:2 adduct as in the analogous cat_2P^+ system. This may indicate weaker acceptor properties of silicon towards pyridine donors, as also found with chloride ion donors in the non-formation of $SiCl_6^{2-}$ and the only partial association of $SiCl_5^-$ in solution [242].

2. ^{31}P n.m.r. spectra

On addition of ligands to the four- and five- co-ordinate phosphorus acceptors, large upfield shifts were observed in the ^{31}P n.m.r. spectra, as found previously for six co-ordinate species. All new six co-ordinate species had shifts within the established range (+82 to+305 ppm) except for $cat_2PCl_2^-$ and $cat_2PCl.py$. These lay slightly to lower field (+66.3, +80.7 ppm respectively).

The shifts of the adducts all occurred to the low field-side of PCl_6^-. They are progressively reduced by substitution of catechyl groups for chlorine, reflecting the constriction of chemical shift differences in species containing phosphorus-oxygen bonds, as already discussed (Chapter 5 section 3(ii)a). The difference in shift between the five co-ordinate phosphorane Z_4PCl and its chloride ion adduct $Z_4PCl_2^-$ reflects the shift

Fig 39 Chemical shift difference between related 4-6 coordinate phosphorus species



Shift difference between $Z_4PCl_x^{(x-1)-}$ and Z_4P^+

difference between the four and five co-ordinate species Z_4P^+ and Z_4PCl (Fig.39), showing the influence of the co-ordinated groups on the spread of ^{31}P chemical shifts. The difference (Z_4PCl_2 - Z_4PCl) is greater than the difference (Z_4PCl - Z_4P^+) by between 5 and 29%. This correlation is rather unexpected, since the change in co-ordination number affects the bonding of the ligands irregularly (e.g. any π bonding found in P-Cl and P-O bonds in four or five co-ordinate species will be suppressed in the six co-ordinate derivatives, whereas π bonding need not be considered with P-C bonds). In some instances, too, there is the possibility of differing 6 co-ordinate shifts for different isomers. These effects thus appear to be relatively small compared with the overall shift differences. The correlation is also only possible because of the relatively fixed bond angles in four, five and six co-ordinate species. Small changes in bond angle in three co-ordinate species have a pronounced effect on the shifts of the molecules [289].

The shift differences between the various adducts of a particular compound ($Z_4PCl_2^-$, $Z_4PCl.py$, Z_4Pphen^+) are much smaller than the range of shifts found for adducts of different compounds but increase with increasing shift of the species. Thus the shift difference between PCl_4phen^+ and PCl_6^- is ~105 ppm, between $PhPCl_3phen^+$ (low field isomer) and $PhPCl_5^-$ ~68 ppm, $catPCl_2phen^+$ and $catPCl_4^-$ ~39 ppm and cat_2Pphen^+ and $cat_2PCl_2^-$ ~ -29 ppm. Indeed a correlation may be made between the chemical shift difference between adducts of a species (e.g. $PZ_4Cl_2^-$ and PZ_4phen^+) and the shift difference

Fig 40 Relationship between shift difference of related 5- and 6-coordinate species and that of their adducts

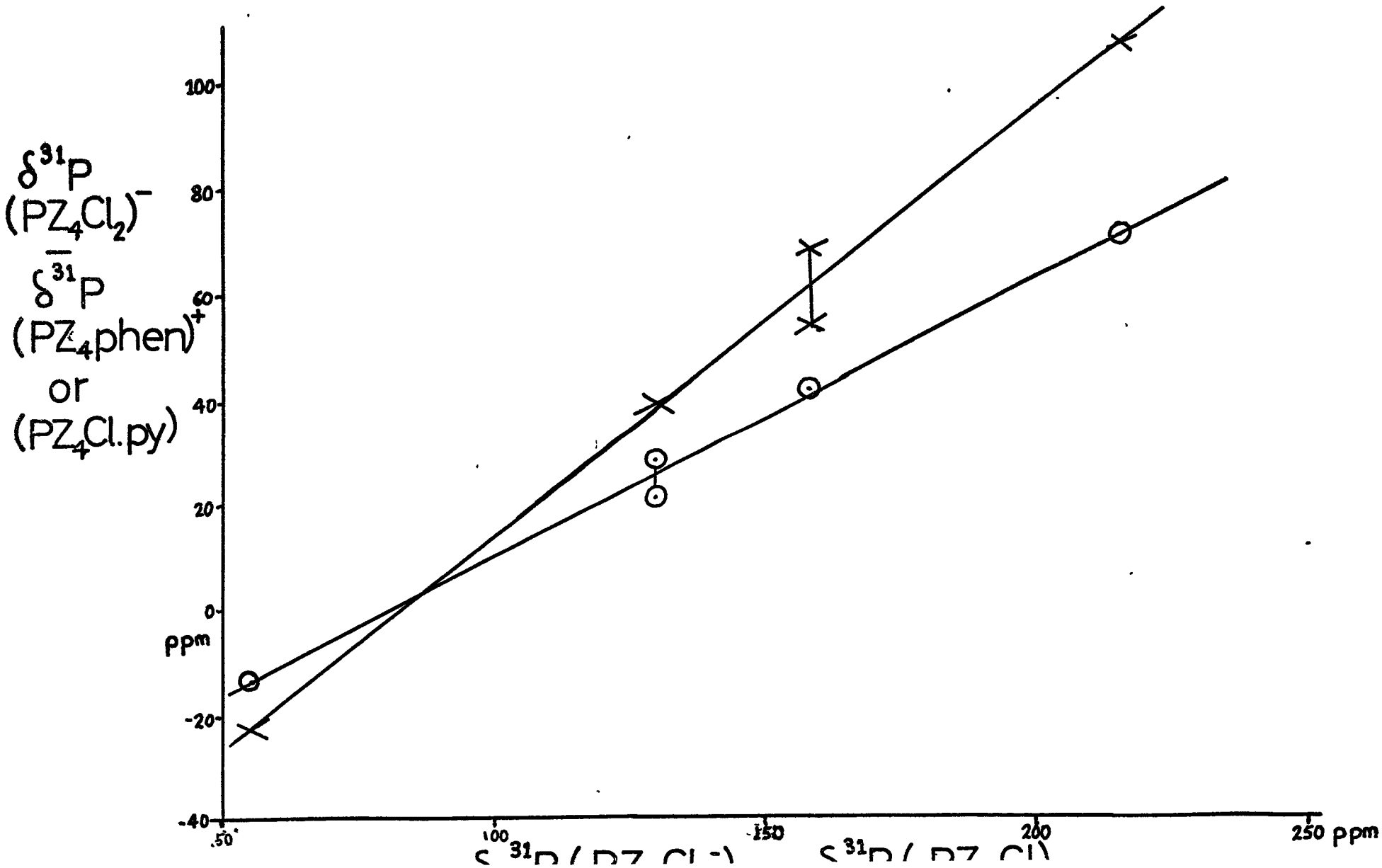
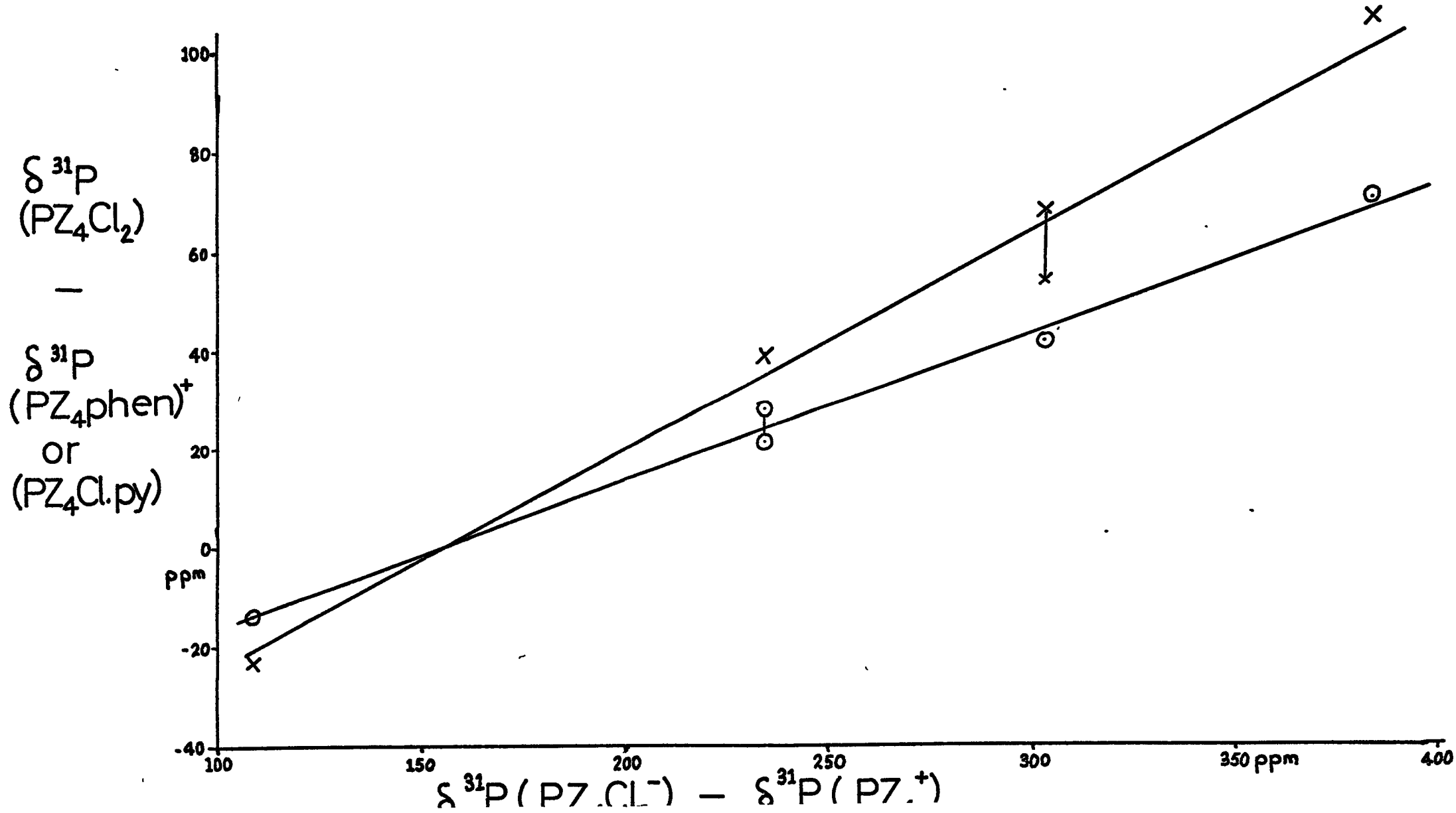


Fig. 41 Relationship between shift difference of related 4- and 6-coordinate species and that of their adducts



between one of the adducts and its 4 or 5 co-ordinate precursor (PZ_4^+ or PZ_4Cl) (Figs. 40,41). Although the reason for such a good correlation is not clear, the graphs are consistent with a changeover of the shift of the adducts:-

$$\delta^{31}P\ Z_4Pphen^+ < Z_4PCl.py < Z_4PCl_2^-$$

for $Z_4P = PCl_4$, $PhPCl_3$, $catPCl_2$

$$\delta^{31}P\ Z_4Pphen^+ > Z_4PCl.py > Z_4PCl_2^-$$

for $Z_4P = cat_2P$

They predict for a $PZ_4Cl_2^-$ - PZ_4Cl shift difference of ~85 ppm (or $PZ_4Cl_2^-$ - PZ_4^+ shift difference of ~163 ppm) that the shifts of all three adducts PZ_4phen^+, $PZ_4Cl.py$, $PZ_4Cl_2^-$ will be identical. As an indication of the shift of an unknown $PZ_4Cl_2^-$ species can be found from the shifts of PZ_4^+ and PZ_4Cl using Fig.39, using Fig.40 or 41 the prediction can be extended to new PZ_4phen^+ or $PZ_4Cl.py$ species. From the shifts of $MePCl_3^+$ and $MePCl_4$ the shifts of $MePCl_5^-$ and $MePCl_3phen^+$ are predicted to be ~ +206 - +246 and +138 - 146 ppm respectively, in good agreement with the limited data known (Chapter 4 section 3(ii)).

The shifts of the species giving the order $Z_4Pphen^+ < Z_4PCl.py < Z_4PCl_2^-$ can be interpreted as the domination of charge effects on the shielding of the phosphorus. The reverse order only appears when the shift range of the 4,5 and 6 co-ordinate species indicates that charge effects are relatively unimportant.

The shifts of the ions $(cat_xPCl_{6-2x})^-$ x=0-3 shows large irregularities from a linear progression, although the series $\left[cat_xP\ (2,2'\text{-biphenylylene})_{3-x}\right]^-$ is approximately linear. In both cases the greatest deviation is at the low field end.

TABLE 72

SHIFTS OF RELATED SIX CO-ORDINATE ADDUCTS

	$\delta^{31}P$ 265	Δ		$\delta^{31}P$	Δ
$biphen_3P^-$	+181		PCl_6^-	+297.9	
$biphen_2Pcat^-$	+147	-1	$catPCl_4^-$	+157.3	-68.7
$biphenPcat_2^-$	+106	-9	$cat_2PCl_2^-$	+66.3	-88.7
cat_3P^-	+82		cat_3P^-	+82	

Δ = Difference between observed shift and shift calculated from linear interpolation between A_3P^- and B_3P^-

biphen = 2,2'-biphenylylene

Although linear variations are found in four [100,101,219] and five [210] co-ordinate phosphorus, large deviations occur in three co-ordinate phosphorus compounds. Deviations have been discussed in terms of σ and π bonding contributions [289]. π-bonding is not expected to be significant in six co-ordinate species, however.

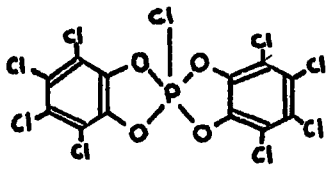
Sharp lines superposed on solid state spectra were found with tetraalkylammonium organochlorophosphates but not with the cationic adducts. This probably reflects the weak lattice energy in the former adducts due to the bulky counter ions. The cationic adducts will have stronger, more compact structures with the smaller chloride or hexachloroantimonate counter-ions.

Due to the proximity of large organic groups or neighboring quadrupoles, the solid state n.m.r. spectra of the adducts were somewhat broader than found with PCl_6^-. This, together with the small percentage of phosphorus in the complexes, made the observation of many of the spectra difficult, which in turn led to difficulties in obtaining accurate shift data. Nonetheless, ^{31}P n.m.r. remained an essential tool for the characterisation of the complexes in the solid state and gave in some cases the only unambiguous evidence for formation of the adducts.

3. Future Work

The ease of formation and stability of pyridine and chloride adducts of the phosphorus(v) chloro-compounds studied suggests that the range of substituted phosphorus(v) compounds exhibiting acceptor properties may be considerable. Molecules with electronegative substituents, e.g.

Cl_3CPCl_4 [290]



[291]

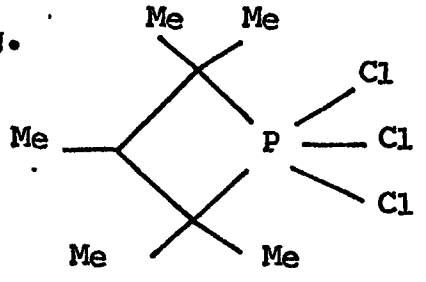
CF_3PCl_4 [292]

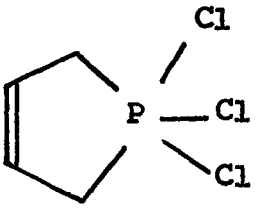
may thus form extremely stable adducts, and polysubstituted species (e.g. $(Cl_3C)_2PCl_3$ [293]) may well retain some acceptor properties. (Adducts between pyridine and $FPCl_4$ and F_2PCl_3 are already known [294]). Moreover molecules with electropositive substituents may possess some degree of acceptor strength. The ability of $MePCl_4$ to act as an acceptor has already been mentioned (Chapter 4 section 3(ii)).

Before more detailed predictions of possible acceptor molecules are attempted, further investigation of the effect of constraining phosphorus in small rings is necessary. The

possibility of using 2,2'-biphenylylene trichlorophosphorane has already been mentioned. (Although this compound has not yet been prepared its synthesis should be possible from the parent chlorophosphine described in Ref.295). If the effect of ring constraint is found to be significant, many compounds with five and four membered rings may possess acceptor properties.

e.g.





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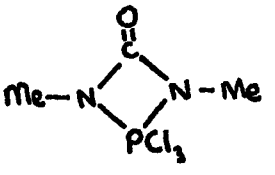
If ligands with 5 membered chelate rings which give the 6 co-ordinate phosphate complexes listed in Appendix 1 form mixed organochlorophosphoranes (c.f. catPCl_3), these species may also possess acceptor properties.

The possibility of small rings enhancing the formation of adducts makes the investigation of four-membered phosphorus-nitrogen heterocycles worthwhile. Perhaps a suitable species to start investigations would be



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and its possible cationic derivative. The possibility of stabilisation of high co-ordination numbers is suggested in these species by their structures which are almost without exception covalent. From the similarity of range of chemical shifts in pyridine and in non-donor solvents [31]

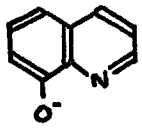
however, some phosphonitrilics seem not to co-ordinate pyridine.

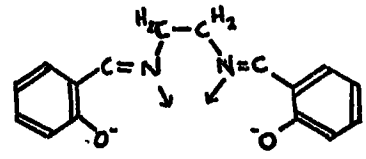
Although the salts $PhPCl_3^+$ $catPCl_4^-$ and $PhPCl_3^+$ PCl_6^- have been isolated, it seems unlikely in view of the reluctance of the catechyl salts to form cations, and the weakness of the chloride acceptor properties of organochlorophosphoranes, that there will be other stable salts between the phosphoranes discussed (except perhaps $PhPCl_3^+$ $cat_2PCl_2^-$). When other phosphoranes are included ($MePCl_4$, Ph_2PCl_3) a larger number of salts should be possible. Salts may also probably be formed by addition of a bidentate ligand to stabilise the cation. Thus, although PCl_5 and $catPCl_3$ do not react, addition of, say, dipyridyl would probably slowly form $catPCl_2dipy^+$ PCl_6^- or PCl_4dipy^+ $catPCl_4^-$.

The acceptor properties of biscatechyl phosphorus monochloride and also the six co-ordinate species based on a biscatechyl framework (Appendix 1), suggests that this framework may be useful in studying the effect of single substituents on the formation of six co-ordinate adducts. Many suitable five co-ordinate structures of the type cat_2PZ are known, e.g. Z=H, [298] Br, [217] Me, Ph [299], OH, [217] OPh [62].

The possibility of investigation of acceptor properties of bromophosphoranes, and mixed chlorobromophosphoranes using $catPBr_{3-x}Cl_x$ was mentioned in Chapter 4 section 3(iii).

Many of the complexes prepared in this work contain phosphorus surrounded by two O^- and two nitrogen ligands. This suggests the possibility of co-ordination complexes containing mixed O^-,N ligands, for instance





as found both in transition metal and main group complexes [300,301]. Difficulties may, however, occur since simple phenoxychlorophosphonium species are unstable with respect to the tetraphenoxyphosphonium ion [217].

The present work has thus shown that a number of new 6 co-ordinate phosphorus compounds may be prepared by co-ordination of donors such as pyridines and chloride ions to suitable phosphoranes, and there clearly remains considerable scope for future investigations in this field.

NOTE

During the final stages of writing the thesis two significant papers [a,b] have been published concerning the formation of weak pyridine adducts with phosphoranes containing five-membered O-P-O rings, usually including one catechol group. These papers are in full accordance with the above discussion and can again be interpreted by the enhancement of acceptor properties by constraining phosphorus in five-membered heterocyclic rings.

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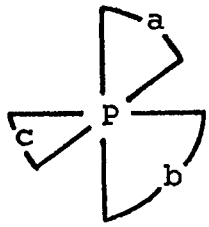
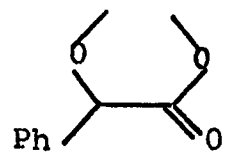
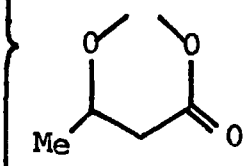
APPENDIX 1

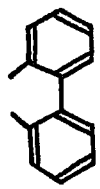
SIX CO-ORDINATE PHOSPHORUS SPECIES CONTAINING NO HALIDE IONS

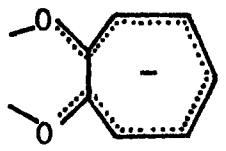
Species of type 

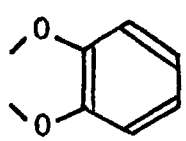
1- or 2+

a	b	c	Overall charge	δ^{31} P	Ref.
Biphen	Biphen	Biphen	1-	a) +186.6 b) +181.2	1 1
Trop	Trop	Trop	2+	-	2
Gly	Gly	Gly	1-	-	9
Cat	Biphen	Biphen	1-	+147	3
Cat	Cat	Biphen	1-	+106	3
Cat	Cat	Cat	1-	+82 +84 -	3 4 5-8, 14
Napdiol	Biphen	Biphen	1-	+168	3
Gly		Benzil	1-	+93	10
Gly		Benzil	1-	+95	10
Pin		Benzil	1-	+97	10

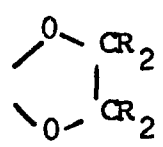
KEY

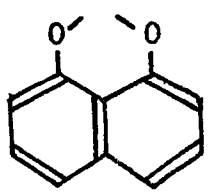
Biphen
2,2' biphenylylene 

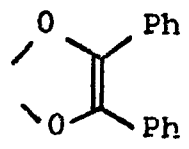
Trop
tropolonate 

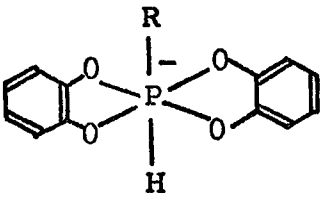
Cat
catechyl
(1,2-phenylenediolate) 

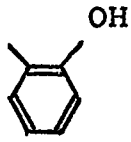
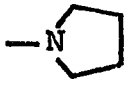
Gly
1,2-ethylene-glycolate R=H

Pin
pinacolate
R=Me 

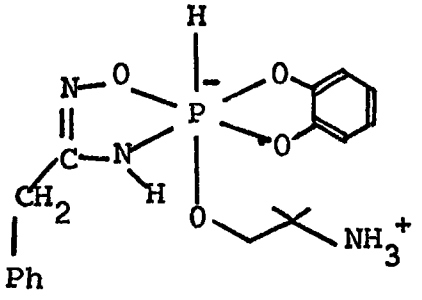
Napdiol
1,8-naphthylene-diolate 

Benzil 



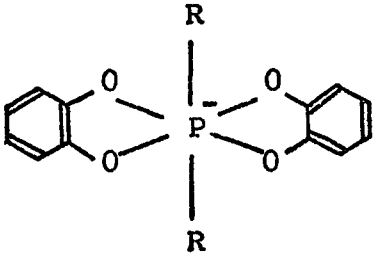
R	δ^{31} P	Ref.	R	δ^{31} P	Ref.
Me	a) +113.5 b) +113.3	11,12 12	t-Bu	-	12
			C_6F_5	+133.45	12
Ph	a) +108.5 +108.8 b) +108.4	11 12 12	OMe	+97.2 +97	12 13
	a) +98 b) +99	8 4	OPh	+98	13
				+97	13
	+99	13		+98	13

a,b refer to complexes with different counter ions



Probably also materials of similar description but with aldoxime side-chain

Ref 8



R = OPh

δ^{31} P +107 ref.3

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APPENDIX 2

CHEMICAL SHIFTS OF POSSIBLE HYDROLYSIS PRODUCTS

Phosphorus(v) compound	Possible hydrolysis products, with chemical shift (ppm)
PCl_5	$POCl_3$ -2.1; $POCl_2OH$ -9.7; $POCl(OH)_2$ -18.2 H_3PO_4 0.0 $Cl_2P(O)OP(O)Cl_2$ 8.0-10.0; $ClOHP(O)OP(O)OHCl$ -18.2 $(O_3POPO_3)^{4-}$ $4H^+$ +11
$(C_6H_4O_2)PCl_3$	$(C_6H_4O_2)P(O)Cl$* -18; H_3PO_4 0.0
Bu_3PCl_2	Bu_3PO -44
Ph_3PCl_2	Ph_3PO -23 - -27
Ph_2PCl_3	$Ph_2P(O)Cl$ -42.7; $Ph_2P(O)OH$ -25.2
$PhPCl_4$	$PhP(O)Cl_2$ -34.1; $PhP(O)(OH)_2$ -17.9
$MePCl_4$	$MeP(O)Cl_2$ -44.4; $MeP(O)(OH)_2$ -30.7

Chemical shifts are taken from:

V. Mark, C. H. Dungan, M. M. Crutchfield, J. R. Van Wazer

Topics in Phosphorus Chemistry, Vol.5 Chapter 4.

* E. Fluck, H. Gross, H. Binder, J. Gloede. Zeit. Nat. 21b, 1125 (1967)

Possible mixed species of type RP(O)OHCl where not reported have not been tabulated.

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A ^{31}P NMR AND ^{35}Cl NQR INVESTIGATION OF SOME HEXACHLOROPHOSPHATES

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Department of Chemistry, University of Durham

(*Received* 20 *April* 1973)

Abstract—The ^{31}P NMR spectra in both solid state and solution, and the ^{35}Cl NQR spectra in the solid, have been recorded for some hexachlorophosphates and for the compounds $[C_8H_{12}N]_2PCl_7$ and $C_{14}H_{14}PCl_7$. The presence of the PCl_6^- ion as the only phosphorus-containing anion has been confirmed in all cases. Data are also reported for the chlorotriphenylphosphonium ion in $Ph_3PCl^+PCl_6^-$.

INTRODUCTION

THE HEXACHLOROPHOSPHATE (PCl_6^-) ion has been characterized by ^{31}P NMR spectroscopy in the ionic form of solid phosphorus(V) chloride [1–5], in solutions of phosphonitrilic compounds[6–8], and in solutions of the reaction products of phosphorus(V) chloride with chlorophosphoranes and aliphatic nitriles[9,10], chemical shifts of between +281 and +305 ppm relative to 85% phosphoric acid were obtained, depending on the system and the experimental method Chlorine nuclear quadrupole resonance (NQR) frequencies have also been measured for this ion in solid PCl_5[11–13] and Et_4NPCl_6[12,14]. We report the results of an investigation of some hexachlorophosphates by ^{31}P NMR in both solid state and solution and by ^{35}Cl NQR in the solid Results are also given for the 2,4,6 collidinium salt $[C_8H_{12}N]_2PCl_7$, and the tropylium compound $C_{14}H_{14}PCl_7$ The latter was first prepared from cycloheptatriene and phosphorus(V) chloride by Bryce-Smith and Perkins[15], who suggested as possible structures either $C_7H_7^+Cl^-$. $C_7H_7^+PCl_6^-$ or $(C_7H_7)_2^+PCl_7^{2-}$ (This reaction had been used previously by Kursanov and Vol'pin[16] in the preparation of tropylium chloride, but their procedure was such as to destroy the intermediate phosphorus complex.) The second structure appears most improbable, however, for a phosphorus compound, because of the number of available bonding orbitals, and its formulation as a hexachlorophosphate is supported by ir data[17]. In addition, the ^{31}P NMR and ^{35}Cl NQR spectra have been recorded for the Ph_3PCl^+ ion in $Ph_3PCl^+PCl_6^-$. A more detailed account of compounds containing this and similar ions will appear in a subsequent publication.

EXPERIMENTAL

Chemicals of the best available commercial grade were used, in general without further purification, except for triphenylphosphine which was recrystallized from acetone Chlorotriphenylphosphonium hexachlorophosphate was prepared by the method of Rozinov *et al* [18] The final stage of this reaction has also been mentioned by Latscha [9] Found C (by wet oxidation)* 39 5, H, 3 08, P, 11 00, Cl, 46 0%, calc for $C_{18}H_{15}P_2Cl_7$ C, 39 9, H, 2 79, P, 11 44, Cl, 45 8% (Rozinov *et al* analysed for Cl only, and their calculated value is incorrect) The compound $C_{14}H_{14}PCl_7$ was prepared by method (b) of Bryce-Smith and Perkins[15] Analyses for P and Cl were consistently high, and those for C were correspondingly low (Found P, 7 18, Cl, 56 98, C, 31 17, H, 3 04%, calc for $C_{14}H_{14}PCl_7$ P, 6 72, Cl, 53 8, C, 36 4, H, 3 03%), suggesting that the product contained tropylium hexachlorophosphate, $C_7H_7PCl_6$, as impurity Tropylium hexachlorophosphate was prepared by a modification of the first literature method for $C_{14}H_{14}PCl_7$[15], the compound was separated without leaving the reaction mixture overnight (Found P, 9 08, Cl, 60 94, C, 26 67, H, 2 71%, calc for $C_7H_7PCl_6$ P, 9 25, Cl, 63 53, C, 25 1, H, 2 11%) The product thus probably contains a small amount of tropylium chloride, which does not affect the spectroscopic results Recrystallization of these products was not attempted because of their instability Bis(2,4,6 collidinium) hexachlorophosphate chloride, $[C_8H_{12}N]_2PCl_7$, was prepared by mixing solutions containing equimolar amounts of phosphorus(V) chloride and 2,4,6 collidine (undried) in carbon tetrachloride The white solid produced was separated in a drybox (Found C, 37 17, H, 4 94, N, 4 97, P, 5 25, Cl, 46 96%, calc for $C_{16}H_{24}N_2PCl_7$ C, 36 7, H, 4 58, N, 5 36, P, 5 92, Cl, 47 4%) A similar pyridinium compound has

* We were not able to obtain satisfactory carbon analyses for this compound by use of the automatic analyser, the reason for this is not clear

been prepared by Beattie *et al* [19], and assigned the structure $C_5H_5NH^+PCl_6^-$ $C_5H_5NH^+Cl^-$ from vibrational spectroscopic evidence Tetraethylammonium hexachlorophosphate was prepared by the method of Gutman and Mairinger[20] All compounds showed a broad, strong i r band (Nujol mull) between 450 and 440 cm^{-1}, as expected for ν_3 of PCl_6^- [17,19], and the absence of bands characteristic of the PCl_4^+ ion or of molecular PCl_5

^{31}P NMR spectra were recorded at 34 2°C on a Perkin–Elmer R10 spectrometer operating at 24 29 MHz, with a Digiac signal averaging accessory Samples were contained in 8 5 mm o d stationary tubes The technique of recording solid state spectra on a high resolution instrument has been described previously[5] Chemical shifts were measured relative to external P_4O_6[21], but are quoted relative to 85% phosphoric acid Values were generally reproducible to better than ±0 3 ppm (solution) and ±2 ppm (solid)

^{35}Cl NQR spectra were recorded at 77K on a Decca spectrometer, using Zeeman modulation Samples were enclosed in tubes of either 13 or 24 mm o d , the larger tubes were used where lines were of low intensity, if sufficient of the compound was available The resonance frequencies were reproducible to better than ±10 kHz

RESULTS AND DISCUSSION

The ^{31}P chemical shifts obtained are given in Table 1 A single peak at high field was observed for each compound, the linewidth in the solid varied considerably with the counter-ion, however An additional peak at lower field from the Ph_3PCl^+ ion was present in $Ph_3PCl^+PCl_6^-$

The values for the anions all lie within the range +295 to +305 ppm, in excellent agreement with solution data for the hexachlorophosphate anion[6–10], and with the shift of +299·7 ppm for this ion in solid phosphorus(V) chloride determined on a high resolution spectrometer[5] We therefore conclude that all of these compounds, including $[C_8H_{12}N]_2PCl_7$ and $C_{14}H_{14}PCl_7$, have PCl_6^- as the only phosphorus-containing anion The tropylium salt is thus correctly formulated as $[C_7H_7]_6^+PCl_6^-,Cl^-$ and the collidinium salt as $[C_8H_{12}N]_2^+PCl_6^-,Cl^-$

There are some differences between the solid and solution values, but this is not surprising in view of changes in diamagnetic susceptibility and crystal packing effects, the spread of values is noticeably greater in the solid Similar differences have been observed previously in other compounds[5] It is perhaps noteworthy that the best agreement is obtained for tetraethylammonium hexachlorophosphate, which has the most symmetrical cation of the species studied There are also minor differences between the shift values of $Ph_3PCl^+PCl_6^-$ in dichloromethane and nitrobenzene solution, but the compound is clearly ionic in both solvents and in the solid The chemical shifts for the Ph_3PCl^+ ion are in very good agreement with previous solution values, which lie in the range −66 to −62 ppm [9,22,23].

Table 2 ^{35}Cl NQR frequencies (MHz) for some hexachlorophosphates at 77K

Compound	ν_{Cl}(MHz) and assignment
$Ph_3PCl^+PCl_6^-$	29 33, 29 53, 29 59, 29 76, 29 93, 30 44, 31 15 (see text)
$C_{14}H_{14}PCl_7$	29 40, multiplet centred at 29 77 Average 29 7 (PCl_6^-)
$C_7H_7^+PCl_6^-$	29 32, multiplet centred at 29 80 Average 29 65 (PCl_6^-)
$[C_8H_{12}N]_2PCl_7$	28 78, 29 31, 29 65, 30 15, 30 55, 30 67 Average 29 85 (PCl_6^-)
$Et_4N^+PCl_6^-$	29 37, 30 025 Average 29 81 (PCl_6^-—see text)

Further confirmation of the solid state structures of these compounds is provided by the ^{35}Cl NQR data, as given in Table 2 above

With the exception of the highest frequency line in $Ph_3PCl^+PCl_6^-$, the values are all within the range (28 4–30·7 MHz) found for the PCl_6^- ion in phosphorus(V) chloride[11–13] and tetraethylammonium hexachlorophosphate[12,14] $Ph_3PCl^+PCl_6^-$ shows seven lines, six of which are assigned to PCl_6^- and the remaining one to the cation If the line at 31 15 MHz is ascribed to Ph_3PCl^+, the average frequency of the remaining signals is 29·76 MHz, in good agreement with the average PCl_6^- frequencies in the other compounds Further evidence is necessary before this provisional assignment can be confirmed, however The compound $[C_8H_{12}N]_2PCl_7$ also shows six lines for PCl_6^-, as observed in the most recent work on ionic PCl_5[13]

Table 1 δ ^{31}P(ppm from 85% H_3PO_4) for some hexachlorophosphates

Compound	Solvent	δ ^{31}P (Soln)	δ ^{31}P (Solid)
$Ph_3PCl^+PCl_6^-$	CH_2Cl_2	−66 3*	−64 3*
		+296 0	+305 0
	$PhNO_2$	−64 7*	−64 3*
		+298 7	+305 0
$C_{14}H_{14}PCl_7$	$PhNO_2$	+299 2	+295 7
$C_7H_7^+PCl_6^-$	$PhNO_2$	+297 3	+296 1
$[C_8H_{12}N]_2PCl_7$	$PhNO_2$	+297 5	+298 7
$Et_4N^+PCl_6^-$	$PhNO_2$	+297 9	+298 5

* Ph_3PCl^+ ion

(Earlier investigators found three signals for this ion in unannealed PCl_5[11,12] and four in annealed PCl_5 [12].)

The tropylium salts $C_{14}H_{14}PCl_7$ and $C_7H_7^+PCl_6^-$ both showed a single line between 29·3 and 29·4 MHz, together with a complex multiplet near 29·8 MHz, which could not be resolved even by using larger samples in 24 mm o.d. tubes, because of the weakness of the signals. The spectra were reproducible in independent scans, and the lines for both compounds are assigned to the PCl_6^- ion, in accordance with the NMR results. Tetraethylammonium hexachlorophosphate produced two lines in a 1:2 intensity ratio, at 29·37 and 30·025 MHz. Di Lorenzo and Schneider reported three lines for this compound at 77K, at 29·32 ± 0·03, 30·06 ± 0·02, and 30·34 ± 0·02 MHz (intensity 1·2:1)[12], and a more accurate determination by Tong[14] gave values of 29·374 ± 0·005, 30·024 ± 0·005 and 30·365 ± 0·005 MHz, in the same intensity ratio. The reason for our non-observance of the third line is not clear, but the frequencies of the other two lines are in excellent agreement.

The crystal structures of the compounds studied are not known, so that it is not possible to correlate the number of NQR lines observed with the structure. The presence of six lines for PCl_6^- in some instances, however, would seem to suggest either a comparatively low crystal symmetry, or else a considerable distortion of the PCl_6^- octahedra at this temperature.

The NMR and NQR results are thus completely in accordance with the formulation of all the compounds studied as hexachlorophosphates.

Acknowledgement—One of us (R.N.R.) thanks the Science Research Council for a Research Studentship. We also thank R. Coult for phosphorus, chlorine and some carbon microanalyses and Dr. Royston for writing the program for the signal averaging accessory.

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