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A STUDY OF
REACTIONS OF TERTIARY PHOSPHINES WITH HALOGENS

A Thesis
presented for the degree of
Doctor of Philosophy
in the Faculty of Science of the
University of St. Andrews

by

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June, 1974

United College of
St. Salvator and
St. Leonard,
St. Andrews

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a higher degree.

The thesis describes results of research carried out in the Chemistry Department of the University of St. Andrews during the three years beginning 1st October 1970, under the supervision of Dr. G.S. Harris

CERTIFICATE

I hereby certify that

David Michael Beaumont

has spent eleven terms at research work under my supervision, has fulfilled the conditions of Ordinance General No. 12 and Resolution of the University Court, No. 1, and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research

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composition $(\text{Me}_3\text{P})_2\text{Br}_2$ and $(\text{Me}_3\text{P})_2\text{I}_2$ were isolated.

The reactions of the halogens Br_2 , I_2 and IBr with methylene-bis-diphenylphosphine, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, and ethylene-bis-diphenylphosphine, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, were investigated using conductometric methods. These studies, coupled with the behaviour of the solid adducts when dissolved in methyl cyanide, showed that ions containing only one phosphonium centre were preferred. The 2:1 compound $\text{Ph}_2\text{P}(\text{Br}_2)\text{CH}_2\text{P}(\text{Br}_2)\text{Ph}_2$ was thought to ionise as $[\text{Ph}_2\text{P}(\text{Br}_2)\text{CH}_2\overset{\oplus}{\text{P}}(\text{Br})\text{Ph}_2]\text{Br}^-$ as it is suggested that ions containing two phosphonium centres in close proximity would be unstable. Halogen exchange reactions have been observed in these systems with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{Br}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{Br}_4$ being isolated from 1:1 and 2:1 mixtures of IBr and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ respectively. When bromine is reacted with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ in the 3:1 ratio a proportion of species containing two phosphonium centres is produced and this is thought to aid substitution of one of the methylene protons.

A conductometric study of the triphenylphosphine-iodine system has shown that the stable species in solution are $(\text{Ph}_3\text{P})_2\text{I}_2$ and Ph_3PI_6 and the solid adducts Ph_3PI_6 and Ph_3PI_8 were isolated. A vapour pressure-composition study of the $\text{Ph}_3\text{P}-\text{Br}_2$ system indicated that $\text{Ph}_3\text{PBr}_{12}$ was formed as a stable solid species.

An automated system for the determination of freezing point depression using solutions of nitrobenzene is described; however, this apparatus was shown to be unsuitable for similar studies using methyl cyanide as solvent.

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I N T R O D U C T I O N

Introduction

The hydrides and halides of phosphorus were some of the first compounds to be discovered and investigated in the late eighteenth century by such notable chemists as Hofmann, Gay Lussac and Michaelis. Gengembre in 1783 and Kirwan¹ in 1786 first prepared phosphine. The phosphorus halides, PCl_3 , PCl_5 and PF_3 were discovered by Gay Lussac, Thénard and Davy² in 1808. Most of the other phosphorus hydrides and halides which are known today were prepared and partially characterised in the nineteenth century. The early chemists had limited and rather crude apparatus and it is to their credit that they obtained so much accurate information on these hydrolytically unstable compounds.

Two distinct series of compounds were found, the trihalides and pentahalides, by reacting phosphorus with halogens. These caused great interest in connection with the theories of valency and pentacoordinate phosphorus. The ease of hydrolysis, whilst hindering the study of most of their chemical and physical properties enabled the analysis and characterisation to be undertaken readily. The hydrides and halides of arsenic, antimony and bismuth were being studied at the same time, producing results analogous to those found for the phosphorus compounds. The next area to be investigated was that of the substituted phosphines, arsines, stibenes and bismuthines³ $\text{R}_n\text{MH}_{(3-n)}$ ($n = 1, 2, 3$) and the substituted pentahalides⁴ $\text{R}_n\text{MX}_{(5-n)}$ ($n = 1, 2, 3, 4$) (where $M = \text{P, As, Sb or Bi}$). One of the first compounds to be made in this series was Et_3PI_2 by Crafts and Silva⁵ in 1871. Mason and Kirkland⁶ were able to produce Et_3PI_4 and Et_4PI_3 as a mixture by heating phosphorus

and ethyl iodide in a sealed tube.

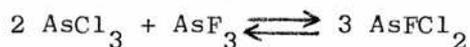
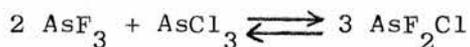
Phosphorus occupies an important place in chemistry today. It is vital to the body's biochemical system and is widely incorporated in such diverse commodities as fertilisers and detergents etc. Much work has been done on compounds of phosphorus using new physical and manipulative techniques and this area still remains one of great interest to chemists.

The Group VB elements form compounds which are 3, 4, 5 or 6 coordinated. By far the most numerous are those which contain pentavalent tetrahedrally coordinated P, As, Sb, Bi atoms (eg. PCl_4^+ , PO_4^{3-} , $(\text{RO})_3\text{PO}$, AsCl_4^+ etc). The trivalent compounds are fairly common and examples of these are PCl_3 , BiCl_3 , AsCl_3 etc. Examples of fivefold trigonal bipyramidal and sixfold octahedral coordination are relatively few in number (eg. PF_5 , SbCl_6^- , PCl_6^- etc). It is of interest to study the halides as they produce a large amount of information about structures and bonding in the Phosphorus group compounds.

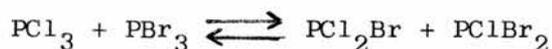
The Trihalides of Group VB

Van Wazer⁷ has outlined the principles of bonding in phosphorus compounds and these can be applied to the rest of the Group VB elements. In the case of trivalent phosphorus, a pyramidal arrangement of three σ -bonds is found. Evidence based on bond-length and enthalpy data⁷ suggests that in the case of phosphorus there are three pure σ -bonds, with little or no π -character (shown by nuclear magnetic resonance studies)⁸ and this may well apply to the remainder of the group. The bond angles lie between 90° and 109.5° (the tetrahedral angle) because the lone pair of electrons on the phosphorus atom causes varying amounts of sp^3 character in these bonds.

The simple halides are formed by reacting the elements with a stoichiometric amount of the halogen. The mixed halides are prepared by a reorganisation reaction eg.



Arsenic trifluoride and arsenic trichloride are immiscible with each other; however Ruff and Paulett⁹ showed from ¹⁹F nuclear magnetic resonance that this exchange equilibrium occurs in the vapour phase. The phosphorus compounds undergo exchange more rapidly. An example is the formation of PCl_2Br and PClBr_2 in an equilibrium

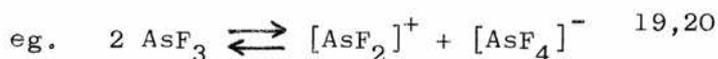


in less than 15 minutes at 25°C from a mixture of phosphorus tribromide and phosphorus trichloride¹⁰. These mixed halides are formed in appreciable amounts only if there is some particular feature of the mixed halide favouring its stability (eg. compounds containing a P-F bond are favoured on account of the strength of the P-F bond).

The trihalides which have been isolated to date are set out in Table 1.

Table 2 shows those mixed halides which have been identified by various physical techniques such as nuclear magnetic resonance, mass spectrometry and Raman spectra.

The halides normally exist as covalent compounds exhibiting low conductivities due to weak dissociation into ions.



The conductivities of the halides AsF_3 , AsCl_3 , AsBr_3 , SbCl_3 and SbBr_3 are increased by substances which can donate halide ions, eg. KF , Me_4NCl , TlBr , or accept them, eg. SbF_5 ,

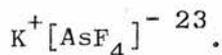
Table 1

Phosphorus	Arsenic	Antimony	Bismuth
PF_3	AsF_3	SbF_3	BiF_3
PCl_3	AsCl_3	SbCl_3	BiCl_3
PBr_3	AsBr_3	SbBr_3	BiBr_3
PI_3	AsI_3	SbI_3	BiI_3
$\text{PF}_2\text{Cl}^{10a}$		SbBrI_2^{12}	
PFCl_2^{10a}			
PF_2Br			
PFCBr_2			
$\text{PCl}_2\text{Br}^{10,11}$			
$\text{PClBr}_2^{10,11}$			

Table 2

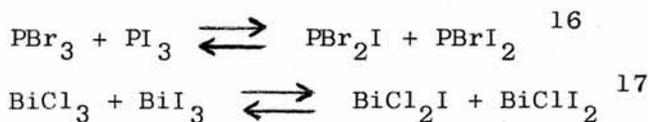
Phosphorus	Arsenic	Bismuth
$\text{PFCIBr}^{13,14}$	AsF_2Cl^9	$\text{BiCl}_2\text{I}^{17}$
$\text{PCl}_2\text{I}^{15}$	AsFCI_2^9	BiClI_2^{17}
PClI_2^{15}	$\text{AsCl}_2\text{Br}^{16}$	$\text{BiBr}_2\text{Cl}^{18}$
$\text{PBr}_2\text{I}^{15}$	AsClBr_2^{16}	BiBrCl_2^{18}
PBrI_2^{15}		

FeCl_3 , AlCl_3 . This has resulted in a variety of complexes being isolated, eg. $[\text{N}(\text{CH}_3)_4]^+[\text{AsCl}_4]^-^{20}$, $[\text{N}(\text{CH}_3)_4\text{Cl}]^+[\text{AsCl}_4]^-$, $2\text{AsCl}_3(\text{solvate})^{21,22}$, $[\text{AsCl}_2]^+[\text{SbCl}_6]^-^{20}$,

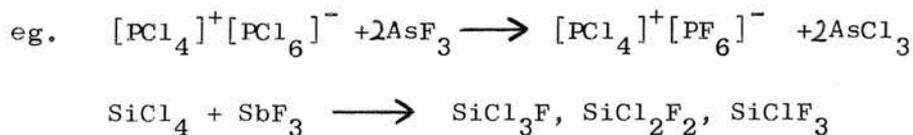


The phosphorus group halides are able to form addition compounds in which the arsenic, antimony and bismuth trihalides accept a pair of electrons from donor molecules such as amines, trimethylphosphine etc. There is some doubt whether the trichlorides or tribromides of arsenic or antimony form complexes with halides of boron, aluminium, or gallium²⁴. However, weak complexes between phosphorus trichloride and the above three halides are found²⁵.

The chemistry of the trihalides is dominated by the 'scrambling' reactions, in which halogen exchange occurs when two different trihalides are mixed eg.



This is especially so in the case of phosphorus. They also act as halogenating agents, the best example being the fluoridation of non-metal chlorides²⁵.



The Pentahalides of Group VB

The pentahalides of phosphorus, arsenic, antimony and bismuth which have been isolated to date are shown in Table 3.

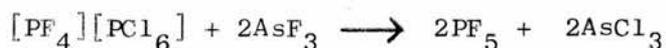
This group of compounds can be represented by MX_5 , $MX_nY_{(5-n)}$. The number of possible compounds is large, only the fluorides and chlorides are well known along with some of the mixed fluorochlorides. Apart from some of the bromides and chlorobromides, the rest of the members of the series have not been investigated.

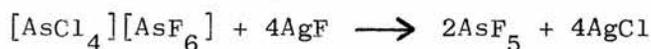
Table 3

Phosphorus	Arsenic	Antimony	Bismuth
PF_5 PCl_5 PBr_5	AsF_5	SbF_5 $SbCl_5$	BiF_5
PF_4Cl ²⁶ PF_3Cl_2 ^{27,28} PF_2Cl_3 ^{29,30} $PFCl_4$ ^{29,30} PF_3Br_2 ³¹ PF_2Br_3 ¹² $PFCBr_4$ ³² $PClBr_4$ ³³		SbF_3Cl_2 ³⁴ SbF_2Cl_3 ³⁵ $SbFCl_4$ ³⁶ SbF_3Br_2 ³⁷	

Phosphorus pentaiodide has not been isolated or even observed. It has been suggested that overcrowding round the phosphorus atom may occur, however, models have shown that steric factors are unlikely to affect the formation of this compound. The reason put forward to explain its absence is the incompatibility of the 3d orbitals on phosphorus with the 7s, p and d orbitals of iodine³⁸.

The simple pentahalides are formed by reaction of a mole of halogen with the corresponding trihalide, and the fluorides are conveniently prepared by fluorination of the chlorides. They can also be obtained by direct combination of the elements. Exchange reactions occur between the pentahalides and other halides and these reactions can be used to prepare PF_5 ³⁹, AsF_5 ⁴⁰ and SbF_5 ⁴¹.





Arsenic pentachloride does not exist⁴², the maximum coordination number of arsenic towards chlorine being less than five. Gutmann⁴² prepared two compounds, AsSbCl_{10} and AsPCl_{10} , when antimony pentachloride or phosphorus pentachloride reacted with excess $\text{AsCl}_3\text{-Cl}_2$ solution and it appears that these compounds probably contain arsenic(V) as AsCl_4^+ .

Structures of the Simple Pentahalides

The structure of pentahalides has been investigated by spectroscopic, X-ray and electron diffraction methods and is found to be trigonal bipyramidal involving $sp^3d_z^2$ hybridisation of the phosphorus atom. A square pyramidal structure involving $sp^3d_{x^2-y^2}$ hybridisation of phosphorus is, on general grounds, almost as probable, but there is no evidence to suggest that this structure is adopted by PX_5 compounds. It is noteworthy however that SbPh_5 adopts it⁴³.

Bonding in these species can also be explained by two sets of hybrids⁴⁴: sp^2 in the planar, and pd bonds in the axial positions of a trigonal bipyramid. As the halogen becomes more electronegative the difference in the energy of these bonds becomes less (eg. $\text{P-Cl}_{\text{axial}} = 2.19 \text{ \AA}$, $\text{P-Cl}_{\text{equat.}} = 2.04 \text{ \AA}$ $\Delta = 0.15 \text{ \AA}$ and $\text{P-F}_{\text{axial}} = 1.577 \text{ \AA}$, $\text{P-F}_{\text{equat.}} = 1.534 \text{ \AA}$ $\Delta = 0.043 \text{ \AA}$).

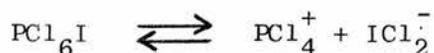
Rundle⁴⁵ has proposed a system of bonding which, using only p-orbitals, excludes any participation by high energy d-orbitals. In his picture there are three normal electron pair bonds formed in the equatorial plane by sp^2 hybridised

orbitals on phosphorus involved in the three equatorial bonds with a p-orbital of the halogen. The remaining p-orbital on the phosphorus atom overlaps with a p-orbital of each of the remaining halogen atoms resulting in a three centre bond in the $X_{axial} - P - X_{axial}$ system.

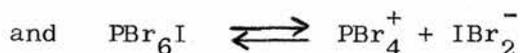
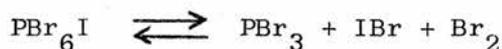
A most significant feature of the chemistry of phosphorus pentahalides is the fact that they may exhibit two different structures depending on their phase and environment. For example gaseous and liquid phosphorus pentachloride shows a trigonal bipyramidal structure, whilst in the solid phase it has been shown by X-ray analysis to be ionic, composed of tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$ units⁴⁶. This structure exhibits sp^3 and sp^3d^2 hybridisation in the cation and anion respectively. In solution the nature of species present, whether covalent or ionic, is determined by the solvent. In non-ionising solvents like carbon tetrachloride and carbon disulphide, the molecular species is present, whereas in solvents of high dielectric constant the ionic species is observed. Payne⁴⁷ has shown by transport number experiments that the PCl_4^+ and PCl_6^- ions are present in methyl cyanide. Beattie and Websters⁴⁸ results are in agreement with this and further evidence is produced by adding iodine monochloride to phosphorus pentachloride. This gives a substance PCl_6I which is ionic in the solid state⁴⁹, $PCl_4^+ \cdot ICl_2^-$. In solution in carbon tetrachloride this compound undergoes molecular dissociation thus:



and in methyl cyanide ions are produced⁵⁰:

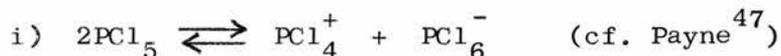


Similar behaviour is reported for PBr_6I , the two equilibria being:

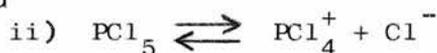


in non-polar and polar solvents respectively.

Shore et al⁵¹, in a recent paper, have shown by laser Raman spectra and freezing point depression that two competing equilibria occur in the ionising solvents, CH_3CN , CH_3NO_2 and $\text{C}_6\text{H}_5\text{NO}_2$. They are:-



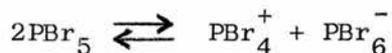
and



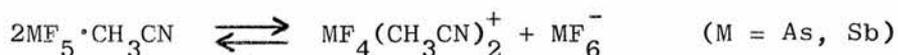
with i) being predominant above about 0.03 M and ii) being predominant at lower concentration.

The solution behaviour of phosphorus pentachloride is thus more complicated than envisaged by Payne⁴⁷.

Phosphorus pentabromide has analogous structures except that the ions present in the solid state are $[\text{PBr}_4]^+$ and Br^- . Powell et al⁵² have shown the phosphonium ion to be tetrahedral. In non-ionising solvents, such as benzene, Kastle et al⁵³ have shown the pentabromide to be completely dissociated into molecular phosphorus tribromide and bromine. In solvents with a high dielectric constant, (eg. phosphoryl chloride and methyl cyanide) the pentabromide undergoes ionic dissociation. Harris and Payne⁵⁴ suggest, on the basis of transport number experiments in methyl cyanide, that the dissociation is:-



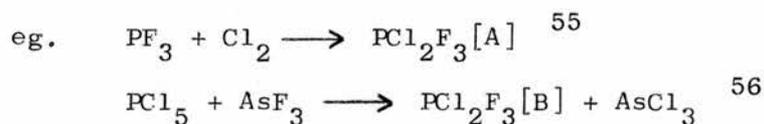
The fluorides of arsenic and antimony have similar ionisation schemes in methyl cyanide:-



The equilibrium lies to the molecular side in the case of antimony and to the ionic side in the case of dilute solutions of arsenic compound.

The Mixed Pentahalides

The mixed halides of phosphorus are prepared by various halogen exchange and addition reactions.



$\text{PCl}_2\text{F}_3[\text{A}]$ and $\text{PCl}_2\text{F}_3[\text{B}]$ are isomers having different physical characteristics. Kennedy et al²⁷ has shown that the conductivity in methyl cyanide of $\text{PCl}_2\text{F}_3[\text{A}]$ is small indicating covalent species whilst Kolditz⁵⁶ reports that $\text{PCl}_2\text{F}_3[\text{B}]$ has a high conductivity, and has formulated the compound as $[\text{PCl}_4^+][\text{PF}_6^-]$.

Ruff et al³⁵ in some early work using phase studies, reported the existence of: $(\text{SbF}_5)_3 \cdot \text{SbCl}_5$, $(\text{SbF}_5)_2 \cdot \text{SbCl}_5$, $\text{SbF}_5 \cdot \text{SbCl}_5$, $(\text{SbF}_5)_2 \cdot (\text{SbCl}_5)_3$, $\text{SbF}_5 \cdot (\text{SbCl}_5)_2$, $\text{SbF}_5 \cdot (\text{SbCl}_5)_3$ in the mixture $\text{SbF}_5 - \text{SbCl}_5$. These results are rather dubious and none of the above compounds have been isolated or structures identified.

The structures of the mixed pentahalides vary according to the medium and conditions in which they exist and these will be dealt with later.

The Reaction of Phosphorus Tribromide and Phosphorus Trichloride with Bromine

It is useful to review the $\text{PBr}_3 - \text{Br}_2$ and $\text{PCl}_3 - \text{Br}_2$ systems, as the same techniques have been used in investigating the phosphine-halogen systems embodied in this thesis. Harris and

Payne^{54,57} have used conductometric titrations in an inert solvent with a high dielectric constant to indicate where compound formation occurs. This is normally signified by a 'break' or change in gradient of the graph as more halogen species is added to the phosphorus trihalide, caused by a change in the nature or number of ions present. Conductance measurements have also been used to show whether the system is covalent or ionic and if the latter to give some indication of the degree of dissociation. To determine the ionisation scheme, transport number experiments have been performed.

In the $\text{PBr}_3\text{-Br}_2$ system a clear break was obtained at the 1:1 mole ratio indicating formation of phosphorus pentabromide. Cryoscopic measurements in nitrobenzene substantiate this evidence and in addition indicate formation of PBr_7 . Absence of inflections in the graph at this ratio suggests that no new type of ions are being formed, the solution being phosphorus pentabromide plus excess bromine. In contrast, the phase diagram of $\text{PBr}_3\text{-Br}_2$ ⁷ shows four crystalline compounds: PBr_3 , PBr_5 , PBr_7 and PBr_{17} . It is postulated that PBr_7 is composed of $[\text{PBr}_4^+]$, $[\text{Br}_3^-]$ units or $[\text{PBr}_4^+]\text{Br}^-(\text{Br}_2)$ and PBr_{17} as $[\text{PBr}_4^+]\text{Br}^-(\text{Br}_2)_n$ in the solid state - ie. the structures may well contain a number of un-ionised bromine molecules in the lattice similar to the water of hydration in many crystalline hydrates. A single-crystal X-ray diffraction study⁵⁸ has shown conclusively that PBr_7 is composed of tetrahedral PBr_4^+ and tribromide ions.

The $\text{PCl}_3\text{-Br}_2$ system is not as clear cut as the $\text{PBr}_3\text{-Br}_2$ system. Harris⁵⁷ found that methyl cyanide was unsuitable for conductometric titrations on $\text{PCl}_3\text{-Br}_2$ and therefore used nitrobenzene and phosphoryl chloride. Neither of these gave

definite inflections in the graph. Cryoscopic work in nitrobenzene indicated PX_5 and PX_7 species (where X = chlorine or bromine). Only one definite compound has been isolated from this system; this is $[PCl_4^+][PCl_5Br^-]$ by Kolditz and Feltz⁵⁹. Two maxima have been observed in the PCl_3 - Br_2 phase diagram by Fialkov and Kuz'menko⁶⁰ indicating PCl_3Br_4 and PCl_3Br_{18} compounds. These compounds are reported as having quasiphosphonium structures $[PCl_3Br^+][Br(Br_2)_n^-]$ with n = 1, 3 and 8²⁵. Popov et al⁶¹ have found no simple compounds, but instead report the formation of a non-stoichiometric substance of composition $PCl_{3.0}Br_{5.7}$, which decomposed to $PCl_{4.67}Br_{0.33}$ at reduced pressure. X-ray analysis indicates that this compound is built up of ions $[PCl_4^+]_8[PCl_6^-]_4[Br^-]_4$ ⁶¹. The compounds formed in this system are all very labile and even this latter compound, $PCl_{4.67}Br_{0.33}$, breaks down in non-polar solvents to phosphorus pentachloride and phosphorus pentabromide. Various other compounds have been reported in the late nineteenth century: $PCl_{3.15}Br_{1.89}$ in 1872⁶², PCl_3Br_8 , PCl_2Br_7 and PCl_3Br_4 ⁶³. These are probably mixtures of PCl_5 and PBr_5 and not genuine bromochlorides. The PCl_3 - Br_2 system is therefore rather complex and may include solvation or inclusion compounds of bromine to give phases of high bromine content eg. PCl_3Br_{18} . Further evidence for this is shown by two relatively stable compounds isolated by Harris⁵⁷, $PCl_3Br_7 \cdot CCl_4$ and $PCl_3Br_7 \cdot 2CCl_4$, which contain carbon tetrachloride of crystallisation.

Attempts have been made to prepare various bromochlorophosphonium ions in the series $[PCl_nBr_{(4-n)}^+]$, ($0 \leq n \leq 4$) using PF_6^- , BCl_4^- and BBr_4^- as anions⁶⁴. $[PCl_3Br^+][PF_6^-]$ and $[PCl_3Br^+][BCl_4^-]$ were the only pure compounds isolated. The ions $PCl_2Br_2^+$ and $PClBr_3^+$ were believed to be present in certain

mixtures of phosphorus trichloride, bromine and boron trichloride in liquid hydrogen chloride. Gabes et al³³ in a recent investigation, successfully prepared PBr_4Cl from a mixture of phosphorus pentachloride and phosphorus pentabromide (4:3). From X-ray powder data and Raman spectra he has shown the structure to be $\text{PBr}_4^+\text{Cl}^-$. Dillon and Gates⁶⁵ have characterised the series $[\text{PCl}_n\text{Br}_{(4-n)}]^+$, ($0 \leq n \leq 4$) using solid state ^{31}P nuclear magnetic resonance.

Structure of the Mixed Pentahalides

The pentahalides in their molecular form exhibit trigonal bipyramidal structures as previously stated. There are various possible configurations for the mixed halides and a study of the stereochemistry of five-coordinate group V element compounds has been extensively reviewed in recent years^{66,67}. Some of the possible stereochemistries for the compounds are shown in Figure 1. $M = \text{P, As, Sb, Bi}$; $X, Y, Z = \text{Halogen}$.

With MX_4Y there are two isomers depending on whether Y is in axial or equatorial position. MX_3Y_2 has three different combinations and MX_3YZ has four.

The compound initially studied with respect to its stereochemistry was PF_3Cl_2 . An early electron diffraction study⁶⁸ of this compound indicated structure (Fig. 2a); this is apparently supported by more recent nuclear magnetic resonance studies³⁰ which show that all the fluorine atoms are equivalent. Other studies using infra-red⁶⁹, low temperature Raman⁷⁰, and low temperature nuclear magnetic resonance (below -80°)^{44,71} indicate however structure (Fig. 2b) with C_{2v} symmetry. It seems that the fluorine atoms prefer the axial sites and Salthouse et al⁶⁹ proposed that the two axial fluorine atoms

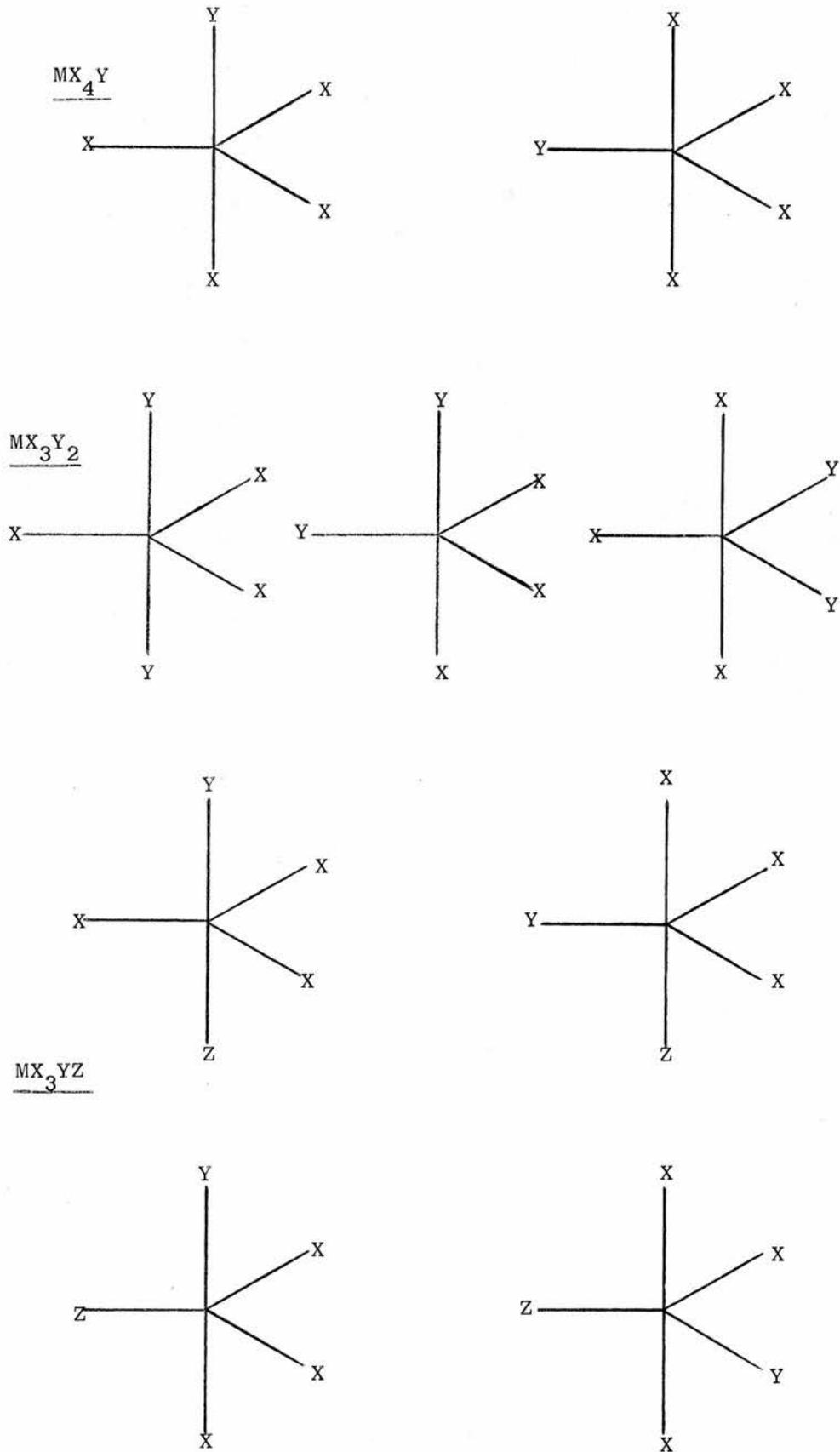


Figure 1

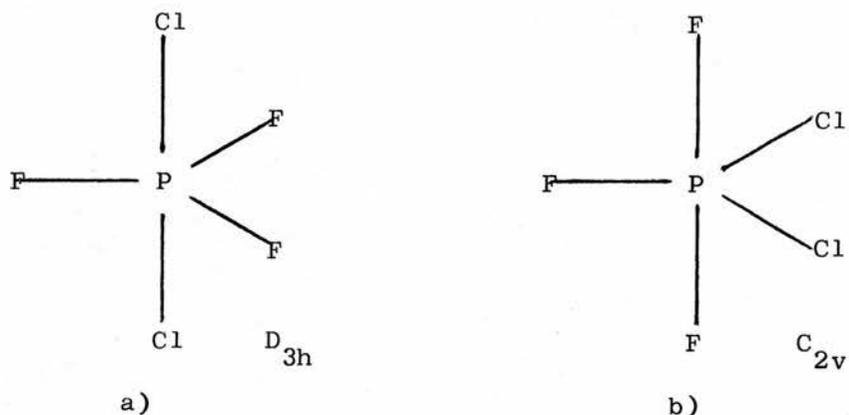


Figure 2: PF_3Cl_2 Structures

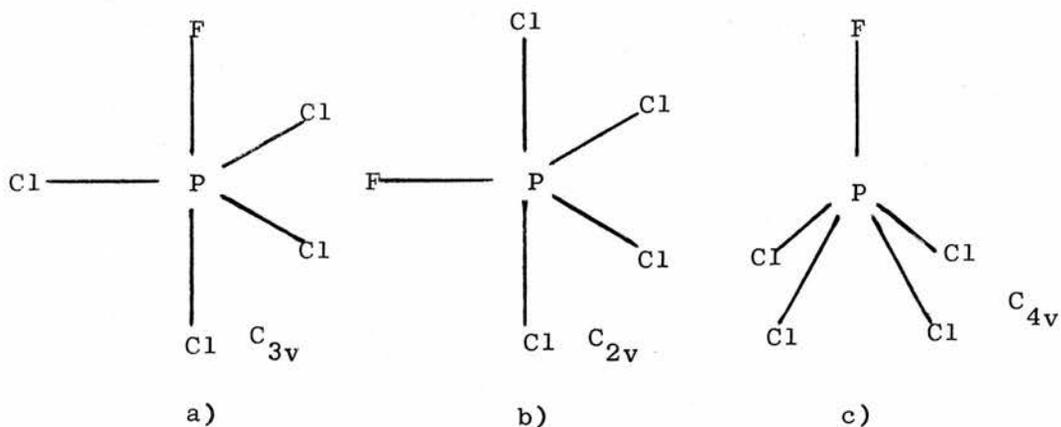


Figure 3: $PFCl_4$ Structures

are bent slightly towards the equatorial one by electron repulsion ($F_{axial} - \hat{P} - F_{axial} = 177.8^\circ$)⁷², which they suggest might account for the equivalence of the fluorine atoms in the room temperature nuclear magnetic resonance studies. A similar scheme is reported for PF_3Br_2 .

Holmes et al⁷¹ considers three possible structures for PFCl_4 and these are shown in Figure 3. Only one isomer is indicated by nuclear magnetic resonance studies and Raman and IR work⁷⁰ suggest C_{3v} symmetry. Structure (c) (Fig. 3), the square pyramidal, can be regarded as arising from an angular distortion of the trigonal bipyramidal structure (b) (Fig. 3). However square pyramidal structures have not been observed in Phosphorus chemistry. In contrast two compounds of Antimony have been shown to contain the square pyramid viz. Ph_5Sb ⁷³ and the SbF_5^{2-} ion in $(\text{NH}_4)_2\text{SbF}_5$ ⁷⁴.

The antimony analogue of PF_3Cl_2 is dichlorotrifluoro-antimony(V), SbF_3Cl_2 , and several views have been put forward to explain its structure. The structure appears to be dependent upon the phase and environment which determines whether SbF_3Cl_2 is covalent or ionic. Kolditz and Lieth⁷⁵ prepared SbF_3Cl_2 as a covalent liquid which on standing formed hygroscopic crystalline $[\text{SbCl}_4^+][\text{SbF}_6^-]$. There was evidence of association in both forms when dissolved in sulfuryl chloride. Later work by Dehnicke and Weidlein³⁴ using IR and Raman gives conflicting results. They suggest that both the liquid and solid are covalent with a trigonal bipyramidal structure possessing axial chlorine atoms. Muetterties et al⁷⁶ consider, however, that SbF_3Cl_2 as a monomeric species is untenable except possibly at high temperature in the gas phase. They have used low temperature¹⁹ ^{19}F nuclear magnetic resonance to show that SbF_3Cl_2 in solution and molten states is associated with hexacoordinate antimony and bridging chlorine or fluorine atoms (similar to SbF_5 ⁷⁷).

A recent study of the crystal structure of solid SbF_3Cl_2

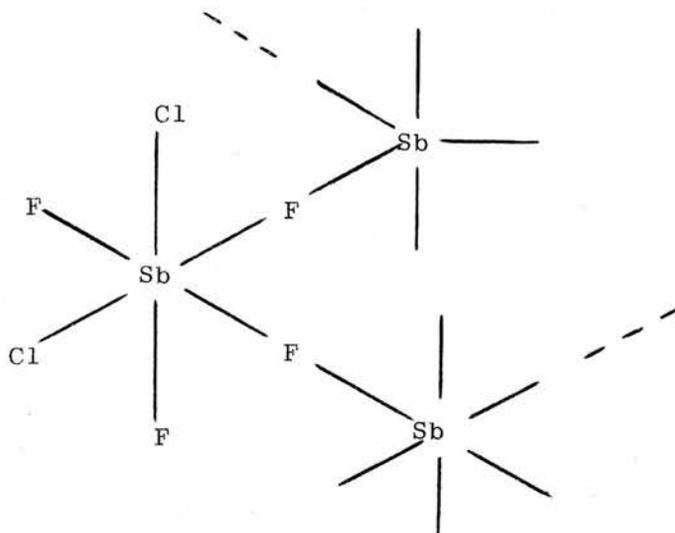


Figure 4: SbF_3Cl_2 structure proposed by
Muetterties⁷⁶

using X-ray has conclusively shown it to be ionic composed of $SbCl_4^+$ cations and $[F_4Sb - F - SbF_4]^-$ anions⁷⁸.

$SbCl_4F$ has been shown to have a trigonal bipyramid structure in non-polar solvents (such as chloroform and carbon tetrachloride) with the fluorine atom occupying an apical position. Analysis of Raman spectra of $SbCl_4F$ proves the ionic structure $SbCl_4^+F^-$ ⁷⁹.

Interchange of Axial and Equatorial Halogen Atoms in PX_5 Molecules

Although covalent structures of compounds such as PF_3Cl_2 can in principle have geometric isomers, the application of separation techniques has never detected the existence of more than one isomer. The stability of one form is obviously much greater than other possibilities.

The nuclear magnetic resonance spectrum of phosphorus pentafluoride shows only one type of fluorine atom (even at low temperature), although it is undoubtedly trigonal bipyramidal in

structure. Likewise at room temperature for PF_3Cl_2 there is only one fluorine resonance. At low temperatures, however, the nuclear magnetic resonance spectrum of PF_3Cl_2 clearly indicates two types of fluorine atoms^{44,76}. It is clear therefore that in PF_5 over the temperature range studied and in PF_3Cl_2 at room temperature that interchange of fluorine atoms is occurring.

There are two possible ways of interchange, one involves bond breaking in a 'scrambling' type of reaction and the other involves internal rearrangement produced by distortion of bond angles.

The exchange reaction has been mentioned in connection with the mixed trihalides. Fluorine has a stabilising effect on the phosphorus halides and this is why so many mixed fluorides have been prepared. Exchange has been observed⁸⁰ between radioactive chlorine and phosphorus pentachloride where three chlorine atoms in the equatorial positions are exchanged rapidly compared to the axial ones. Intermolecular exchange is not however thought to be responsible for interchange of axial and equatorial halogen atoms in the trigonal bipyramidal structures of molecules like phosphorus pentafluoride.

Two main mechanisms have been postulated for the interchange process. These are the 'Berry' pseudorotation mechanism⁸¹ and the 'Turnstile Rotation'⁸² which is slightly less favourable energetically. These are both illustrated in Figures 5 and 6. They both involve angle compressions and rotations of a pair of ligands against a trio. This is the reason why some of the mixed fluorides of phosphorus have been observed to have equivalent atoms at room temperature when they should show two types, the axial and equatorial. Strich and

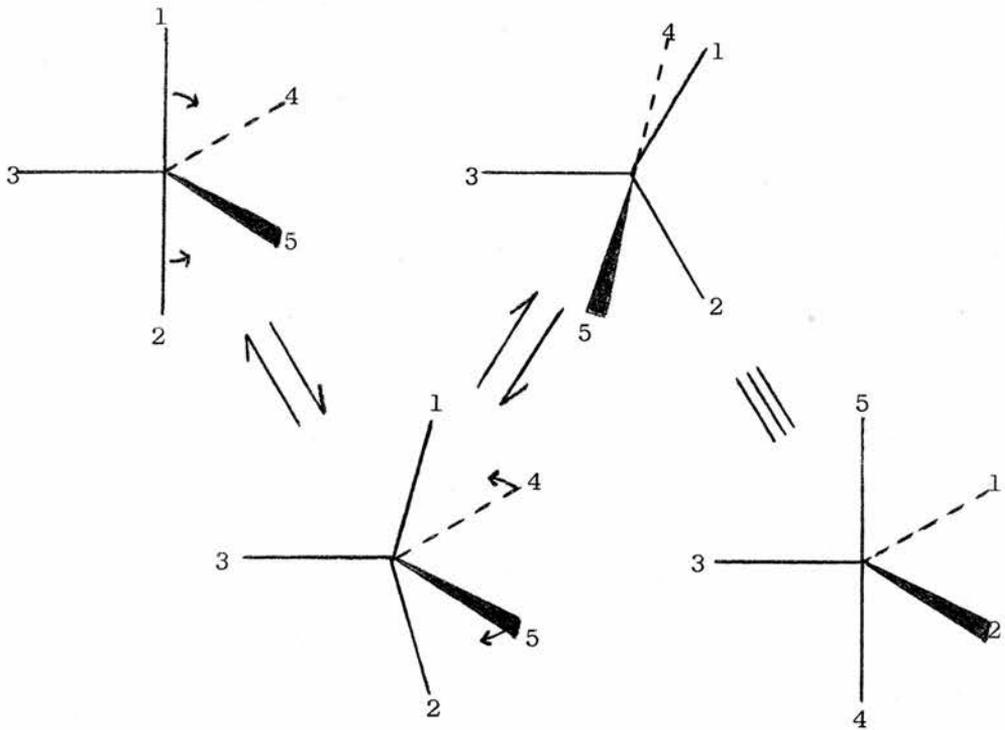


Figure 5: The Berry Pseudorotation

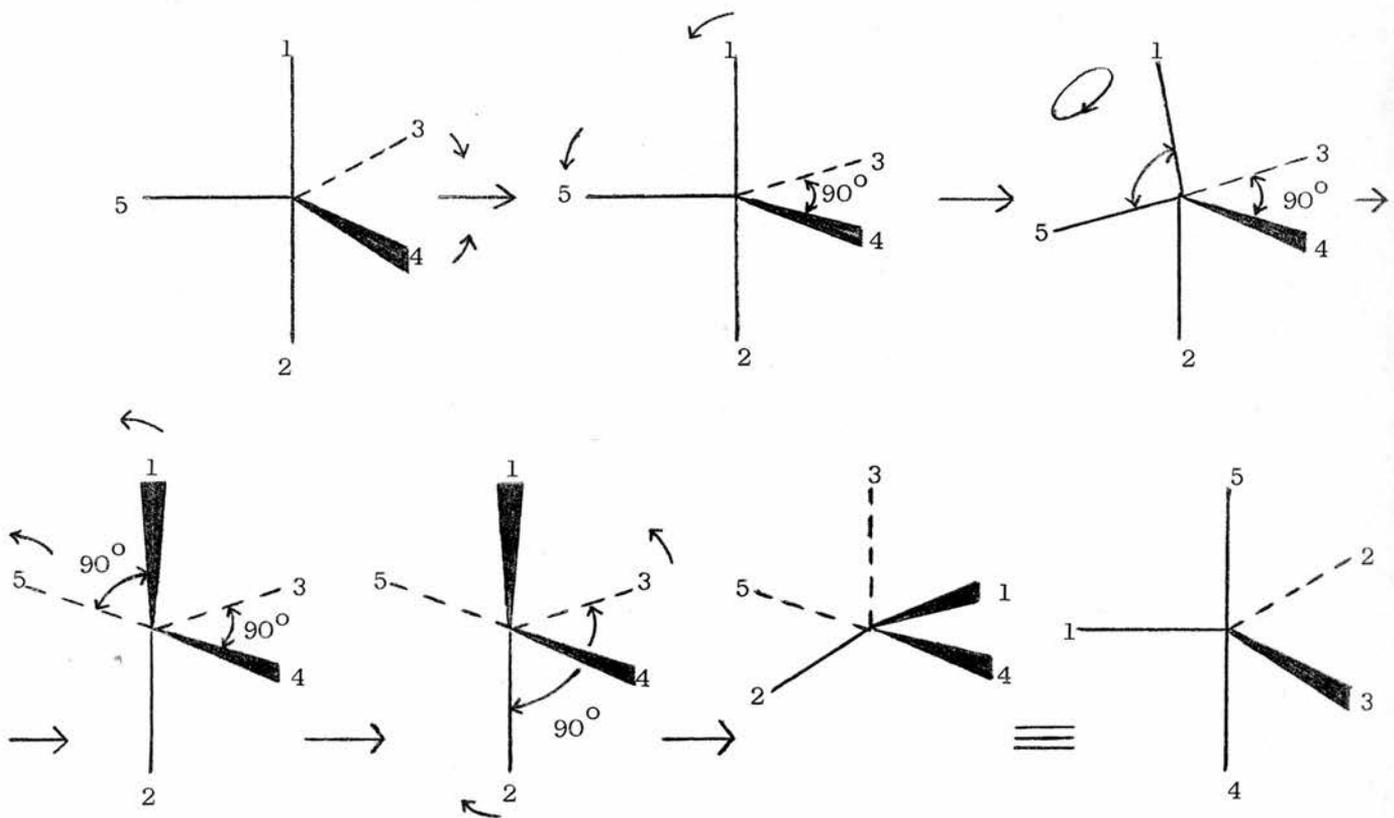


Figure 6: The Turnstile Rotation

Veillard⁸³, in a recent paper, indicate that ligand interchange on phosphorus pentafluoride occurs by a Berry mechanism and not by turnstile rotation.

Bonding in Pentacoordinate Structures

The bonding in pentacoordinate structures has been referred to previously. The valence bond theory assumes sp^3d hybridisation. If a d_z^2 orbital is involved then a trigonal bipyramidal structure results whereas a tetragonal pyramidal configuration is obtained using a $d_{x^2-y^2}$ orbital. The predominant structure in the Group VB series is trigonal bipyramidal. The rather diffuse d-orbitals would appear to disallow effective hybridisation with s- and p-orbitals. Because of this high energy of the d-orbitals and the influence of electronegative groups on the stability of penta-covalent molecules, Pauling⁸⁴ concluded that d-orbitals are not used and suggested resonance between the following twelve structures illustrated in Figure 7. However

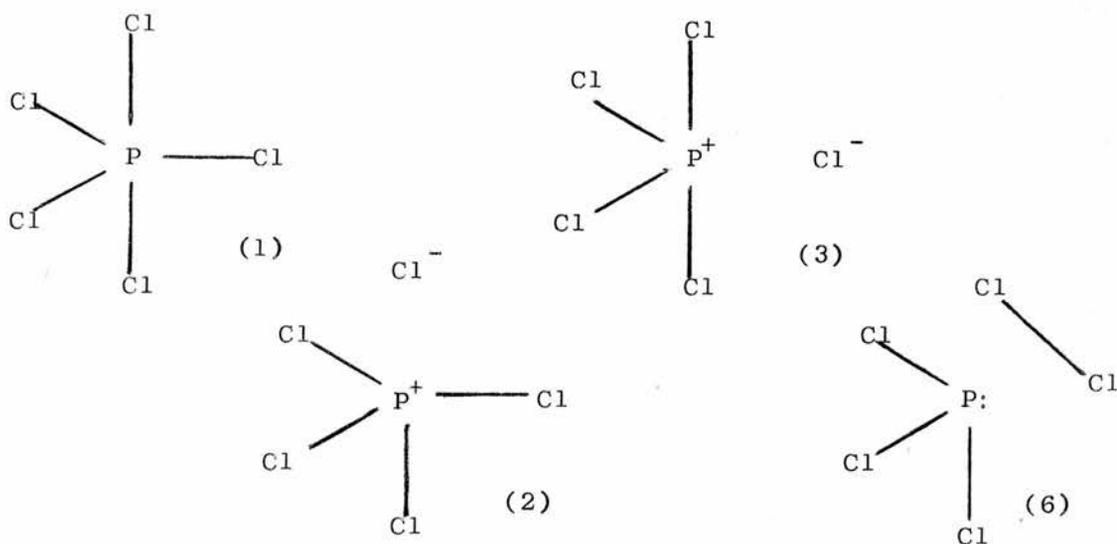


Figure 7: Structures proposed by Pauling for PCl_5 ⁸⁵ (with number of isomers in brackets)

electronegative ligands are thought to contract the d-orbitals

to allow effective overlap with s- and p-orbitals⁸⁵.

The more qualitative "valence shell electron pair repulsion" (VSEPR) theory⁸⁶ predicts the same result as above. It states that electron pairs around a central atom occupy positions giving the minimum electrostatic repulsion. This produces a trigonal bipyramidal structure with the axial bond slightly longer than the equatorial one. This is in keeping with details of structures of phosphorus pentafluoride etc ($P-F_{\text{axial}} = 1.577 \text{ \AA}$, $P-F_{\text{equat.}} = 1.534 \text{ \AA}$).⁶⁸

Attempts have been made to produce a model which excludes the use of high energy d-orbitals. An example is the Rundle three centre bond picture which was mentioned earlier⁴⁵. From the above résumé it can be seen that there is no single interpretation of the bonding and stereochemistry in phosphorus (V) compounds. The subject is still being discussed and new theories developed.

The Organo-Substituted Halides of Phosphorus

Fluorophosphoranes

The fluorophosphoranes constitute one of the largest group of pentasubstituted phosphorus compounds, and they have been very useful in studies of the chemistry and permutational isomerisations of pentacoordinate phosphorus compounds. The majority of the fluorophosphoranes are covalent exhibiting molecular structures, although some of the chlorofluoro-phosphoranes and chlorophosphoranes show ionic structures. Compounds in the series $Me_n PF_{5-n}$ ($n = 1 - 4$) have been prepared. Me_4PF has recently been reported⁸⁷ and is thought to exist in the form $[R_4P^+]F^-$ similar to Ph_4PF ⁸⁸. The vibrational spectra⁸⁹

of CH_3PF_4 indicates that this molecule approximates to a trigonal bipyramid with the methyl group assuming an equatorial position. Downs and Schmutzler⁸⁸ have investigated $(\text{CH}_3)_2\text{PF}_3$ and $(\text{CH}_3)_3\text{PF}_2$ using vapour state infrared, liquid state Raman, and ^1H , ^{19}F and ^{31}P NMR to evaluate their structures. They indicate trigonal bipyramidal frameworks in both molecules with the fluorine atoms occupying two axial and one equatorial site in the case of Me_2PF_3 and two axial sites in Me_3PF_2 . The introduction of methyl groups produces a weakening in the axial P-F bonds as shown by infrared measurements. The extent of this decrease in bond order is considerable and for Me_3PF_2 has been estimated to be half that of the P-F bond in phosphorus trifluoride⁸⁸. Similar correlations are obtained between PF_5 , $(\text{CH}_3)_3\text{CPF}_4$ and $[(\text{CH}_3)_3\text{C}]_2\text{PF}_3$ ^{90,91} where substitution with tert-butyl groups produces lengthening and weakening of the P-F bond through addition of electron-releasing groups. The bis(tert-butyl)trifluorophosphorane is again trigonal bipyramidal with the tert-butyls in equatorial positions⁹¹, producing electron-pair repulsion effects on the axial bonding pairs thus causing the lengthening of the P-F bond as stated above. It would seem reasonable to expect that the replacement of another fluorine in Me_3PF_2 by a methyl group would result in an ionic structure and not a pentacoordinate molecule. This can be explained by assuming that the orbitals of phosphorus forming the equatorial bonds are mainly sp^2 and those forming the axial bonds are largely pd_{z^2} in character. Because there is only one fluorine atom, d-orbital participation is not likely and therefore $\text{Me}_4\text{P}^+\text{F}^-$ is preferred.

The tetrafluorophosphoranes of type RPF_4 all show magnetically equivalent fluorine atoms even at low temperatures which is

thought to result from fast pseudorotation in the trigonal bipyramidal molecules.

Chlorophosphoranes

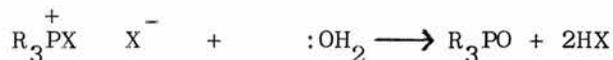
Another series of compounds which has been fairly well investigated, are the chlorophosphoranes which form part of the series PCl_5 , PRCl_4 , PR_2Cl_3 , PR_3Cl_2 . Baumgärtner et al.⁹², by analysing the vibrational spectra of the compounds $\text{P}(\text{CH}_3)_n\text{Cl}_{(5-n)}$, have shown the existence of phosphonium salts of the form $[\text{P}(\text{CH}_3)_n\text{Cl}_{4-n}]^+\text{Cl}^-$. MePCl_4 is ionic in the solid state ($\text{MePCl}_3^+\text{Cl}^-$), but is a pentacoordinate species with C_{2v} symmetry in non-polar solvents⁹³.

Hydrolytic Stability

These organohalophosphoranes, like phosphorus halides, in general are moisture sensitive compounds and some hydrolysis studies have been reported. An order of stability towards hydrolysis has been suggested: $\text{R}_3\text{PF}_2 > \text{R}_2\text{ArPF}_2 \cong \text{Ar}_2\text{PF}_3 \gg \text{R}_2\text{PF}_3 > \text{RPF}_4 > \text{PF}_5 > \text{ArPF}_4$ ^{66,94}. The same progression occurs in the chlorophosphoranes and it appears that stability to hydrolysis of these halophosphoranes increases with the presence of trihaloalkyl and aryl substituents. $(\text{CCl}_3)_2\text{PCl}_3$ and $\text{Ph}_2(\text{CF}_3)\text{PBr}_2(\text{I}_2)$ are reported to be unaffected by water.

This stability order is similar to that proposed by Murray and Schmutzler⁹⁵ to explain the general reactivity of penta-coordinated phosphorus compounds: $\text{PF}_5 > \text{ArPF}_4 > \text{AlkPF}_4 \gg \text{R}_2\text{PF}_3 \sim \text{R}_3\text{PF}_2$. Fluorophosphoranes, like PF_5 , are Lewis acids, and their reactivity depends on the factors influencing their acceptor properties. In this case inductive and steric effects are jointly responsible for the decrease of acceptor character in the above list.

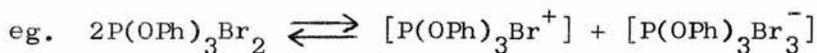
The ionic structures are clearly very unstable hydrolytically due to ease of nucleophilic attack by water on the phosphonium ion.



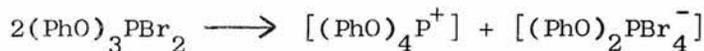
This probably explains why comparatively little work has been reported on systems other than fluorophosphoranes.

Effect of the Nature of R on the Behaviour of R_nPX_{5-n} Compounds

Adducts such as R_3PX_2 may display ionic or covalent properties depending on the nature of the group R and a number of studies designed to throw light on what types of groups induce ionic properties have been made by Harris and co-workers^{96,97}. It has been found for example that when R is the electron attracting phenoxy group, the pentacovalent adducts undergo ionic dissociation⁹⁸.



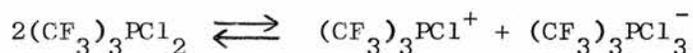
Rydon and Tonge⁹⁹ have proposed an alternative explanation for the ionisation of $(\text{PhO})_3\text{PBr}_2$ involving phenoxy group migration thus:



However their conclusions are somewhat suspect, as they used hydrolysis and alcoholysis of the products to characterise species present in solution and it is well known that in phosphorus chemistry, hydrolysis reactions often result in migration of groups attached to phosphorus, eg. hydrolysis of PhOPCl_4 gives some $(\text{PhO})_3\text{PO}$.

In a study of compounds containing the electronegative CF_3 group, Eméleus and Harris¹⁰⁰ have shown that $\text{PCl}_2(\text{CF}_3)_3$ is a conductor and, surprisingly, $\text{PCl}_3(\text{CF}_3)_2$ is a non-conductor

in methyl cyanide. The ionisation of $\text{PCl}_2(\text{CF}_3)_3$, by analogy with previous systems^{47,54,98}, is thought to be:

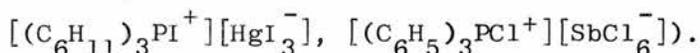


The difference in conductance of these two phosphoranes is thought to be connected with the structure of the covalent molecules believed to be present in the solid state of these compounds. $(\text{CF}_3)_2\text{PCl}_3$ is thought to have a structure similar to $(\text{CF}_3)_2\text{PF}_3$ ⁴⁴ in which the (CF_3) groups occupy axial positions. It has also been postulated that phosphorus pentahalides ionise, in a suitable environment, by ionisation of the apical bond^{101,102}. Since no $[\text{CF}_3]^-$ ion has been observed in any system, this must explain the non-ionic behaviour of $(\text{CF}_3)_2\text{PCl}_3$. $(\text{CF}_3)_3\text{PCl}_2$, accordingly, is assumed to contain an apical phosphorus-chlorine bond through which ionisation takes place.

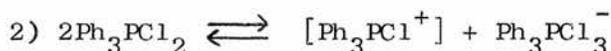
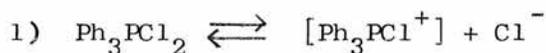
Phosphorus trihalides are able to add two molecules of halogen in certain cases. Harris and Payne⁹⁸ obtained a definite inflection in the conductometric titration graph of bromine against triphenylphosphite in methyl cyanide and they were able to prepare a tetrabromide with a structure $[(\text{PhO})_3\text{PBr}^+]\text{Br}^-$. Forsman and Lipkin¹⁰³ obtained an analogous iodine adduct $[(\text{PhO})_3\text{PI}^+]\text{I}_3^-$ along with an enneaiodide, $(\text{PhO})_3\text{PI}_9$. This is thought to have a molecular formula $\text{C}_{36}\text{H}_{30}\text{O}_6\text{P}_2\text{I}_{18}$ with the crystal structure composed of $[(\text{PhO})_3\text{PI}^+]$ cations and equal numbers of the polyiodide ions I_7^- and I_9^- .

Issleib and Seidel¹⁰⁴ reported addition reactions of tertiary aliphatic, as well as aromatic phosphines, with elemental chlorine, bromine and iodine in the mole ratio of 1:1 (including R = Et, n-Bu, cyclohexyl and phenyl)¹⁰⁵. These adducts are extremely moisture sensitive with the exception of

$(C_6H_{11})_3PI_2$ and $(C_6H_5)_3PI_2$, which is probably due to shielding of the central phosphorus atom by the large cyclic groups and iodine atoms. The R_3PX_2 compounds act as halide ion donors to acceptor halides such as $SbCl_5$, $SbBr_3$ and HgI_2 . The resulting phosphonium salts contain the cation R_3PX^+ and their conductivity corresponds with that of binary electrolytes, (eg.



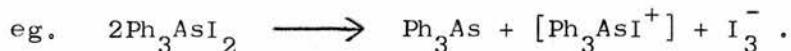
There are various plausible ionisation pathways for the dihalides, R_3PX_2 . Wiley and Stine¹⁰⁶ have used ^{31}P nuclear magnetic resonance to evaluate the ionisation pattern of triphenylphosphine dichloride. By analogy with phosphorus pentahalides^{25,48,51} they proposed two possibilities:



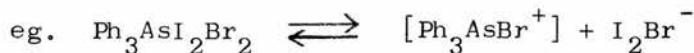
They report that equation 1 occurs in methyl cyanide, whilst in nitrobenzene equation 2 operates. Harris and Ali¹⁰⁷, using transport number experiments and conductance measurements in methyl cyanide, have shown the reverse result indicating equation 2 as the ionisation pathway. The strong chloride ion donor $\text{Et}_4\text{N}^+\text{Cl}^-$ was used in an attempt to see if a Ph_3PCl_2 molecule could accept a chloride ion to give $[\text{Ph}_3\text{PCl}_3^-]$. However, a conductometric titration of Et_4NCl against Ph_3PCl_2 in methyl cyanide failed to produce an inflection and thus there was no indication of $[\text{Ph}_3\text{PCl}_3^-]$ formation. Further ^{31}P nuclear magnetic resonance work in nitrobenzene¹⁰⁸ shows that Ph_3PCl_2 exists as a pentacoordinate material, although addition of excess chlorine promotes dissociation to a phosphonium cation, trichloride anion ion pair.

Organo-Substituted Pentahalides of Arsenic, Antimony and Bismuth

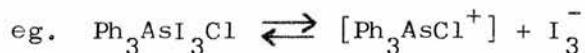
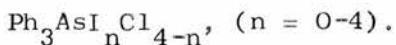
This type of halogen adduct formation is not limited to phosphorous compounds but is exhibited by all members of Group VB to a greater or smaller extent. For example the triphenyl-arsine-halogen systems have been evaluated by Beveridge and Harris¹⁰⁹ using conductometric titrations, conductance measurements¹¹⁰ and transport number experiments in ionising solvents. The resulting dihalides show different modes of ionisation, with the dichloride producing $[\text{Ph}_3\text{AsCl}^+]$ and $[\text{Ph}_3\text{AsCl}_3^-]$ ions whilst the dibromide gave $[\text{Ph}_3\text{AsBr}^+]$ and Br^- ions. The diiodide and iodine monobromide adducts appeared to disproportionate.



The diiodide and dibromide were shown to undergo a further addition reaction with the appropriate halogens to form a series of tetrahalides of general formula $\text{Ph}_3\text{AsI}_n\text{Br}_{4-n}$, ($n = 0-4$). From a transport number study of compounds in this series the mode of ionisation is always that in which the halogen of lower atomic number resides in the cation.



Further supporting evidence¹¹¹ that the cation containing the arsenic-halogen bond of greater strength is the favoured process, comes from the mode of ionisation of the series

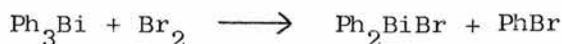


In this latter series of compounds the mode of ionisation was confirmed from ultraviolet spectra since trihalide ions show characteristic absorptions in methyl cyanide.

Triphenyl stibine, when titrated with solutions of bromine, iodine and iodine monobromide in methyl cyanide gave virtually

no rise in conductance as far as the 1:1 ratio⁹⁶. This indicates formation of the molecular dihalide. Similar behaviour is shown by $(C_6H_5)_3SbCl_2$ which is soluble in both non-polar and polar solvents without ionisation¹¹² and has no tendency to form ions by halide transfer. Kolditz et al¹¹³ reports similar findings for tribenzyl antimony dichloride and trimethyl antimony dichloride¹¹⁴. Infrared spectra have shown these compounds to have a trigonal bipyramidal structure with the most electro-negative ligands in the axial position^{76,115}. Such a geometry has been established for Me_3SbX_2 where X is chlorine, bromine or iodine¹¹⁶. This is substantiated by X-ray investigations on $(C_6H_5)_3SbCl_2$ by Polynova et al¹¹⁷.

Very few pentacoordinate compounds of bismuth have been observed. The pentaphenyl derivative was prepared by Wittig and Clauss¹¹⁸ and is thought to have a trigonal bipyramidal structure similar to Ph_5P and Ph_5As ⁴³, and unlike that of Ph_5Sb which possesses a molecular lattice of square pyramidal units⁷³. Few compounds of the type R_3BiX_2 have been isolated. Wittig¹¹⁸ reported the preparation of Ph_3BiBr_2 by adding bromine to triphenylbismuthine in chloroform and also by recrystallising Ph_4BiBr_3 from chloroform/methanol. Beveridge et al⁹⁶ carried out conductometric titrations of triphenylbismuthine-bromine in methyl cyanide, but found no increase in conductance. It appeared that the reaction occurring was:



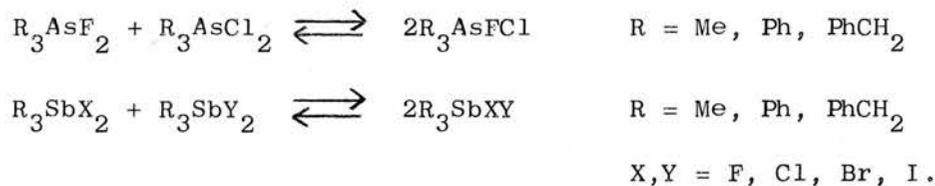
The dichloride and difluoride of triphenylbismuthine are both covalent, even in solvents of high dielectric constant.

Jensen¹¹⁵ found that triphenylbismuth dichloride has a zero dipole moment in benzene and suggested a trigonal bipyramidal

structure which has recently been confirmed by X-ray diffraction studies¹¹⁹. Likewise for Ph_3BiF_2 , where ^{19}F nuclear magnetic resonance and cryoscopic studies suggest, but do not firmly establish, a trigonal bipyramidal structure⁷⁶.

Halogen Exchange Reactions in Organo-Substituted Halides of Group VB

Halogen exchange reactions have been mentioned earlier in connection with the trihalides and pentahalides of phosphorus, arsenic, antimony and bismuth. The organo-substituted halides of phosphorus undergo similar scrambling reactions. Examples of these are the equilibration of mixtures of PhPCl_2 and PhPBr_2 to yield PhPClBr ; this system has been studied by phase diagram methods¹²⁰. Low temperature ^1H and ^{19}F nuclear magnetic resonance have been used to elucidate the following reactions between pentavalent substituted halides¹²¹.



Compounds containing PX_4^+ or PX_6^- in general

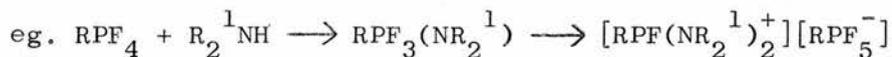
PX_4^+ compounds

Compounds containing PX_4^+ have been mentioned previously in connection with the pentahalides. The largest group containing the PX_4^+ species is the quaternary phosphonium salts, $[\text{R}_n\text{H}_{(4-n)}\text{P}^+]\text{X}^-$ where $n = 0-4$. They are very similar to the phosphonium salts $\text{R}_3\text{PX}^+\text{X}^-$ and form part of the series $\text{PX}_n\text{R}_{(5-n)}$, ($n = 0-5$). An example is Ph_4PI which has been shown by X-ray crystallography to be composed of tetrahedral Ph_4P^+ and

I⁻ ions¹²².

PX₆⁻ compounds

As yet there are few compounds which contain a hexavalent phosphorus atom. The most familiar PX₆⁻ species are PF₆⁻ and PCl₆⁻. Recently some organo-substituted PX₆⁻ species have been prepared.



These ions, of the type RPF₅⁻ (eg. in Cs⁺[MePF₅⁻] and Cs⁺[PhPF₅⁻])¹²⁴, have been shown to have an octahedral structure with, in the case [PhPF₅⁻], the phenyl group in an axial position¹⁴⁰. This behaviour is allied to that of phosphorus pentachloride in which the anion has an octahedral structure.

Related Studies

Harris and co-workers have investigated several systems of the type R₃P-halogen, mainly using conductometric methods. They have shown by comparing (Me₂N)₃P-X₂, (C₆H₅)₃P-X₂ and (C₆F₅)₃P-X₂ that the molar conductance of dihalides of the type R₃PX₂ increases with the decrease in the electronegativity of the organic groups attached to phosphorus. The work described in this thesis is comprised of two parts. The first part forms a study of the reaction of halogens with Me₃P, PhMe₂P and Ph₂MeP. Much information is already known about Ph₃P-X₂ systems, and it was thought worthwhile to study the effect of replacement of a phenyl group by an electron releasing methyl group on the properties of halogen adducts of MePh₂P, Me₂PhP and Me₃P. The second part of the thesis is concerned with the reaction of the biphosphines, Ph₂PCH₂PPh₂ and Ph₂PCH₂CH₂PPh₂ with halogens.

R E S U L T S A N D D I S C U S S I O N

PART 1

The Reaction of Halogens with some Tertiary Phosphines

Results and Discussion

Part 1

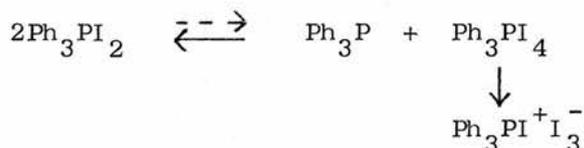
The Reaction of Halogens with some Tertiary Phosphines

Introduction

The reactions of triphenylphosphine with halogens have been extensively studied, using mainly conductometric methods, by Harris and co-workers. The conductance of the triphenylphosphine dihalides indicates that they are strong 1:1 electrolytes in methyl cyanide. There are two probable modes of ionisation of the dihalides:

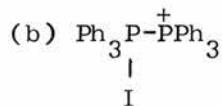
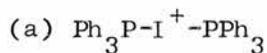


However, as mentioned previously^{96,106,107}, the dichloride and dibromide have been shown to ionise according to equation 2. The diiodide follows a similar scheme apart from there being slight disproportionation giving triiodide and triphenylphosphine.



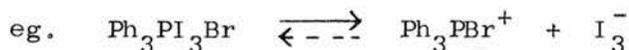
The iodine monobromide adduct, Ph_3PIBr , was not isolated but instead a compound of stoichiometry $\text{Ph}_3\text{PI}_{1.5}\text{Br}_{0.5}$ was found. The ultraviolet spectrum of solutions of this substance indicated the formation of triiodide ion and so the structure $[(\text{Ph}_3\text{P})_2\text{Br}]^+\text{I}_3^-$ was postulated. A similar chloriodide of elemental composition $\text{Ph}_3\text{PCl}_{0.5}\text{I}_{1.5}$ was isolated and believed to have an ionic structure $[(\text{Ph}_3\text{P})_2\text{Cl}]^+\text{I}_3^-$ ¹²⁵. The structure of $(\text{Ph}_3\text{P})_2\text{X}^+$ ions has not been determined. There are two likely structures for these ions; structure (a) is composed of I^+ ions coordinated by two

triphenylphosphine molecules, whilst structure (b) contains a phosphorus-phosphorus bond^{125,126}.



An analogous structure to that given in example (a) is found in $[\text{Ipy}_2^+]\text{I}_3^-\text{I}_2$ which has been shown by X-ray studies¹³⁹ to contain the planar ion, $[\text{pyIpy}]^+$.

All of the tetrahalides in the series $\text{Ph}_3\text{PI}_n\text{Br}_{(4-n)}$ ($n = 0,1,2,3,4$) have been prepared and characterised. The compounds are strong electrolytes in methyl cyanide in which the anions were characterised by ultraviolet absorption spectra. They have ionisation schemes analogous to those of the arsenic compounds, where the 'onium cation contains the halogen of lower atomic number.



In general these compounds are very moisture sensitive but Issleib and Seidel¹⁰⁴ report that Ph_3PI_2 and tricyclohexylphosphine diiodide are fairly stable towards hydrolysis; this is probably due to the screening of the central phosphorus atom by the bulky iodine, phenyl or cyclohexyl groups.

Little work has been done on the reaction of trimethylphosphine with halogens. Goubeau and Baumgärtner¹²⁷ have isolated trimethylphosphine dichloride, dibromide and diiodide and have shown, by infrared and Raman spectra, that the structures of the solids are ionic, of the form $[\text{Me}_3\text{PX}]^+\text{X}^-$. Baumgärtner et al⁹² using vibrational spectra have also proved that Me_3PFCl in the solid state has an ionic structure, $[\text{Me}_3\text{PF}]^+\text{Cl}^-$, similar to the series of phosphonium salts $[(\text{Me})_n\text{PCl}_{(4-n)}]^+\text{Cl}^-$ ($n = 0,1,2,3,4$) mentioned in the introduction.

No studies of trimethylphosphine with halogens in solution have been reported. It was of interest to compare the values of conductance for the halogen adducts of Me_3P , Me_2PhP and MePh_2P with those obtained by Harris and co-workers for triphenylphosphine halogen adducts. In addition there has been no previous work on the reaction of halogens with Me_2PhP and MePh_2P apart from studies of the difluorides of these phosphines⁶⁷.

These phosphine-halogen systems are extremely sensitive towards moist air and thus require in their investigation extensive precautions to exclude oxygen and water vapour. Conductometric titrations of Ph_2MeP -halogen systems were carried out in an apparatus developed by Harris⁹⁶ in which contact with moist air, tap grease, and rubber is avoided. Titrations of all other phosphine-halogen systems were performed inside the dry-box using an apparatus developed by McKechnie¹²⁹.

A. The Reactions of Diphenylmethylphosphine with Halogens

(1) The Ph_2MeP -Bromine System

The results of the conductometric titration of diphenylmethylphosphine with bromine in methyl cyanide are recorded in Table 22 and illustrated graphically in Figure 8. The graph shows definite breaks close to the 0.5:1 and 1:1 mole ratio $\text{Br}_2:\text{Ph}_2\text{MeP}$. The solution was colourless until the 1:1 ratio when it became pale yellow and gradually darkened upon further addition of bromine solution. After the 1:1 ratio the conductance rose steadily until the region of the 3:1 ratio when it slowly tailed off. From the graph it appears that species of the stoichiometries $[\text{Ph}_2\text{MeP}]_2\text{Br}_2$ and $[\text{Ph}_2\text{MeP}]\text{Br}_2$ and possibly $[\text{Ph}_2\text{MeP}]\text{Br}_6$ exist in methyl cyanide solution. To explain the 0.5:1 and 1:1 breaks it is suggested that the reaction proceeds by the following

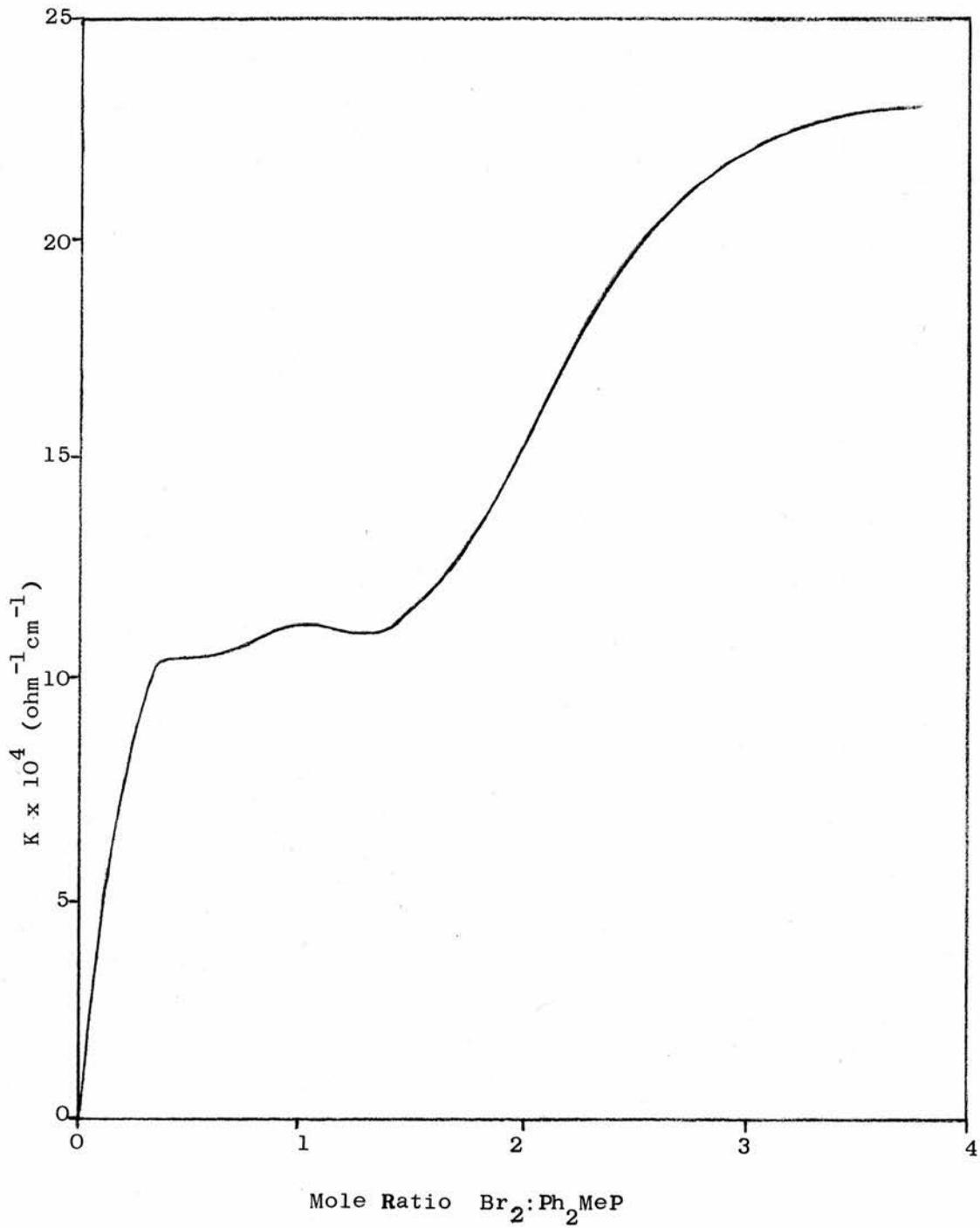
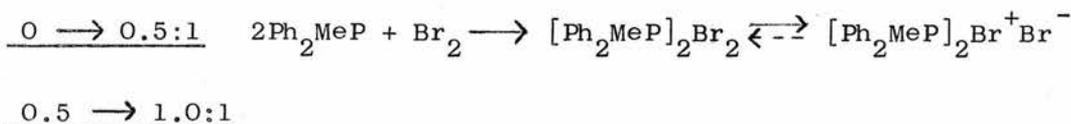
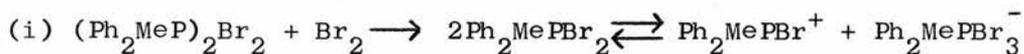


Figure 8 : Conductometric Analysis of the System $\text{Br}_2\text{-Ph}_2\text{MeP}$
in Methyl Cyanide

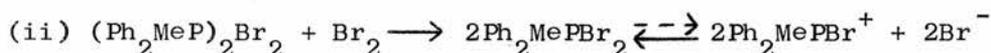
scheme:



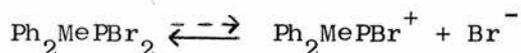
There are two possible explanations of the small change in K in this mole ratio range.



This scheme does not alter the number of ions already existing in solution at the 0.5:1 ratio.



It seems reasonably well enough established that ionisation of R_3PX_2 compounds in solvents such as methyl cyanide involves simple halide ions^{106,107} so that scheme (ii) is favoured. However this scheme implies a doubling of the number of ions in solution unless the 1:1 compound $\text{Ph}_2\text{MePBr}_2$ is incompletely ionised; it is thus suggested that reaction (ii) occurs in the 0.5 \rightarrow 1.0:1 mole ratio range.



The molar conductance values at the 0.5:1 and 1:1 mole ratios ($\text{Br}_2:\text{Ph}_2\text{MeP}$) are:

$$0.50:1 \quad \Lambda_m = 124.20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}, \quad (c_m = 0.00848 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on formula } [\text{Ph}_2\text{MeP}]_2\text{Br}^+\text{Br}^-)$$

$$1.00:1 \quad \Lambda_m = 72.74 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}, \quad (c_m = 0.01578 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on formula } \text{Ph}_2\text{MePBr}^+\text{Br}^-)$$

These values of molar conductance indicate strong electrolytes.

The cation formed at the 0.5:1 ratio is probably of the type

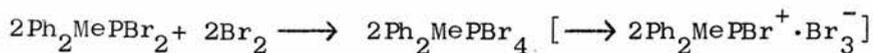
$[(\text{Ar}_3\text{P})_2\text{Hal}]^+$ similar to that obtained by Ali¹²⁵, MacPherson¹³⁰ and McKechnie¹²⁹ where Ar = Ph, p-tol, n-(C_4H_9) respectively.

This scheme is further substantiated by the absence of tribromide

ion (colourless solution) until after the 1:1 mole ratio.

Attempts were made to isolate solids at the 0.5:1 and 1:1 ratios which were obtained with difficulty. They were both extremely hydrolytically unstable and the solutions had to be freeze dried and pumped to remove traces of methyl cyanide as no solids could be precipitated by addition of ether (the procedure previously used⁹⁶ to obtain phosphine-halogen adducts). Both these solids analysed as the dibromide although the solid obtained at the 0.5:1 ratio contained unreacted phosphine.

From what is known of other phosphine-halogen systems (eg. $\text{Ph}_3\text{P}-\text{Br}_2$, $(\text{cyclohexyl})_3\text{P}-\text{Br}_2$) it would be expected that addition of bromine solution beyond the 1:1 stage would give the following reaction:



and hence a break at the 2:1 ratio. The absence of a 2:1 break is probably due to the above reaction being an equilibrium and complete production of the tetrabromide is not achieved until excess bromine is present in the solution. This behaviour would delay the break beyond the 2:1 ratio and produce an indistinct break as is observed. Isolation of a compound at the 2:1 ratio was achieved by freeze drying a methyl cyanide solution containing a 2:1 ratio of $\text{Br}_2:\text{Ph}_2\text{MeP}$. The value of the molar conductance at the 2:1 ratio ($\text{Br}_2:\text{Ph}_2\text{MeP}$) taken from the conductometric titration graph indicated a strong 1:1 electrolyte.

$$2.00:1 \quad \Lambda_m = 110.23 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}, \quad (c_m = 0.01388 \text{ mole litre}^{-1})$$

(c_m based on formula $\text{Ph}_2\text{MePBr}^+ \text{Br}_3^-$)

Examination of the ultraviolet spectrum of methyl cyanide solutions of the dibromide and tetrabromide showed that tribromide ion was present in the tetrabromide only. Trihalide anions have

characteristic absorptions in the uv range and these have been reported by Popov and Swensen¹³¹ (see Table 4). The only absorbing species present at the 1:1 mole ratio is the phosphine.

Table 4

Anion	Maximum λ (m μ)	Absorption Coefficient (ϵ)	Maximum λ (m μ)	Absorption Coefficient (ϵ)
Br ₃ ⁻	269	55,000		
I ₃ ⁻	360	22,500	291	38,800
I ₂ Br ⁻	351	11,600	280	40,600
IBr ₂ ⁻	370	606	256	54,000

The infrared spectrum of the tetrabromide showed a very similar absorption pattern to the phosphine. The finger-print region clearly indicated that no substitution of the phenyl groups by bromine had taken place. Two peaks appeared to be missing on passing from Ph₂MeP to Ph₂MePBr₄. They were the shoulder at 1420 cm⁻¹ (s) and the peak at 1025 cm⁻¹ (m), whilst the absorption at 1479 cm⁻¹ (s) was reduced in intensity to 1484 cm⁻¹ (w) and that at 1098 cm⁻¹ (m) increased in the tetrabromide to 1107 cm⁻¹ (s). In addition, there were three peaks which were shifted to higher frequency by the addition of bromine. The rocking band characteristic of the P-Me group¹³² shifted and broadened from 878 cm⁻¹ to 902 cm⁻¹ (mb) with the shoulder at 745 cm⁻¹ moving to 784 cm⁻¹ (m) and the peak at 705 cm⁻¹ (s) going to 720 cm⁻¹ (m). The band at 693 cm⁻¹ (s) moves to a lower frequency 682 cm⁻¹ (s).

Vapour Pressure Study of the Br₂-Ph₂MeP System

In view of the general lability of these phosphine-bromine

adducts and their tendency to lose bromine it was thought that a vapour pressure-composition study would yield some information on the nature of solid phases present in this system. Vapour pressures of various mixtures of $\text{Br}_2:\text{Ph}_2\text{MeP}$ were measured at 20°C , (ie. just below room temperature), in an all glass system involving a spiral gauge null-meter. The phase diagram obtained is illustrated in Figure 9. This shows with certainty the formation of a solid adduct of stoichiometry $\text{Ph}_2\text{MePBr}_{10}$ only. From the values obtained it would appear that the dibromide and tetrabromide have ~~vapour~~ ^{dissociation} pressures less than 2mm Hg. These two adducts were therefore not detected by this technique as it would be impossible to distinguish two phases at these low pressures. The decabromide can be written as $\text{Ph}_2\text{MePBr}^+\text{Br}_9^-$ by analogy with other compounds containing the enneabromide ion $\text{Me}_4\text{N}^+\text{Br}_9^-$ ¹³³, $(\text{C}_6\text{F}_5)_3\text{PBr}^+\text{Br}_9^-$ ¹³⁵ and $(\text{C}_6\text{H}_{11})_3\text{PBr}^+\text{Br}_9^-$ ¹²⁹.

Table 5: Vapour Pressure-Composition for the System $\text{Br}_2-\text{Ph}_2\text{MeP}$ at 20°C

Mole Ratio $\text{Br}_2:\text{Ph}_2\text{MeP}$	Vapour Pressure (mm Hg)
7.371	100.26
7.109	98.77
6.431	96.82
6.148	91.25
5.872	87.51
5.622	77.63
5.359	59.77
5.150	36.32
4.862	7.53
4.226	6.27
3.996	5.14
3.724	4.85
3.542	3.36
3.452	2.97
3.274	2.28

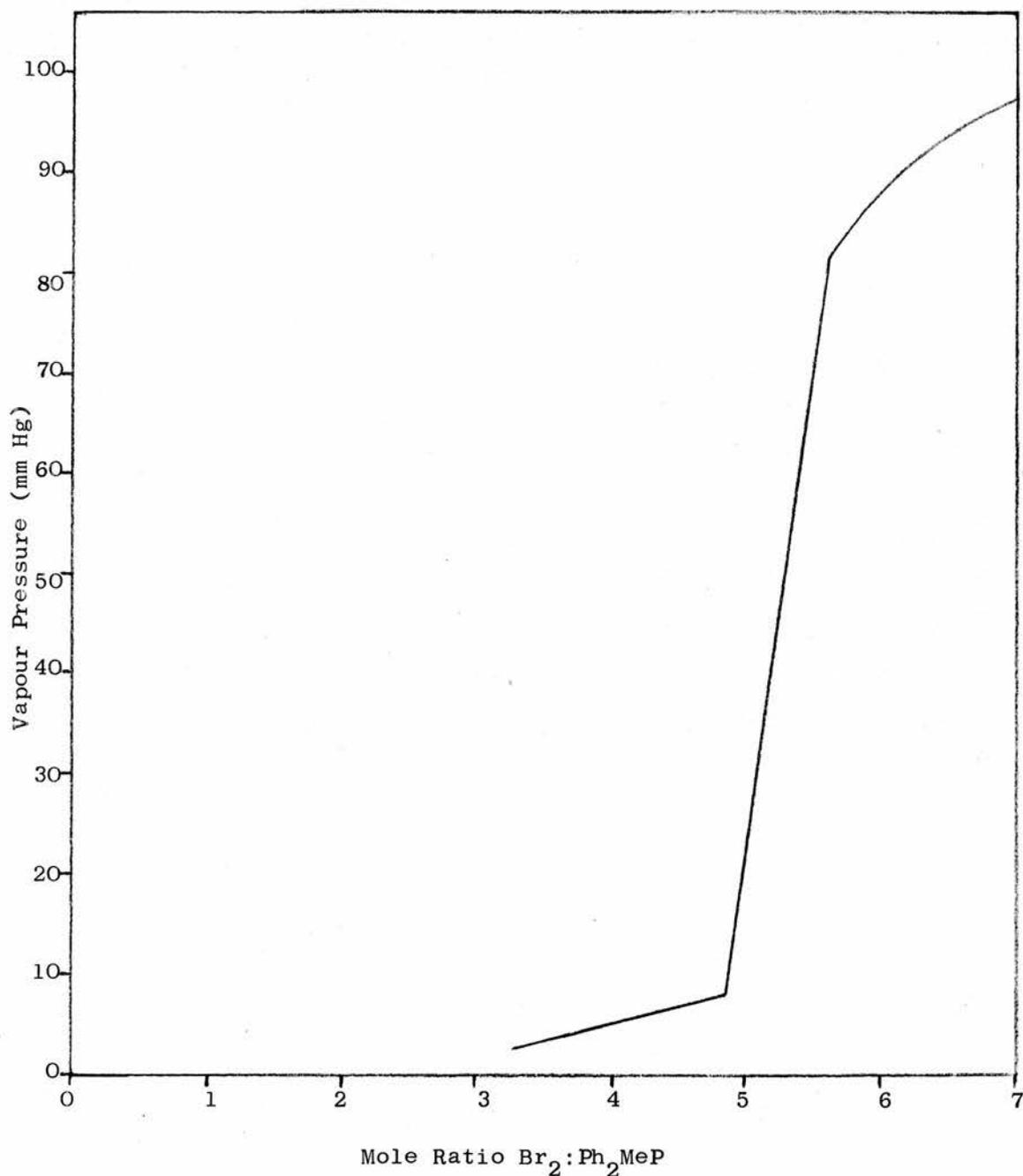


Figure 9: Vapour Pressure Study of the Br₂-Ph₂MeP System at 20°C

The enneabromide ion has been characterised only in solution using phase studies¹³³ and not by X-ray studies of the crystalline state. The corresponding polyiodide ion, I₉⁻¹³⁶, has been shown by X-ray structure analysis to have a structure composed of iodine molecules attached to a triiodide ion in a three dimensional array¹³⁷.

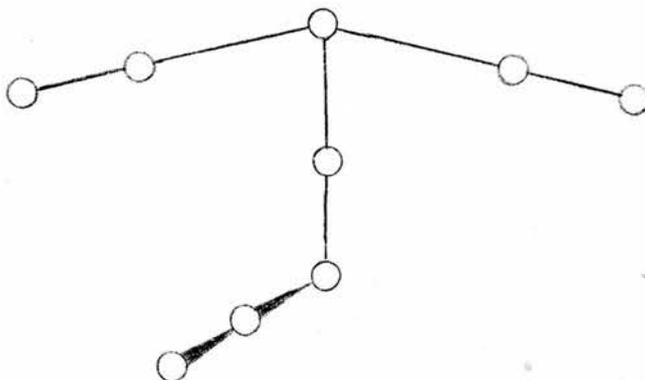


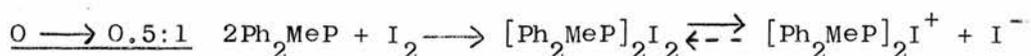
Figure 10: The ennea-halide species in Me_4NI_9 134

From the high molar conductances measured in the system $\text{Ph}_2\text{MeP-Br}_2$ in methyl cyanide it appears that the dibromide and tetrabromide exist as ionic entities $[\text{Ph}_2\text{MePBr}^+]\text{Br}^-$, $\text{Ph}_2\text{MePBr}^+\text{Br}_3^-$ and that there may well be a series of higher bromides $\text{Ph}_2\text{MePBr}^+\text{Br}_{(2n+1)}^-$ ($n=2,3,4$) up to the decabromide.

(2) The Reaction of Iodine with Diphenylmethylphosphine

The conductance composition graph for the system $\text{Ph}_2\text{MeP-I}_2$ in methyl cyanide is reproduced in Figure 11 and the data recorded in Table 23.

The graph showed discontinuities at the 0.5:1 and 1:1 (rather indefinite) I_2 - Ph_2MeP mole ratios with a rather diffuse break between the 2:1 and 2.5:1 mole ratios. Further addition of iodine solution caused the conductance to slowly decrease after the 2.5:1 mole ratio. These results suggest the formation of the adducts $(\text{Ph}_2\text{MeP})_2\text{I}_2$, Ph_2MePI_2 and Ph_2MePI_4 . In the titration the solution remained colourless until the 0.5:1 mole ratio when it turned yellow and gradually darkened, suggesting the formation of triiodide ion after the 0.5:1 ratio. The reactions proposed for this system are as follows:



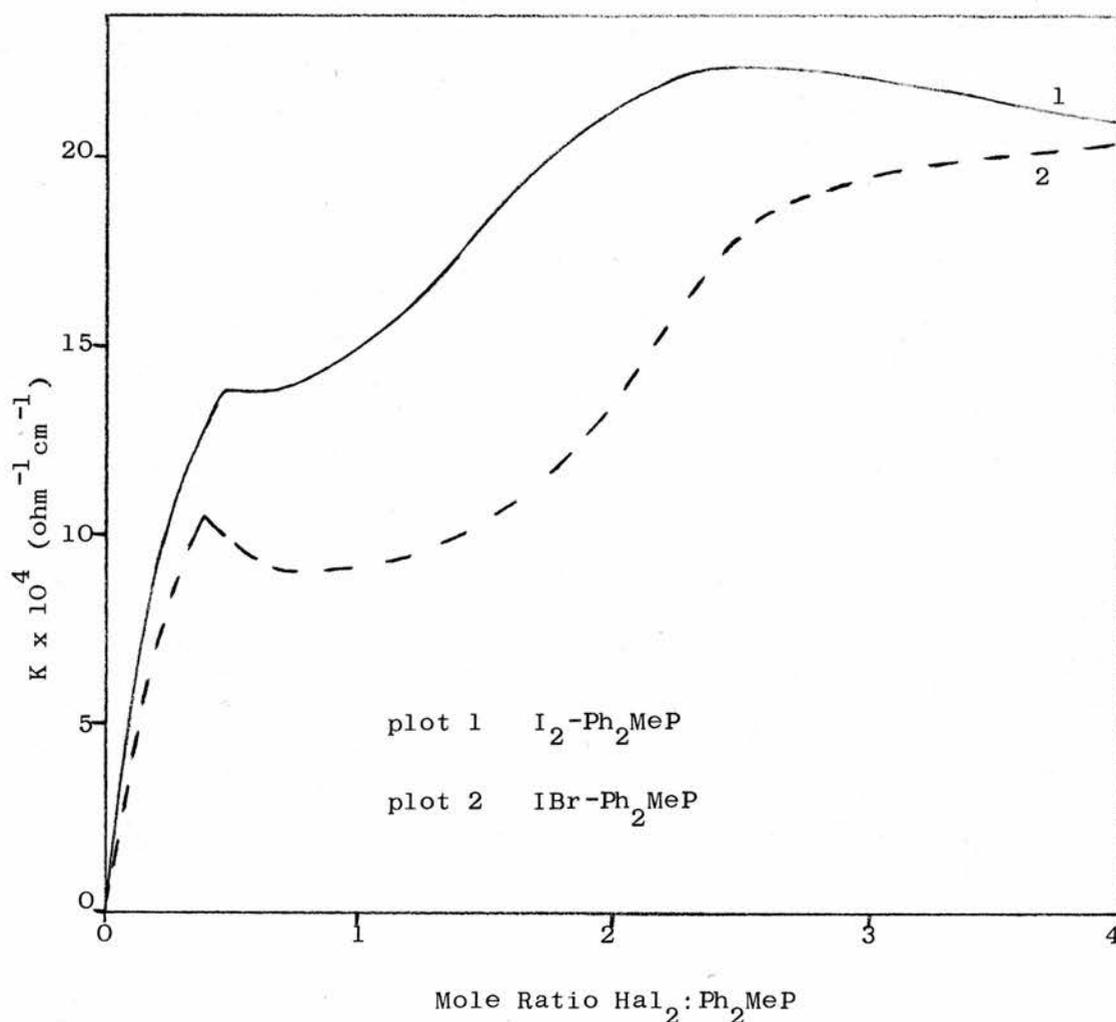
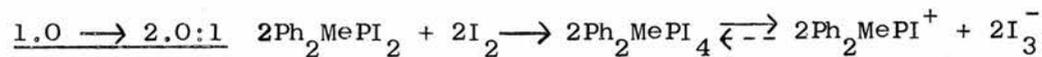
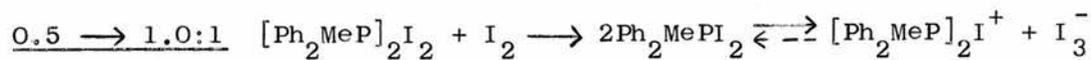


Figure 11: Conductometric Titration of the Systems I_2 - Ph_2MeP and IBr - Ph_2MeP in Methyl Cyanide



The values of molar conductance indicate strong 1:1 electrolytes at the 0.5:1, 1:1 and 2:1 mole ratios. (Strong 1:1 electrolytes have an average value for Λ_m of $\sim 140 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ at $\sim 10^{-3} \text{ M}$ in methyl cyanide)¹³⁸.

$$0.50:1 \quad \Lambda_m = 153.50 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}, \quad (c_m = 0.00899 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } [Ph_2MeP]_2I^+I^-)$$

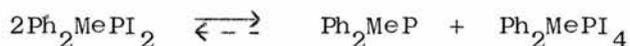
$$1.00:1 \quad \Lambda_m = 176.96 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}, (c_m = 0.00842 \text{ mole litre}^{-1})$$

(c_m based on $[\text{Ph}_2\text{MeP}]_2\text{I}^+\text{I}_3^-$)

$$2.00:1 \quad \Lambda_m = 143.05 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}, (c_m = 0.01496 \text{ mole litre}^{-1})$$

(c_m based on $\text{Ph}_2\text{MePI}^+\text{I}_3^-$)

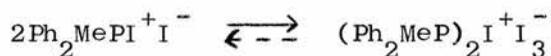
During conductometric titrations the conductance rose sharply to the 0.5:1 ratio and remained constant to the 1:1 ratio indicating that no further ions were being formed between 0.5 and 1:1 mole ratios. The reaction occurring was the complexing of iodine molecules with iodide ions to form triiodide ions. The increase in conductance beyond the 1:1 ratio can be attributed to a doubling of the number of ions present in solution. By analogy with the system $(n\text{-C}_4\text{H}_9)_3\text{P-I}_2$ ¹²⁹ isolation of a colourless diiodide and a yellow/brown tetraiodide from appropriate mixtures of the reactants was expected. A pale yellow solid was in fact isolated at the 1:1 mole ratio but darkened rapidly, even in the dry-box, to a soft brown solid. It was thought the solid 1:1 adduct, which from colour is probably $\text{Ph}_2\text{MePI}^+\text{I}^-$, was undergoing disproportionation to the phosphine and tetraiodide. The tetraiodide was obtained as a black



semi-crystalline solid after freeze drying a mixture of iodine and phosphine (2:1 ratio) in methyl cyanide.

Attempts to isolate a 0.5:1 adduct by addition of iodine (0.5 mole) to a suspension of the phosphine (1 mole) in methyl cyanide resulted in the separation of a black oil which on shaking dissolved to give a pale yellow solution. From this solution pale yellow crystals formed and analysis showed that they were the 1:1 adduct Ph_2MePI_2 . Clearly, equilibria occur in solution and the species predominately present in solution is not necessarily the same as the material which crystallises.

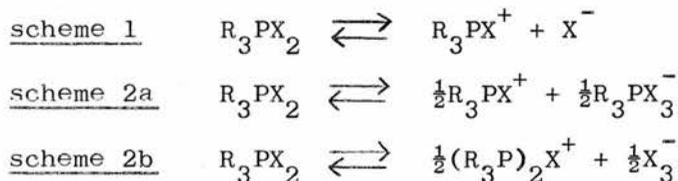
The ultraviolet spectrum of the tetraiodide Ph_2MePI_4 , dissolved in methyl cyanide, showed characteristic triiodide ion absorption which is in keeping with the proposed structure $\text{Ph}_2\text{MePI}^+\text{I}_3^-$. The solid 1:1 adduct, on the other hand, when redissolved in methyl cyanide showed no triiodide ion absorption straight away, although on standing the solution turned pale yellow and the uv indicated triiodide ions. This suggests that the solid diiodide should be formulated as $\text{Ph}_2\text{MePI}^+\text{I}^-$ and when this is dissolved in methyl cyanide the equilibrium



is set up. In order to gain more information on the species present in solution at the 1:1 mole ratio, transport number experiments were performed.

Quantitative Electrolysis of Diphenylmethylphosphorus diiodide in Methyl Cyanide

There are three plausible modes of ionisation for phosphine dihalides, and all three have been encountered in connection with the dihalides of triphenylphosphine^{96,125}. They are:



Transport number experiments are able to distinguish between scheme 1 and scheme 2, by electrolysing a solution of the dihalide in a Hittorf cell, and measuring any changes in the iodine content of the solution near the electrodes after the passage of a measured amount of current. It is impossible to distinguish between the two ionisation patterns for scheme 2, as it can be seen that in each case the cation and anion both contain the

same number of iodine atoms. Ultraviolet spectra are the only readily available means for deciding whether trihalide ions are present and thus enables a distinction to be made between schemes 2a and 2b.

The observed change in iodine content of each cell compartment can be compared with changes calculated for the possible values of transport numbers for each ionisation scheme; the transport numbers can thus be obtained.

In systems like the ones being investigated where large singly charged ions are present and the passage of current does not occur by a chain transfer process, the cation and anion will carry roughly equivalent amounts of current. Values in the range 0.35 - 0.65 are expected for the transport numbers.

The relationship between the change in halogen content (ΔHal) and transport number can be expressed as follows:

scheme 1

$$\text{at anode: } \Delta\text{Hal} = x(1-2t^+)$$

$$\text{at cathode: } \Delta\text{Hal} = x(2t^+-1)$$

scheme 2

$$\text{at anode: } \Delta\text{Hal} = x(3-4t^+)$$

$$\text{at cathode: } \Delta\text{Hal} = x(4t^+-3)$$

where ΔHal = change in gram atoms of Hal at the electrode

t^+ = transport number of the cation

x = quantity of electricity passed (Faradays).

When $x = 1$ Faraday, these expressions give rise to the following values of ΔHal , for values of t^+ between 0 and 1, (Tables 6 and 7).

The results of the electrolysis of Ph_2MePI_2 in a methyl cyanide solution are recorded in Table 8.

From the values of the transport numbers it appears that

Table 6: Ionisation scheme 1

t ⁺	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
+ ΔHal	1.0	0.8	0.6	0.4	0.2	0.0	-0.2	-0.4	-0.6	-0.8	-1.0
- ΔHal	-1.0	-0.8	-0.6	-0.4	-0.2	0.0	0.2	0.4	0.6	0.8	1.0

Table 7: Ionisation scheme 2

t ⁺	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
+ ΔHal	3	2.6	2.2	1.8	1.4	1.0	0.6	0.2	-0.2	-0.6	-1.0
- ΔHal	-3	-2.6	-2.2	-1.8	-1.4	-1.0	-0.6	-0.2	0.2	0.6	1.0

Table 8: Electrolysis of Ph₂MePI₂ in Methyl Cyanide

Electrode	ΔI g atoms/F	t ⁺	
		scheme 1	scheme 2
anode	1.146	-0.073	0.464
cathode	-0.923	0.039	0.519

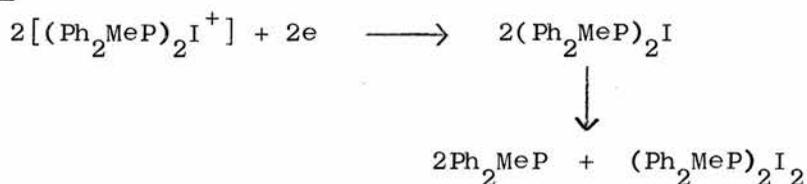
ionisation in methyl cyanide occurs by scheme 2(a) or (b)



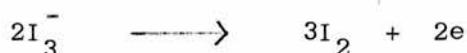
This result agrees with the postulated reactions in the conductometric titration. The initial solution was too dark to observe any noticeable colour change during electrolysis.

However, by analogy with the Ph₃AsCl₂ system¹¹¹, the following processes are assumed to occur at the electrodes during electrolysis.

At cathode:



At anode:



Infrared spectrum of Ph_2MePI_2 -

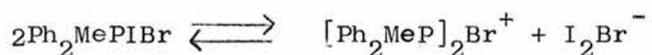
The infrared spectrum of Ph_2MePI_2 showed several changes to that of the starting phosphine, Ph_2MeP . The phosphine peak at 1583 cm^{-1} was split into a doublet at 1581 (m) cm^{-1} and 1570 (m) cm^{-1} , whilst the peak at $878 \text{ (s)(b) cm}^{-1}$ was split, giving two sharp absorptions at 890 (s) cm^{-1} and 883 (s) cm^{-1} in the diiodide. The peak at 1279 (w) cm^{-1} in the phosphine increased in intensity and moved to a higher frequency at 1291 (m) cm^{-1} whilst the absorption at 693 (s) cm^{-1} moved to 681 (s) cm^{-1} .

(3) The Reaction of Iodine Monobromide with Diphenylmethylphosphine

The conductometric titration of diphenylmethylphosphine with a solution of iodine monobromide in methyl cyanide showed discontinuities at the 0.5 and 1:1 mole ratios. There was a slight inflexion in the graph at the 2:1 ratio with an indistinct break at 3:1 caused by a gradual decrease in the rise in conductance. The results of the conductometric titration are illustrated graphically in Figure 11 and recorded in Table 24. The phosphine solution remained colourless until the 0.5:1 mole ratio when it became yellow and gradually deepened in colour to a reddish brown. The titration curve indicated definite compound formation at the following stoichiometries, $(\text{Ph}_2\text{MeP})_2\text{IBr}$, Ph_2MePIBr .

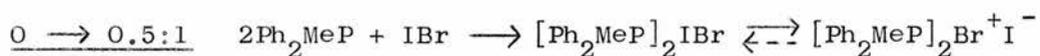
A pale yellow solid of composition close to Ph_2MePIBr was isolated by freeze drying, as treatment of the solution with dry ether and carbon tetrachloride failed to precipitate any product, when equimolar quantities of the phosphine and iodine

monobromide solution were mixed together. It was impossible to remove the last traces of methyl cyanide by pumping, and as a result of pumping the solid decomposed slightly due to loss of halogen. This solid, when redissolved in methyl cyanide showed no trihalide ion absorption. This is in contrast to the behaviour of a methyl cyanide solution containing a 1:1 mixture of Ph_2MeP and IBr , in the conductometric titration, where the solution was coloured after the 0.5:1 ratio, indicating trihalide ions. The redissolved solid showed no trihalide ions on standing and it is surprising that on dissociation of Ph_2MePIBr in methyl cyanide the equilibrium



is not set up.

A proposed scheme of reaction to explain the breaks at the 0.5 and 1:1 ratios is:



The values of the molar conductances at these stoichiometries were:

$$0.50:1 \quad \Lambda_m = 136.94 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1}, \quad (c_m = 0.00723 \text{ mole litre}^{-1})$$

(c_m based on $[\text{Ph}_2\text{MeP}]_2\text{Br}^+ \text{I}^-$)

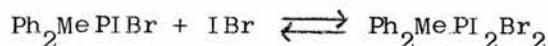
$$1.0:1 \quad \Lambda_m = 132.98 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1}, \quad (c_m = 0.00680 \text{ mole litre}^{-1})$$

(c_m based on $[\text{Ph}_2\text{MeP}]_2\text{Br}^+ \text{I}_2\text{Br}^-$)

In the conductometric titration, the conductance remains fairly constant between the 0.5:1 and 1:1 ratios, which agrees with the above scheme of reaction where the number of ions remains constant between these ratios.

There appears to be a break at the 3:1 ratio $\text{IBr}:\text{Ph}_2\text{MeP}$. However, this is probably a delayed 2:1 break caused by the

equilibrium



similar to that postulated in the Br_2 - Ph_2MeP system. The value of the molar conductance at the 2:1 ratio was

$$\Lambda_m = 109.11 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}, \quad (c_m = 0.01219 \text{ mole litre}^{-1})$$

(c_m based on $[\text{Ph}_2\text{MePBr}^+][\text{I}_2\text{Br}^-]$)

which indicates strong 1:1 electrolyte behaviour characteristic of tetrahalides.

A solid tetrahalide, $\text{Ph}_2\text{MePI}_2\text{Br}_2$, was isolated by freeze-drying from a 2:1 ratio iodine monobromide-phosphine mixture. The compound was a dark red oil which solidified just below room temperature. The ultraviolet spectrum showed two absorptions (at $\lambda_{\text{max}} = 286 \text{ m}\mu$ and $358 \text{ m}\mu$). This indicated the presence of I_2Br^- ions ($\lambda_{\text{max}} = 280, 351 \text{ m}\mu$)¹³¹. However, as the absorptions were shifted to a higher wavelength, it appears that a small amount of triiodide ion ($\lambda_{\text{max}} = 360, 291 \text{ m}\mu$) was present. The formation of triiodide ions can be explained by the following equilibrium:



(4) Electrolytic Conductance of Diphenylmethylphosphine Dihalides in Methyl Cyanide

The molar conductances of diphenylmethylphosphine dihalides, dissolved in methyl cyanide at 25°C , were measured at different concentrations. The values obtained gave some indication of the electrolyte strength of the compounds.

Methyl cyanide was again chosen as the solvent because of its high dielectric constant (36.7 at 25°C) and also to enable a direct comparison with values obtained by Beveridge et al.⁹⁶ for triphenylphosphine dihalides.

Solutions of each dihalide were prepared and placed in the conductance cell which was immersed in a thermostat at 25°C. The solids were sparingly soluble and readings were taken after about thirty minutes when steady values were obtained. The molar concentration (c_m) of these solutions was based on the formula $\text{Ph}_2\text{MePBr}_2$ in the case of the dibromide compound and the doubled formula $[\text{Ph}_2\text{MeP}]_2\text{X}_2$ in the case of the diiodide and iodine monobromide compounds. The doubled formula $[\text{Ph}_2\text{MeP}]_2\text{X}_2$ was used as the conductometric titrations mentioned earlier had indicated that the cations $(\text{R}_3\text{P})_2\text{X}^+$ were present in methyl cyanide solution. The molar conductance in each case increased with decreasing concentration and the results are shown in Table 9 and displayed in Figure 12. This enabled values for the molar conductance at 0.01 mole litre⁻¹ concentration to be obtained by extrapolation; they could therefore be compared with Λ values at this concentration for other phosphines reported by Beveridge⁹⁶.

The values of molar conductance at 0.01 mole litre⁻¹ are :-

$$\text{Ph}_2\text{MePBr}_2 \quad \Lambda_m = 34.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\text{Ph}_2\text{MePI}_2 \quad \Lambda_m = 108.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\text{Ph}_2\text{MePIBr} \quad \Lambda_m = 76.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

It can be seen that the values of molar conductance for the dibromide are considerably lower than is usually found in methyl cyanide for strong 1:1 electrolytes of similar concentration ($\Lambda_m = 100 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$). This suggests that the dibromide is a fairly weak electrolyte in methyl cyanide:

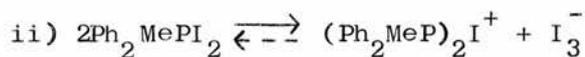
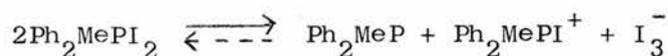


Table 9 : Electrolytic Conductance of Diphenylmethylphosphine
Dihalides in Methyl Cyanide at 25°C

Compound	c_m mole litre ⁻¹	$\sqrt{c_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mole ⁻¹
Ph ₂ MePBr ₂	0.00294	0.0542	1.365	46.43
	0.00509	0.0713	2.105	41.39
	0.00636	0.0798	2.470	38.83
	0.00801	0.0895	2.974	37.14
Ph ₂ MePI ₂	0.001004	0.03168	3.923	390.50
	0.001823	0.04269	5.939	325.78
	0.002864	0.05352	7.879	275.06
	0.003995	0.06321	9.994	250.14
Ph ₂ MePIBr	0.000683	0.02613	1.837	268.72
	0.001068	0.03269	2.630	246.30
	0.001905	0.04365	4.080	214.10
	0.002777	0.05270	5.442	195.92

The diiodide when dissolved in methyl cyanide produced a coloured solution and the presence of triiodide ions was confirmed by the ultraviolet spectrum. There are two possible schemes of ionisation for the diiodide:

- i) Disproportionation to the phosphine and tetraiodide:



It has been shown that compounds of the type R₃PX₄ are strong 1:1 electrolytes in methyl cyanide⁹⁶. However the results of the conductometric titration support scheme (ii).

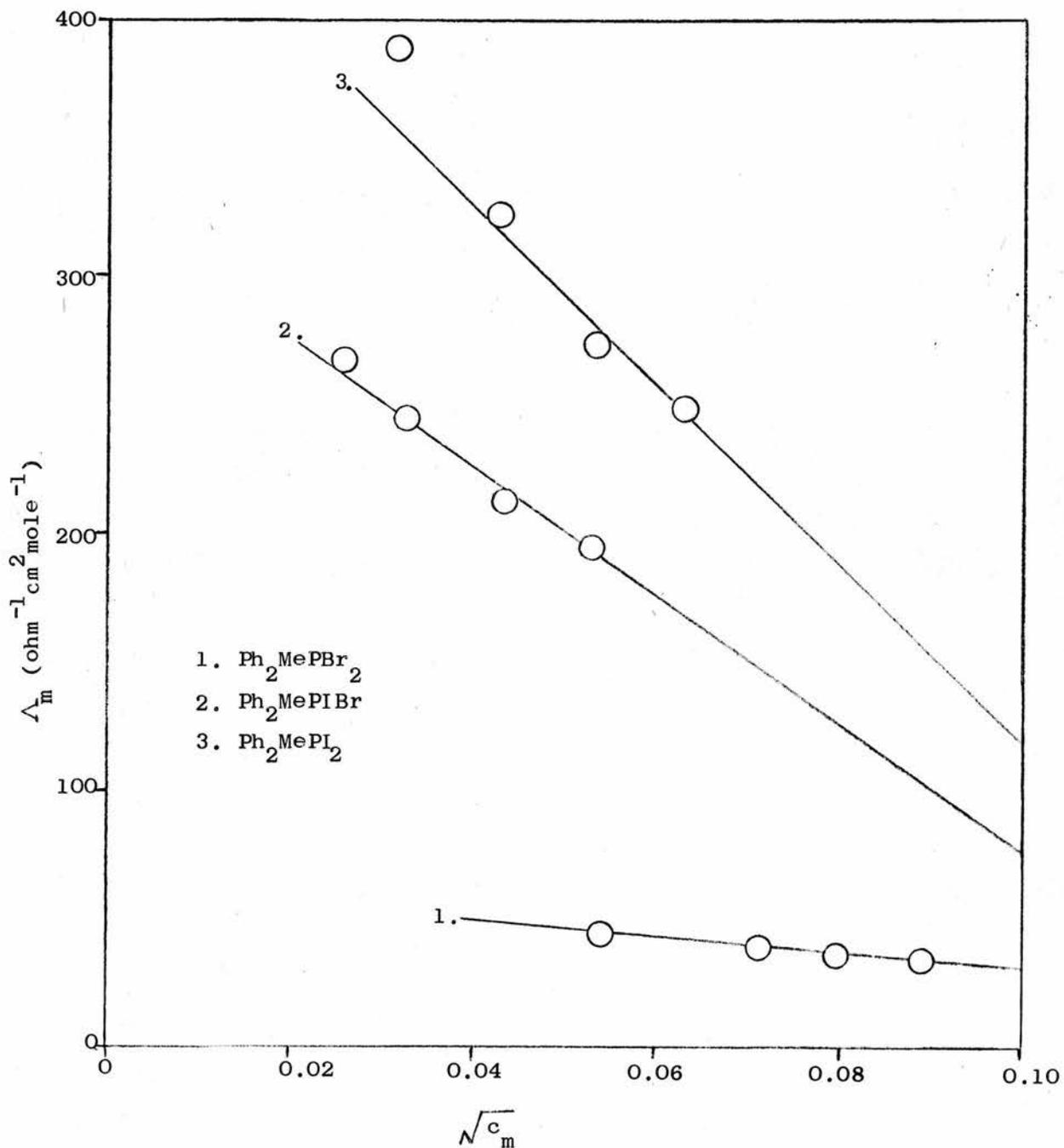


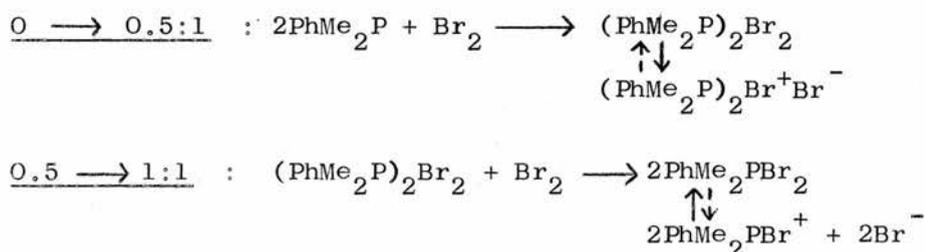
Figure 12 : Electrolytic Conductance of Diphenylmethylphosphine
Dihalides in Methyl Cyanide at 25°C

B. The Reactions of Dimethylphenylphosphine with Halogens

1) The PhMe₂P-Bromine System

The reaction of dimethylphenylphosphine with bromine appears to proceed in the same manner as that of the diphenylmethylphosphine-bromine system previously studied. The graph of the conductometric titration (see Figure 13) shows distinct breaks close to the 0.5:1 and 1:1 mole ratios. After the 1:1 mole ratio the conductance increases sharply but there is a gradual slowing down of the increase in conductance after the 2.5:1 mole ratio. A noticeable feature of the graph is the decrease in conductance between the 0.5:1 and 1:1 mole ratios. It is clear that at the 0.5:1 ratio the species present in solution is highly conducting. The titration was carried out at two widely differing concentrations and the graphs are displayed in Figure 13; the results are recorded in Tables 25 and 26. These show a close correspondence.

It is suggested that the reaction up to the 1:1 ratio in the conductometric titration proceeds in an analogous fashion to that outlined for the Br₂-Ph₂MeP system. That is:



with the 1:1 species, PhMe₂PBr₂, only partially ionised in solution.

1:1 ratio onward:

During the titration the solution remained colourless until just before the 1:1 ratio when it turned yellow, presumably due

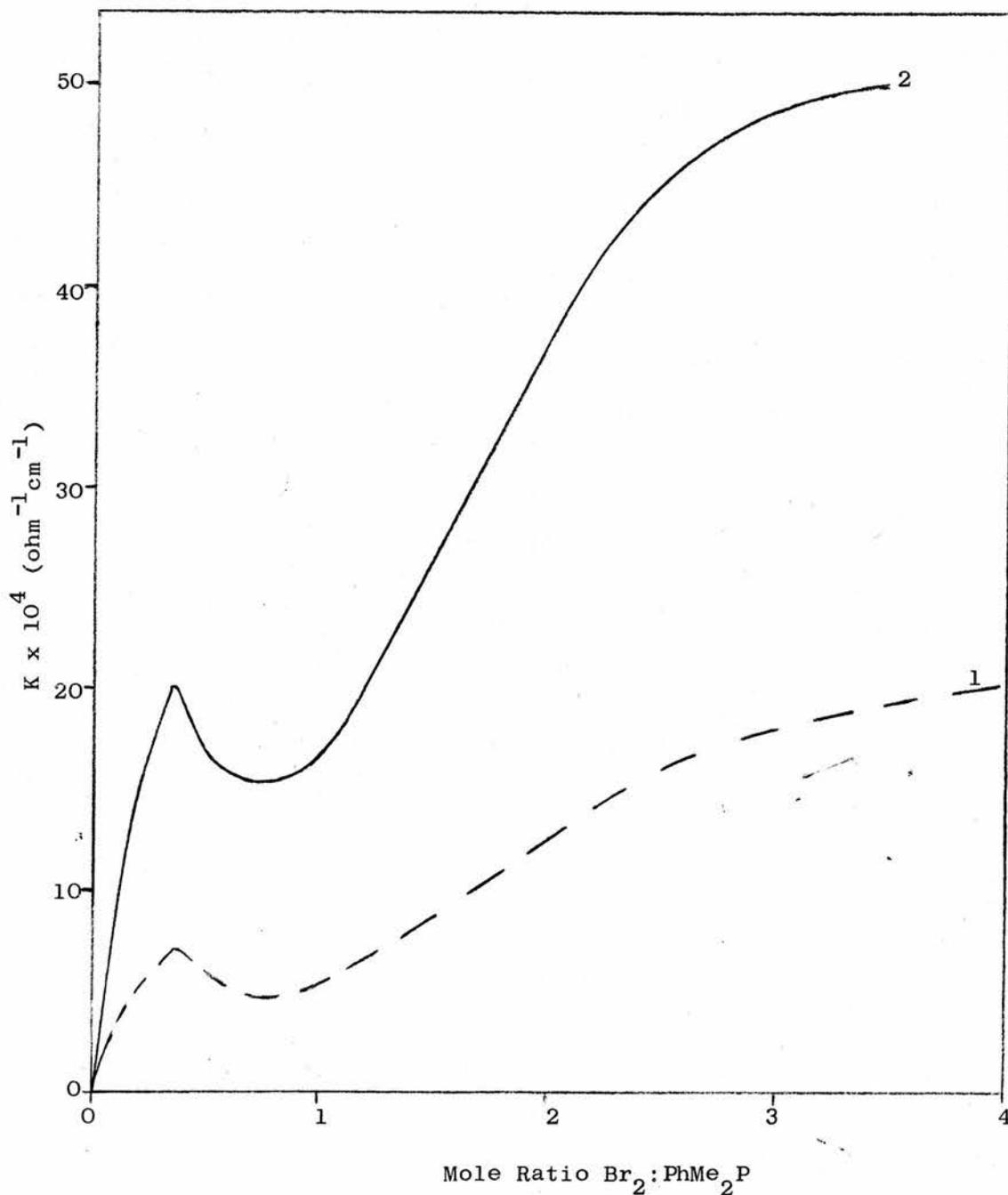
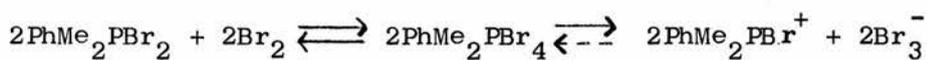


Figure 13 : Conductometric Titration of the System $\text{Br}_2\text{-PhMe}_2\text{P}$ in Methyl Cyanide

to tribromide ion formation. The increase in conductance observed after the 1:1 ratio must be due to the formation of $\text{PhMe}_2\text{PBr}_4$ in solution.



The absence of a sharp break for reasons similar to those discussed in the previous section, along with the premature colouration of the solution and the 1:1 break occurring slightly earlier than expected, can be attributed to this reaction commencing before completion of the reaction leading to $\text{PhMe}_2\text{PBr}_2$ (0.5 \rightarrow 1:1 stage).

Molar conductance values were calculated for the solution at the 0.5:1, 1:1 and 2:1 ratios: these were based on the formulae $(\text{PhMe}_2\text{P})_2\text{Br}_2$, $\text{PhMe}_2\text{PBr}_2$, and $\text{PhMe}_2\text{PBr}_4$ for the conducting species. The values obtained were:

<u>0.50:1</u>	Graph 1 $\Lambda_m = 133.18 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ($c_m = 0.004655 \text{ mole litre}^{-1}$)
	Graph 2 $\Lambda_m = 107.96 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ($c_m = 0.01584 \text{ mole litre}^{-1}$)
<u>1.00:1</u>	Graph 1 $\Lambda_m = 62.13 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ($c_m = 0.008852 \text{ mole litre}^{-1}$)
	Graph 2 $\Lambda_m = 57.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ($c_m = 0.02986 \text{ mole litre}^{-1}$)
<u>2.00:1</u>	Graph 1 $\Lambda_m = 157.69 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ($c_m = 0.008054 \text{ mole litre}^{-1}$)
	Graph 2 $\Lambda_m = 140.40 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ($c_m = 0.02679 \text{ mole litre}^{-1}$)

Values for the 0.5:1 and 2:1 ratios are consistent with strong electrolyte behaviour. Note that the values at the 1:1 ratio, whilst reasonably high, are in keeping with the suggestion that $\text{PhMe}_2\text{PBr}_2$ is not completely ionised.

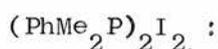
Attempts were made to obtain solids from methyl cyanide solutions containing PhMe_2P and bromine in the ratios 0.5:1, 1:1, and 2:1. The solid isolated at 0.5:1 ratio, when analysed, was found to have a 1:1 stoichiometry, $\text{PhMe}_2\text{PBr}_2$. The two other adducts which were isolated from the 1:1 and 2:1 solutions were respectively, the dibromide and tetrabromide. The dibromide was

formed as a white solid immediately the bromine solution was added to the phosphine leaving a colourless mother liquor. The ultraviolet spectrum of the solid when redissolved in methyl cyanide showed the absence of tribromide ion, thus substantiating the proposed reaction sequence. The tetrabromide was extremely soluble, as opposed to the dibromide which formed initially as a precipitate during the preparation of the tetrabromide and only redissolved on stirring for approximately one hour. The mixture had therefore to be "freeze-dried", whereupon orange crystals were observed. The tetrabromide compound can be formulated as $\text{PhMe}_2\text{PBr}^+\text{Br}_3^-$ as the ultraviolet spectrum showed that tribromide ions were present.

2) The PhMe_2P -Iodine System

The graph of the conductometric titration of dimethylphenylphosphine with a solution of iodine in methyl cyanide is very similar to that obtained for the system $\text{Ph}_2\text{MeP-I}_2$, and is shown in Figure 14 with the results recorded in Table 27. There is a clear break at the 0.5:1 mole ratio up to which the solution is colourless; thereafter the solution acquires a yellow colour indicating formation of triiodide ions after this point. The conductance rises sharply after the 0.5:1 mole ratio to a maximum at the 2:1 ratio and there is definitely no break at the 1:1 stoichiometry. After the 2:1 ratio the conductance decreases linearly, this being caused by the poor conductance of molecular iodine in methyl cyanide solution, the volume of which is constantly increasing.

From the graph it appears that there are two reactions occurring. The first is formation of the 0.5:1 species,



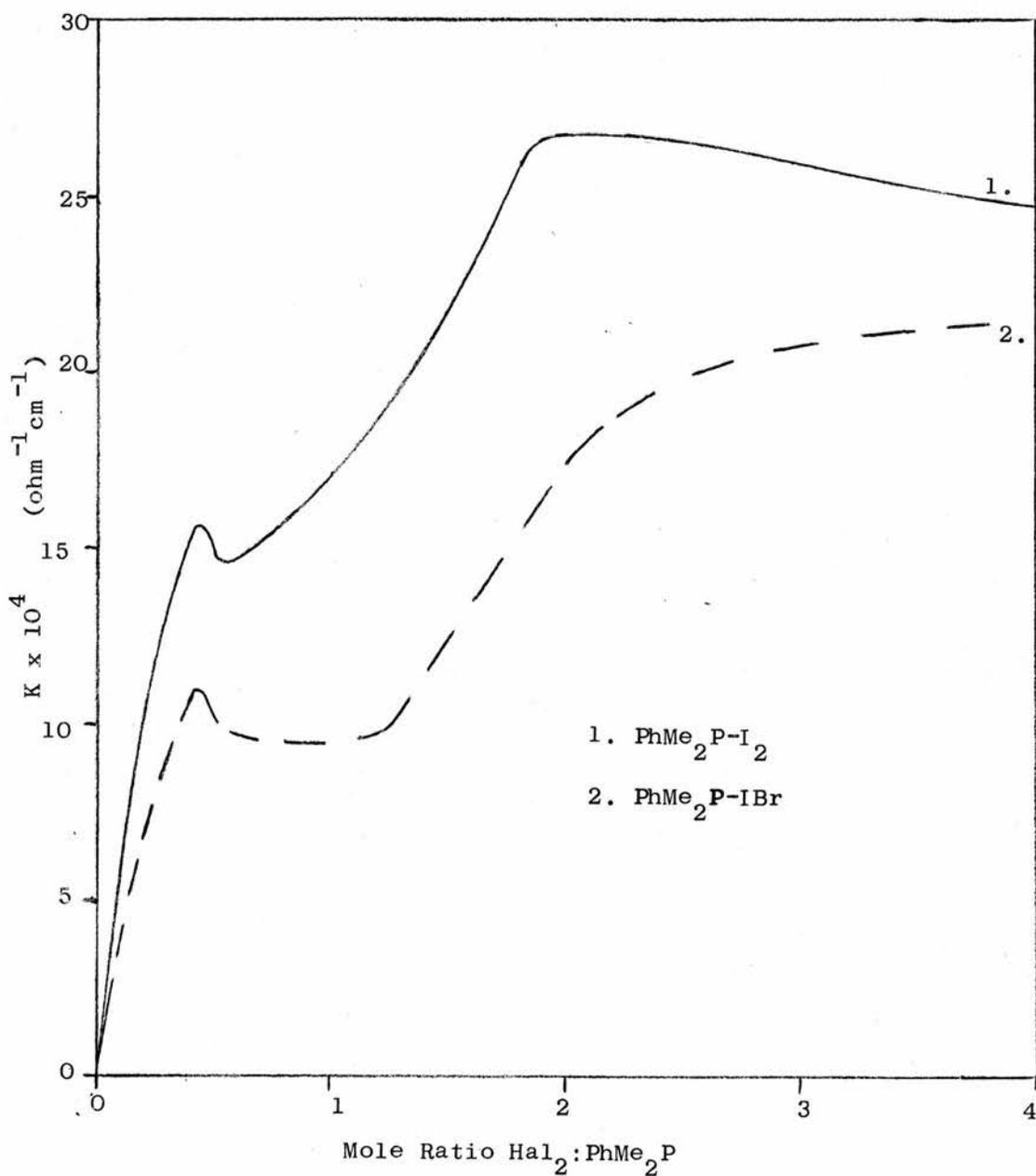
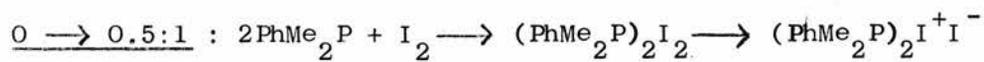
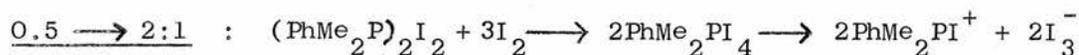


Figure 14 : Conductometric Titration of the System I_2 - $PhMe_2P$ and IBr - $PhMe_2P$ in Methyl Cyanide



After the 0.5:1 ratio the solution became coloured indicating triiodide ion formation, and coupled with the absence of a break at the 1:1 ratio it is suggested that the tetraiodide species is formed between the 0.5 and 2:1 ratios:



The values of molar conductance at the 0.5:1 and 2:1 mole ratios which were calculated from the conductometric titration graph are both characteristic of strong 1:1 electrolytes.

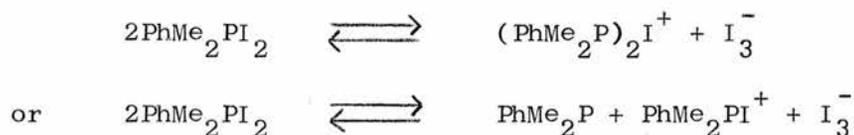
$$0.5:1 \quad \Lambda_m = 188.02 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.00768 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } (\text{PhMe}_2\text{P})_2\text{I}^+\text{I}^-)$$

$$2.0:1 \quad \Lambda_m = 200.15 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.01339 \text{ mole litre}^{-1})$$

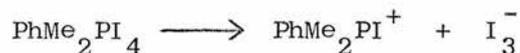
$$(c_m \text{ based on } \text{PhMe}_2\text{PI}^+\text{I}_3^-)$$

Attempts were made to isolate compounds at the 0.5:1, 1:1 and 2:1 mole ratios of iodine to phosphine. The white solid which precipitated from the 0.5:1 solution had a composition which lay between that of the 0.5 compound $(\text{PhMe}_2\text{P})_2\text{I}_2$ and the 1:1 compound PhMe_2PI_2 . This solid decomposed quickly even in the dry-box and was analysed immediately after preparation. The solid is assumed to be the 1:1 compound PhMe_2PI_2 which has lost iodine. The diiodide compound, PhMe_2PI_2 , was precipitated from an equimolar solution of phosphine and iodine in methyl cyanide, leaving a pale yellow solution. The white solid gradually became pale yellow and darkened even in the dry-box. The ultraviolet spectrum of the diiodide in methyl cyanide showed triiodide ion absorption which gradually increased due to decomposition.



This indicates the instability of the diiodide in methyl cyanide and ties in with the absence of a break at the 1:1 ratio in the conductometric titration curve. The tetraiodide was extremely soluble and the solution had to be freeze-dried to reduce the solvent volume whereupon a dark-brown solid remained. Strong

triiodide ion absorption was observed in the ultraviolet spectrum indicating that the tetraiodide ionises thus:



Quantitative Electrolysis of a Solution of Dimethylphenylphosphine Diiodide in Methyl Cyanide

A methyl cyanide solution (ca. 0.05 M) of dimethylphenylphosphine diiodide was electrolysed, and using the same symbols and relationships given previously (see Table 6 and 7) values for the transport numbers (t^+) were obtained (Table 10) for the following postulated reaction schemes:

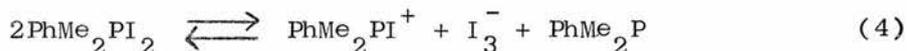
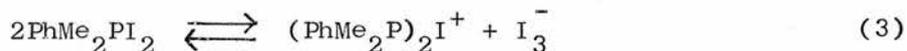
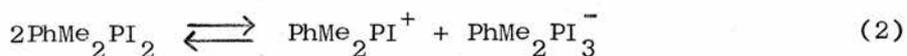
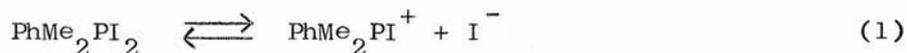


Table 10 : Electrolysis of PhMe_2PI_2 in Methyl Cyanide

Electrode	ΔI g atoms/F	t^+	
		scheme 1	schemes 2,3,4
anode	1.143	-0.071	0.464
cathode	-0.960	1.071	0.510

From the results it is clear that there is a net transfer of iodine to the anode and the t^+ values obtained are in keeping with the schemes (2), (3) and (4). Scheme (2) can be eliminated since triiodide ions were detected in solution (strong absorption band at 291 and 360 μ) as can scheme (3) since the

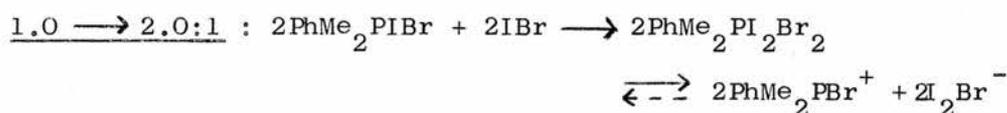
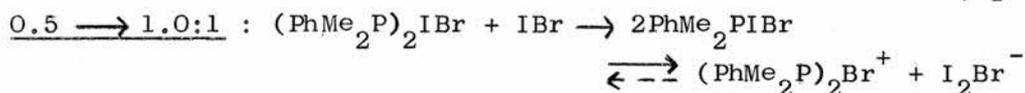
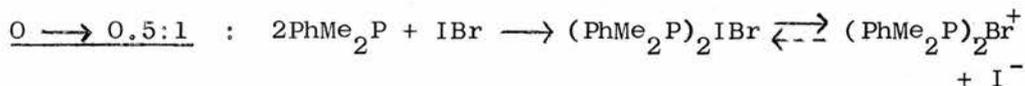
conductometric titration data did not support the existence of a 1:1 adduct [PhMe_2PI_2 or $(\text{PhMe}_2\text{PI}_2)_2$] in methyl cyanide solution. It would seem therefore that the behaviour of PhMe_2PI_2 (s) when dissolved in methyl cyanide is best described by scheme (4) ie. tetraiodide is formed and a molecule of PhMe_2P is released.

In an attempt to distinguish further between the possible schemes of ionisation, the ^{31}P nuclear magnetic resonance of solutions of PhMe_2PI_2 was investigated. However no peaks were observed. This was probably due to one or both of two reasons. Firstly the diiodide was fairly insoluble and therefore only weak solutions could be obtained - too weak for a signal to be recorded; and secondly, the iodine has a spin of 5/2 and therefore a quadrupole moment. This would be expected to broaden the lines and hence make them difficult to distinguish from the background noise.

3) The PhMe_2P -Iodine Monobromide System

The dimethylphenylphosphine-iodine monobromide system shows behaviour which is rather like that of the $\text{PhMe}_2\text{P-Br}_2$ system. The results of the conductometric titration are displayed in Figure 14 and recorded in Table 28. The graph (plot 2) shows a sharp initial rise in conductance to the 0.5:1 ratio which is followed by a plateau and a further break at the 1:1 ratio. Then the conductance roughly doubles in value to the 2:1 ratio after which the rate of increase slows down until it is practically constant at the 4:1 ratio. The solution assumed a yellow colour at the 0.5:1 ratio which presumably indicates the start of trihalide ion formation.

The proposed scheme of reaction to explain the results of the conductometric titration is:



The values of molar conductance abstracted from the titration graph are:-

$$\underline{0.5:1} \quad \Lambda_m = 168.14 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0060 \text{ mole litre}^{-1})$$

(c_m based on (PhMe₂P)₂Br⁺I⁻)

$$\underline{1.00:1} \quad \Lambda_m = 166.78 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.00572 \text{ mole litre}^{-1})$$

(c_m based on (PhMe₂P)₂Br⁺I₂Br⁻)

$$\underline{2.00:1} \quad \Lambda_m = 165.87 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.01049 \text{ mole litre}^{-1})$$

(c_m based on PhMe₂PBr⁺I₂Br⁻)

These values each indicate strong 1:1 electrolyte behaviour at the respective ratios.

From the titration curves the following compounds were expected: (PhMe₂P)₂IBr, PhMe₂PIBr and PhMe₂PI₂Br₂. In fact only two distinct adducts could be isolated as solid compounds - the dihalide and the tetrahalide.

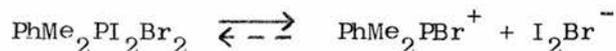
The iodine monobromide adduct was precipitated immediately equimolar solutions of phosphine and iodine monobromide were mixed together. It was isolated as a pale yellow solid which turned orange on standing, even in the dry-box, due to decomposition. The ultraviolet spectrum of a solution of the solid showed mainly phosphine absorption but triiodide ions were also detected. A possible explanation for these findings could be the decomposition of the iodine monobromide adduct to the dibromide and diiodide compounds,



with subsequent disproportionation of the diiodide to the phosphine and tetraiodide (as is known to occur) thus producing triiodide ions:

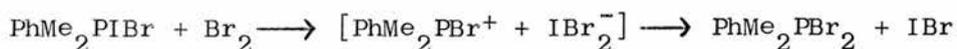


A pale yellow solid was precipitated when phosphine and iodine monobromide solutions were mixed during the preparation of the tetrahalide compound. This redissolved on shaking for approximately one hour. The solution during freeze-drying fractionally crystallised to give a dark brown solid and a pale yellow solid (1:1 adduct). The dark brown solid analysed as $\text{PhMe}_2\text{PI}_2\text{Br}_2$ and ultraviolet studies showed that in methyl cyanide it ionised as follows:-



This is in accord with previous observations mentioned in the general introduction which state that the smaller halogen atom is attached to the phosphorus atom in tetrahalides containing two different halogens.

In the above systems three tetrahalides were obtained viz $\text{PhMe}_2\text{PBr}_4$, $\text{PhMe}_2\text{PI}_2\text{Br}_2$ and PhMe_2PI_4 . These are members of the series $\text{PhMe}_2\text{PI}_n\text{Br}_{(4-n)}$, (n=0-4). In an attempt to prepare the missing member $\text{PhMe}_2\text{PIBr}_3$ the iodine monobromide adduct was redissolved and an equimolar portion of bromine solution added. The solid which was obtained on precipitation analysed as $\text{PhMe}_2\text{PBr}_2$ and it therefore appears that a simple exchange of the halogen atoms is taking place:



A similar experiment was performed using equimolar amounts of PhMe_2PIBr and iodine in an attempt to obtain $\text{PhMe}_2\text{PI}_3\text{Br}$ as a solid compound. The solution was freeze dried to remove methyl cyanide giving a low melting solid which existed as an oil at room temperature. This preparation was therefore not pursued any further.

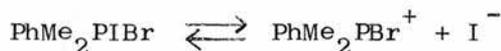
Infrared spectra of PhMe_2P and PhMe_2P -Halogen adducts

The dihalide adducts of dimethylphenylphosphine were extremely moisture sensitive and as a result precautions were taken to exclude water vapour by preparing the mull in the dry-box and sealing the edges of the KBr plates with "Sellotape". KBr discs were used because CsI plates were attacked by the mulls. As a direct consequence no P-X stretching frequencies could be measured as the KBr 'window' did not extend to a low enough frequency, (the cut-out occurs at approximately 600 cm^{-1}). The observed shifts and variations in intensity are recorded in Table 11.

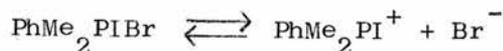
Table 11 : IR shifts on going from PhMe_2P to PhMe_2PX_2 .

PhMe_2P	$\text{PhMe}_2\text{PBr}_2$	PhMe_2PI_2	PhMe_2PIBr
1484(w)			
1433(s)	1443(s)	1440(s)	1440(s)
1290(vw)	1300(m)	1303(w)	1290(m)
	1134(s)		1132(m)
1107(w)	1114(m)	1118(m)	1113(m)
	1010(s)		1009(m)
1000(vw)	1000(m)	970(s)	1000(m)
940(m)	948(sb)	930(sb)	933(sb)
865(w)	870(w)	865(s)	869(w)
		756(s)	

It can be seen that the infrared spectrum of $\text{PhMe}_2\text{PBr}_2$ and PhMe_2PIBr are nearly identical. This can be taken as indicating closely similar structures of these compounds. Since it is assumed that the solid phase of the dihalides of this type is ionic, of the form $\text{R}_3\text{PX}^+\text{X}^-$, it would seem reasonable to conclude that the bromine and iodine monobromide adducts contain the same cation which must be $\text{PhMe}_2\text{PBr}^+$. Therefore the iodine monobromide adduct ionises as



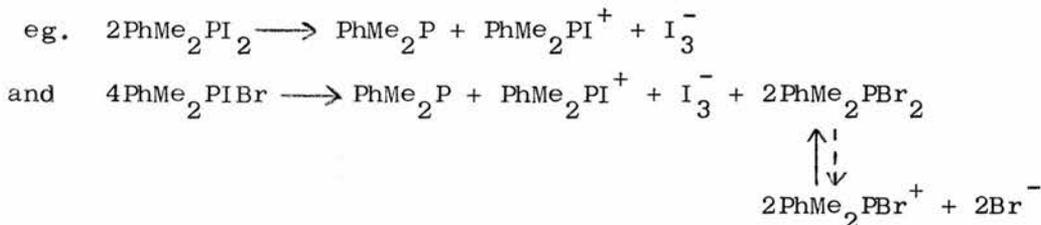
and not as



4) Electrolytic Conductance of Dimethylphenylphosphine Dihalides in Methyl Cyanide

The molar conductances of the various dihalides of dimethylphenylphosphine were measured in methyl cyanide at 25°C . The values of conductance at various concentrations are recorded in Table 12 and displayed in Figure 15.

The values for c_m were calculated on the basis of the formula PhMe_2PX_2 as all previous experiments had indicated that the species present in solution were $\text{PhMe}_2\text{PBr}^+\text{Br}^-$ in the case of the dibromide, $\text{PhMe}_2\text{PBr}_2$, whilst PhMe_2PI_2 and PhMe_2PIBr decomposed in methyl cyanide to give a mixture of species.



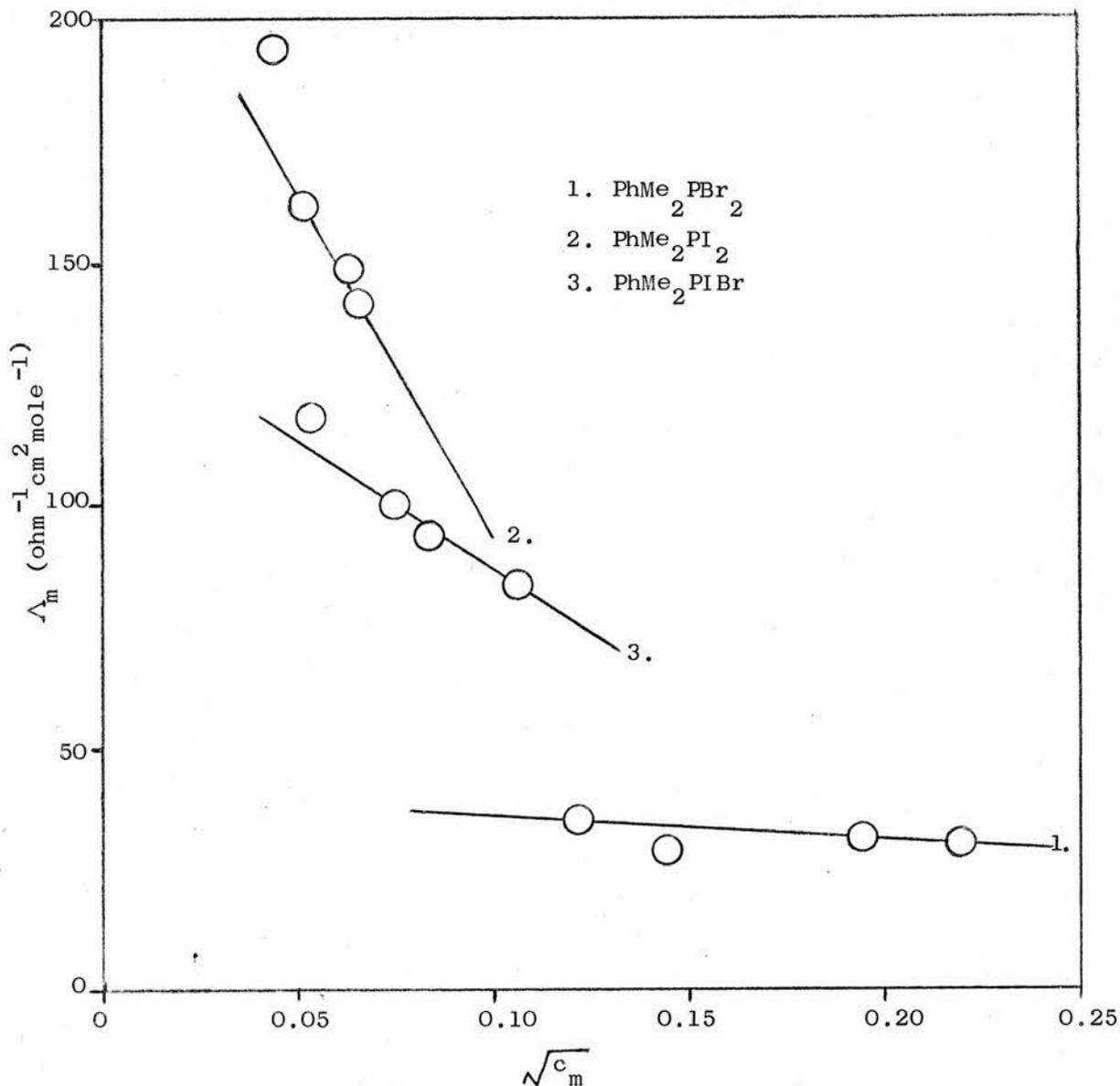


Figure 15 : Electrolytic Conductance of Dimethylphenylphosphine Dihalides in Methyl Cyanide at 25°C

A plot of molar conductance against $\sqrt{c_m}$ showed, in each case, that the molar conductance decreased with increasing concentration. The rate of decrease was greatest for the diiodide and least for the dibromide. From the graph it is possible to obtain values of conductance at 0.01 M by extrapolation.

Table 12 : Electrolytic Conductance of Dimethylphenylphosphine
Dihalides in Methyl Cyanide at 25°C

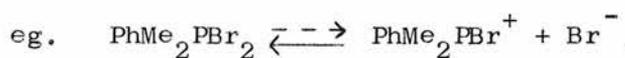
Compound	c_m mole litre ⁻¹	$\sqrt{c_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mole ⁻¹
PhMe ₂ PBr ₂	0.01497	0.1223	5.241	35.01
	0.02080	0.1442	5.939	28.55
	0.03773	0.1942	11.845	31.39
	0.04845	0.2201	14.707	30.35
PhMe ₂ PI ₂	0.002105	0.0459	4.079	193.77
	0.002789	0.0528	4.49	161.11
	0.004089	0.0639	6.09	148.88
	0.004517	0.0672	6.41	141.99
PhMe ₂ PIBr	0.002969	0.0545	3.499	117.85
	0.005701	0.0755	5.695	99.90
	0.007205	0.0849	6.740	93.55
	0.01140	0.1068	9.540	83.69

$$\text{PhMe}_2\text{PBr}_2 \quad \Lambda_m = 36.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\text{PhMe}_2\text{PI}_2 \quad \Lambda_m = 98.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\text{PhMe}_2\text{PIBr} \quad \Lambda_m = 86.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

The observed molar conductance value for the dibromide, PhMe₂PBr₂, is lower than is usual for similar solutions of strong 1:1 electrolytes in methyl cyanide; this could be due to the presence in solution of an equilibrium involving molecular PhMe₂PBr₂ units which is supported by the results of the conductometric titration.



As mentioned above the compounds PhMe₂PI₂ and PhMe₂PIBr decompose

in methyl cyanide to give a mixture of species, and therefore the only conclusion that can be drawn from the values of molar conductance at 0.01 M is that the species present are strong electrolytes. The ionisation schemes of the PhMe_2PX_2 systems are different in each case and therefore comparison of molar conductances (Λ 's) is not particularly meaningful.

C. The Reactions of Trimethylphosphine with Halogens

Trimethylphosphine is a volatile liquid, b.pt. 37-40°C, which is spontaneously inflammable in air. To avoid contact with air and moisture and to facilitate accurate measurement of known amounts, the phosphine was stored in weighed ampoules similar to those used for bromine. To prepare a solution of the phosphine, the ampoules were broken below the surface of the solvent. All operations and manipulations of the phosphine and related compounds were carried out either in the nitrogen filled dry-box or on the vacuum line.

The extreme lability of trimethylphosphine is underlined by the fact that despite all the precautions taken to exclude moisture and air, a white solid residue remained in the distillation flask after ampouling all of a portion of the phosphine. An infrared spectrum showed a large broad peak at 1168 cm^{-1} which was absent in the spectrum of trimethylphosphine. This is believed to be the P=O stretching frequency and results of microanalysis showed that the solid may be trimethylphosphine oxide. The trimethylphosphine had therefore picked up traces of oxygen and oxidised to Me_3PO .

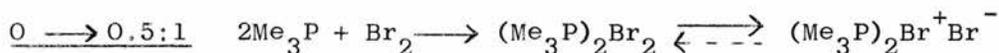
To check whether any oxidation products of the phosphine were present in the ampoules, one ampoule was broken under vacuum and the sample was distilled into an IR gas cell. The gas phase infrared spectrum gave an identical spectrum to that reported by Wagstaffe et al¹⁴¹ for trimethylphosphine and there was no residue left after distillation. These observations showed a complete absence of oxidation products.

1) The Me_3P -Bromine System

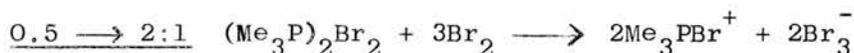
A conductometric titration study of the Br_2 - Me_3P system in methyl cyanide gave the results recorded in Table 29 and graph illustrated in Figure 16. The graph shows a steep rise in the

conductance until just before the 0.5:1 ratio, followed by a noticeable dip before the conductance rises gradually to the region of the 2:1 ratio after which the rate of increase is reduced. There is a definite break in the conductance close to the 0.5:1 ratio with a rather indistinct break around the 2:1 ratio. The solution became coloured after the 0.5:1 ratio indicating tribromide ion formation.

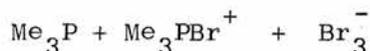
The scheme for the reaction of the phosphine with 0.5 mole of bromine is



There was no indication of a break at the 1:1 ratio in the conductometric titration and therefore the reaction occurring between the 0.5:1 and 2:1 ratios is the production of the tetrabromide species, Me_3PBr_4 .



Thus the solution at the 1:1 ratio will have the composition



The values of molar conductance taken from the titration graphs are:

$$0.50:1 \quad \Lambda_m = 170.70 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0087 \text{ mole litre}^{-1}) \\ (c_m \text{ based on } (\text{Me}_3\text{P})_2\text{Br}^+\text{Br}^-)$$

$$2.00:1 \quad \Lambda_m = 186.95 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0152 \text{ mole litre}^{-1}) \\ (c_m \text{ based on } \text{Me}_3\text{PBr}^+\text{Br}_3^-)$$

These values both indicate extremely strong 1:1 electrolyte behaviour in methyl cyanide at the 0.5 and 2:1 ratios.

Solids were isolated from solutions containing a 0.5:1, 1:1 and 2:1 mole ratio of bromine to phosphine.

The fine white solid isolated at the 0.5:1 ratio had the composition $(\text{Me}_3\text{P})_2\text{Br}_2$. An ultraviolet analysis of the solid

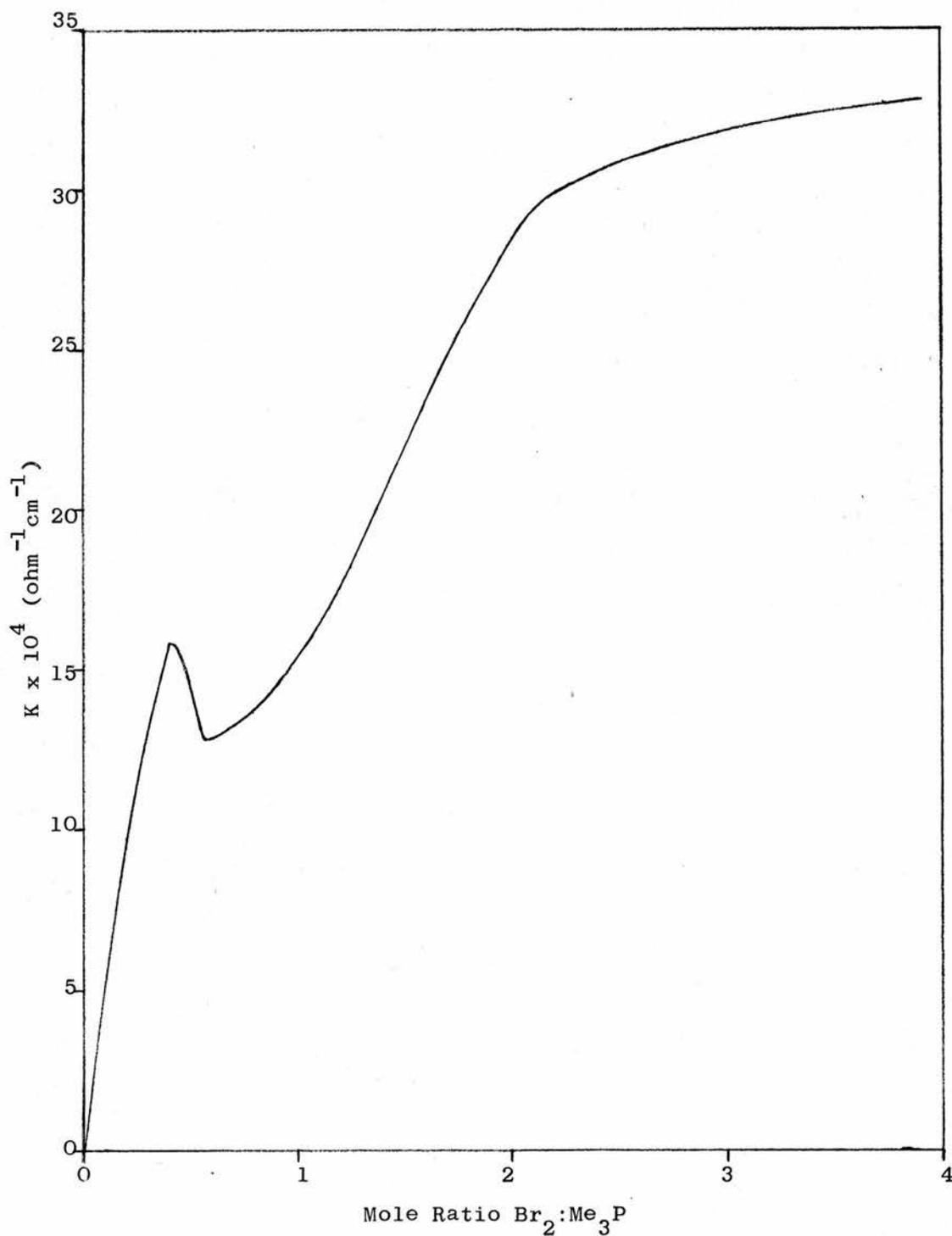
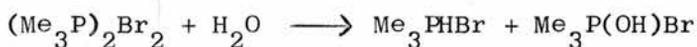


Figure 16 : Conductometric Titration of the System $\text{Br}_2\text{-Me}_3\text{P}$ in Methyl Cyanide

dissolved in methyl cyanide showed no tribromide ion absorption. The solid, however, was extremely moisture sensitive and, despite all precautions taken to exclude water vapour, the IR spectrum

showed a broad O-H absorption centred on 2650 cm^{-1} . There was no discernible P-Br absorption around 400 cm^{-1} , but instead a small peak at 337 cm^{-1} . This could be attributed to either of two different factors. If the compound is $(\text{Me}_3\text{P})_2\text{Br}_2$, then a possible structure contains a cation with a configuration $\text{Me}_3\overset{+}{\text{P}}\text{-Br-PMe}_3$ or $\text{Me}_3\overset{+}{\text{P}}\text{-PMe}_3$ which would lower the frequency of the P-Br stretching mode. The alternative explanation is an exchange of halogen atoms between the phosphine adduct and the CsI plates thus giving P-I stretching. The infrared spectrum was similar to that obtained for $\text{Me}_3\text{P(OH)Br}$, and $(\text{Me}_3\text{P})_2\text{Br}_2$ is thought to hydrolyse as follows



Trimethylphosphonium bromide, Me_3PHBr , could be produced by moisture present in the methyl cyanide in a similar manner to that suggested by Beveridge et al¹⁴² for the triphenylphosphonium halides. P-H stretching was not, however, observed in the region $2200\text{-}2450 \text{ cm}^{-1}$ ¹⁴³ presumably because of masking by the O-H absorption. Neither Me_3PHBr nor $\text{Me}_3\text{P(OH)Br}$ contains a P-Br bond as their structures are $\text{Me}_3\text{PH}^+\text{Br}^-$ and $\text{Me}_3\text{P(OH)}^+\text{Br}^-$ respectively.

A white solid was obtained by mixing equimolar quantities of phosphine and bromine solutions. Analysis showed the compound to be Me_3PBr_2 and the IR spectrum contained a peak at 412 cm^{-1} which was attributed to the P-Br stretching mode. The UV spectrum of the solid Me_3PBr_2 redissolved in methyl cyanide showed initially no tribromide ion absorption which is in agreement with Goubeau and Baumgärtner¹²⁷ who showed, by solid state infrared and Raman spectra, that the structure is $\text{Me}_3\text{PBr}^+\text{Br}^-$. However on standing the solution of Me_3PBr_2 showed traces of tribromide ion.

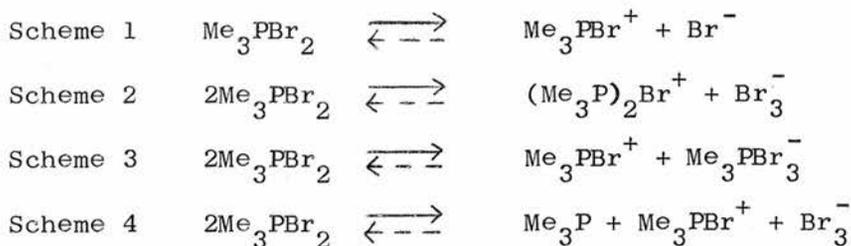
Transport Number Measurements on Methyl Cyanide Solutions of Me₃PBr₂

In order to gain more information on the nature of the species present when the dibromide, Me₃PBr₂, is dissolved in methyl cyanide solution a transport number experiment was performed.

Table 13 : Electrolysis of Me₃PBr₂ in Methyl Cyanide

Electrode	ΔBr g atoms/F	t ⁺	
		Scheme 1	Schemes 2,3,4
anode	+ 1.499	- 0.249	0.375
cathode	- 0.601	0.199	0.599

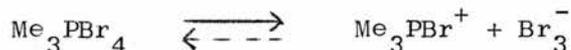
The results recorded in Table 13 are not as consistent as previously. The possible schemes of ionisation of Me₃PBr₂ are as follows



The results favoured ionisation by Schemes 2, 3, or 4 although, in this case, the experiment was fraught with error because of the extreme lability of the dibromide and the dilute solutions used on account of the low solubility of Me₃PBr₂. The presence of tribromide in solutions of Me₃PBr₂ rules out Scheme 3 and the absence of a break at the 1:1 ratio in the conductometric titration eliminates Scheme 2. Therefore Scheme 4, which was indicated by the conductometric titration, appears to be the correct ionisation for Me₃PBr₂ in methyl cyanide.

An orange solid was isolated when a methyl cyanide solution containing bromine and phosphine in the ratio of 2 mole:1 mole was

freeze dried. The compound analysed as the tetrabromide, Me_3PBr_4 , and UV spectra detected strong tribromide ion absorption showing that it ionised as



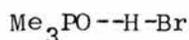
in methyl cyanide. The infrared spectrum of the tetrabromide was similar to that of the dibromide with a peak at 415 cm^{-1} (s) attributed to the P-Br stretching frequency. A noticeable addition to the spectrum of Me_3PBr_4 over that of Me_3PBr_2 was the occurrence of a shoulder at 426 cm^{-1} (m). The tetrabromide was extremely moisture sensitive, with hydrolysis occurring in the samples used for infrared analysis even though the CsI plates were sealed with "Sellotape".

The indistinctness of the break at the 2:1 ratio in the titration is possibly caused by an equilibrium reaction occurring between the tetrabromide and some higher polybromide. Vapour pressure-composition studies at 20°C were used to try and detect higher polybromides in this system. The vapour pressure-composition graph failed to reveal any steps, thus showing that no stable solid entities other than Me_3PBr_2 and Me_3PBr_4 existed at that temperature.

Atmospheric Hydrolysis of Me_3PBr_2 and Me_3PBr_4

It has already been mentioned that the compounds Me_3PBr_2 and Me_3PBr_4 are extremely labile, losing bromine, and reacting very readily with traces of moisture even when handled in the dry-box and between sealed caesium iodide plates. Copious fumes of bromine and hydrogen bromide were evolved when the compounds were exposed to the open atmosphere. The dibromide remained white and analysis of the solid showed it to be $\text{Me}_3\text{P(OH)Br}$. The infrared spectrum of this hydrolysis product contained a very broad absorption band in the region $2700\text{-}2000 \text{ cm}^{-1}$ indicative of hydrogen bonded O-H,

similar to that found by Inglis and Harris¹⁴⁴ in their work on triarylarsonic hydroxyhalides, $\text{Ar}_3\text{AsOH Hal}$. Inglis has shown that hydroxyhalides of this type are more correctly represented as simple hydrogen bonded adducts of the oxide and hydrogen halide, thus $\text{Ph}_3\overset{\delta+}{\text{As}}\text{--O--H--}\overset{\delta-}{\text{Hal}}$ where -- represented a bond order of less than one and all bonds are covalent, though polar. A prominent peak in the infrared spectrum of the hydroxyhalide is the broad band at 1015 cm^{-1} (sb) which is attributable to the P=O stretching. The frequency of P=O stretching normally lies in the region $1440\text{--}1140 \text{ cm}^{-1}$ and it seems likely that this is lowered on account of hydrogen bonding. By analogy with the structure proposed by Inglis the hydrolysed product of Me_3PBr_2 is probably more correctly represented,



The tetrabromide Me_3PBr_4 readily absorbed traces of moisture to give an orange solid which analysed as $\text{Me}_3\text{P(OH)Br}_3$. The infrared spectrum showed O-H and P-O absorption and the ultraviolet spectrum showed tribromide ions; therefore the compound can be formulated as $\text{Me}_3\text{POH}^+\text{Br}_3^-$

The tetrabromide was exposed to the open atmosphere for several days. After pumping on the vacuum line for about four hours to remove excess water, the colourless oil turned to a white solid. Analysis and infrared spectrum of this solid showed it to be $\text{Me}_3\text{P(OH)Br}$. It was possible to assign the major peaks in the infrared spectrum of $\text{Me}_3\text{P(OH)Br}$: (P)-O-H, 1400 cm^{-1} ; P-Me, 1295 cm^{-1} ; P-O-(H) stretching, 1015 cm^{-1} ; P-Me-rocking, 960 cm^{-1} ; P-Me, 870 cm^{-1} ; P-C, 775 cm^{-1} . There was no absorption in the region where P-Br stretching would be expected to occur and this concurs with the proposed structure for $\text{Me}_3\text{P(OH)Br}$ mentioned above.

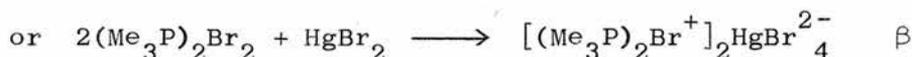
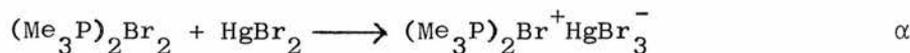
Complexes of Trimethylphosphine Bromides with Mercuric Bromide

To explain the 0.5:1 breaks in conductometric titrations ions of the type $(R_3P)_2X^+$ are envisaged as occurring in solution. However there have been very few compounds isolated which are thought to contain the cation $[(R_3P)_2X]^+$. One of these is the adduct $(Ph_3P)_2HgBr_2, Br_2$ obtained by Ali et al¹²⁵ from an equimolar mixture of $(Ph_3P)_2HgBr_2$ and bromine in methyl cyanide. The structure of this compound can be written as $[(Ph_3P)_2Br]^+HgBr_3^-$.

In an attempt to clarify the structure of the Me_3P-Br_2 adducts isolated at the 0.5:1 and 1:1 ratio $Br_2:Me_3P$, various experiments were conducted using mixtures of Me_3P , Br_2 and $HgBr_2$ in an attempt to isolate a solid containing the ion $(Me_3P)_2Br^+$.

The System $HgBr_2-(Me_3P)_2Br_2$

A conductometric titration was performed on the system $HgBr_2-(Me_3P)_2Br_2$ to give some indication of possible compound formation. It was thought probable that one of the following two reactions might occur.



Trimethylphosphine was titrated with a methyl cyanide solution of bromine until the 0.5:1 mole ratio was reached. Burettes were changed and the titration was continued using a solution of mercuric bromide in methyl cyanide. The results of the conductometric titration $HgBr_2-(Me_3P)_2Br_2$ are illustrated in Figure 17, plot 2 and recorded in Table 30.

The graph shows a slight initial drop in conductance with the first addition of mercuric bromide solution followed by a large linear increase to the 2:1 mole ratio. There was a clear

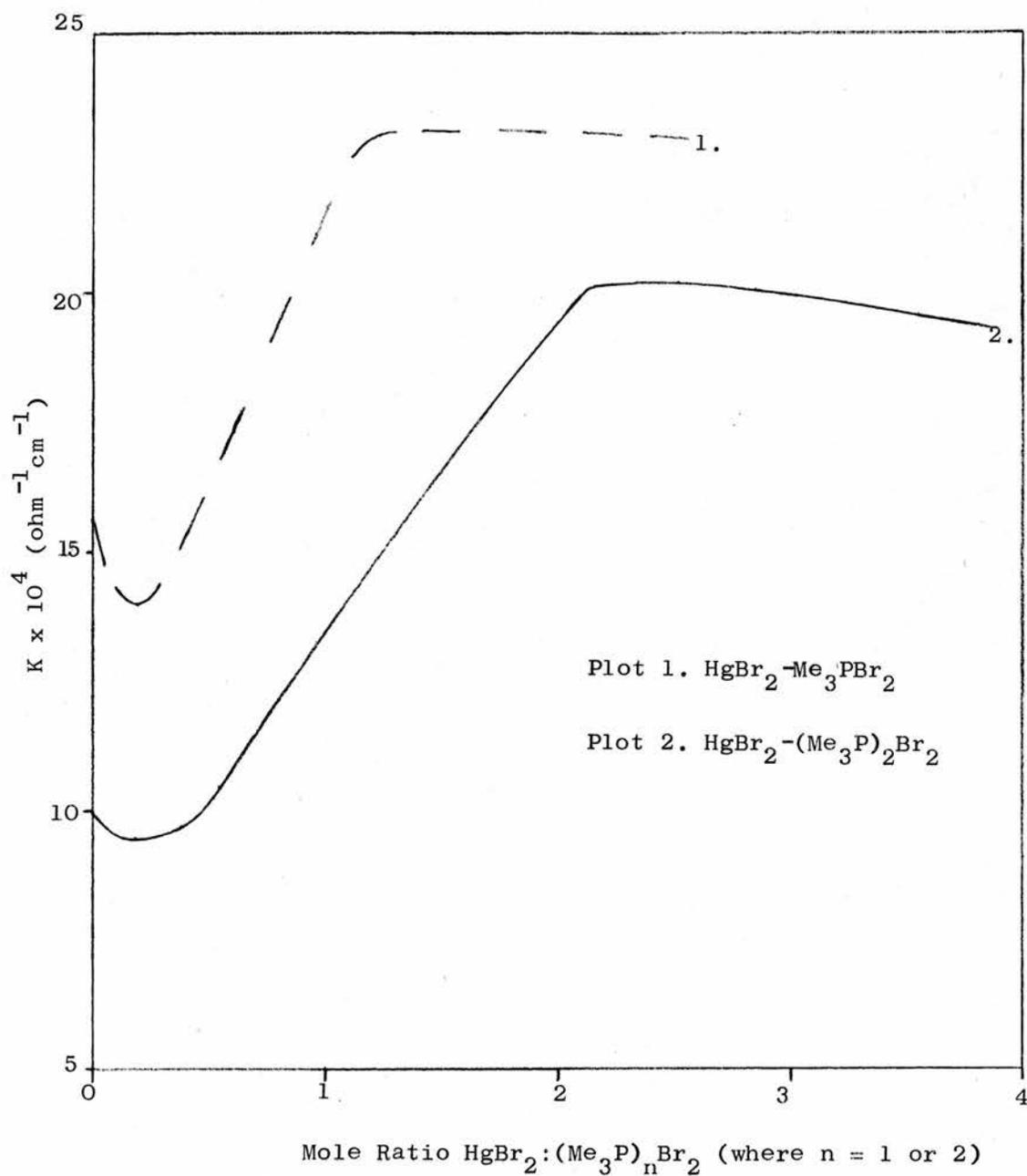
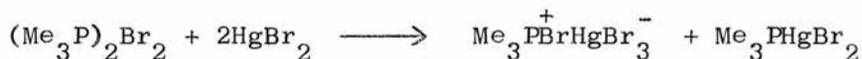


Figure 17 : Conductometric Titration of the Systems

$\text{HgBr}_2 - (\text{Me}_3\text{P})_2\text{Br}_2$ and $\text{HgBr}_2 - \text{Me}_3\text{PBr}_2$ in Methyl Cyanide

break at the 2:1 ratio after which there was a slow decrease in the conductance. The solution was a pale straw colour after the addition of bromine but on titrating with mercuric bromide this colour gradually disappeared. Since there was no break at the 1:1

ratio or the 0.5:1 ratio there is therefore no evidence from this experiment for the existence of a mercuric bromide complex containing the $(\text{Me}_3\text{P})_2\text{Br}^+$ ion. The suggested scheme of reaction to explain the break at the 2:1 ratio ($\text{HgBr}_2:(\text{Me}_3\text{P})_2\text{Br}_2$) is:



A compound of composition $\text{Me}_3\text{PHgBr}_4$ [ie. $\text{Me}_3\text{PBr}^+\text{HgBr}_3^-$] which is postulated as occurring at the 2:1 ratio in the conductometric titration was not isolated. The compound, $\text{Me}_3\text{PHgBr}_2$ was, however, isolated as a white solid when excess mercuric bromide solution was added to trimethylphosphine in methyl cyanide. The solid was washed with ether before pumping for five hours on the vacuum line to remove traces of solvent. The infrared spectrum of $\text{Me}_3\text{PHgBr}_2$ showed few absorptions and was similar to the spectrum of trimethylphosphine. There was a slight difference between the two spectra; the broad peaks at 945 and 950 cm^{-1} in Me_3P were clearly split into a doublet at 978 and 964 cm^{-1} in $\text{Me}_3\text{PHgBr}_2$; the broad peak centred on 710 cm^{-1} (s) in Me_3P was reduced in intensity and shifted to 762 cm^{-1} (m) in $\text{Me}_3\text{PHgBr}_2$ along with the appearance of two new peaks at 863 cm^{-1} (m) and 678 cm^{-1} (w).

In an attempt to isolate a solid of composition $(\text{Me}_3\text{P})_2\text{Br}_2, \text{HgBr}_2$, a mixture of $\text{Me}_3\text{PHgBr}_2$ and bromine (2 mole:1 mole Br_2) in methyl cyanide was prepared. A white solid precipitated from this solution and analysis showed it had a composition $(\text{Me}_3\text{P})_2\text{HgBr}_4$. This compound is thought to have the structure $(\text{Me}_3\text{P})_2\text{Br}^+\text{HgBr}_3^-$ by analogy with the proposed structure for $(\text{Ph}_3\text{P})_2\text{HgBr}_2, \text{Br}_2$ ¹²⁵ mentioned earlier. Therefore it seems almost certain that a compound containing the cation $(\text{Me}_3\text{P})_2\text{Br}^+$ was in fact prepared. This corresponds to a 1:1 mole ratio but no break was observed here in the conductometric titration; therefore this species is presumably not stable in solution but is stable in the

solid phase. The suggested reaction for the formation of

$(\text{Me}_3\text{P})_2\text{HgBr}_2 \cdot \text{Br}_2$ is :

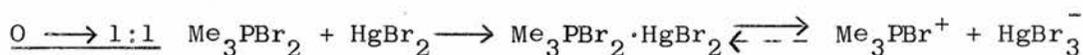


The System HgBr_2 - Me_3PBr_2

Trimethylphosphine was first titrated with an equimolar amount of bromine before changing burettes and continuing the titration with a solution of mercuric bromide in methyl cyanide. The results of this titration are illustrated in Figure 17, plot 1, and recorded in Table 31. The graph shows a slight decrease in conductance for the first two additions of mercuric bromide solution before a sharp rise to the 1:1 ratio. After a clear break close to the 1:1 ratio, the conductance remained roughly constant on further addition of mercuric bromide solution.

To account for the break observed at the 1:1 ratio

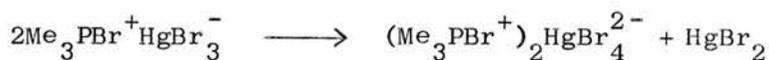
$(\text{Me}_3\text{PBr}_2:\text{HgBr}_2)$ the following reaction scheme is proposed:



The species present at the 1:1 mole ratio has a molar conductance value of $\Lambda_m = 145.50 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ at $c_m = 0.01491 \text{ mole litre}^{-1}$ which is characteristic of a strong 1:1 electrolyte.

A compound of composition $\text{Me}_3\text{PBr}_2 \cdot \text{HgBr}_2$ could not however be isolated when equimolar solutions of $\text{Me}_3\text{PHgBr}_2$ and bromine in methyl cyanide were mixed. A white precipitate was, however, isolated and this was found to have the composition $(\text{Me}_3\text{P})_2\text{HgBr}_6$. This can be formulated as $(\text{Me}_3\text{PBr}^+)_2\text{HgBr}_4^{2-}$ and corresponds to a 0.5:1 mole ratio $(\text{HgBr}_2:\text{Me}_3\text{PBr}_2)$ but no break was observed at this ratio in the conductometric titration; thus it is presumed that this compound is not stable in solution but is stable in the solid form.

The isolation of $(\text{Me}_3\text{P})_2\text{HgBr}_6$ from a 1:1 solution ($\text{HgBr}_2:\text{Me}_3\text{PBr}_2$) can be attributed to the breakdown of $\text{Me}_3\text{PBr}^+\text{HgBr}_3^-$.



2) The Me_3P -Iodine System

The conductometric titration of trimethylphosphine with iodine in methyl cyanide differs from that of the bromine and iodine monobromide (which appears later). Breaks occur at the 0.5 and 1.5:1 mole ratios of $\text{I}_2:\text{Me}_3\text{P}$. The graph illustrated in Figure 18, plot 1, (with results recorded in Table 32), shows a sharp initial rise in conductance to the 0.5 ratio followed by a less steep rise to the 1.5 ratio. The solution, which was initially colourless, became yellow at the 0.5 ratio suggesting that polyiodide ion formation must start at this point. After the 1.5 ratio the conductance decreases slowly on further addition of iodine solution which is attributable to a dilution effect. There is a complete absence of a break at the 1:1 ratio. To verify this result and confirm the position of the breaks in the graph, a further titration was carried out using solid iodine as titrant. This avoided any dilution in the solution which may cause indistinctness in the breaks. The results of this titration are given in Table 33 and plotted in Figure 18, curve 2. These two graphs show a close correspondence with clear breaks occurring at the 0.5 and 1.5 ratios in the solid iodine titration.

McKechnie¹²⁹ has reported a practically identical graph with breaks

at the 0.5 and 1.5:1 ratios for the system iodine-triethylphosphine.

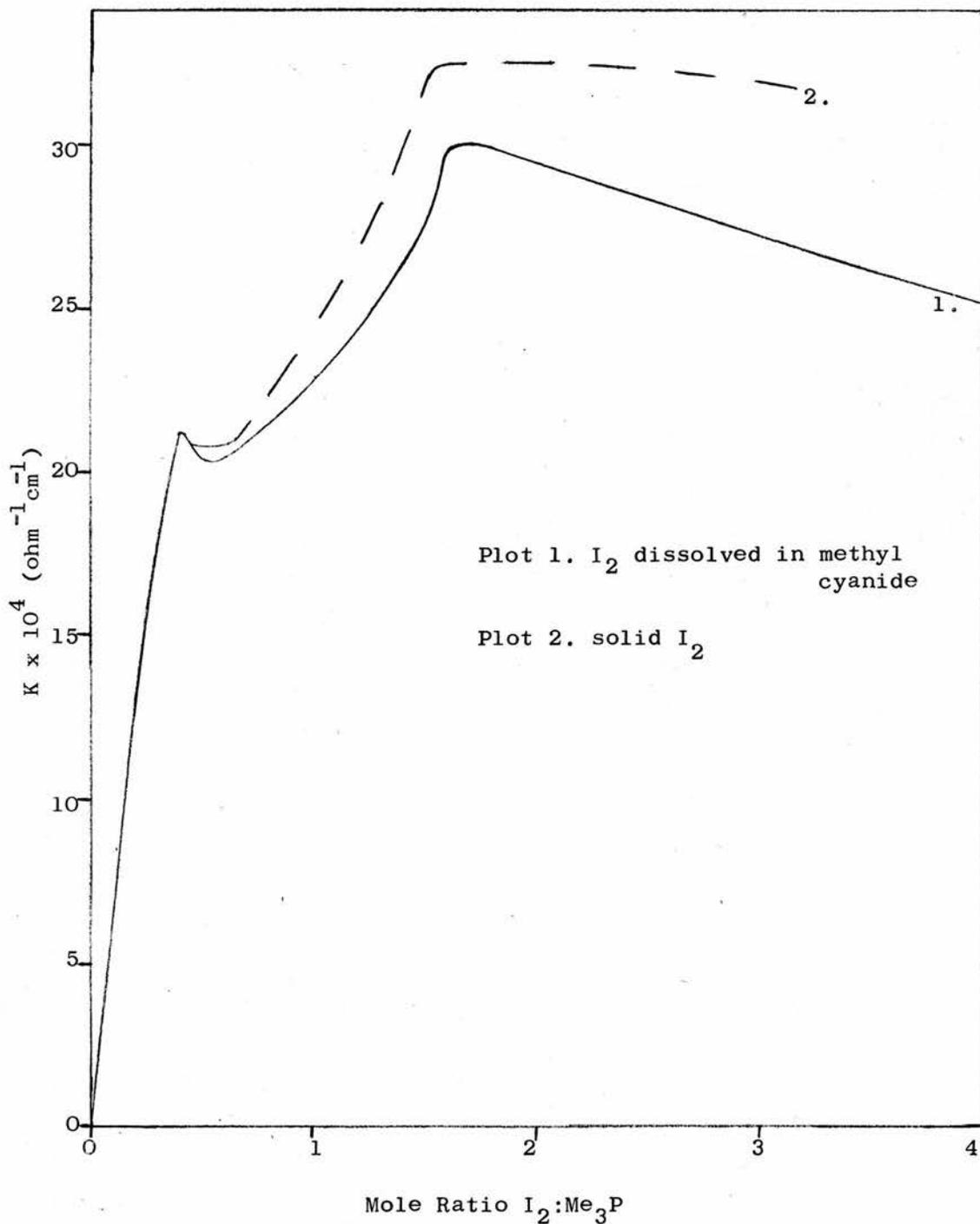
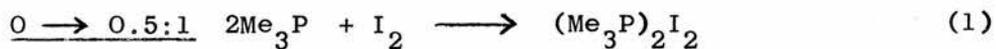
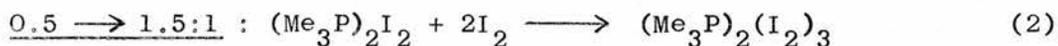


Figure 18 : Conductometric Titration of the System I_2 - Me_3P in Methyl Cyanide

The position of the breaks indicates that there are two reactions, corresponding to the stoichiometries

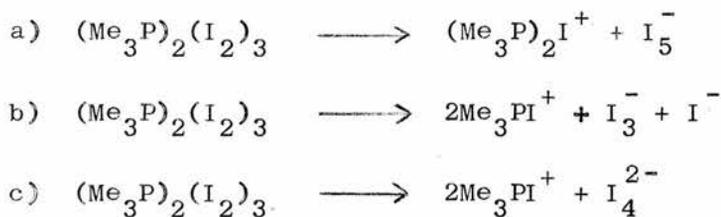




The high values of conductance suggest that the products of these reactions are ionising in methyl cyanide. The first of these can be represented in a way which is in keeping with previous systems, namely



The second reaction however is more difficult to represent. There are several possibilities:

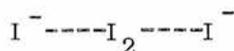


Considering each of these in turn:

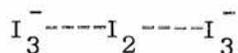
a) This is not in keeping with the increase in conductance between the 0.5 and 1.5 mole ratios since the number of ions in solution is not changing; also on going from triiodide ion to the larger penta-iodide ion one might expect a drop in Λ because of the expected decrease in mobility of the larger penta-iodide ion.

b) This would account for the increase in conductance between the 0.5:1 and 1.5:1 ratios but it would seem unlikely that all of the iodide formed at stage (1) would not be converted to triiodide unless half of the iodide were "tied up" in some way so as to be unavailable for conversion to triiodide (see c) below).

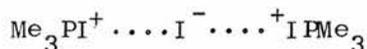
c) This postulates the interaction of two iodide ions with one iodine molecule to give the polyhalide ion I_4^{2-}



Although this has not been reported, a somewhat similar situation exists in I_8^{2-} which involves the interaction of an iodine molecule with two triiodide ions¹⁴⁵



Alternatively the iodide ion might be "tied up" by interaction with two cations thus:



although there is no supporting evidence of this kind of interaction from other systems.

Apart from these ideas it has to be admitted that there is no obvious chemically sensible way of formulating the addition compound, $(Me_3P)_2(I_2)_3$.

The molar conductance values taken from both titrations were:-

a) Iodine added in methyl cyanide solution

$$0.5:1 \quad \Lambda_m = 208.20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.00994 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } (Me_3P)_2I^+I^-)$$

$$1.5:1 \quad \Lambda_m = 304.40 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.00906 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } (Me_3P)_2(I_2)_3)$$

b) Iodine added as solid

$$0.5:1 \quad \Lambda_m = 230.20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0091 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } (Me_3P)_2I^+I^-)$$

$$1.5:1 \quad \Lambda_m = 340.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0091 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } (Me_3P)_2(I_2)_3)$$

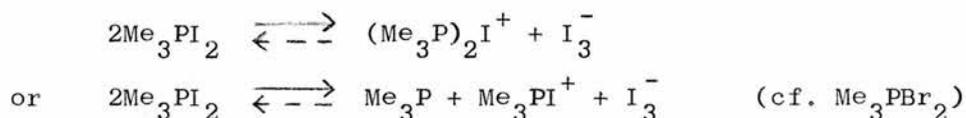
These values clearly indicate that the species present at the 0.5:1 and 1.5:1 mole ratios are both extremely strong electrolytes.

Compounds of stoichiometry $(Me_3P)_2I_2$, Me_3PI_2 and Me_3PI_4 were isolated from solutions containing iodine and phosphine in the appropriate mole ratios, (0.5:1, 1:1 and 2:1).

A white solid was formed at the 0.5:1 ratio (iodine to phosphine) with a composition $(Me_3P)_2I_2$. The ultraviolet spectrum of this solid when dissolved in methyl cyanide showed a minute amount of triiodide ion absorption possibly caused by partial decomposition. This solid is presumed to have the structure

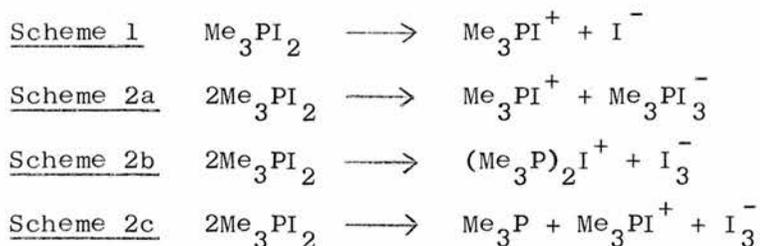
$(\text{Me}_3\text{P})_2\text{I}^+\text{I}^-$ which is in line with previous systems although there was no peak attributable to P-I stretching in the infrared spectrum.

The diiodide, Me_3PI_2 , was formed as a white solid whose structure has been established by Goubeau and Baumgärtner¹²⁷ to be $\text{Me}_3\text{PI}^+\text{I}^-$. The infrared spectrum of Me_3PI_2 contained a peak at 359 cm^{-1} which could be indisputedly allocated as the P-I stretching mode. The UV spectrum initially showed no sign of triiodide absorption, but on standing triiodide ions were formed indicating that the diiodide in methyl cyanide solution behaves thus:



Transport Number Measurements on Methyl Cyanide Solutions of Me_3PI_2

A transport number experiment was carried out on a solution of Me_3PI_2 in methyl cyanide to provide further evidence and verification for the postulated ionisation of Me_3PI_2 . The solution containing the diiodide was electrolysed in a Hittorf cell and afterwards each cell was analysed to find the change in iodine content. The solution initially was a deep wine red colour and this remained throughout the experiment, there being no visible colour changes during electrolysis. The results were calculated using the formulae and equations mentioned in connection with the electrolysis of Ph_2MePI_2 . The possible schemes of ionisation for Me_3PI_2 are:-



From the results of this experiment it appears that ionisation occurs by Schemes 2a, 2b or 2c; most likely by Scheme 2b or 2c for

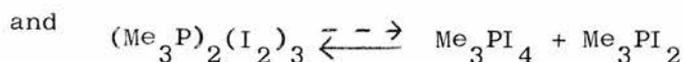
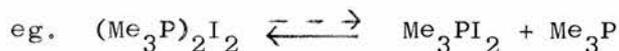
Table 14 : Electrolysis of Me_3PI_2 in Methyl Cyanide

Electrode	ΔI g atoms/F	t^+	
		Scheme 1	Schemes 2a,b,c
anode	1.161	-0.08	0.435
cathode	-0.731	0.135	0.567

the same reasons as mentioned earlier in conjunction with Me_3PBr_2 - but see cryoscopic study later on page 84 .

The tetraiodide, Me_3PI_4 , was prepared from a methyl cyanide solution containing iodine and phosphine in the ratio 2:1 mole. As normal methods for inducing precipitation, such as addition of dry carbon tetrachloride or dry ether, failed the solution was freeze dried. Crystals with a reddish tinge were observed on the walls of the flask above the level of the solution, however these disappeared when the flask warmed up. The remaining solvent was removed leaving a reddish-black, semi-crystalline solid. The infrared spectrum of this solid contained a strong peak at 365 cm^{-1} which is clearly the P-I stretching mode and the ultraviolet spectrum showed strong triiodide ion absorption. From the available evidence the tetraiodide can be formulated as $\text{Me}_3\text{PI}_3^+ \text{I}_3^-$.

As the diiodide and tetraiodide are isolated as solids from this system even though their existence is not suggested by the conductometric titration, it appears that the above picture is much simplified and that at least two more equilibria are present in solution. The diiodide and tetraiodide must be formed in equilibria of minor significance.



Cryoscopic Measurements on Solutions Containing Iodine Adducts of Trimethylphosphine

It was thought that cryoscopic measurements on solutions of trimethylphosphine-iodine adducts would enable an average molecular weight to be determined and thus give some information on the species present in solution. Nitrobenzene was chosen as solvent partly because it is a good ionising solvent and also because of its high molal freezing point depression constant ($K_f = 7.05 \text{ } ^\circ\text{C mole}^{-1} \text{ kg}^{-1}$)¹⁴⁶ and its high freezing point (+ 5.7 $^\circ\text{C}$) compared to other suitable solvents. Better temperature control can therefore be maintained during experiments through the use of an ice-salt bath.

As nitrobenzene was being used as a solvent it was essential to see if the behaviour of the system $\text{I}_2\text{-Me}_3\text{P}$ in nitrobenzene was analogous to that observed in methyl cyanide. Consequently a conductometric titration was performed, the results of which are displayed in Figure 19, plot 1 and recorded in Table 34. A solid-iodine-addition titration was again conducted in order to verify the shape of the graph and the position of the breaks; the graph of this titration is shown in Figure 19, plot 2. In each case the graph shows an important difference from the titration using methyl cyanide as solvent in that the second break occurs close to the 2:1 ratio ($\text{I}_2:\text{Me}_3\text{P}$) and not at the 1.5:1 ratio.

Apart from a sharp rise in conductance after the first addition of iodine the conductance remains constant until the 0.5:1 ratio. Between the 0.5:1 and 1.8:1 ratios the conductance rises sharply and after the break at the 1.8:1 ratio there is a slow decrease on further addition of iodine. The colour of the solution in the titration vessel changed from yellow to red at the 0.5:1 ratio and gradually deepened in colour as the titration

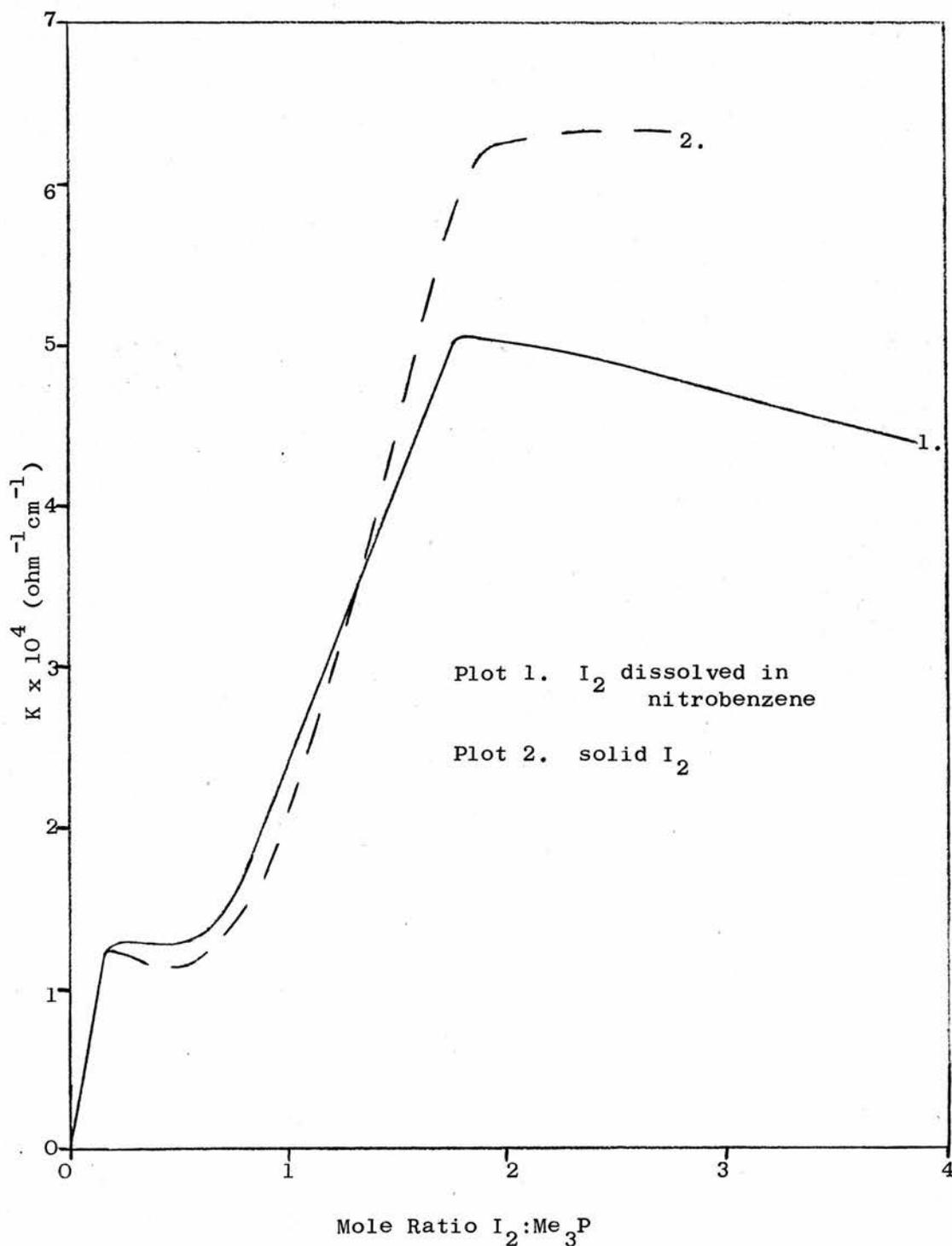
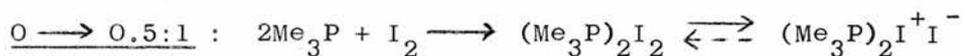


Figure 19 : Conductometric Titration of the System I_2 - Me_3P in Nitrobenzene

progressed. It is interesting to note that the graph does not show a break at the 1:1 ratio and therefore Me_3PI_2 is not indicated as a stable species in nitrobenzene.

The reaction of iodine and trimethylphosphine in nitrobenzene can therefore be interpreted in terms of the following stages:



The values of molar conductance taken from the respective titration graphs are:-

a) Iodine added in nitrobenzene solution

$$0.5:1 \quad \Lambda_m = 14.02 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1} \quad (c_m = 0.00915 \text{ mole litre}^{-1}) \\ (c_m \text{ based on } (\text{Me}_3\text{P})_2\text{I}^+\text{I}^-)$$

$$2.0:1 \quad \Lambda_m = 31.32 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1} \quad (c_m = 0.0160 \text{ mole litre}^{-1}) \\ (c_m \text{ based on } \text{Me}_3\text{PI}^+\text{I}_3^-)$$

b) Iodine added as solid

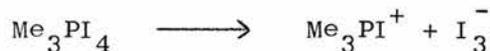
$$0.5:1 \quad \Lambda_m = 11.16 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1} \quad (c_m = 0.0103 \text{ mole litre}^{-1}) \\ (c_m \text{ based on } (\text{Me}_3\text{P})_2\text{I}^+\text{I}^-)$$

$$2.0:1 \quad \Lambda_m = 30.44 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1} \quad (c_m = 0.0206 \text{ mole litre}^{-1}) \\ (c_m \text{ based on } \text{Me}_3\text{PI}^+\text{I}_3^-)$$

Since strong 1:1 electrolytes when dissolved in nitrobenzene have a value for their molar conductance of approximately $20 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ at $0.01 \text{ mole litre}^{-1}$, it is clear that the species present at the 0.5:1 ratio is a moderately strong electrolyte. The tetraiodide, Me_3PI_4 , shows high values of molar conductance characteristic of this type of compound and can therefore be formulated as $\text{Me}_3\text{PI}^+\text{I}_3^-$ in nitrobenzene solution.

Details of the method used for measuring the freezing-point depression and a description of the automated recording system are contained in Appendix 2. Difficulties, however, were encountered because of the low solubility of the $(\text{Me}_3\text{P})_2\text{I}_2$ and Me_3PI_2 adducts. Even in very dilute solutions (ca. 0.01 M) precipitation of the compound started well before the freezing point of nitrobenzene was

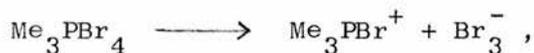
reached. As a result of this behaviour no valid conclusions could be drawn from the value obtained for the freezing point depression of $(\text{Me}_3\text{P})_2\text{I}_2$ and Me_3PI_2 . Experiments on the extremely soluble tetraiodide Me_3PI_4 were more successful producing a value for the average molecular weight of 377.3. This is larger than expected on the basis of the complete ionisation



Mol. Wt. = 583.68 Average molecular weight = 291.8

As good reproducibility of results was obtained this higher value could be due to incomplete dissociation of Me_3PI_4 (ie. ion pairing).

Cryoscopic measurements conducted on Me_3PBr_4 gave a value of 252 for the average molecular weight. Again this is between the molecular weight of Me_3PBr_4 (395.7) and the average molecular weight (197.9) calculated on the basis of complete ionisation,



probably for the same reason proposed above for Me_3PI_4 .

Cryoscopic studies of the $\text{Me}_3\text{P-I}_2$ system in nitrobenzene were therefore not able to throw any light on the species present in nitrobenzene solutions of $(\text{Me}_3\text{P})_2\text{I}_2$ and Me_3PI_2 .

3) The Me_3P -Iodine Monobromide System

The trimethylphosphine-iodine monobromide system appears to be more straightforward than either the bromine or iodine- Me_3P systems. It follows the same pattern as that established for the $\text{Ph}_2\text{MeP-IBr}$ and $\text{PhMe}_2\text{P-IBr}$ reactions. The conductometric titration illustrated in Figure 20 (with results recorded in Table 36) shows clear breaks at the 0.5 and 1:1 mole ratios with a less distinct discontinuity at the 2:1 ratio. After a sharp rise in conductance to the 0.5:1 ratio there is a level portion between the 0.5 and 1:1

ratios. The conductance doubles between the 1:1 and 2:1 ratios and after the break remains constant upon further addition of iodine monobromide.

The solution became coloured at the 0.5 ratio which indicates that polyhalide ion formation begins at this point.

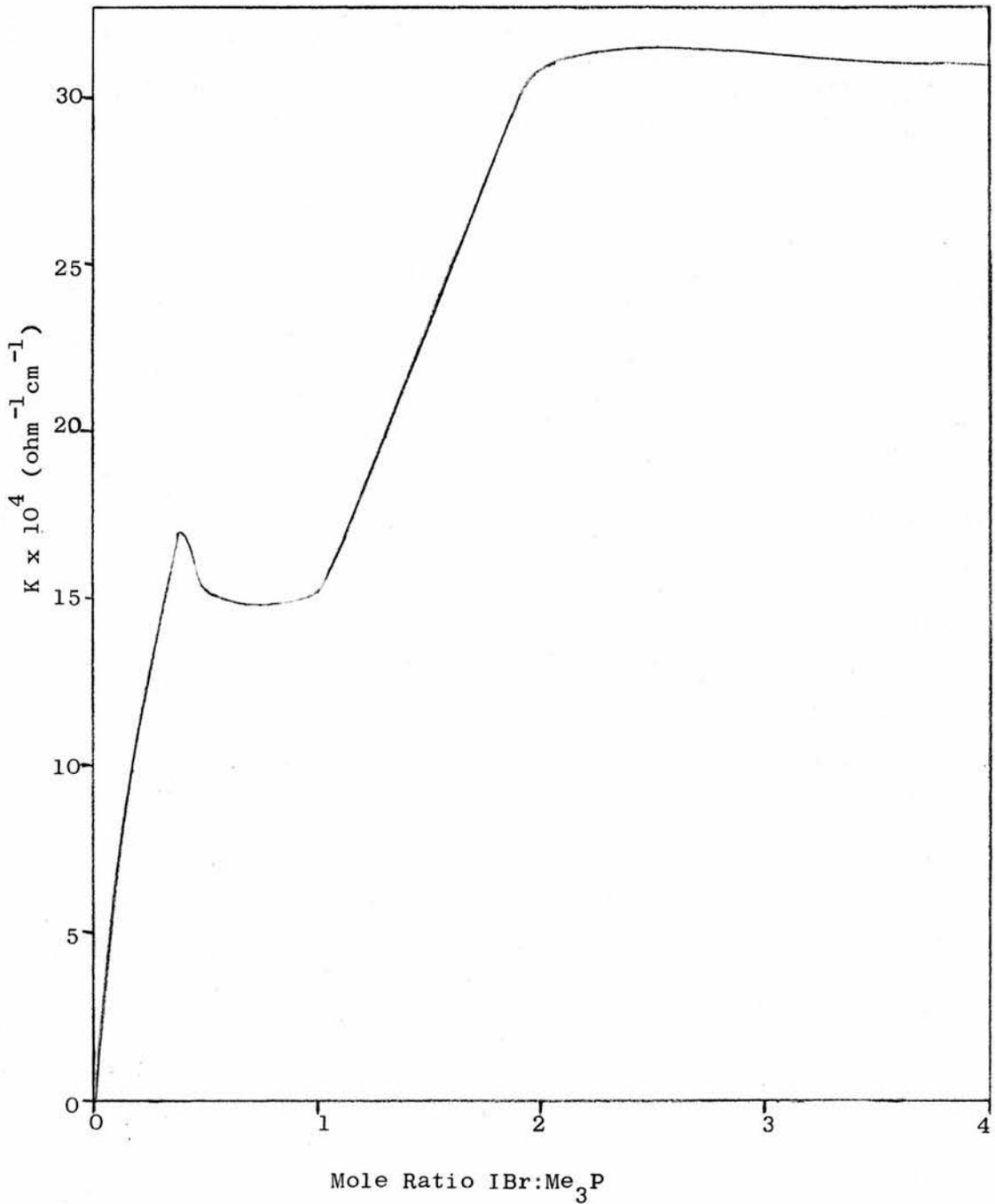
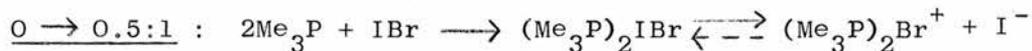
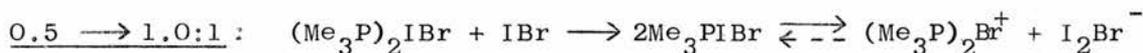


Figure 20 : Conductometric Titration of the System IBr-Me₃P in Methyl Cyanide

The reaction occurring in the conductometric titration when 0.5 mole of iodine monobromide is added to one mole of phosphine can be written as

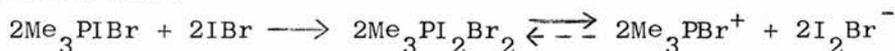


The conductance remains roughly constant on addition of another 0.5 mole of iodine monobromide indicating no additional formation of ions is occurring. The iodine monobromide is reacting with iodide ions giving trihalide ions.



The addition of a mole of iodine monobromide to Me_3PIBr causes a doubling in the conductance and consequently a doubling in the number of ions. The production of the tetrahalide species can be written as

1.0 \rightarrow 2.0:1 :



The values of the molar conductances at the 0.5:1, 1:1 and 2:1 ratios are all typical of strong electrolytes:

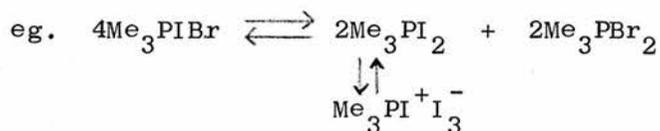
$$0.5:1 \quad \Lambda_m = 195.90 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1} \quad (c_m = 0.00837 \text{ mole litre}^{-1}) \\ (c_m \text{ based on } (\text{Me}_3\text{P})_2\text{Br}^+\text{I}^-)$$

$$1.0:1 \quad \Lambda_m = 194.52 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1} \quad (c_m = 0.00795 \text{ mole litre}^{-1}) \\ (c_m \text{ based on } (\text{Me}_3\text{P})_2\text{Br}^+\text{I}_2\text{Br}^-)$$

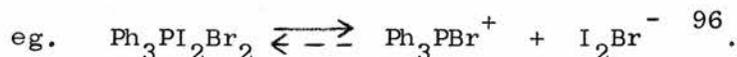
$$2.0:1 \quad \Lambda_m = 211.43 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1} \quad (c_m = 0.0145 \text{ mole litre}^{-1}) \\ (c_m \text{ based on } \text{Me}_3\text{PBr}^+\text{I}_2\text{Br}^-)$$

The adduct Me_3PIBr , which was isolated as a white solid when methyl cyanide solutions containing equimolar amounts of phosphine and iodine monobromide were mixed together, is thought to have a structure $\text{Me}_3\text{PBr}^+\text{I}^-$ in line with those for Me_3PBr_2 and Me_3PI_2 established by Goubeau and Baumgärtner¹²⁷. The infrared spectrum of

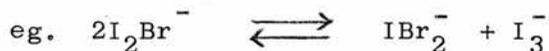
Me_3PIBr clearly shows the P-Br peak at 418 cm^{-1} . However when this solid is dissolved in methyl cyanide and allowed to stand, the ultraviolet spectrum indicates the presence of triiodide ions. It appears therefore that Me_3PIBr is reorganising to give Me_3PBr_2 and Me_3PI_2 in a similar fashion to that postulated earlier for PhMe_2PIBr .



The tetrahalide, $\text{Me}_3\text{PI}_2\text{Br}_2$, was prepared by the same method used to obtain Me_3PI_4 , namely by freeze drying, as the adduct was extremely soluble in all the common solvents. The infrared spectrum of the soft reddish brown solid contained the characteristic P-Br peak at 424 cm^{-1} . This clearly agrees with earlier work mentioned in the introduction where the halogen atom of lower atomic number is always attached to the phosphorus atom.



The ultraviolet spectrum of a solution of $\text{Me}_3\text{PI}_2\text{Br}_2$ in methyl cyanide contains an intense absorption peak centred on $271 \text{ m}\mu$. This peak is probably attributable to I_2Br^- ions ($280 \text{ m}\mu$) which have undergone reorganisation giving IBr_2^- ($256 \text{ m}\mu$) and I_3^- ions ($291 \text{ m}\mu$)



4) Electrolytic Conductance of Trimethylphosphine Dihalides in Methyl Cyanide

The electrolytic conductance of the dihalides was measured at 25°C using methyl cyanide solutions prepared in the dry-box. Solutions of various concentrations were used thus enabling Λ_m to be plotted against $\sqrt{c_m}$ (c_m used was based on the formula Me_3PX_2). For each compound the points lay approximately on a straight line

and in each case there is a decrease in molar conductance with increasing concentration; the rate of decrease being greatest in the case of Me_3PI_2 and least in the case of Me_3PBr_2 . All three lines have a point which is slightly higher than the line and in each case this corresponds to the most dilute solution. These points are the least reliable as the effect of minute traces of moisture at these low concentrations of dihalide (causing hydrolysis of the halide) will be more noticeable.

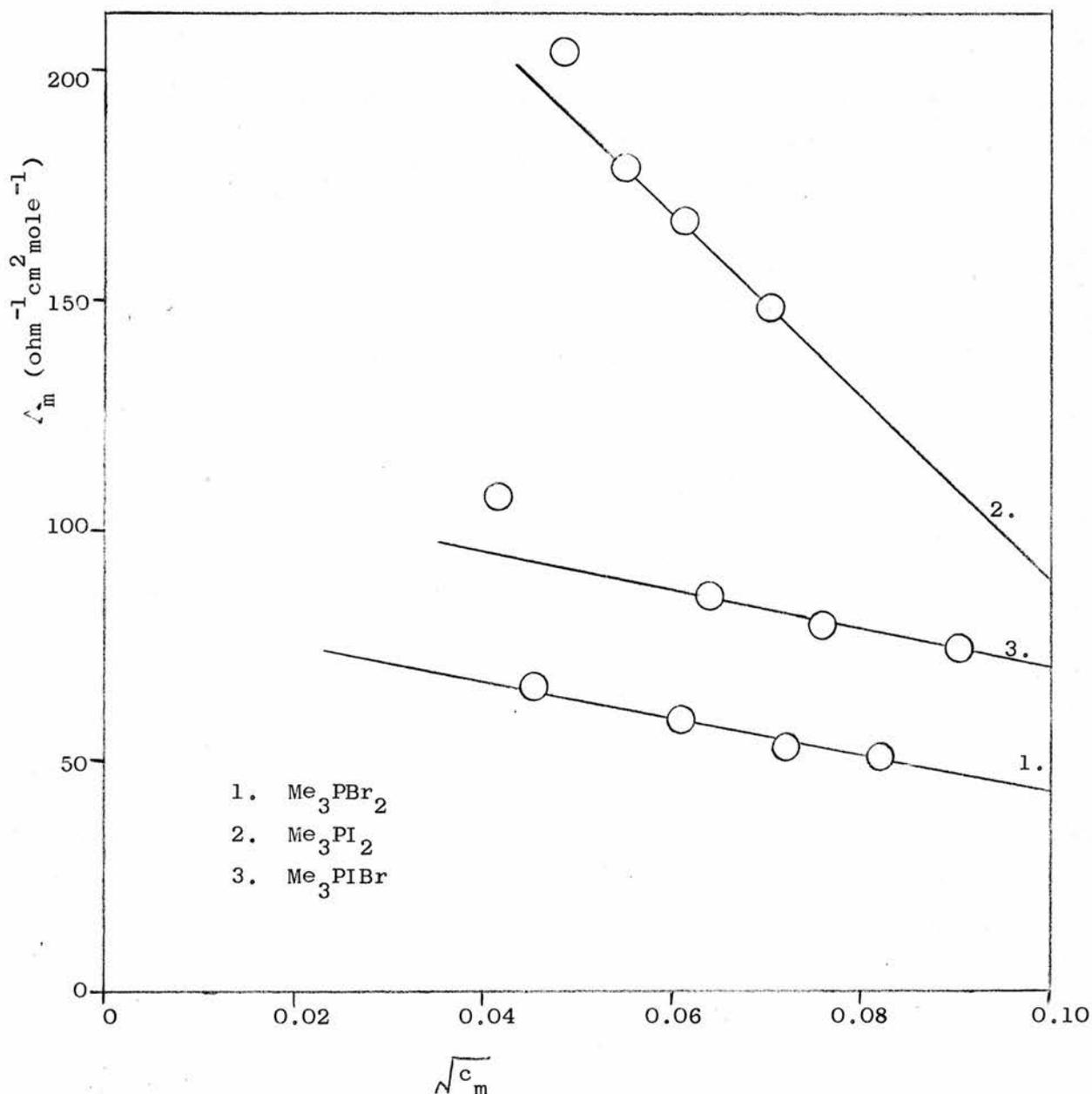


Figure 21 : Electrolytic Conductance of Trimethylphosphine Dihalides
in Methyl Cyanide at 25°C

Table 15 : Electrolytic Conductance of Trimethylphosphine Dihalides
in Methyl Cyanide at 25°C

Compound	c_m mole litre ⁻¹	$\sqrt{c_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mole ⁻¹
Me ₃ PBr ₂	0.002040	0.0452	1.355	66.42
	0.003735	0.0611	2.180	58.37
	0.005200	0.0721	2.746	52.81
	0.006722	0.0820	3.392	50.46
Me ₃ PI ₂	0.002376	0.0487	4.83	203.39
	0.003017	0.0549	5.39	178.83
	0.003782	0.0615	6.32	167.16
	0.004939	0.0703	7.31	147.93
Me ₃ PIBr	0.001713	0.0414	1.839	107.35
	0.004106	0.0641	3.52	85.73
	0.005771	0.0760	4.56	78.99
	0.008188	0.0905	6.08	74.29

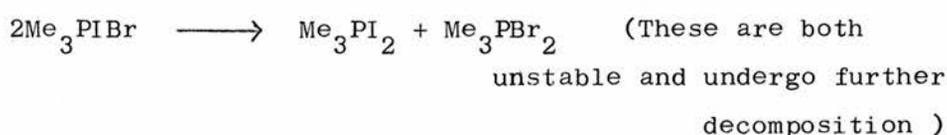
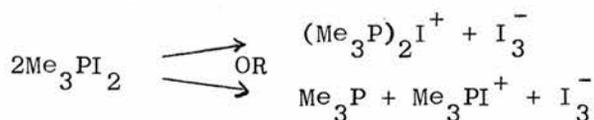
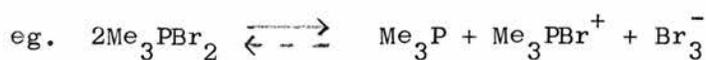
The values for the molar conductance at 0.01 M obtained by extrapolation of the graphs are:-

$$\text{Me}_3\text{PBr}_2 \quad \Lambda_m = 43.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\text{Me}_3\text{PI}_2 \quad \Lambda_m = 89.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\text{Me}_3\text{PIBr} \quad \Lambda_m = 69.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

It appears that the dihalides of trimethylphosphine are all unstable when dissolved in methyl cyanide (shown by the absence of a break in the conductometric titration at the 1:1 mole ratio).



Therefore the values of molar conductance at 0.01 M quoted above give some idea of the electrolyte strength of the decomposition products produced from the dihalides. The value for Me_3PBr_2 is rather low for a strong electrolyte but this could be due to either the existence of molecular units of Me_3PBr_2 , or to ion pairing of the tetrabromide $[\text{Me}_3\text{PBr}^+\text{Br}_3^-]$ which has been indicated by cryoscopic measurements on Me_3PBr_4 in nitrobenzene. The values for Me_3PI_2 and Me_3PIBr both indicate that species present in solution are moderately strong electrolytes. Again since the species present in solution are different in each case, a direct comparison of Λ 's is not meaningful.

General Conclusion

The phosphine-halogen systems reported in Part 1 of this thesis each produce two distinct sets of solid compounds. These are the dihalides, R_3PX_2 , and the tetrahalides, R_3PX_4 . The electrolytic properties of the dihalides were studied in methyl cyanide, with a view to relating the effect of progressively replacing the phenyl groups in triphenylphosphine by methyl groups on the structure and ionic properties of the dihalides. Table 16 contains the values of molar conductance at 0.01 M for the Ph_2MePX_2 , PhMe_2PX_2 and Me_3PX_2 compounds along with values obtained by Beveridge et al.⁹⁶ for the Ph_3PX_2 compounds.

The values of Λ indicate that the compounds are behaving as electrolytes in methyl cyanide. It can be seen from Table 16 that it is impossible to draw any direct correlations between these Λ values and the degree of substitution of phenyl groups

Table 16 : The Electrolytic Conductance (Λ ohm⁻¹ cm² mole⁻¹) of R_3PX_2 Compounds in Methyl Cyanide at a Concentration of 0.01 M

Phosphine \ Halogen	-Br ₂	-I ₂	-IBr
	Ph ₃ P	73.2	65.3
Ph ₂ MeP	34.3	108.0	76.0
PhMe ₂ P	36.0	98.5	86.8
Me ₃ P	43.1	89.0	69.2

by the electron releasing methyl group. The addition of methyl groups would be expected to increase the molar conductance of the methyl-substituted compounds possibly through stabilisation of the cation, R_3PX^+ . The compounds, $(Me_2N)_3PX_2$, containing the electron releasing dimethylamino group have high Λ values, whilst low Λ values are found for the compounds $(C_6F_5)_3PX_2$ which incorporate the electron withdrawing pentafluorophenyl group.

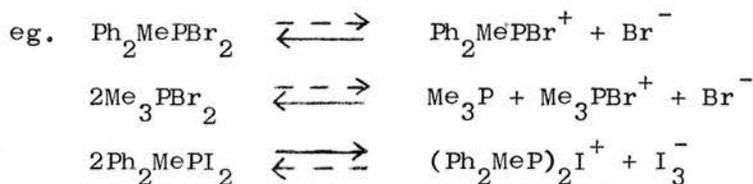
A notable feature of the data is that the molar conductance value for Ph_3PBr_2 is appreciably larger than for any of the other R_3PBr_2 compounds. This is surprising and not readily explained because, as mentioned above, other work suggests that electron releasing groups increase the tendency towards ionisation. The molar conductances for Ph_2MePBr_2 , $PhMe_2PBr_2$ and Me_3PBr_2 are all approximately the same.

The compounds R_3PI_2 all have approximately similar values of molar conductance at 0.01 M and no regular trend is observed. It is however not very meaningful to draw comparisons between these values as the ion types are not the same in each case.

The values of Λ for the R_3PIBr adducts are again roughly the same with no significant trend and therefore no definite

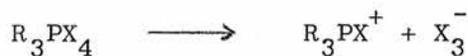
conclusions can be drawn.

The random nature of these results is likely to arise from the fact that the R_3PX_2 adducts ionise in different modes, and also because some undergo rearrangements when dissolved in methyl cyanide.



As mentioned earlier each phosphine produced a solid dihalide and tetrahalide when reacted with appropriate amounts of iodine, bromine or iodine monobromide. The solubility of the dihalides in methyl cyanide was in the order $\text{Ph}_2\text{MeP} > \text{PhMe}_2\text{P} > \text{Me}_3\text{P}$ as determined qualitatively from the fact that solutions of Ph_2MePX_2 had to be freeze dried to obtain solids whereas the dihalide adducts of Me_3P precipitated immediately from solution. All these compounds are extremely sensitive towards moisture, and it appears that replacement of the phenyl groups in Ph_3P (which gives fairly stable Ph_3PX_2 adducts) by methyl groups increases lability probably due to a decrease in the 'shielding' of the phosphorus atom, thus allowing hydrolysis to occur.

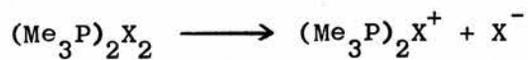
When the solid tetrahalides are dissolved in methyl cyanide they have been shown by ultraviolet analysis to ionise as



and the conductometric titrations indicate that they are strong 1:1 electrolytes in methyl cyanide.

The conductometric titrations indicated that a 0.5:1 species was present in solution, however, attempts to prepare 0.5:1 compounds of the type $(R_3P)_2X_2$ were unsuccessful in the case of the $\text{Ph}_2\text{MeP-X}_2$ and $\text{PhMe}_2\text{P-X}_2$ systems; the dihalide, R_3PX_2 , was

isolated each time. However $(\text{Me}_3\text{P})_2\text{Br}_2$ and $(\text{Me}_3\text{P})_2\text{I}_2$ were isolated as white solids from the $\text{Me}_3\text{P-X}_2$ system. They are thought to ionise as



in methyl cyanide solution.

R E S U L T S A N D D I S C U S S I O N

PART 2

The Reaction of Halogens with Some Tertiary Biphosphines

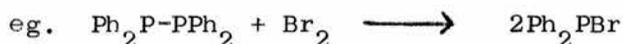
Part 2

The Reaction of Halogens with some Tertiary Biphosphines

Introduction

Harris and co-workers have previously studied phosphine-halogen systems in which the phosphine contained only one phosphorus centre. The reaction of halogens with biphosphines, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, ($n = 0, 1, 2$, etc), has not been investigated in any real depth. The monophosphines when reacted with halogen produce two main distinct sets of compounds, the dihalides R_3PX_2 and tetrahalides R_3PX_4 . However in a biphosphine-halogen system there would appear to be a greater number of possible compounds depending on whether dihalide and tetrahalide formation occurs independently at each phosphorus atom.

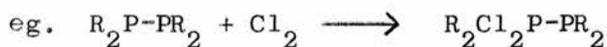
The simplest member of the series $\text{R}_2\text{P}(\text{CH}_2)_n\text{-PR}_2$ is the diphosphine $\text{R}_2\text{P-PR}_2$, which when reacted with an equivalent amount of bromine (or chlorine or iodine) causes cleavage of the phosphorus-phosphorus bond to form the corresponding phosphinous halides.



Excess halogen must be avoided to prevent the subsequent formation of phosphoranes^{128,147,148}.

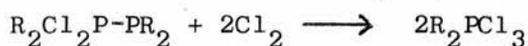


Ang and Miller¹⁴⁹ report, contrary to the above findings, that quaternisation not cleavage occurs when phosphino substituted diorganylphosphines are chlorinated.

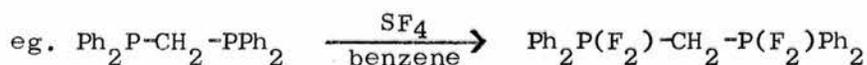


Addition of further chlorine gives, as above, halophosphoranes

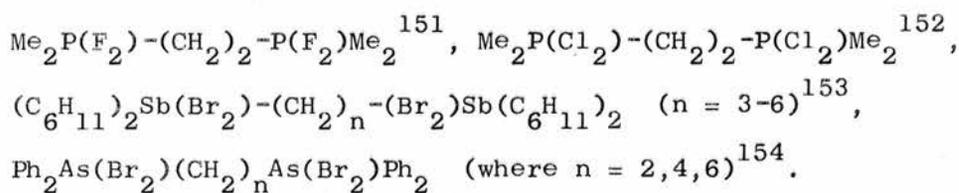
as final product.



When methylene groups are introduced between the two phosphorus atoms in biphosphines straightforward dihalides are produced, which contain one mole of halogen attached to each phosphorus atom. An example of this is the fluorination of methylene-bis-diphenylphosphine using sulphur tetrafluoride¹⁵⁰



Other compounds of this type which have been isolated are



This section of the thesis deals with the reaction of halogens with methylene-bis-diphenylphosphine and ethylene-bis-diphenylphosphine in methyl cyanide solution. These reactions are studied with a view to evaluating the effect on adduct formation of the introduction of one and two methylene groups between the phosphorus atoms in biphosphines, and to study any possible mutual interaction between the two phosphorus centres in these systems.

A. The Reactions of Methylene-bis-diphenylphosphine with Halogens

(1) The $Ph_2PCH_2PPh_2$ -Bromine System

The results of the conductometric analysis of the $Ph_2PCH_2PPh_2-Br_2$ system are contained in Table 39 and depicted graphically in Figure 22. The graph shows a sharp initial rise in the conductance as far as the 0.5:1 ratio with a break at this ratio. Another break occurs around the 2:1 ratio with the conductance remaining constant between the two breaks. Further addition of bromine solution after the 2:1 ratio causes the solution to become a yellow colour, and

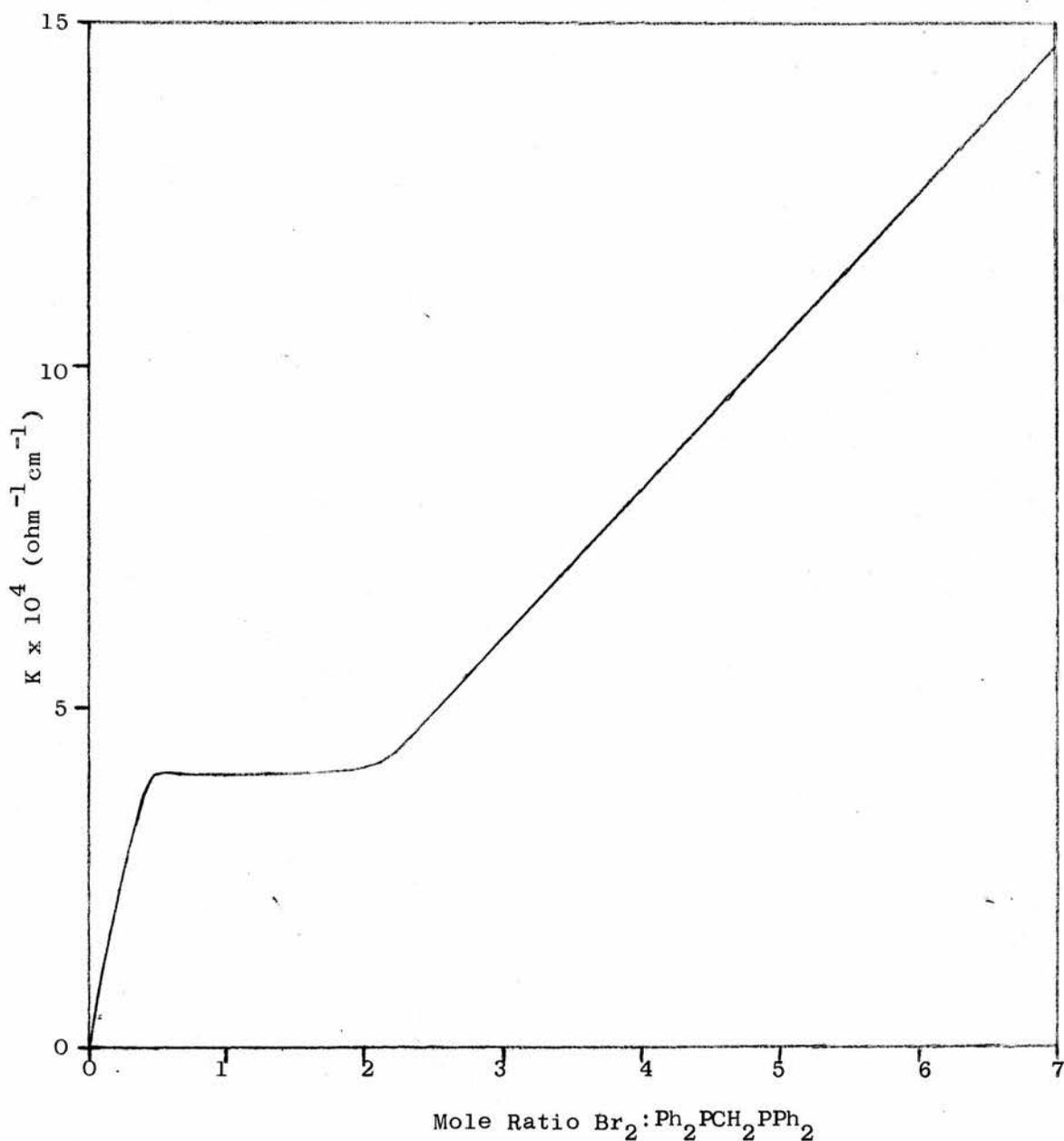
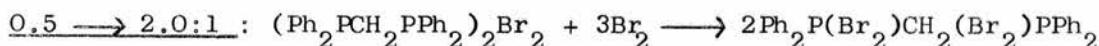
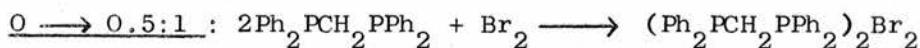


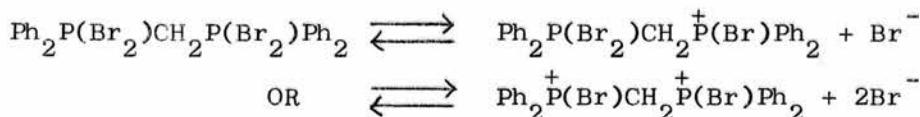
Figure 22 : Conductometric Titration of the System Br₂-Ph₂PCH₂PPh₂-
in Methyl Cyanide

the conductance to increase steadily with no sign of tailing off even as far as the 7:1 ratio. From these observations it would appear that compounds of stoichiometries (Ph₂PCH₂PPh₂)₂Br₂ and Ph₂PCH₂PPh₂·Br₄ are formed in methyl cyanide solution.

The scheme of reaction suggested by the conductometric titration is:

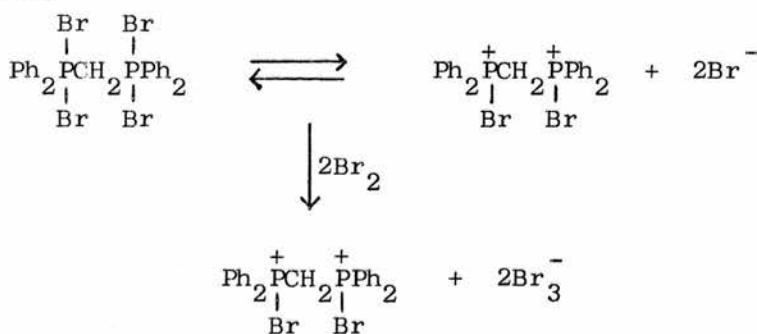


The solution is colourless up to the 2:1 break and therefore it can be deduced that no tribromide ions are present. The species present at the 2:1 mole ratio would be expected to ionise as:



The value of molar conductance at the 2:1 ratio ($\Lambda = 131.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ at $c_m = 0.003298 \text{ mole litre}^{-1}$), suggests that ionisation occurs predominantly to the first stage only and that further ionisation to a dipositive cation must be negligible.

After the 2:1 break the solution becomes a yellow colour and tribromide ions are formed. The sharp rise in conductance after this ratio would be expected to be due to an increase in the degree of ionisation accompanying the formation of tribromide ions:



or the 1:1 electrolyte adding bromine to give tribromide ions. It is surprising that there is no break at the 4:1 ratio or slightly beyond: the conductance rises steadily even up to the 8:1 ratio. Hence either

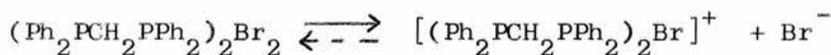
(a) this reaction does not proceed to completion within the range of stoichiometries studied, or

(b) the reaction is not proceeding as expected.

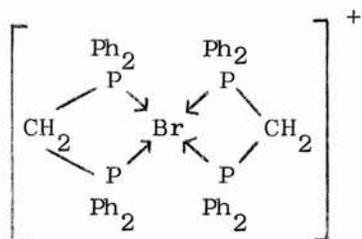
A white solid was isolated by freeze drying a 0.5:1 mixture of bromine and phosphine. The nature of this compound is unclear although it appears to be an electrolyte with a relatively high value of molar conductance

$$\Lambda_m = 103.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.003868 \text{ mole litre}^{-1})$$

The ultraviolet spectrum of this compound, when redissolved in methyl cyanide, shows no tribromide ion absorption and based on previous assumptions the structure in solution of the species at the 0.5:1 ratio could be

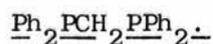


It is known that diphosphines can act as good chelating agents with positively charged metal ions suggesting that the structure of the cation is possibly



Another white solid was obtained by freeze drying an equimolar mixture of the diphosphine and bromine. Analysis showed this to be the dihalide $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{Br}_2$. It is noteworthy that the conductometric titration did not indicate compound formation at this stoichiometry. Again there is no tribromide ion absorption in the ultraviolet solution-spectrum. The structure of this compound by analogy with monophosphine-halogen adducts is likely to be $[\text{Ph}_2\text{PCH}_2\text{P}(\text{Br})\text{Ph}_2]^+\text{Br}^-$. However the mass spectrum, recorded in Table 17 does not accord with this but suggests that during transfer to the mass spectrometer hydrolysis has occurred. The mass spectrum tends to indicate that the following mixture of hydrolysis products is present -

Table 17 : The Mass Spectrum of $\text{Ph}_2\text{PCH}_2\text{PPh}_2\cdot\text{Br}_2$ (hydrolysed) and

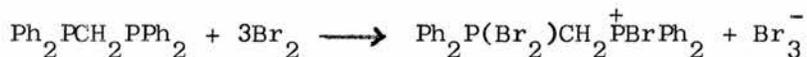


$\text{Ph}_2\text{PCH}_2\text{PPh}_2\cdot\text{Br}_2$		$\text{Ph}_2\text{PCH}_2\text{PPh}_2$	
m/e	Proposed ions	m/e	Proposed ions
416	$\text{Ph}_2\text{PCH}_2\text{PPh}_2\cdot(\text{O})_2^+$		
400	$\text{Ph}_2\text{PCH}_2\text{PPh}_2\cdot(\text{O})^+$		
384	$\text{Ph}_2\text{PCH}_2\text{PPh}_2^+$	384	$\text{Ph}_2\text{PCH}_2\text{PPh}_2^+$
339	$\text{Ph}_2\text{PCH}_2\text{PPh}\cdot(\text{O})_2^+$		
323	$\text{Ph}_2\text{PCH}_2\text{PPh}\cdot(\text{O})^+$		
292	$\text{Ph}_3\text{POCH}_2^+$		
291	Ph_3POCH^+		
276	$\text{Ph}_3\text{PCH}_2^+$		
275	Ph_3PCH^+		
262	Ph_3P^+	262	Ph_3P^+
217			
215	$\text{Ph}_2\text{POCH}_2^+$		
201	Ph_2PO^+		
200		200	
199	$\text{Ph}_2\text{PCH}_2^+$	199	$\text{Ph}_2\text{PCH}_2^+$
185	Ph_2P^+	197	
183		185	Ph_2P^+
165		184	
152		183	
121	PhPCH^+	165	
108	PhP^+	152	
107		122	
95		121	PhPCH^+
91	PhCH_2^+	108	PhP^+
82	H^{81}Br^+	107	
81	$^{81}\text{Br}^+$	95	
80	H^{79}Br^+	91	PhCH_2^+
79	$^{79}\text{Br}^+$	79	
78		78	
77	C_6H_5^+	77	C_6H_5^+
59		65	
51		63	
47		59	
44		52	
43		51	



Attempted isolation of a 2:1 compound, $\text{Ph}_2\text{P}(\text{Br}_2)\text{CH}_2\text{P}(\text{Br}_2)\text{Ph}_2$, as predicted by the conductometric titration was unsuccessful. A substance of unknown constitution was however precipitated when bromine and phosphine (2:1 mole ratio) were mixed together. The analysis of this substance did not agree with figures calculated for the expected compound $\text{Ph}_2\text{P}(\text{Br}_2)\text{CH}_2\text{P}(\text{Br}_2)\text{Ph}_2$, although they were near to values calculated for $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot (\text{OH})_2\text{Br}_2$. It is thought that several hydrolysis products are present and the infrared spectrum shows peaks that can only be attributed to these products. This underlines the extreme lability of these compounds which absorb minute traces of moisture even in the dry-box.

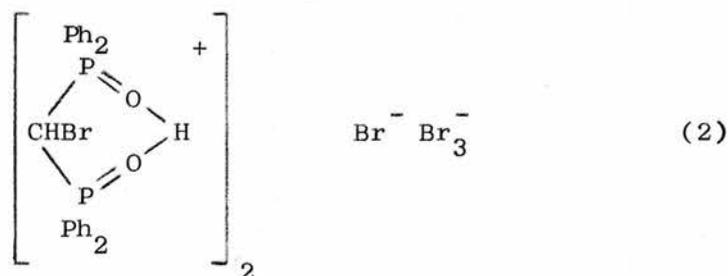
Addition of three moles of bromine to one mole of phosphine resulted in the formation of a yellow crystalline substance, m.pt. 189-191^o: the high value of specific conductance in methyl cyanide points to an ionic formulation. The simplest interpretation of these observations is that a 3:1 adduct is formed and this undergoes ionisation in methyl cyanide



However, the following nuclear magnetic resonance, infrared, and mass spectral studies show that this simple picture is untenable. The empirical formula of this substance based on the results of elemental analysis is $\text{C}_{25}\text{H}_{24}\text{P}_2\text{O}_3\text{Br}_3$.

Proton nuclear magnetic resonance studies of this substance (called compound A), using d_6 dimethylsulphoxide as a solvent are recorded in Table 18. The peaks at 5.66 and 7.50 τ in compound A were due to water and DMSO respectively. It can

The infrared spectrum of the solid contains two strong broad absorptions in the regions 1300-1550 cm^{-1} and 850-1000 cm^{-1} but the strong broad absorption in the region 2500-3000 cm^{-1} , characteristic of R_3POH^+ ion (OH stretching), is totally absent. In addition there is no indication of the HBr_2^- ion (1670-1700 cm^{-1} , 1170 cm^{-1})¹⁵⁵ which could be formed when substitution of the methylene proton occurs. Further study of the infrared spectrum reveals the absence of the P=O stretching absorption (1170-1380 cm^{-1}) showing that the compound must be reformulated as

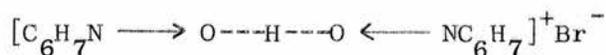


Compounds containing mixed anions are not unknown; for example, Inglis¹⁴⁴ has isolated $[\text{Ph}_3\text{AsOH}^+]_2 \text{Br}^- \text{Br}_3^-$. In summary, therefore, a cation involving hydrogen bonding as shown in structure 2 is supported by the following features of the infrared spectrum, viz :-

- 1) the absence of an observable OH stretching frequency above 1700 cm^{-1} .
- 2) the presence of strong broad absorptions in the range 1600-600 cm^{-1} .
- 3) the presence of a transmission window at ca. 1200 cm^{-1} , the P=O stretching frequency in Ph_3PO .
- 4) the absence of any strong absorption around 420 cm^{-1} attributable to P-Br stretching.

These features correspond closely to those described by Hadži et al as being characteristic of strongly hydrogen bonded species

with nearly symmetrical H-bonds. It seems likely that the broad absorption at 850-1000 cm^{-1} is the P=O stretching frequency which has been lowered and considerably broadened by the action of hydrogen bonding, thus reducing the bond order. On very similar spectral evidence to that outlined above Hadži¹⁵⁶ assigned the structure



to the 2:1 adduct of 2-picoline-N-oxide with HBr, and this has been confirmed¹⁵⁷ by Mills and Speakman's crystal structure analysis.

The ultraviolet spectrum of this compound shows strong tribromide ion absorption and quantitative analyses of this spectrum gave an average of 63,420 for the extinction coefficient. This is reasonably close to the reported value of ϵ for the tribromide ion, 55,000¹³¹. The value for the extinction coefficient of compound A is based on the formula shown in structure 2 and therefore indicates that there is one tribromide ion per two diphosphine residues in compound A.

The bromide ions postulated in structure 2 would be expected to add another molecule of bromine to give tribromide ions. In order to verify this assumption, a conductometric titration was performed, the results of which are shown in Figure 23 and recorded in Table 40. The graph shows a linear increase in conductance as far as the 1:1 ratio (Br_2 :Compound A). There is a break at this ratio followed by a gradual 'tailing off' of the conductance on further addition of bromine solution.

The molar conductance taken from the graph at the 1:1 ratio is

$$\Lambda_m = 373.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}, (c_m = 0.002520 \text{ mole litre}^{-1})$$

which agrees with values for strong 2:1 electrolytes¹³⁸.

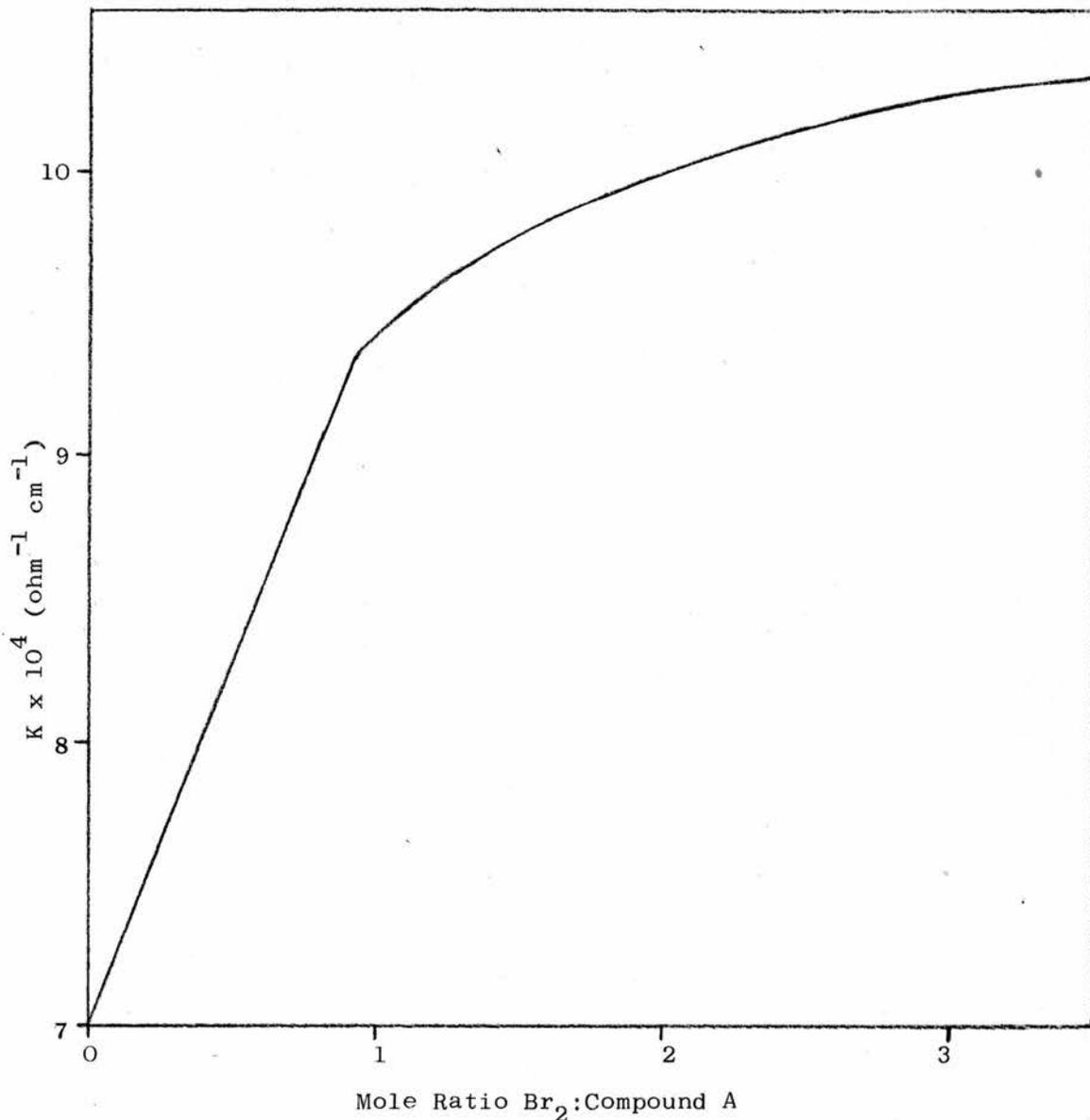
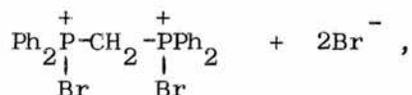


Figure 23 : Conductometric Titration of the System
Br₂-Compound A in Methyl Cyanide

The mass spectrum of a complex substance such as compound A contains a large number of lines due to the great number of possible splitting patterns and recombination of fragments inside the spectrometer. The spectrum is not reproduced here, however various lines could be assigned to specific fragments, eg.

495	Ph ₂ P(O)CHBrP(O)Ph ₂ ⁺	416	Ph ₂ P(O)CH ₂ P(O)Ph ₂ ⁺
415	Ph ₂ P(O)CHP(O)Ph ₂ ⁺	293	Ph ₂ P(O)CBr ⁺
	262	Ph ₃ P ⁺	

Substitution of CH₂ by bromine in Ph₂PCH₂PPh₂ was not expected to occur, and therefore the reaction of bromine and Ph₂PCH₂PPh₂ beyond the 2:1 mole ratio does not go as expected. Assuming that the 2:1 compound forms in solution and that this undergoes partial ionisation thus

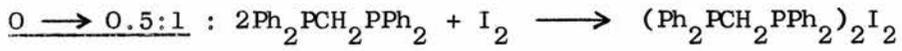
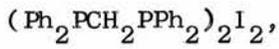


there are therefore two phosphonium centres in the molecule, and consequently the methylene protons lie between two positively charged atoms, thus making these protons more easily removed by bromine in a substitution reaction which is possibly catalysed by traces of moisture. Only one methylene proton is replaced by bromine as steric reasons preclude the replacement of the second proton. This species seems to readily undergo oxidation by absorbing minute traces of moisture and oxygen present in the dry-box to give compound A.

(2) The Ph₂PCH₂PPh₂-Iodine System

The results of the conductometric titration of Ph₂PCH₂PPh₂ with iodine in methyl cyanide solution are shown in Figure 24 and recorded in Table 41. The graph shows a sharp initial rise in conductance up to the 0.5:1 ratio, (iodine:phosphine). After a break at the 0.5:1 ratio, the conductance steadily increases to the 4:1 ratio where the second break occurs. Following the discontinuity at the 4:1 ratio there is a slow decrease in conductance as more iodine solution is added.

There appear to be two reactions occurring during the titration. The first is the production of the 0.5 species



The structure of the compound $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{I}_2$ is not known, but by analogy with previous systems where the phosphine contained only one phosphorus centre, it could be $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{I}^+\text{I}^-$.

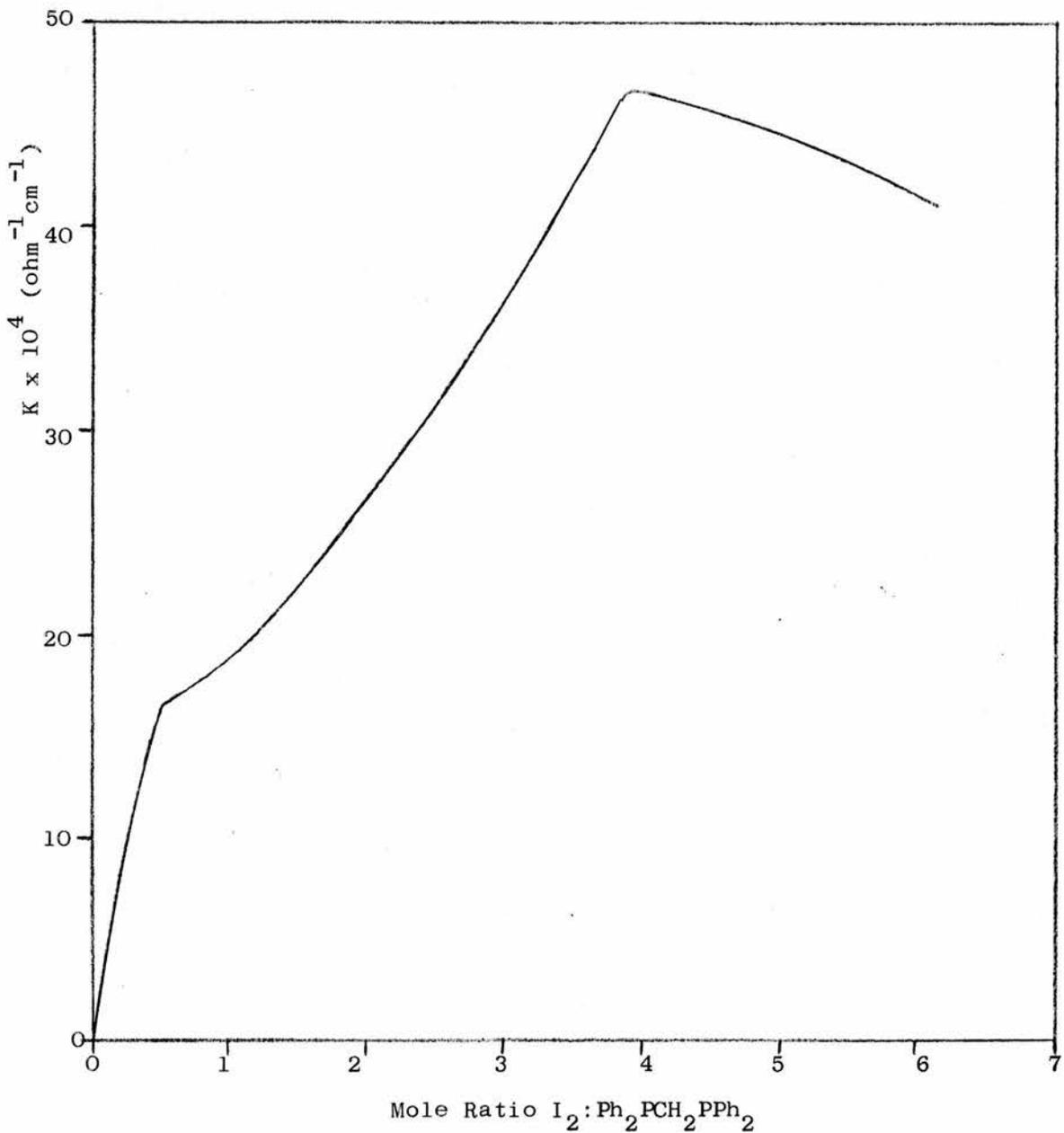
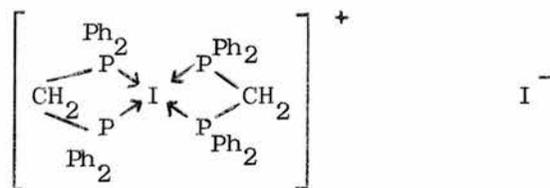


Figure 24 : Conductometric Titration of the System

I₂ - Ph₂PCH₂PPh₂ in Methyl Cyanide

and the phosphine molecule is unclear but it would seem not unreasonable to assume that the phosphine, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, is behaving as a bidentate ligand attached to a I^+ cation



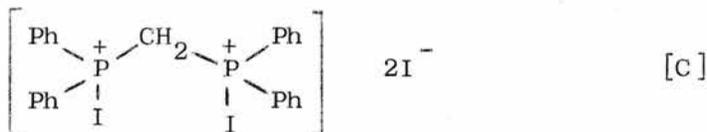
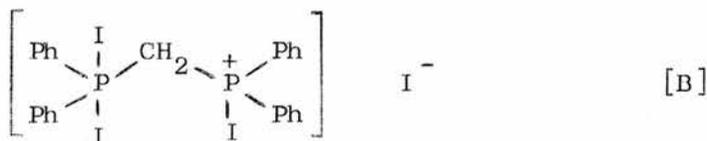
(cf. M^{n+} complexes with diphosphines).

When equimolar amounts of solutions containing iodine and a suspension of phosphine were mixed together a yellow precipitate formed. This precipitate on analysis was found to have a composition $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$. The solutions containing iodine and phosphine in the ratio of 2:1 and 3:1 also gave a yellow precipitate of the composition $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$. The solid obtained at the 1:1 ratio was slightly impure due, it is thought, to contamination by unreacted phosphine (the phosphine is relatively insoluble in methyl cyanide).

There are three possible structures for $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$



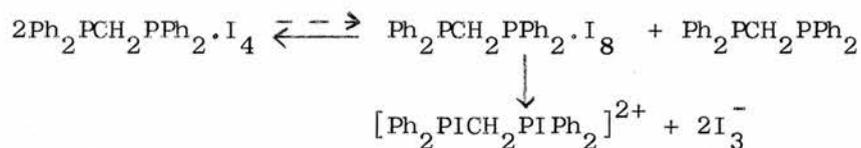
Covalent



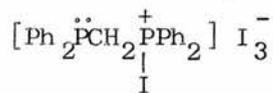
Experiments performed here are not able to say unambiguously what the nature of the solid is. The mass spectrum of $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$ contained a peak at m/e of 637 which can be allocated as the fragment $\text{Ph}_2\text{PICH}_2\text{PIPh}_2^+$. No peak of higher m/e

was observed and this therefore tends to indicate structure [C]. This is what would be expected by analogy with the monophosphine dihalides but it is perhaps not expected that an ion with two phosphonium centres in close proximity would be stable. It is of course possible that even if the structure was [A] or [B], that ionisation to $\text{Ph}_2\overset{+}{\text{P}}\text{CH}_2\overset{+}{\text{P}}\text{IPh}_2$ would occur in the electron beam of the mass spectrometer.

The ultraviolet spectrum of $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$ when dissolved in methyl cyanide showed absorption attributable to triiodide ions. As there is no break in the conductometric titration graph at the 2:1 mole ratio (iodine:phosphine), this indicates that the compound $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$ is not stable when dissolved in methyl cyanide solution. It is therefore suggested that the triiodide ions, which were detected in the ultraviolet spectrum, are formed by decomposition of $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$ to the octaiodide compound, $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_8$ (indicated by conductometric titration) and phosphine.



An alternative explanation is that a rearrangement of iodine occurs to give



The infrared spectrum of the compound $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$ contained a peak at 356 cm^{-1} but this could not be unambiguously assigned as the P-I stretching because the spectrum of the phosphine itself has a peak close to this at 348 cm^{-1} .

A light brown solid was precipitated from the 4:1 mixture of iodine and phosphine. Analysis of this solid did not correspond with the composition of the compound $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_8$,

which was indicated by the conductometric titration, but was close to that expected for $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$. It seems that $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_8$ is not stable in the solid state.

The 6:1 mixture of iodine and phosphine produced a dark green precipitate which was shown to have the composition $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_{10}$. The ultraviolet spectrum of this solid showed strong triiodide ion absorption and, in addition, the mass spectrum contained a peak at m/e of 638 which can be attributed to the $\text{Ph}_2\text{PICH}_2\text{PIPh}_2^+$ species. It is suggested, therefore, that the compound $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_{10}$ has the ionic structure $[\text{Ph}_2\text{PICH}_2\text{PIPh}_2]^{2+} \text{I}_3^- \text{I}_5^-$. A peak in the infrared spectrum at 362 cm^{-1} was thought to be the P-I stretching frequency.

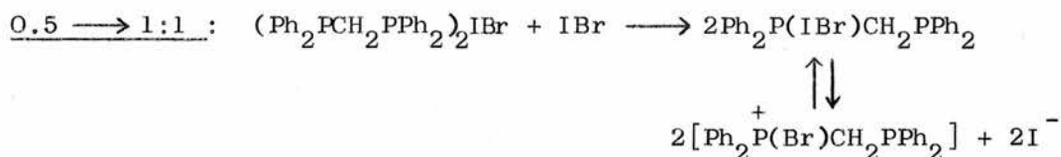
In the $\text{Ph}_2\text{PCH}_2\text{PPh}_2 - \text{I}_2$ system it has therefore been shown that the stable solids are $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$ and $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_{10}$. It is also clear that these undergo rearrangement when dissolved in methyl cyanide.

(3) The $\text{Ph}_2\text{PCH}_2\text{PPh}_2 - \text{Iodine Monobromide System}$

The graph for the conductometric titration of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ with iodine monobromide is displayed in Figure 25 with the results recorded in Table 42. The addition of iodine monobromide solution to a suspension of the phosphine gave an initial sharp rise in conductance as far as the 0.5:1 ratio. Following a break at the 0.5:1 ratio the conductance rose less steeply to the 2:1 ratio where the second break occurred. There was a further clear discontinuity in the graph close to the 3:1 mole ratio followed by a linear increase in conductance prior to precipitation at the 6.5:1 ratio.

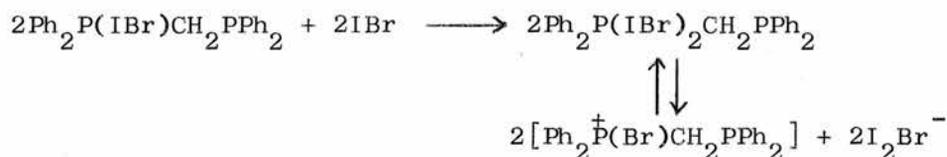
As there are several discontinuities in the graph it appears that there are various reactions occurring during the titration.

The 0.5:1 species is assumed to ionise in the same manner as outlined in previous systems, although again the way the two phosphine molecules and the bromine atom are bonded in the unionised product is not known.



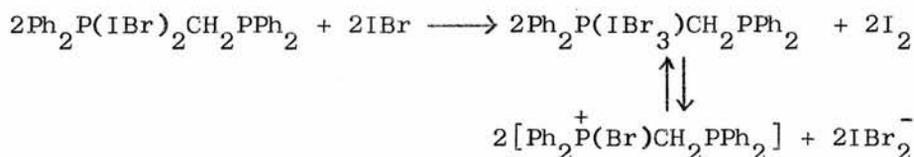
1:1 \longrightarrow 2:1 :

The solution became coloured after the 1:1 ratio indicating that trihalide ions were being formed.



2:1 \longrightarrow 3:1 :

To account for the negligible increase in conductance in this mole ratio region, it is suggested that a halogen exchange reaction occurs in which iodine atoms are replaced by bromine atoms



The values of the molar conductance taken from the conductometric titration graph at the 0.5:1, 2:1 and 3:1 mole ratios are:-

$$0.5:1 \quad \Lambda_m = 178.56 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.00521 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } (\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Br}^+\text{I}^-)$$

$$2:1 \quad \Lambda_m = 156.9 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.009116 \text{ mole litre}^{-1})$$

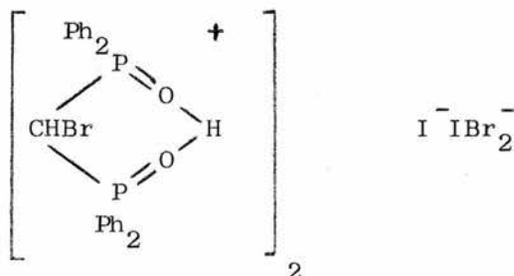
$$(c_m \text{ based on } (\text{Ph}_2\text{P}(\text{Br})\text{CH}_2\text{PPh}_2)^+\text{I}_2\text{Br}^-)$$

$$3:1 \quad \Lambda_m = 190.1 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.008416 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } (\text{Ph}_2\text{P}(\text{Br})\text{CH}_2\text{PPh}_2)^+\text{IBr}_2^-)$$

It can be seen in each case that the compounds are strong 1:1 electrolytes.

The solid which precipitated from the conductometric titration at the 6.5:1 mole ratio was filtered off and analysed. The results of analysis favoured a compound of composition $C_{25}H_{23}P_2Br_2IO_3$. An infrared and mass spectrum of this compound were obtained and both were identical to the spectra of "compound A" which was mentioned in connection with the $Ph_2PCH_2PPh_2-Br_2$ system. This indicates that the cations are identical in these two compounds and coupled with the observation of I^- ion absorption in the ultraviolet spectrum, the following structure is proposed for this compound:



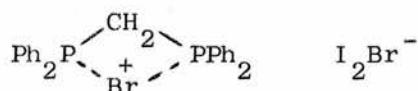
Presumably after the 3:1 ratio substitution of a methylene proton takes place, and that the compound formed is extremely sensitive to traces of moisture and oxygen which probably catalyse the replacement of the methylene proton by a bromine atom.

Attempts were made to isolate compounds from methyl cyanide solutions containing iodine monobromide and phosphine in the ratios, 1:1, 2:1 and 3:1.

A dark yellow solid precipitated when equimolar quantities of iodine monobromide and phosphine were mixed together. This solid was found to have the composition $Ph_2PCH_2PPh_2 \cdot IBr$, and as the ultraviolet spectrum showed no trihalide ion absorption when the compound was dissolved in methyl cyanide, it is thought that the structure is most probably $[Ph_2P^+(Br)CH_2PPh_2]I^-$.

The solid isolated at the 2:1 ratio (iodine monobromide to

phosphine) was brownish yellow in colour and was found to have the composition $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_2 \cdot \text{Br}_2$. The structure of this compound is believed to be $[\text{Ph}_2\overset{+}{\text{P}}(\text{Br})\text{CH}_2\text{PPh}_2]\text{I}_2\text{Br}^-$. The infrared spectrum of $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_2 \cdot \text{Br}_2$, however, shows no absorption directly attributable to P-Br stretching. There is therefore another possible structure for this compound which involves a bridged bromine atom between the two phosphorus atoms eg.



The ultraviolet spectrum shows that a mixture of trihalide ions are present which probably occur through rearrangement when the compound is dissolved in methyl cyanide.

The compound formed at the 3:1 ratio precipitated as a yellow/brown solid from a methyl cyanide solution containing iodine monobromide and phosphine in the appropriate ratio.

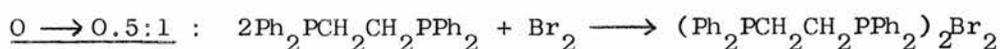
Analysis of this solid showed that its constitution was $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{IBr}_3$. The infrared spectrum of the compound gave no clue to its structure but it is assumed to be $[\text{Ph}_2\text{PCH}_2\overset{+}{\text{P}}(\text{Br})\text{Ph}_2]\text{IBr}_2^-$. The ultraviolet spectrum of the solid when dissolved in methyl cyanide showed triiodide ions were present. The origin of these triiodide ions is not known but presumably they occur through some rearrangement process, and it appears that the solid does not exhibit the same behaviour as that encountered during the conductometric titration in solution.

B. The Reactions of Ethylene-bis-diphenylphosphine with Halogens

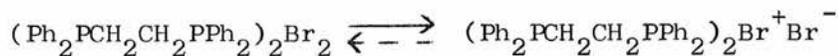
(1) The $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ -Bromine System

The conductometric titration of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ with a solution of bromine in methyl cyanide gave the results which are plotted in Figure 26 and recorded in Table 43. The graph shows a sharp rise in conductance at low mole ratios of bromine to phosphine. There is a clear break at the 0.5:1 ratio with the conductance remaining roughly constant between the 0.5:1 and 2:1 ratios. There is no pronounced break at the 1:1 ratio but instead the graph shows a dip in conductance which is centred on the 1:1 ratio. Following the break close to the 2:1 ratio, further addition of bromine solution caused the conductance to increase linearly until, in the region of the 5:1 ratio, the slope gradually tailed off.

The scheme of reaction which is proposed to explain the results of the conductometric titration is as follows:



Again the exact nature of the species at the 0.5:1 ratio is not known, however it is assumed to be analogous to other 0.5:1 species which were encountered earlier in connection with the systems $\text{Ph}_n\text{Me}_{(3-n)}\text{P-X}_2$ ($n = 0, 1, 2, 3$) and should therefore ionise thus:



0.5 \rightarrow 2.0:1 :

The solution is colourless in this mole ratio region, therefore the formation of the simple dihalide type compound is suggested:

The second stage of ionisation of the 2:1 compound is not likely, because the formation of a 2:1 electrolyte would result in a large increase in conductance in the 0.5:1 to 2:1 mole ratio region, which is not found in practice.

2:1 onwards

After the 2:1 ratio the solution became coloured indicating the start of polybromide ion formation. There are no breaks in the conductometric titration graph after the 2:1 ratio and it is therefore impossible to use this to predict the scheme for the remainder of the titration.

The molar conductance values which were calculated from the titration graph at the 0.5:1 and 2:1 ratios are listed below:

$$0.5:1 \quad \Lambda_m = 144.52 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.00789 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } (\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Br}^+\text{Br}^-)$$

$$2.0:1 \quad \Lambda_m = 86.82 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.01382 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } \text{Ph}_2\text{P}(\text{Br}_2)\text{CH}_2\text{CH}_2\text{P}(\text{Br})\text{Ph}_2^+\text{Br}^-)$$

It is clear from these values that the species present at the 0.5:1 and 2.0:1 ratios are both strong 1:1 electrolytes.

Two distinct compounds were prepared with the stoichiometries $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_4$. The compound $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_2$ was isolated as a white precipitate when equimolar amounts of bromine and phosphine were mixed in methyl cyanide solution. The ultraviolet spectrum of this compound when dissolved in methyl cyanide showed no tribromide ion absorption, and therefore a possible structure is $[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}^+(\text{Br})\text{Ph}_2] \text{Br}^-$. However there is no peak in the infrared spectrum between 300 and 500 cm^{-1} which can be assigned as the P-Br stretching mode.

Attempts were made to prepare the compound

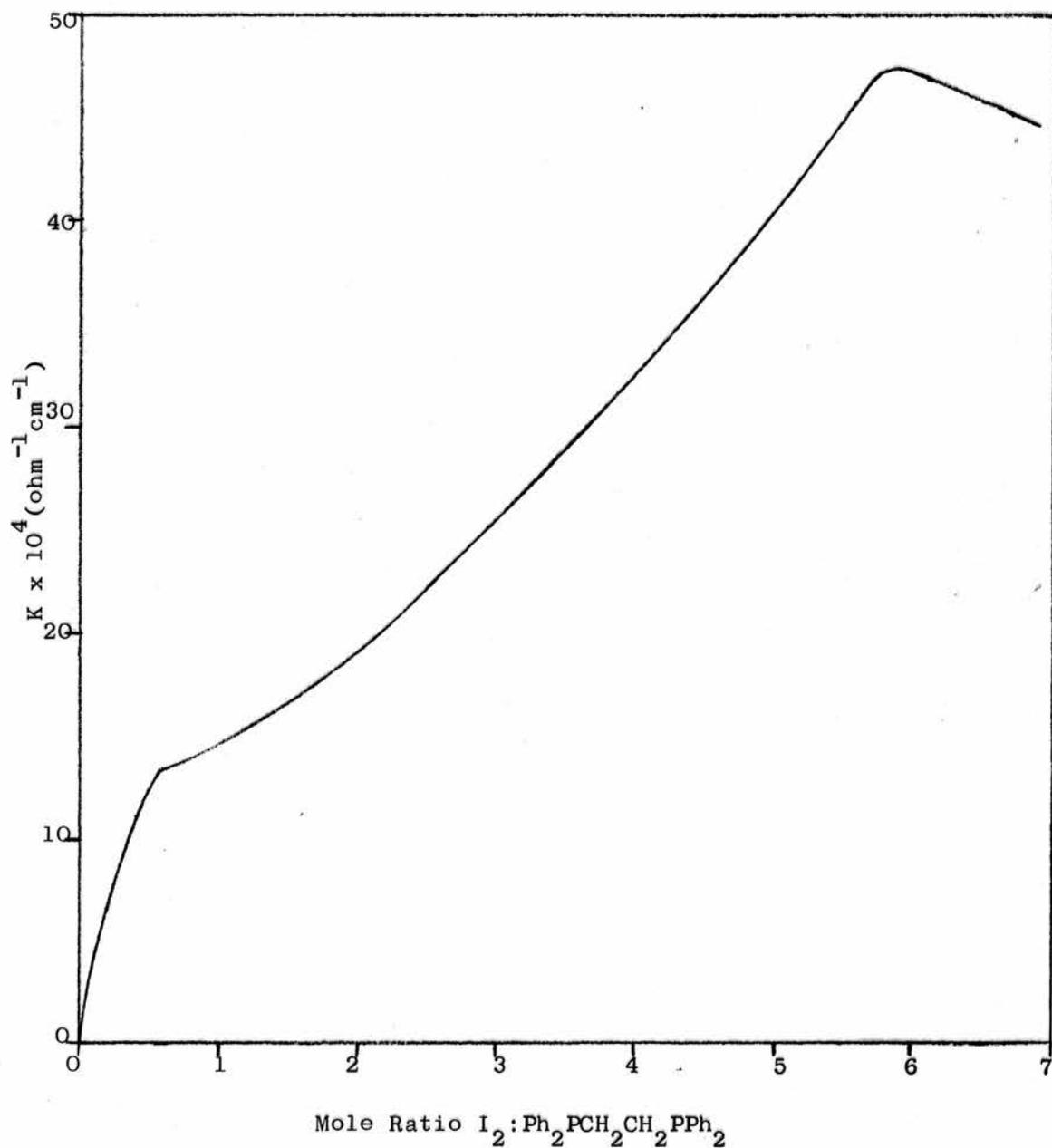
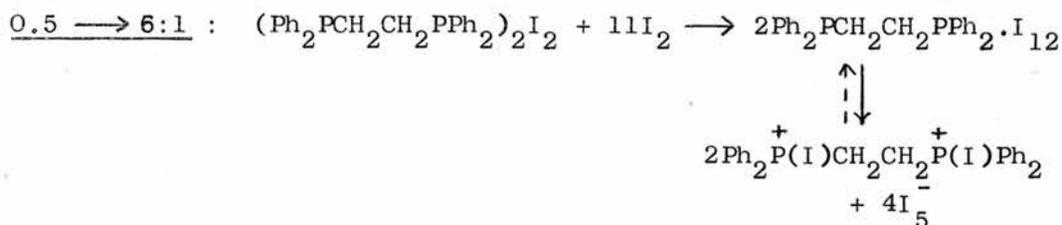


Figure 27 : Conductometric Titration of the System

$I_2 - Ph_2PCH_2CH_2PPh_2$ in Methyl Cyanide

coloured, indicating the presence of polyiodide ions, and as there were no intermediate breaks between the 0.5:1 and 6:1 ratios it would appear that the reaction proceeds in the following manner:-



ie. direct formation of the species $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{I}_{12}$ by addition of iodine to the 0.5:1 compound, $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{I}_2$.

The values of molar conductance at the 0.5:1 and 6:1 ratios calculated on the basis of the formulae $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{I}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{I}_{12}$ are:

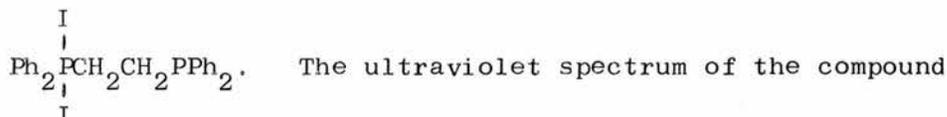
$$0.5:1 \quad \Lambda_m = 208.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.00604 \text{ mole litre}^{-1})$$

$$6.0:1 \quad \Lambda_m = 594.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.00792 \text{ mole litre}^{-1})$$

which are indicative of strong 1:1 and 2:1 electrolytes respectively.

Attempts were made to isolate compounds from methyl cyanide solutions containing iodine and phosphine in the mole ratios 1:1, 2:1, 4:1 and 5:1.

Yellow crystals were deposited when an equimolar solution of iodine was added to the phosphine; the composition of the solid was close to $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{I}_2$. It was extremely difficult to remove the last traces of solvent from this solid (as shown by a fractional % of nitrogen in the microanalysis results) even by pumping on the vacuum line for a considerable time. Further supporting evidence for this composition is contained in a mass spectrum of the solid which has a molecular ion peak at m/e of 652. (Molecular Weight of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{I}_2 = 652$). This suggests a covalent structure for this compound viz.

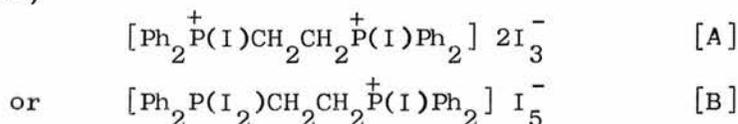


dissolved in methyl cyanide showed no absorption due to triiodide ions, and therefore the structure in solution is either covalent

or ionic of the form $\text{Ph}_2\text{PCH}_2\text{CH}_2\overset{+}{\text{P}}(\text{I})\text{Ph}_2 + \text{I}^-$. In the infrared spectrum there was no peak in the range $200-400 \text{ cm}^{-1}$ which could be attributed to the P-I vibration.

The brown solid which was deposited from a 2:1 mole ratio solution of iodine and phosphine in methyl cyanide had the composition $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{I}_4$. The ultraviolet spectrum of the compound in methyl cyanide showed moderately strong triiodide absorption. The structure of this compound is thought to be $[\text{Ph}_2\text{PCH}_2\text{CH}_2\overset{+}{\text{P}}(\text{I})\text{Ph}_2] \text{I}_3^-$.

A soft reddish-brown solid was isolated when a 4:1 mixture of iodine and phosphine was freeze dried. Repeated pumping on the vacuum line failed to remove traces of methyl cyanide, however, the analysis for C, H and I appeared to support the composition $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{I}_8$. A similar reddish-brown solid was immediately deposited when a methyl cyanide solution of iodine and phosphine in a 5:1 mole ratio was mixed. This second solid again contained traces of methyl cyanide which could not be removed by pumping. The ultraviolet spectra of these solids showed strong triiodide absorption which is consistent with the following structures,



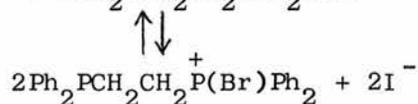
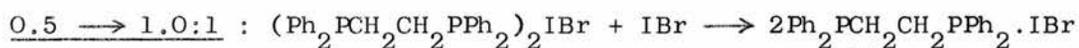
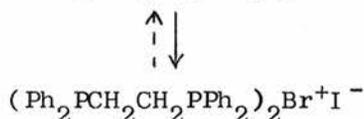
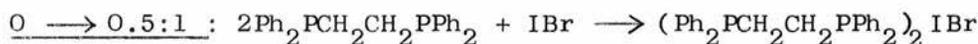
Structure [A] has the objection of two positively charged centres in the same ion whereas [B] is a singly charged ion. However in this system, in contrast to those involving $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, the charges are more widely separated and hence their mutual repulsive effect will be less.

(3) The $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ -Iodine Monobromide System

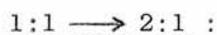
The conductometric titration of the system $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ -IBr

in methyl cyanide contains three discontinuities at mole ratios corresponding to the stoichiometries $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{I}^+\text{Br}^-$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{I}^+\text{Br}^-$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{I}_3\text{Br}_3$. There is also a slight inflection at the 2:1 ratio. The results of the titration are shown in Figure 28 with the data recorded in Table 45. The conductance increases sharply at low mole ratios with the first break occurring at the 0.5:1 ratio of iodine monobromide to phosphine. This is followed by a plateau-region between the 0.5:1 and 1:1 ratios after which the conductance increases slowly to the 3:1 ratio (with the slight inflection at 2:1) where a further break occurs. After the 3:1 ratio the conductance again increases steeply to a "rounded" maximum in the region of the 7:1 ratio.

It appears from the shape of the titration graph that the reaction occurs in four distinct stages.



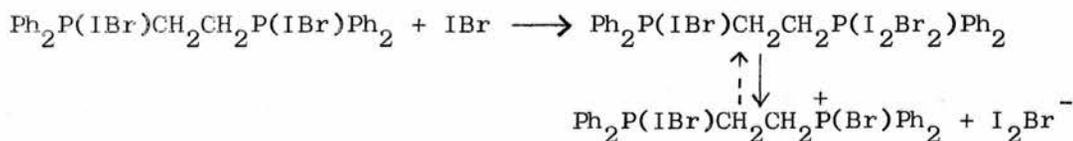
This scheme implies a doubling in the number of ions between the 0.5:1 and 1:1 ratios whereas the conductance remains constant between these mole ratios. It appears therefore that the species at the 1:1 ratio is incompletely ionised.



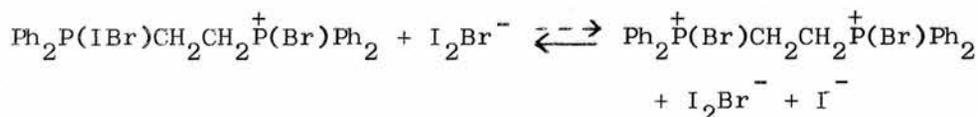
There is a slight increase in conductance between these ratios with the colour appearing just before the 2:1 ratio which suggests that the reaction proceeds as

2:1 → 3:1 :

From the 2:1 to 3:1 ratio it appears that polyhalide ions are formed in solution. This reaction occurs prematurely, the solution becoming coloured just before the 2:1 ratio.



The bromodiiodide ion was detected using ultraviolet analysis in a 3:1 mixture of iodine monobromide and phosphine in methyl cyanide. The relatively high value of molar conductance at the 3:1 ratio might imply a partial ionisation of the iodine on the second phosphorus atom



3:1 onwards :

Addition of iodine monobromide beyond the 3:1 ratio would be expected to produce additional polyhalide ions. However, as there is no clear break at higher mole ratios it is impossible to quantify the reaction sequence in this mole ratio region.

The molar conductance values, which were calculated from the graph on the basis of the formulae $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{IBr}$,

$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{I} \cdot \text{Br}$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{I}_2 \cdot \text{Br}_2$ and

$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{I}_3 \cdot \text{Br}_3$, are as follows:-

$$0.5:1 \quad \Lambda_m = 189.38 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.00591 \text{ mole litre}^{-1})$$

$$1.0:1 \quad \Lambda_m = 109.8 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.01128 \text{ mole litre}^{-1})$$

$$2.0:1 \quad \Lambda_m = 150.8 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.01035 \text{ mole litre}^{-1})$$

$$3.0:1 \quad \Lambda_m = 182.8 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.00954 \text{ mole litre}^{-1})$$

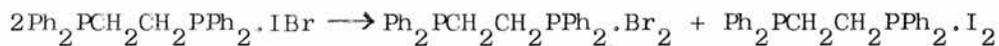
These figures suggest that the species present at the 0.5:1,

1:1, 2:1 and 3:1 ratios are all strong 1:1 electrolytes, with the

3:1 species possibly undergoing further partial ionisation to give a 2:1 electrolyte.

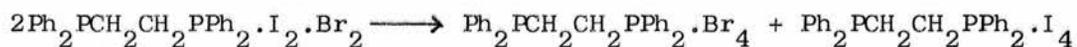
Solids of stoichiometry $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{Br}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{Br}_4$ were obtained by mixing a methyl cyanide solution of iodine monobromide with phosphine in the ratios 1:1 and 2:1 respectively. It appears therefore that the compounds $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{IBr}$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{I}_2\cdot\text{Br}_2$ which were postulated as occurring at the 1:1 and 2:1 ratios in the conductometric titration (ie. in methyl cyanide solution) are not formed as stable solids. Instead the bromine analogues of these compounds were isolated. This implies that a halogen interchange is occurring during the isolation of solid compounds from mixtures containing diphosphine and iodine monobromide.

In the preparation which led to the isolation of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{Br}_2$, an equimolar solution of iodine monobromide and phosphine was allowed to stand overnight with the result that a pale yellow precipitate was formed. This solid was filtered off and washed with a little methyl cyanide to produce a white solid. Analysis of this solid showed it to be the dibromide, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{Br}_2$. The melting point was $206-208^\circ$ which is identical to that of the solid $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{Br}_2$ isolated from the $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2-\text{Br}_2$ system. The infrared spectrum was also identical in all respects and the ultraviolet spectrum contained no tribromide ion absorption. It thus appears that the compound $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{IBr}$ is unstable in the solid form and decomposes to give the dibromide, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{Br}_2$.



Yellow crystals were formed when a 2:1 mixture of iodine monobromide and phosphine was allowed to stand for a few days.

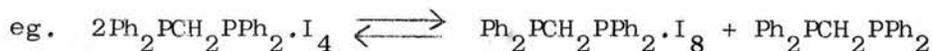
The resulting compound was found to have a composition $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_4$ and the infrared spectrum was identical to that of the adduct $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_4$ prepared by the direct reaction of bromine with the phosphine. The ultraviolet spectrum of the solid dissolved in methyl cyanide showed no tribromide ion absorption which is surprising as $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_4$ mentioned in the $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_2$ system contained tribromide ions. The absence of tribromide ions in this compound, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_4$, prepared above tends to indicate that the structure is the ionic one $[\text{Ph}_2\text{P}^+(\text{Br})\text{CH}_2\text{CH}_2\text{P}^+(\text{Br})\text{Ph}_2]2\text{Br}^-$. Again it appears that the species $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{I}_2 \cdot \text{Br}_2$ is unable to exist as a stable solid and undergoes a halogen rearrangement to give:



The attempted preparation of solids at the 3:1 and 4:1 mole ratios of iodine monobromide to phosphine was unsuccessful. Oils were formed and analysis of these showed that appreciable quantities of methyl cyanide were present even after pumping on the vacuum line. Their composition could not therefore be accurately determined.

General Conclusion

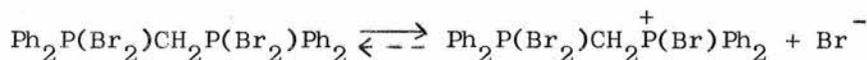
The reaction of halogens with the biphosphines, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, is not as straightforward as the systems investigated in Part 1 of this thesis. In many cases the compounds predicted by the conductometric titration were not isolated, probably due to their instability in the solid state; conversely other compounds were isolated which were shown to rearrange in solution:



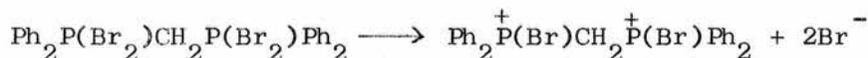
Both phosphines formed 1:1 and 2:1 compounds with bromine. The 1:1 compounds were shown to be strong electrolytes in methyl cyanide,



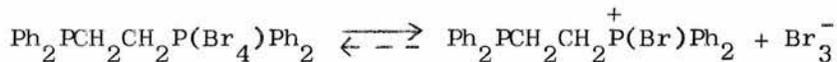
The 2:1 compound, $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{Br}_4$ is also a strong electrolyte and is thought to ionise thus



and not



In contrast the 2:1 compound, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Br}_4)\text{Ph}_2$, was found to contain tribromide ions



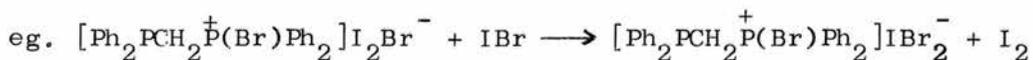
It is suggested that ions containing two phosphonium centres in close proximity would be unstable.

A compound was isolated at the 3:1 ratio ($\text{Br}_2:\text{Ph}_2\text{PCH}_2\text{PPh}_2$) in which one of the methylene group hydrogens was substituted by bromine. The addition of bromine to $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ beyond the 2:1 ratio is thought to produce a proportion of species with two phosphonium centres, which in turn would tend to assist the substitution of one of the methylene protons by bromine. This reaction is probably catalysed by traces of moisture. This substitution reaction is not observed in the $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_2$ system presumably due to the fact that the phosphonium centres are more widely separated thus reducing their combined effect on individual methylene protons and thereby decreasing the acidic nature of these protons. All of the $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{Br}_2$ adducts are extremely labile; hydrolysis and oxidation occurs even in the dry-box. The $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_2$ compounds appear to be less sensitive towards moisture.

The solid adducts isolated from the $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{-I}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{-I}_2$ systems were $\text{Ph}_2\text{PCH}_2\text{PPh}_2\cdot\text{I}_4$, $\text{Ph}_2\text{PCH}_2\text{PPh}_2\cdot\text{I}_{10}$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{I}_2$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{I}_4$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{I}_8$; they were less easily hydrolysed than the bromine compounds mentioned above, possibly due to a screening effect on the phosphorus atoms by the bulky iodine atoms. Again singly charged cations seem to be preferred, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{I}_4$ ionising as $[\text{Ph}_2\text{PCH}_2\text{CH}_2\overset{\oplus}{\text{P}}(\text{I})\text{Ph}_2]\text{I}_3^-$.

The reaction of iodine monobromide with the two biphosphines involves various halogen rearrangements. For example the compounds $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{Br}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{Br}_4$ were isolated from 1:1 and 2:1 mixtures of iodine monobromide and phosphine respectively.

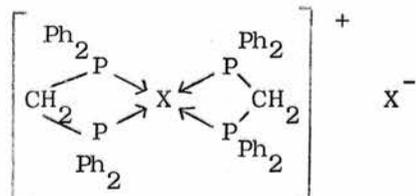
The stable solids obtained from the $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{-IBr}$ system were $\text{Ph}_2\text{PCH}_2\text{P}(\text{IBr})\text{Ph}_2$, $\text{Ph}_2\text{PCH}_2\text{P}(\text{I}_2\text{Br}_2)\text{Ph}_2$ and $\text{Ph}_2\text{PCH}_2\text{P}(\text{IBr}_3)\text{Ph}_2$ from appropriate mixtures of halogen and phosphine. In the latter case, $\text{Ph}_2\text{PCH}_2\text{P}(\text{IBr}_3)\text{Ph}_2$ is formed by an interchange of halogens when $\text{Ph}_2\text{PCH}_2\text{P}(\text{I}_2\text{Br}_2)\text{Ph}_2$ reacts further with iodine monobromide



The iodine monobromide adducts of the phosphine, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, seem to be more susceptible to hydrolysis and a methylene substituted compound is formed during the reaction in methylene cyanide, analogous to the solid isolated during the investigation of the $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{-Br}_2$ system.

All of the conductometric titration graphs possess a break at the 0.5:1 mole ratio (halogen:phosphine) indicating compound formation at this point. Two solids of composition $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{X}_2$ (where X = Br or I) were obtained by freeze drying 0.5:1 mixtures of halogen and phosphine and it

is suggested that they may have the structure,



APPENDIX 1

Some Reactions of Triphenylphosphine with Halogens

and

APPENDIX 2

An Automated Apparatus for the Measurement of Depression of Freezing
Point

Appendix 1

Some Reactions of Triphenylphosphine with Halogens

The study of the $\text{Ph}_2\text{MeP-I}_2$, $\text{PhMe}_2\text{P-I}_2$ and $\text{Me}_3\text{P-I}_2$ systems showed in each case a break at the 0.5:1 mole ratio in the conductometric titrations indicating the species $(\text{R}_3\text{P})_2\text{I}_2$. On the other hand, previous work by Beveridge⁹⁶ on triphenylphosphine-iodine, the remaining member of the series $\text{Ph}_n\text{Me}_{(3-n)}\text{P}$, ($n = 0-3$), failed to indicate a break at the 0.5 ratio. As Beveridge's conductometric titrations were performed using an apparatus⁹⁶ designed for operation in the open laboratory, the results could have been affected by traces of moisture and oxygen. It was decided to repeat the experiments using an apparatus developed by McKechnie¹²⁹, where the entire titration is carried out inside the dry-box thus reducing the chances of interference by moist air or oxygen.

1. Results and Discussion

Conductometric Titration

A conductometric titration study of the $\text{Ph}_3\text{P-I}_2$ system (using I_2 in solution as titrant) in methyl cyanide gave the results listed in Table 37 and illustrated in Figure 29, plot 1. To verify the shape of the curve and position of the breaks a second titration was performed using solid iodine as titrant to avoid any dilution effect which could cause indistinctness in the breaks; the results of this titration are shown in Figure 29 plot 2 with the results recorded in Table 38. Unlike Beveridge's results, the graph shows without any doubt a clear break at the 0.5:1 ratio and a definite break in the region of the 3:1 ratio

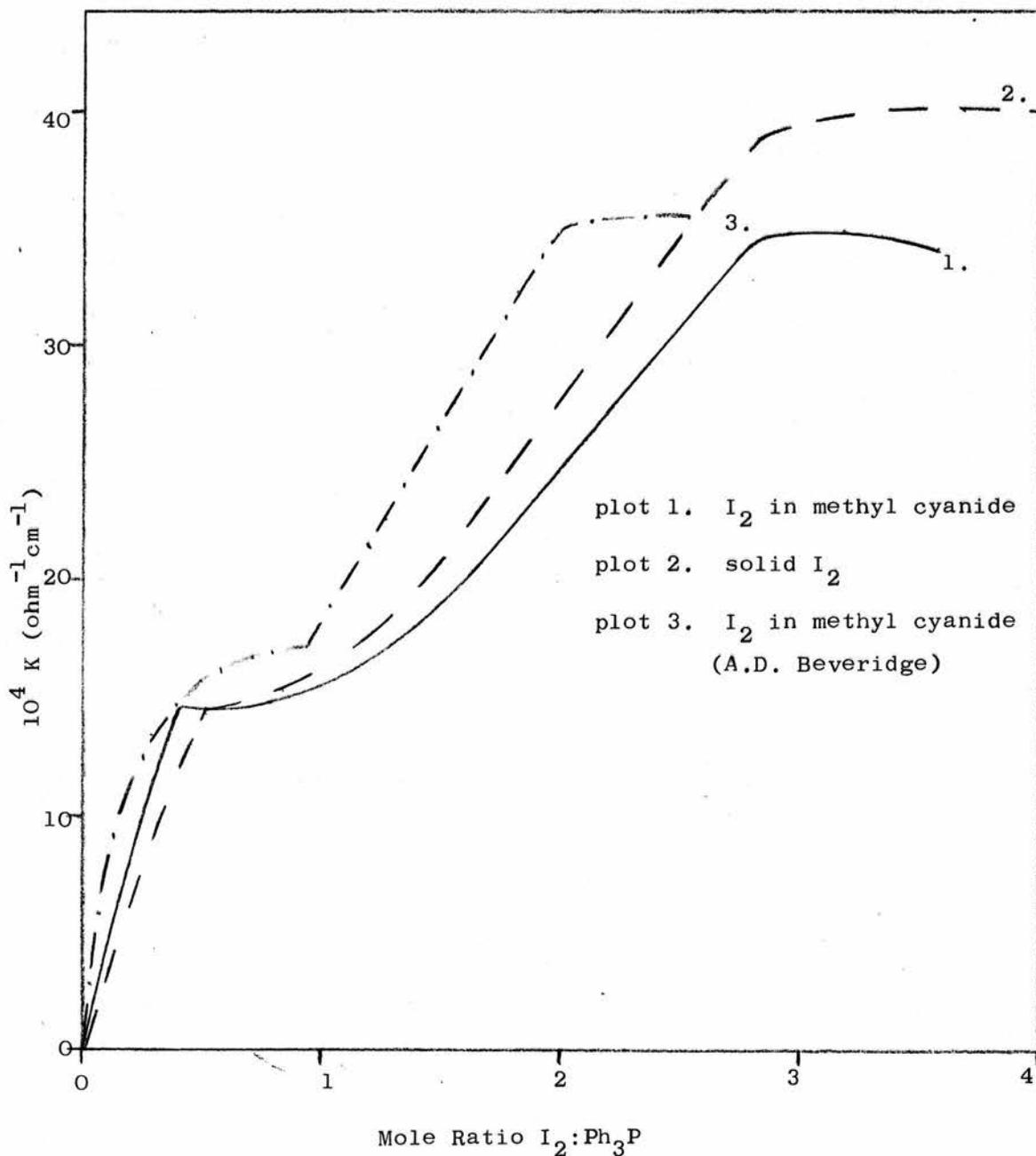


Figure 29 : Conductometric Titration of the System I_2-Ph_3P
in Methyl Cyanide

suggesting that compounds of the stoichiometries $(Ph_3P)_2I_2$ and Ph_3PI_6 are probably formed in solution. The conductance rose sharply up to the 0.5:1 ratio, the solution being colourless at

low mole ratios and only assuming a pale yellow colouration at the 0.5 ratio. Beyond 0.5:1 the colour darkened with the conductance increasing slightly to the 1:1 ratio followed by a steady rise in slope until the 3:1 ratio. The molar conductance values at the 0.5:1 and 1:1 ratios for the titrations using iodine in methyl cyanide and solid iodine were respectively:

First Titration (I_2 dissolved in methyl cyanide)

$$0.5:1 \quad \Lambda_m = 170.62 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.00855 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } (\text{Ph}_3\text{P})_2\text{I}^+\text{I}^-)$$

$$1.0:1 \quad \Lambda_m = 190.52 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.00815 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } (\text{Ph}_3\text{P})_2\text{I}^+\text{I}_3^-)$$

Second Titration (solid I_2)

$$0.5:1 \quad \Lambda_m = 180.80 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0078 \text{ mole litre}^{-1})$$

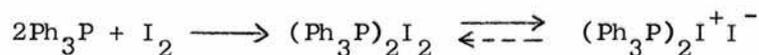
$$(c_m \text{ based on } (\text{Ph}_3\text{P})_2\text{I}^+\text{I}^-)$$

$$1.0:1 \quad \Lambda_m = 205.70 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0078 \text{ mole litre}^{-1})$$

$$(c_m \text{ based on } (\text{Ph}_3\text{P})_2\text{I}^+\text{I}_3^-)$$

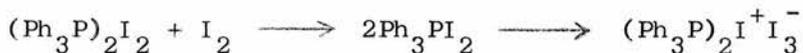
These values suggest that the species present at the 0.5 and 1:1 ratios were strong electrolytes.

The results of the conductometric titration differ from those obtained by Beveridge et al⁹⁶, (see Figure 29, plot 3) in that they show clear breaks at the 0.5:1 and 3:1 ratios whereas Beveridge's graphs contain discontinuities at the 1:1 and 2:1 ratios. The production of the 0.5 species can be assumed to occur as

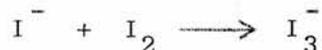


in line with previous systems.

It appears however from the colour of solution and existence in it of triiodide ion at the 1:1 ratio break, that the reaction between the 0.5:1 and 1:1 ratio is best represented as

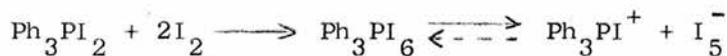


and the effective change is

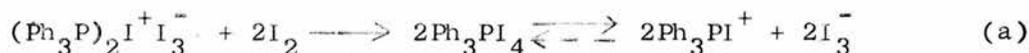


Beveridge also found the presence of triiodide ions in solution at the 1:1 ratio⁹⁶. On the basis of this scheme there is no increase in the number of ions between the 0.5 and the 1:1 ratio, consequently little change in conductance between these ratios would be expected and this is found in practice.

The break at the 3:1 ratio points to the reaction between 1:1 and 3:1 being



Alternatively, and in line with previous systems, it could be that the reaction after the 1:1 ratio is the one leading to triphenylphosphine tetraiodide Ph_3PI_4 , viz



This should give a break at 2:1 but if the reaction (a) were not complete a delayed break in the graph would be expected.

Support for the first interpretation comes from the isolation of Ph_3PI_6 . However it must also be noted that a 2:1 solution and a 4:1 solution (iodine to triphenylphosphine) gave the tetraiodide and octaiodide respectively. The polyiodides Ph_3PI_6 , Ph_3PI_8 were isolated as relatively stable black solids and are assumed to contain higher polyiodide ions, eg. $\text{Ph}_3\text{PI}^+\text{I}_5^-$ and $\text{Ph}_3\text{PI}^+\text{I}_7^-$.

Vapour Pressure Study of the System $\text{Ph}_3\text{P-Br}_2$

A vapour pressure-composition study of the $\text{Ph}_2\text{MeP-Br}_2$ system (described in an earlier section) demonstrated the existence of higher polybromide species of the type R_3PX_n , ($n = 6, 8, 10$) were capable of existing as solid phases. Similar experiments on the $\text{PhMe}_2\text{P-Br}_2$ and $\text{Me}_3\text{P-Br}_2$ systems failed to indicate any such formation and it is suggested that the phenyl groups have a stabilising effect on these higher adducts.

Triphenylphosphine, possessing three phenyl groups, would be expected to behave in a similar manner to Ph_2MeP . Also as the higher polyhalide compounds, Ph_3PI_6 and Ph_3PI_8 , were obtained from the $\text{Ph}_3\text{P-I}_2$ system it was thought probable that additional higher bromides would be present in the $\text{Ph}_3\text{P-Br}_2$ system. Ordinary preparative techniques could not be used to show the existence of these bromine compounds as they are more unstable than their iodine counterparts and lose bromine readily. A vapour pressure-composition study was the only readily available means of indicating the existence of higher polybromides, and the results of this experiment are noted in Table 19 and shown in Figure 30.

Table 19 : Vapour Pressure-Composition of the $\text{Br}_2\text{-Ph}_3\text{P}$ System at 20°C

Mole Ratio $\text{Br}_2:\text{Ph}_3\text{P}$	Vapour Pressure (mm Hg)
7.437	81.62
7.271	75.57
7.016	67.53
6.734	59.72
6.455	53.52
6.199	46.59
5.970	9.58
5.915	1.54
5.871	1.02

There is a clear step in the graph at the 6:1 mole ratio $\text{Br}_2:\text{Ph}_3\text{P}$. This shows, without doubt, the presence of the solid phase of composition $\text{Ph}_3\text{PBr}_{12}$. This can be written in the form $[\text{Ph}_3\text{PBr}^+][\text{Br}_{11}^-]$. The $[\text{Br}_{11}^-]$ ion is as yet not firmly

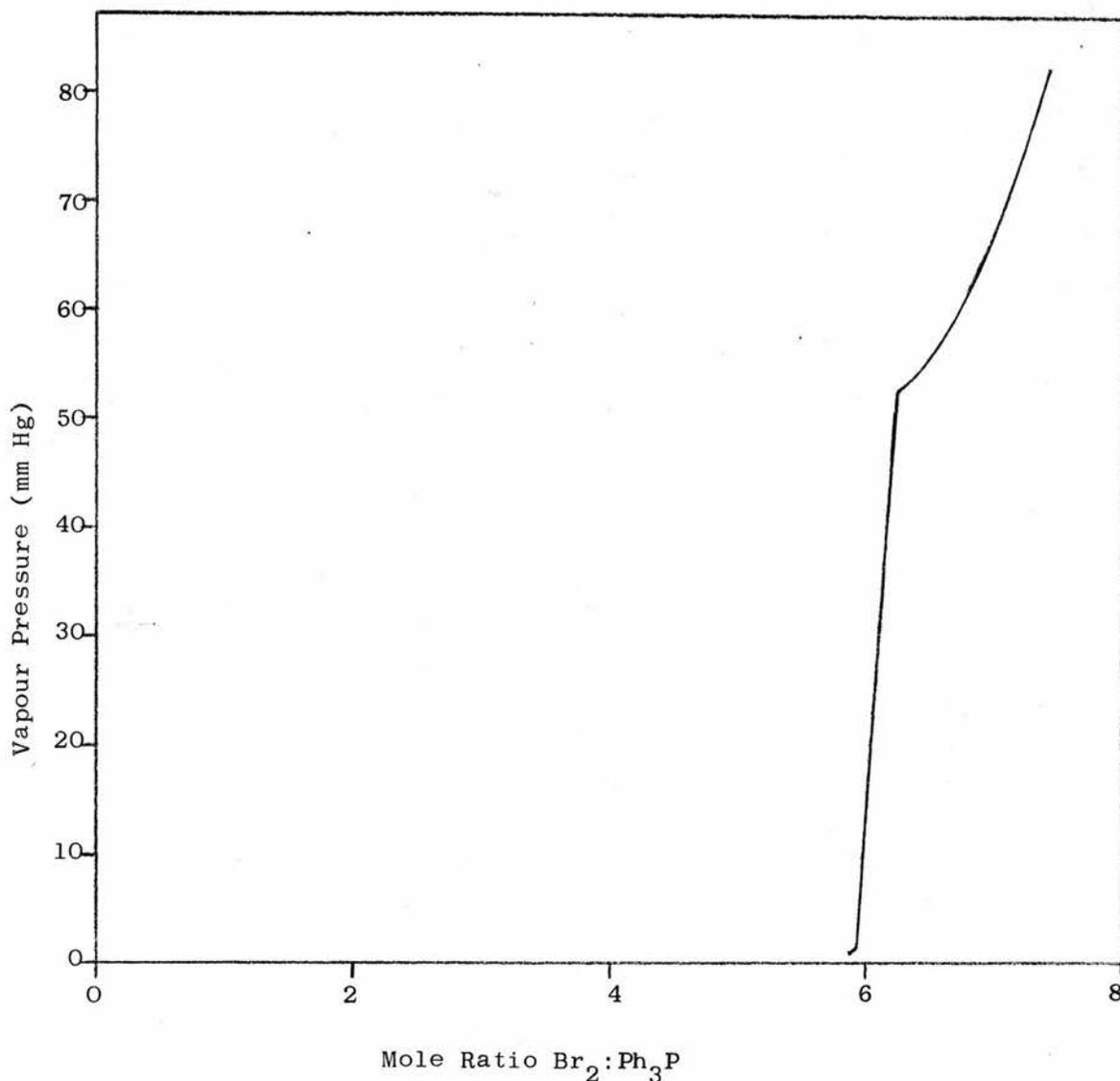


Figure 30 : Vapour Pressure Study of the Br₂-Ph₃P System at 20°C

established but MacPherson¹³⁰ found evidence for its formation in $[(p\text{-tol})_3\text{PBr}^+][\text{Br}_{11}^-]$. It should be noted too that the I_{11}^- ion is known in $\text{Me}_4\text{N}^+\text{I}_{11}^-$. Below the 6:1 ratio the vapour pressure is very low (less than 1 mm) so no lower polybromides could be identified by this method.

2. Experimental

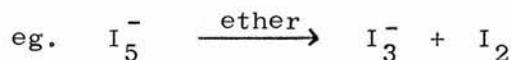
(a) Conductometric titration and vapour pressure titration apparatus were as described in the main "Experimental" portion of this thesis.

(b) The purification and handling of methyl cyanide, bromine, iodine and triphenylphosphine are also described in the main "Experimental" part.

(c) Preparations:

(i) Ph₃P-I₂ in 3:1 mole ratio

Iodine (0.6528 g) was dissolved in methyl cyanide (10 ml) by stirring in the dry-box for two hours. This was added to triphenylphosphine (0.2053 g) with stirring producing a clear solution. The solution was shaken overnight and the resulting black solid was filtered off and dried in the dry-box. M.p. 81-84^oC. (Found: C, 20.93; H, 1.52; I, 76.46. Ph₃PI₆ requires C, 21.12; H, 1.48; I, 74.38%.) Washing with ether was avoided as ether tends to remove iodine from the higher polyhalides.



(ii) Ph₃P-I₂ in 4:1 mole ratio

A solution containing iodine (0.6565 g) in methyl cyanide (10 ml) was stirred with triphenylphosphine (0.1677 g) until the solution became clear. A black solid was precipitated after this mixture was shaken overnight. This was filtered (but not washed) and dried in the dry-box. M.p 76-77^oC. (Found: C, 16.75; H, 1.17; I, 78.68. Ph₃PI₈ requires C, 16.92; H, 1.18; I, 79.47%).

Appendix 2

An Automated Apparatus for the Measurement of Depression of Freezing Point

The average molecular weight of a species in solution can be used to distinguish between possible ionisation schemes and was mentioned in Part 1 of this thesis in connection with the trimethylphosphine-iodine compounds. The results in that particular case were inconclusive because of the inherent low solubility of the compounds. The apparatus used in the determination of freezing point depression is described in this section. The depression of freezing point was measured indirectly by use of a thermistor whose resistance alters with temperature and this variation is assumed to be linear over a small range ca. 3°C. Linear calibration graphs were obtained relating conductance and molality using substances of known molecular weight. This enabled average molecular weights to be calculated for unknown species.

The Apparatus

The freezing point cell (Figure 31) used in this investigation was originally designed to be used in conjunction with a Beckmann thermometer. The Beckmann thermometer was discarded as inconsistent results were obtained due, it is thought, to crystallisation on the wall of the vessel around the freezing point. This was replaced with a finger of the same overall dimensions as the thermometer, containing a thermistor (with a resistance of ca. 2k Ω at room temperature) sitting in a pool of mercury (about 1/3 inch long) with a layer of paraffin oil above. Stirring was achieved by vertical agitation using a

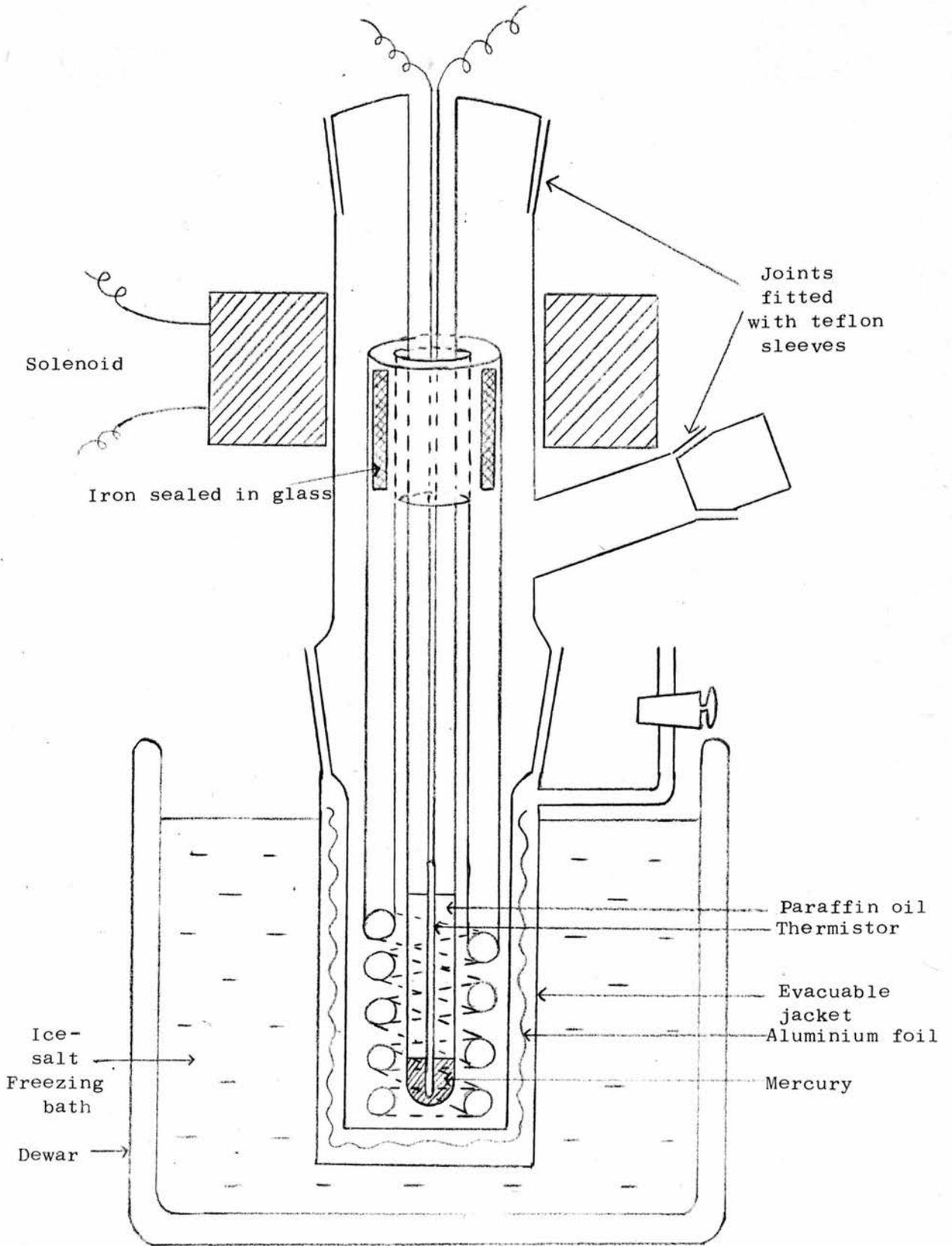


Figure 31 : Freezing Point Cell and Cryostat Cooling System

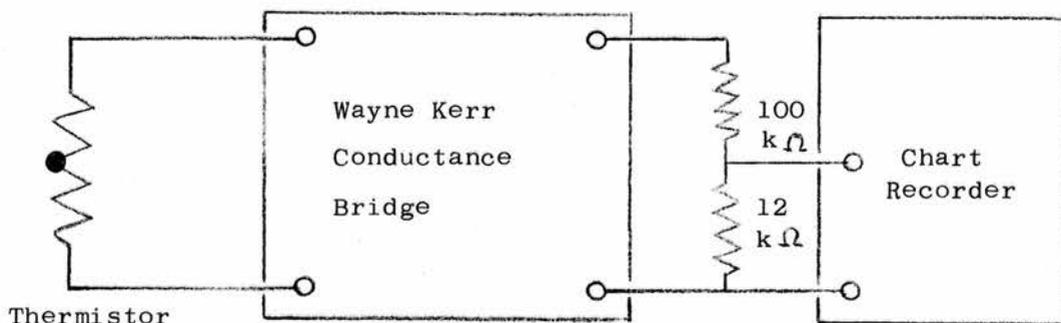


Figure 32 : The Automated System for Measuring and Recording
the Change in Conductance of a Thermistor

glass spiral which fitted snugly between the thermistor housing and the outer wall of the apparatus. A lump of iron was sealed in the glass at the upper end and this was surrounded by a solenoid energised by an oscillator. Solute could be added through a stoppered side arm with all ground glass joints being fitted with teflon sleeves to exclude moisture. The cryoscopic apparatus was fitted with an evacuable jacket to control the rate of cooling and aluminium foil was sandwiched between the inner apparatus and jacket to prevent transfer of heat by radiation. The whole apparatus was immersed in a Dewar flask containing an ice-salt mixture whose temperature was kept around -1.0°C ($\pm 1^{\circ}\text{C}$) for nitrobenzene as solvent.

The variation in conductance with temperature of the thermistor was measured using a Wayne Kerr B641 Autobalance Bridge. The output from this bridge was fed through a voltage dividing network to a Leeds and Northrup Speedomax 'W' recorder (as outlined in Figure 32) with a chart speed of 12 inches per hour.

Cryoscopic Measurements using Nitrobenzene as Solvent

About 17 ml of nitrobenzene was used, so that the stirrer was just covered on its upward stroke but never broke the surface of the liquid, and the apparatus was filled with dry nitrogen. The value of the conductance of the thermistor at the freezing point of the solvent was taken as the highest point after the supercooling. The solute was added to the solvent in the form of weighed pellets which were introduced through the side arm. Between five and ten consecutive runs were performed after each addition of solute with consistent results being obtained.

The equation used to calculate the average molecular weight

is

$$M_a = \frac{K_f \times 1000 \times W_{\text{solute}}}{\Delta T \times W_{\text{solvent}}} \quad \text{Equation 1}$$

where M_a = average molecular weight

K_f = molal freezing point constant (degree/mole/kg)

W_{solute} = weight of solute (grams)

W_{solvent} = weight of solvent (grams)

ΔT = freezing point depression ($^{\circ}\text{C}$).

This equation only holds for solutions containing less than 1% of solute.

Equation 1 can be rewritten as

$$\Delta T = K_f \times S \quad \text{Equation 2}$$

where S = Molality of solute (moles of solute/kg of solvent).

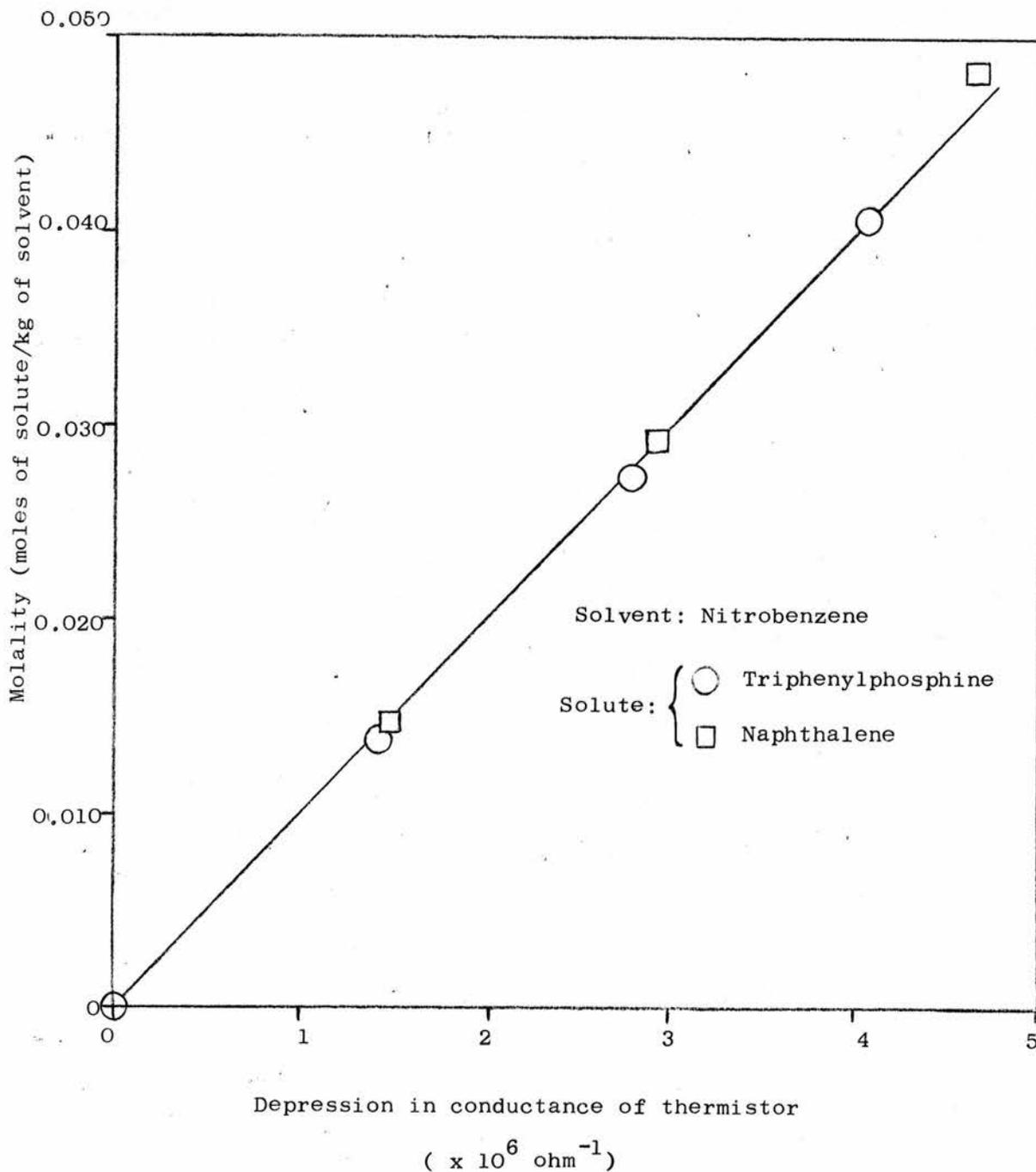


Figure 33 : The Depression in Conductance Measured by Thermistor in the Systems Nitrobenzene-Triphenylphosphine and Nitrobenzene-Naphthalene

In this investigation ΔT is measured in terms of a depression in conductance of a thermistor and there is a direct linear relationship with S, the molality of the solute.

Table 20 : Cryoscopic Measurements on the Systems Nitrobenzene-Triphenylphosphine and Nitrobenzene-Naphthalene using a Thermistor

Wt. of Triphenylphosphine added (g)	Molality (moles/kg solvent)	Depression in Conductance x 10 ⁶ (ohm ⁻¹)
0	0	0
0.0884	0.0139	1.43
0.1737	0.0274	2.79
0.2573	0.0406	4.09

Wt. of Naphthalene added (g)	Molality (moles/kg solvent)	Depression in Conductance x 10 ⁶ (ohm ⁻¹)
0	0	0
0.0367	0.0148	1.47
0.0728	0.0293	2.91
0.1194	0.0481	4.65

Both triphenylphosphine and naphthalene were used as the solute with nitrobenzene as solvent; the results show an ideal straight-line calibration plot and are illustrated in Figure 33 and listed in Table 20. The sensitivity of the thermistor at the freezing point of nitrobenzene (5.7 °C) was $0.144 \times 10^{-4} \Omega^{-1}/^{\circ}\text{C}$ or $120 \Omega/^{\circ}\text{C}$. The accuracy of freezing point determination using this method is roughly a factor of ten times greater than similar experiments employing a Beckman thermometer.

Cryoscopic Measurements using Methyl Cyanide as Solvent

The use of nitrobenzene as a solvent for studying the depression of freezing point on the phosphine-halogen systems

reported in this thesis was unsatisfactory because of the low solubility of the compounds in nitrobenzene. It was thought that methyl cyanide would be a better solvent for cryoscopic measurements on these systems as the compounds were more soluble in methyl cyanide than in nitrobenzene. Also all the other experiments, conductometric titrations, transport number determinations etc, had been performed using methyl cyanide as the solvent and a direct correlation could be obtained between these experiments and the cryoscopic work.

Table 21 : Cryoscopic Measurements on the System Methyl Cyanide-Triphenylphosphine using a Thermistor

Wt. of Triphenylphosphine added (g)	Molality (moles/kg solvent)	Depression in Conductance x 10 ⁸ (ohm ⁻¹)
0	0	0
0.0340	0.0101	5.9
0.0757	0.0226	14.7
0.1217	0.0363	18.0

Minor modifications were made to the apparatus to take account of the low freezing point of methyl cyanide (-45.7°C). The mercury and paraffin oil surrounding the thermistor were replaced with alcohol and the cryostat was a chloroform slush bath (-63.5°C).

About ten separate determinations of the freezing point were performed. The methyl cyanide was allowed to warm up between each run until the solvent had completely re-liquefied. There was a certain amount of scatter in the readings and an average of the results is listed in Table 21 and displayed in Figure 34. The triphenylphosphine was added as weighed pellets,

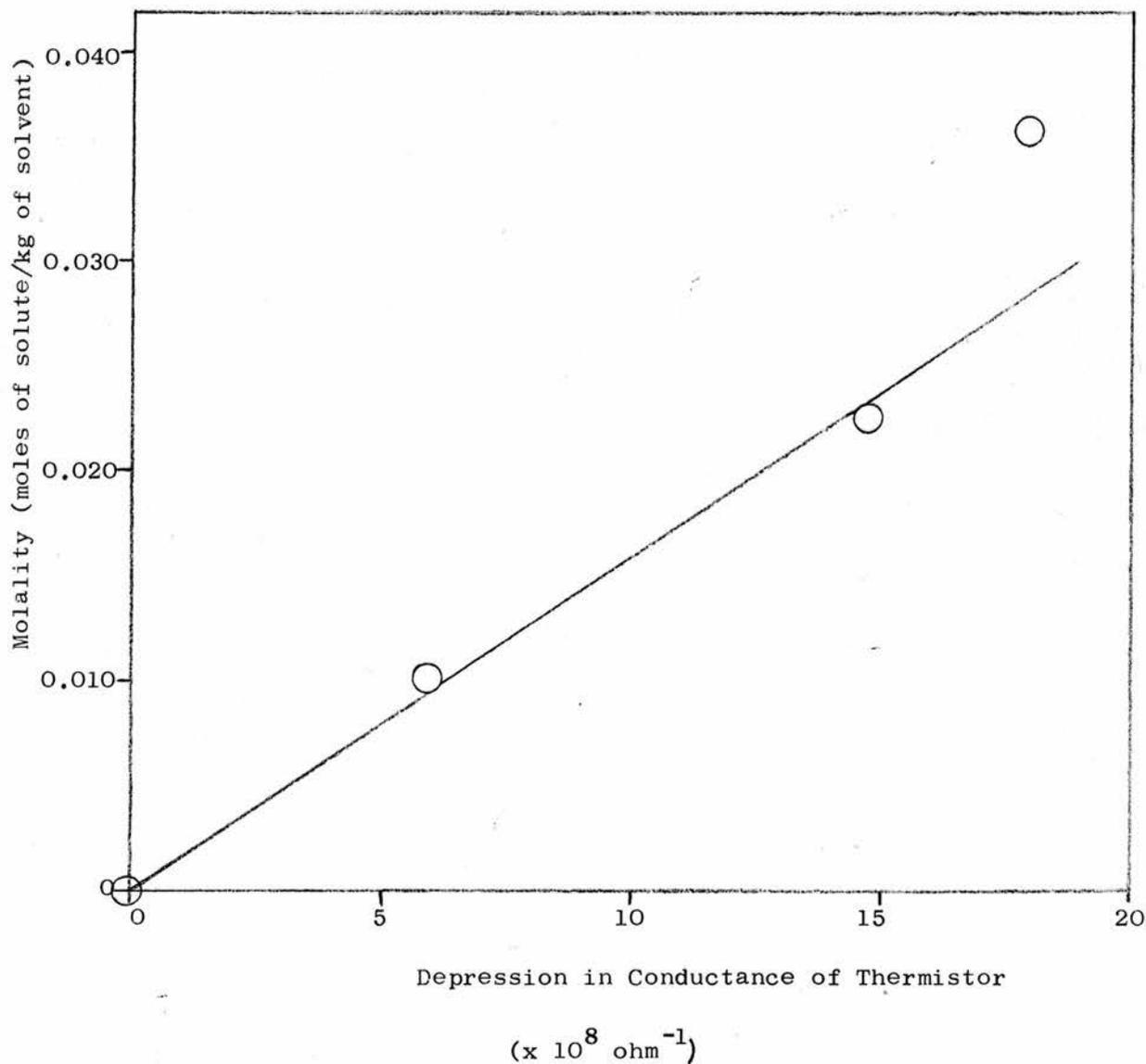


Figure 34 : The Depression in Conductance Measured by Thermistor
in the System Methyl Cyanide-Triphenylphosphine

care being taken to exclude moisture during the addition. The sensitivity of the thermistor at ca. -46°C was $1700 \text{ ohm}/^{\circ}\text{C}$ which is an increase of roughly fourteen times the figure at ca. 5°C . However, conductance was being measured, not resistance, and the sensitivity at -46°C was $0.223 \times 10^{-5} \text{ ohm}^{-1}/^{\circ}\text{C}$ which is a factor

of seven less than that previously obtained at the higher temperatures used in the nitrobenzene experiments. It can be seen from the graph that the results are less consistent than those obtained using nitrobenzene as a solvent, and on the basis of this it was decided that methyl cyanide was unsuitable for cryoscopic measurements without a complete redesign of the apparatus to achieve better temperature control of the cooling bath, and therefore a more even rate of cooling of the methyl cyanide solution.

E X P E R I M E N T A L

EXPERIMENTAL

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Experimental

1. General Techniques

(a) Handling of Materials

As the majority of the compounds studied in this work were extremely moisture-sensitive, strict precautions were required to ensure the absence of moisture and air at all times. This was achieved by the extensive use of a nitrogen-filled dry-box containing trays of phosphorus pentoxide. The nitrogen was commercial oxygen-free nitrogen, dried by passage through a column of molecular sieve (AEI-Birlec Ltd, adsorber type AB 12.5). Certain manipulations, chiefly removal of solvents, were carried out in a simple vacuum line, thus avoiding exposure of the sensitive halides to both atmospheric moisture and elevated temperatures. Compounds so handled were stored in sample tubes sealed with plastic stoppers and kept either in the dry-box or in a partially evacuated desiccator over silica gel.

(b) Vacuum System

The vacuum system consisted of a rotary oil pump connected via two protective sludge traps to a main line from which branched various sub-sections designed for special operations, eg. vapour pressure measurement and freeze-drying.

Vapour Pressure Measurements

The vapour pressure studies were performed using an all-glass system which is illustrated in Figure 35. The spiral gauge (C) in this system was used as a null instrument in which the deflection of the pointer was magnified by the optical lever principle. The pointer of the gauge was made to actuate a small

delicately-balanced mirror which reflected a parallel beam of light on to a scale situated at a distance of one metre. The zero point of the instrument on the scale was adjusted.

The phosphine under investigation was kept in flask A, and initially this flask also contained a known excess of bromine which had been vacuum distilled from the weighed flask B. Before the vapour pressure titration began, flask B was carefully re-evacuated and weighed, in preparation for receiving aliquots of the excess bromine over the phosphine. The taps and joints incorporated in the vacuum system were of the greaseless type, manufactured by J. Young (Acton) Ltd, and contained halogen resistant rubber and teflon 'O'-rings. For vapour pressure readings during the titration, flask A was kept immersed in a Dewar vessel containing water at 20°C (just below room temperature). The vapour pressure of the contents of flask A having deflected the mirror on gauge C, this pressure was compensated by admitting air through capillary leak E and the surge chamber D. Full compensation was monitored by the return of the light signal to the original zero point on the scale: vapour pressure could then be obtained as a difference in mercury levels between manometers F and G, arranged close to one another and using a common mercury reservoir. Having closed tap T_4 before the start of the titration, with tube G fully evacuated, manometer G was employed as an ordinary barometer. A cathetometer was used to obtain accurate measurement of the mercury levels.

Having read the vapour pressure for given contents of flask A, some of the excess bromine was then distilled off into flask B by temperature difference, liquid nitrogen being used to surround B during this process. Flask B was allowed to assume room temperature, after closing taps T_5 and T_8 , and re-weighed.

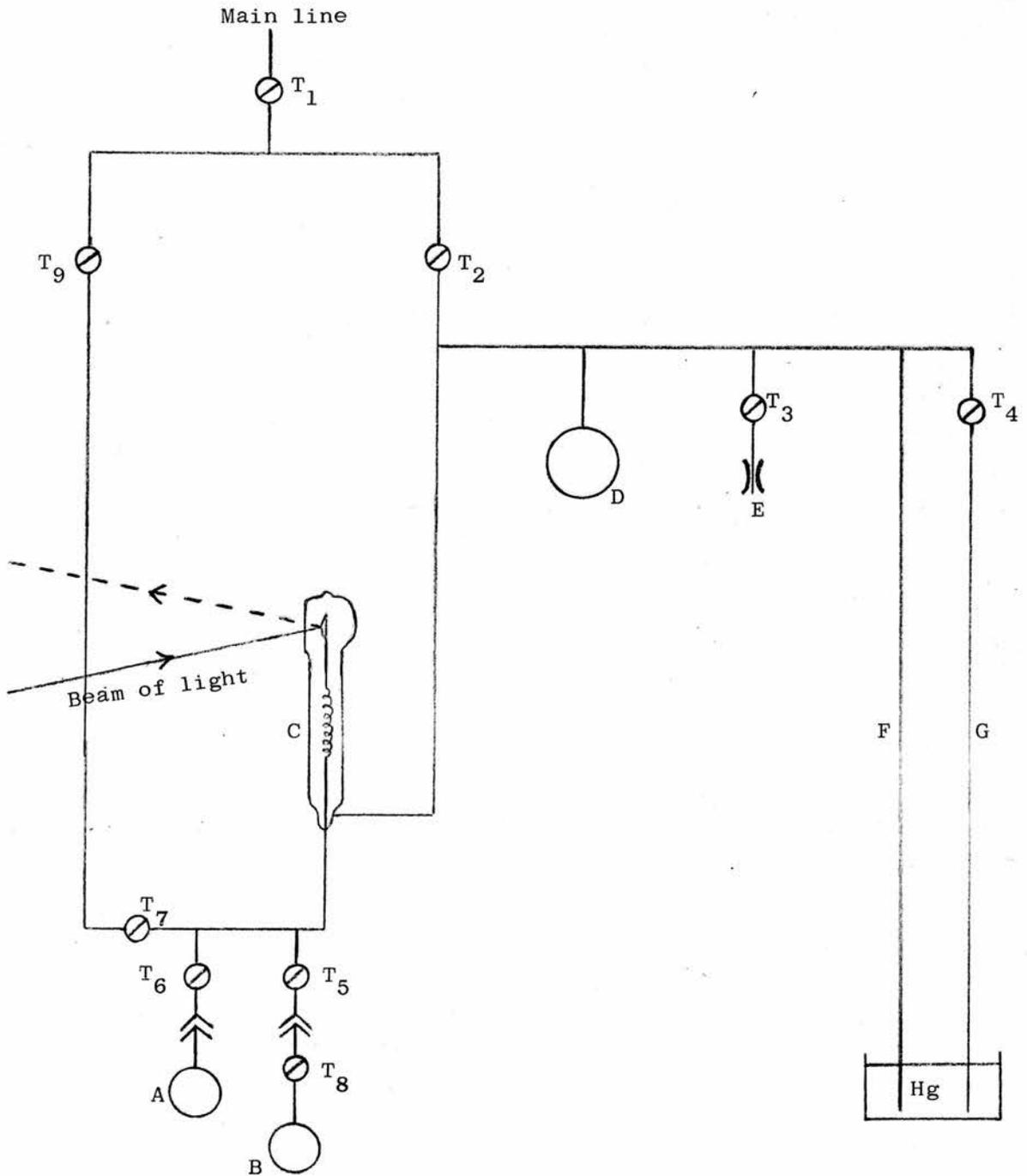


Figure 35 : Vacuum System for Vapour Pressure Study

Thus the new mole ratio of bromine to phosphine in flask A could be ascertained, and the process of obtaining the vapour pressure repeated as before. When it was necessary to reduce the pressure in , or pump directly any part of the system, taps

T_2 and T_1 , which gave access to the main line, were used.

(c) Conductance Measurements

A standard pair of smooth platinum dipping electrodes was used in a sealed cell. The cell constant was determined by using a standard potassium chloride solution. A weighed amount of dry solvent was placed in the cell, and successive additions of the solid from small sample tubes were always made inside the dry-box. After each addition the cell was placed in a thermostat bath at 25°C and complete solution allowed to take place. The conductance of these solutions was measured using a Wayne Kerr B641 Autobalance Bridge; therefore molar conductances could be calculated and plotted against $\sqrt{c_m}$.

(d) Conductometric Titrations

A convenient technique for studying the reactions of the triarylphosphines and their derivatives with halogens has been shown to be the conductometric titration^{96,109}. Information may be obtained not only on the stoichiometry of the reaction products but also on their electrolytic nature.

Methyl cyanide was usually employed as a solvent as its high dielectric constant (36.7 at 25°C) results in high conductances of electrolytes and consequent easy distinction between non-electrolytes and weak electrolytes. Strong 1:1 electrolytes have Λ_m ca. 100 ohm⁻¹ cm² mole⁻¹, and weak electrolytes have Λ_m ca. 10-20 ohm⁻¹ cm² mole⁻¹ in methyl cyanide.

The apparatus used to study the $\text{Ph}_2\text{MeP-X}_2$ system was designed to prevent the solutions coming into contact with atmospheric moisture or tap grease. A description of the apparatus and its operation has been published⁹⁸. However, because of its

size this apparatus could only be used in the open laboratory; in order to reduce the chance of interference by oxygen and atmospheric moisture, another apparatus was developed by McKechnie¹²⁹ to enable the entire titration to be performed within the confines of the nitrogen filled dry-box. The conductometric titrations of all the other phosphine-halogen systems reported in this thesis were performed using this apparatus which is displayed in Figure 36.

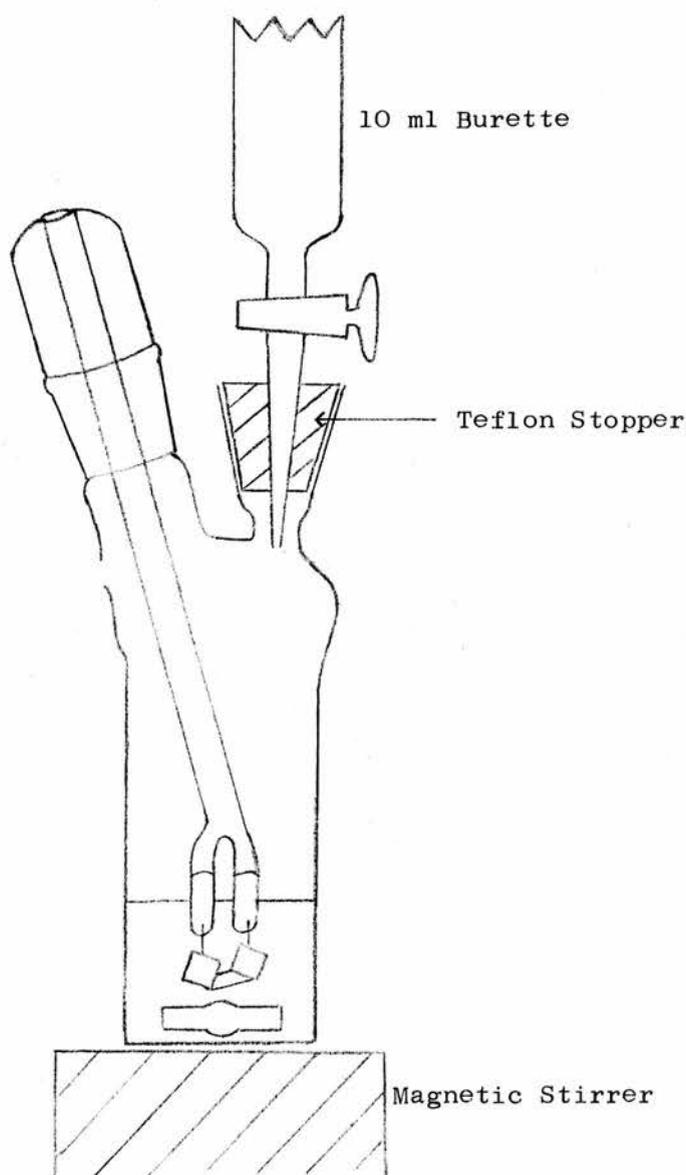


Figure 36 : Dry Box Conductometric Titration Apparatus

The dipping electrodes and the conductance bridge used were the same ones previously mentioned for conductance measurements. The conductance was measured when equilibrium had been attained after each addition of halogen solution.

(e) Transport Number Determinations

Transport numbers were determined by the Hittorf method, which involves the measurement of small changes in the concentration of the electrolyte, which occur in the vicinity of the electrodes when a solution is electrolysed. The design of the apparatus reflects the experimental difficulties which have to be overcome. One of the major problems is mixing of the anode and cathode solutions which may take place by diffusion, convection or vibration. Attempts to reduce these errors by, for example, interposing a partition of sintered glass, or lengthening the column of the solution, only results in an increased resistance of the system, and consequently smaller concentration changes. Conversely, attempts to increase the concentration changes by prolonged electrolysis or increased currents, results in an enhancement of the above errors. Therefore, the apparatus must have optimum dimensions, resulting in a maximum current, with minimum diffusion.

The electrolysis cell was of the H-type with a middle (U-shaped) compartment as shown in Figure 37. The compartments of the cell were emptied using taps greased with 'Kel-F' fluorocarbon grease. The electrodes consisted of smooth platinum foil (coiled) and each had a total surface area of 37.5 cm^2 ; their separation was about 40 cm. The remainder of the apparatus was designed to allow the solutions to be manipulated by pressure difference in a closed circuit. The following procedure was adopted in using the cell.

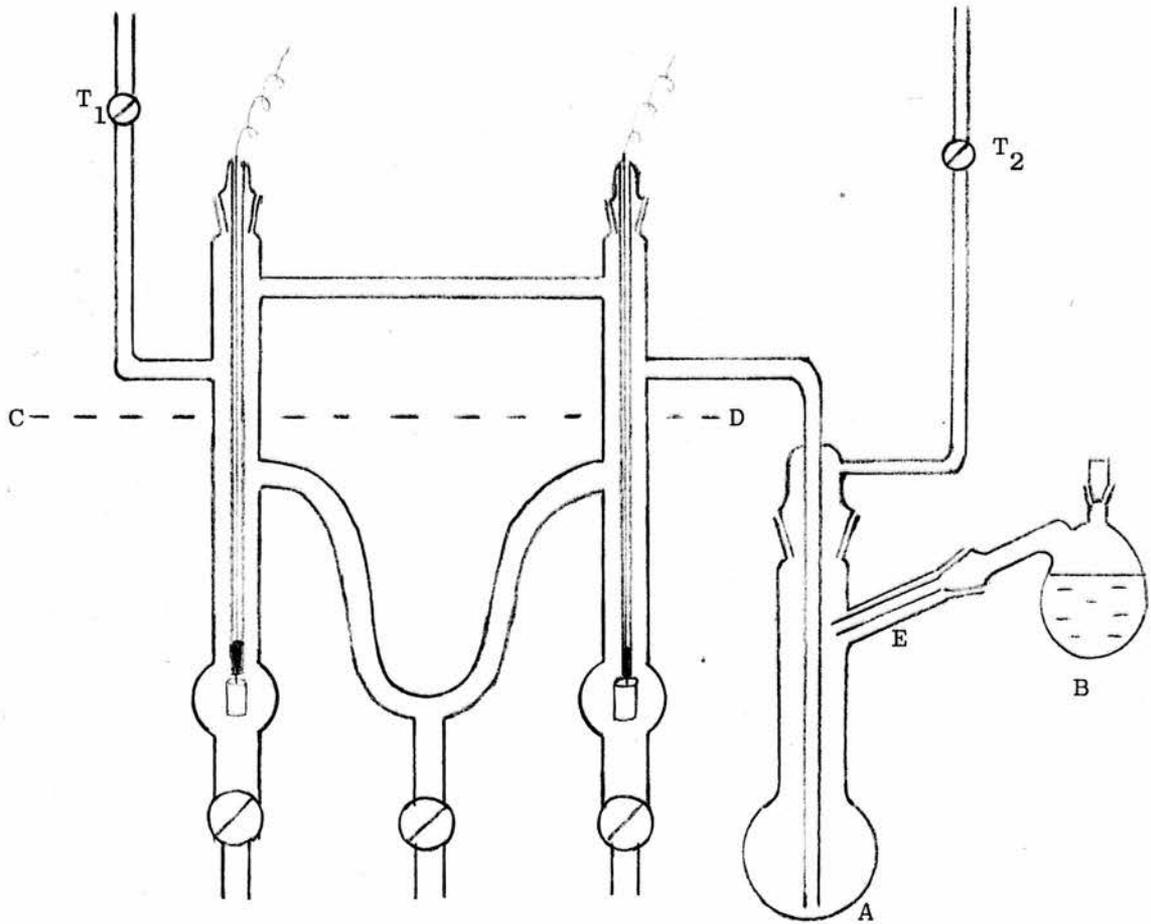


Figure 37 : Electrolysis Cell

The apparatus was attached to the vacuum line through taps T_1 and T_2 and was evacuated for several hours before use. Dry oxygen-free nitrogen was then allowed into the system. Flask B

was then removed and the openings stoppered. The solution to be electrolysed was prepared, and transferred to flask B in the dry-box. Flask B was rejoined to the apparatus enabling the solution to be transferred to flask A by rotating B about the throughjoint E. The cell was filled by suction to the level C-D by opening tap T_1 , and the pressure difference was compensated by admitting dry nitrogen to the system through tap T_2 . The solution was then electrolysed for thirty to forty-five minutes by the passage of direct current (12 V).

After electrolysis the compartments were emptied (middle first) and the separate solutions analysed for halogen content. The amount of current passed was determined from the increase in weight of a silver coulometer incorporated in the circuit. An 'AVO' meter showed that during electrolysis the current was 1-2 mA.

The silver coulometer consisted of a glass crucible sitting in a beaker containing 0.1 M silver nitrate solution so that the crucible was about half filled with solution. A piece of silver foil interposed between the crucible and the inner wall of the beaker formed the anode, whilst the cathode was a platinum electrode (area 1 cm^2) immersed in the solution within the crucible. The crucible served to trap any silver which became disengaged from the cathode.

The cathode and crucible were weighed before the experiment. After the current had passed, cathode and crucible were washed with distilled water, then acetone, before finally drying in an oven at 100°C . Reweighing enabled the weight of silver deposited to be calculated.

(f) Infrared Spectra

Infrared spectra were recorded on a Perkin-Elmer model 621 Grating Infrared Spectrophotometer over the range $4000\text{-}200 \text{ cm}^{-1}$.

The samples were prepared in the dry-box as mulls in nujol or Kel-F oil, and placed between plates of potassium bromide or caesium iodide using "Sellotape" to seal the plates around the edge to prevent attack by atmospheric moisture.

(g) Ultraviolet Spectra

Ultraviolet spectra were recorded on a Unicam SP800B UV/visible recording spectrophotometer. Stoppered quartz cells of 10 mm path length were used, measurements being made at room temperature (ca. 20°C).

(h) Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance spectra were recorded on a Varian Associates HA100 spectrometer. The compounds were dissolved in either d_6 dimethylsulphoxide or deuterio-chloroform for ^1H NMR and dry methyl cyanide for ^{31}P NMR. All ^1H NMR chemical shifts were based on tetramethylsilane and phosphorus trioxide was used as the reference compound for ^{31}P NMR studies.

(i) Mass Spectra

Mass spectra were recorded on an AEI MS902 mass spectrometer. Samples were submitted in sealed tubes, however, contact with atmospheric moisture was unavoidable during injection into the spectrometer, and therefore many of the spectra of bromine and iodine monobromide adducts showed hydrolysis products.

(j) Analyses

Microanalyses for carbon, hydrogen and nitrogen were performed in the Chemistry Department of St. Andrews University on a Perkin-Elmer model 240 Elemental Analyzer by Mr James Bews.

Analysis for phosphorus was performed by Alfred Bernhardt of West Germany.

Halogen analyses were carried out potentiometrically using an adaption of the method described by Lingane¹⁵⁸. Approximately 50 mg of sample was accurately weighed into a stoppered 50 ml quickfit conical flask. The sample was then hydrolysed with 20 ml of 2M sodium hydroxide (an excess), the hydrolysis being performed in a closed system to prevent the possible escape of hydrogen halide. The solution was allowed to stand for one hour before boiling for twenty minutes to ensure complete hydrolysis. It was then cooled, made just acidic with conc sulphuric acid before immediate treatment with sulphur dioxide to reduce any hypohalite ion present. The excess sulphur dioxide was boiled off and the solution was made neutral with conc ammonia. The solution was transferred to a 100 ml beaker along with washings using distilled water, 2.4 g A.R. barium nitrate added, followed by 10 ml A.R. acetone, and 3-5 drops of boiled out 6 N nitric acid, before titrating against 0.1 M silver nitrate. The solution was stirred for the duration of the titration by a magnetic stirrer. A silver wire was used as an indicator electrode and a calomel electrode as reference electrode, the salt bridge to the latter containing 3M NH_4NO_3 solution.

The electrode potential (mV) of the initial halide solution was determined, and corresponding measurements taken at intervals of 0.1 ml addition of silver nitrate from the burette. A more rapid increase in the change in potential signified that the end-point was being approached, and the potential readings were taken at more frequent intervals. A graph was plotted of mV readings against ml of silver nitrate added, the points of inflection being regarded as the end-points of the titration.

NOTE:- Good analytical data were not obtained for some of the compounds reported in this thesis, partly because of the inherent instability of these compounds at room temperature, and partly because of experimental difficulties.

2. Source and Purification of Materials

(a) Solvents

(i) Methyl Cyanide: Pure anhydrous methyl cyanide suitable for conductance studies was prepared by a modification of the method described by Smith and Witten¹⁵⁹. The commercial material (Hopkins and Williams) was stirred over potassium hydroxide pellets for twenty-four hours. It was then filtered and distilled on to calcium chloride (14-20 mesh) before stirring for a further twenty-four hours. It was again filtered before being repeatedly and alternately refluxed over, and distilled on to, phosphorus pentoxide until dry, when the P_2O_5 did not cake and turn yellow, but formed a fine suspension in the liquid. Finally, after adding some fresh P_2O_5 , the methyl cyanide was refluxed and distilled on to oven dried Type 4A Molecular Sieves, using a nine inch column of glass helices. The fraction boiling between $81-82^{\circ}C$ was collected. The dry solvent was distilled on the vacuum line as required, to remove any traces of sieve powder. The specific conductance of methyl cyanide purified by this method was always ca. 10^{-7} ohm⁻¹ at $25^{\circ}C$.

(ii) Nitrobenzene: AR grade nitrobenzene was distilled twice, once at atmospheric pressure, when the fraction boiling at $207-208^{\circ}C$ was collected, and the other at reduced pressure (2.5 mm Hg) incorporating a nitrogen leak and a fourteen inch Vigreux column. The fraction boiling at $62^{\circ}C$ was collected. The specific conductance of this nitrobenzene was less than 10^{-7} ohm⁻¹ cm⁻¹ at $25^{\circ}C$.

(iii) Carbon Tetrachloride: Pure carbon tetrachloride was obtained by a variation of the method of Popov and Schmor⁵⁰. The crude

solvent (500 ml) was refluxed for ten hours with a saturated solution of potassium permanganate in 2M sodium hydroxide solution (100 ml). The carbon tetrachloride was then separated and washed several times with water. After a preliminary drying with anhydrous magnesium sulphate, the carbon tetrachloride was filtered and distilled onto phosphorus pentoxide, and then distilled several times onto fresh P_2O_5 . The fraction boiling between 75.5-76.0°C was collected.

(iv) Diethyl Ether: Diethyl ether was preliminary dried over calcium chloride before adding sodium wire. The ether was allowed to stand over the sodium wire for several days before use.

(b) Reagents

(i) Bromine: AR bromine was first stored over calcium bromide. It was filtered into a small flask under a nitrogen hood, attached to the vacuum system and pumped off to remove the more volatile impurities. The bromine was then cooled to ca. $-3^{\circ}C$ and distilled in vacuo into small ampoules cooled to liquid nitrogen temperature. Thus, known weights of bromine were stored in sealed ampoules. Solutions were made by breaking a given ampoule under a known weight of solvent.

(ii) Iodine: AR grade iodine was resublimed and stored in a desiccator over phosphorus pentoxide.

(iii) Iodine Monobromide: Iodine monobromide was always freshly prepared before use by breaking a bromine ampoule alongside its

molar equivalent of finely powdered iodine, under a known weight of solvent.

(c) Starting Materials

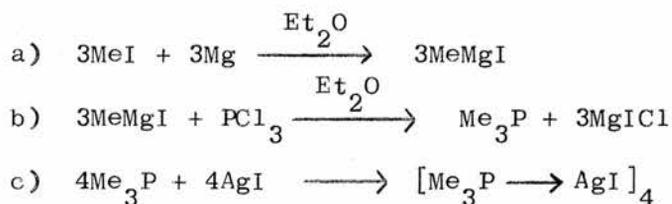
(i) Diphenylmethylphosphine: The commercial grade material (from Maybridge Research Chemicals, Launceston, Cornwall) was redistilled once under reduced pressure using a nitrogen leak. The fraction collected had b.p. range 113-114°C/0.5 mm.

(ii) Dimethylphenylphosphine: The commercial grade material (also from Maybridge Research Chemicals, Launceston, Cornwall) was redistilled once at the water pump using a nitrogen leak. The fraction collected had b.p. range 81-82°C/13 mm.

(iii) Trimethylphosphine: Trimethylphosphine was prepared by the method outlined by Mann and Wells¹⁶⁰, and because of its extreme reactivity it was prepared by making the silver iodide adduct $[\text{Me}_3\text{P} \rightarrow \text{AgI}]_4$. Methyl iodide was distilled (b.p. 43°C); ether was dried over calcium chloride for 24 hours, then filtered and sodium wire added before refluxing for one hour followed by distillation (b.p. 34.5°C). The ether was stored over fresh sodium wire. High purity magnesium turnings suitable for Grignard reagents were used. 24 g (1 mole) Magnesium turnings and 200 ml diethyl ether were placed in a one litre three-necked flask equipped with a teflon paddle stirrer, condenser, dropping funnel and nitrogen inlet. A solution of 138 g (1 mole) methyl iodide in 100 ml diethyl ether was added slowly with constant stirring over a period of ninety minutes. The mixture was cooled to ca. -65°C (ethanol-Drikold bath) and 22.5 g (0.16 mole) phosphorus

trichloride in 50 ml diethyl ether was slowly added with vigorous stirring. Beg and Clark¹⁶¹ state that the reaction normally gives low yields, but it was found that, with strong cooling of the reaction vessel in ethanol/Drikold, yields of 60% could be achieved. The flask was allowed to attain room temperature before distillation from an oil bath was commenced, the temperature of which was finally taken to 210°C until no further distillate was obtained. The ethereal distillate was, without delay, shaken with a solution of silver iodide in aqueous potassium iodide solution. The white solid was filtered, washed with water until the washings were clear and air dried. This silver iodide derivative is too unstable to be recrystallised and must be protected from light. The overall reaction scheme is:

is:



The solid was heated under vacuum to 100°C to drive off any moisture. The temperature was gradually raised to 210°C to decompose the complex, the condensate being collected in a freeze drying apparatus. The colourless volatile liquid was placed in weighed ampoules, similar to those used for bromine, to facilitate handling. (Found: C, 47.42; H, 12.11%. Me_3P requires C, 47.36; H, 11.92%.)

(iv) Methylene-bis-diphenylphosphine: The methylene-bis-diphenylphosphine (BDH Ltd, Poole) was pumped on the vacuum line for several hours to remove any volatile impurities and moisture. M.p. 117.5-118°C. (Found: C, 78.02; H, 5.73%. $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ requires C, 78.11; H, 5.77%.)

(v) Ethylene-bis-diphenylphosphine: The phosphine was also purchased from BDH Ltd, Poole. Volatile impurities and moisture were removed by pumping on the vacuum line for several hours. M.p. 139-140°C. (Found: C, 78.37; H, 6.29%. $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ requires C, 78.38; H, 6.07%.)

3. Preparations of Phosphine-Halogen Adducts

All the procedures described in the following preparations were performed in the nitrogen filled dry-box. Samples were transferred between the dry-box and vacuum line and vice versa using a sealed adaptor to avoid contact with moisture.

(a) Part 1 : A. Diphenylmethylphosphine adducts

(i) Br₂-Ph₂MeP

Mole ratio Br₂:Ph₂MeP = 0.5:1. Bromine (0.061 g) was dissolved in methyl cyanide (5 ml) and added slowly to diphenylmethylphosphine (0.1528 g). The resulting solution was colourless, and as addition of dry diethyl ether or carbon tetrachloride failed to produce a precipitate, it was freeze dried. An unstable white solid was produced which was believed to be contaminated by unreacted phosphine. M.p. 139-143°C. (Found: C, 52.15; H, 4.67. Ph₂MePBr₂ requires C, 43.37; H, 3.64%.)

Mole ratio Br₂:Ph₂MeP = 1:1. The procedure directly above was repeated, with a mole ratio Br₂:Ph₂MeP = 1:1. Again a colourless solution was formed and as normal methods of inducing precipitation failed, the solution was freeze dried leaving a white crystalline solid. The solid was washed with a small amount of carbon tetrachloride in an attempt to remove any unreacted phosphine. Repeated pumping on the vacuum line failed to remove the last traces of methyl cyanide. M.p. 145-153°C decomp. (Found: C, 45.02; H, 3.55; N, 0.45; Br, 40.88. Ph₂MePBr₂ requires C, 43.37; H, 3.64; Br, 44.39%.) UV spectrum - no trihalide ion absorption.

Mole ratio Br₂:Ph₂MeP = 2:1. An excess of bromine dissolved in methyl cyanide was added slowly to diphenylmethylphosphine (Br₂:Ph₂MeP = 4:1). The orange solution was freeze dried as addition of carbon tetrachloride or diethyl ether failed to produce

any precipitate. The excess bromine evaporated off on pumping for several hours leaving an orange crystalline solid. M.p. 60-63°C. (Found: C, 30.05; H, 2.33; Br, 59.50. $\text{Ph}_2\text{MePBr}_4$ requires C, 30.04; H, 2.52; Br, 61.48%.) UV spectrum shows Br_3^- ions (peak at $\lambda_{\text{max}} = 271 \text{ m}\mu$).

(ii) $\text{I}_2\text{-Ph}_2\text{MeP}$

Mole Ratio $\text{I}_2:\text{Ph}_2\text{MeP} = 0.5:1$. Solid iodine (0.4560 g) was added to a suspension of diphenylmethylphosphine (0.7223 g) in methyl cyanide (10 ml). A black tar was formed initially which on shaking gradually disappeared to give a pale yellow solution and on standing pale yellow crystals were deposited. These were filtered off and washed with dry ether. This compound was analysed immediately as the solid darkened to a pale brown colour in a matter of minutes even though it was within the confines of the dry-box. M.p. 182-187°C, decomp. (Found: C, 34.31; H, 2.78. Ph_2MePI_2 requires C, 34.39; H, 2.89%.)

Mole Ratio $\text{I}_2:\text{Ph}_2\text{MeP} = 1:1$. Iodine (0.9598 g) was added to a suspension of diphenylmethylphosphine (0.7580 g) in methyl cyanide (10 ml). A black tar was formed which slowly disappeared on shaking to give a port coloured solution. Addition of dry ether produced pale yellow crystals and a dark red mother liquor. The crystals were filtered off and washed with dry ether. Again the compound was analysed immediately because it darkened quickly. M.p. 184-188°C, decomp. (Found: C, 34.45; H, 2.78; I, 55.46. Ph_2MePI_2 requires C, 34.39; H, 2.89; I, 55.90%.) UV spectrum shows traces of I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $362 \text{ m}\mu$).

Mole ratio $\text{I}_2:\text{Ph}_2\text{MeP} = 2:1$. see page 177

(iii) IBr-Ph₂MeP

Mole Ratio IBr:Ph₂MeP = 1:1. An equimolar solution of iodine monobromide in methyl cyanide was added to diphenylmethylphosphine to give a pale yellow solution. Again carbon tetrachloride or ether failed to induce precipitation and the solution was freeze dried to give a pale yellow solid. This solid was pumped to remove traces of methyl cyanide and as a direct consequence, loss of halogen occurred. M.p. 50-55°C decomp. (Found: C, 40.82; H, 3.39; N, 0.56; I, 29.16; Br, 17.57. Ph₂MePIBr requires C, 38.36; H, 3.22; I, 31.18; Br, 19.63%) UV spectrum shows no trihalide ion absorption even on standing.

Mole Ratio IBr:Ph₂MeP = 2:1. The procedure directly above was repeated using a mole ratio IBr:Ph₂MeP = 2:1. The resulting red solution was freeze dried to give a dark red oil. This oil was repeatedly pumped on the vacuum line to remove traces of solvent with the result that halogen was also pumped off. The oil when cooled solidified, but returned to an oil just below room temperature. (Found: C, 26.35; H, 2.45; N, 0.86; I, 40.61. Ph₂MePI₂Br₂ requires C, 25.44; H, 2.13; I, 41.36%). UV spectrum contains peaks at $\lambda_{\max} = 286$ and $358 \text{ m}\mu$ (I₂Br⁻ plus other trihalides).

Part 1 : B. Dimethylphenylphosphine adducts

(i) Br₂-PhMe₂P

Mole Ratio Br₂:PhMe₂P = 0.5:1. A solution of bromine dissolved in methyl cyanide was added to dimethylphenylphosphine in the mole ratio Br₂:PhMe₂P = 0.5:1. Clouds of dense white fumes were produced, which slowly disappeared on shaking, and the reaction was exothermic. A white solid formed immediately leaving a colourless solution. The solid was filtered off and washed with

a little ether. M.p. 243-245°C. (Found: C, 32.22; H, 3.70.

$\text{PhMe}_2\text{PBr}_2$ requires C, 32.25; H, 3.72%.)

Mole ratio $\text{Br}_2:\text{PhMe}_2\text{P} = 1:1$. Equimolar quantities of bromine and dimethylphenylphosphine were combined using the same procedure outlined for $\text{Br}_2-\text{PhMe}_2\text{P} = 0.5:1$. A white solid was precipitated immediately leaving a colourless solution. The solid, after filtration, was washed with dry ether and on standing slowly turned pale yellow, due to decomposition. M.p. 239-242°C. (Found: C, 32.63; H, 3.89; Br, 54.01. $\text{PhMe}_2\text{PBr}_2$ requires C, 32.25; H, 3.72; Br, 53.63%.) UV spectrum shows absence of trihalide ions.

Mole ratio $\text{Br}_2:\text{PhMe}_2\text{P} = 2:1$. When a 2:1 mole ratio ($\text{Br}_2:\text{PhMe}_2\text{P}$) solution was prepared a white precipitate (obviously $\text{PhMe}_2\text{PBr}_2$) appeared immediately coupled with clouds of dense white fumes. This precipitate was dissolved by shaking for one hour to give an orange solution. Normal methods failed to produce a solid 2:1 compound and therefore the solution was freeze dried, whereupon fractional crystallisation occurred. The 2:1 compound was deposited as orange crystals on the side of the flask, and a white solid appeared on the bottom of the flask. M.p. 69-73°C. (Found: C, 20.47; H, 2.66; Br, 68.09. $\text{PhMe}_2\text{PBr}_4$ requires C, 20.99; H, 2.42; Br, 69.82%.) UV spectrum shows Br_3^- ions ($\lambda_{\text{max}} = 270 \text{ m}\mu$).

(ii) $\text{I}_2-\text{PhMe}_2\text{P}$

Mole ratio $\text{I}_2:\text{PhMe}_2\text{P} = 0.5:1$. Iodine solution was added to dimethylphenylphosphine in the mole ratio of $\text{I}_2:\text{PhMe}_2\text{P} = 0.5:1$. An exothermic reaction resulted and clouds of white fumes were produced which gradually disappeared on shaking to leave a pale yellow solution and a pale yellow solid. The solid was filtered off and washed with ether to give a white solid which was extremely unstable, losing bromine readily. M.p. 200-225°C. (Found: C, 31.44; H, 3.94. PhMe_2PI_2 requires C, 24.52; H, 2.83%.)

Mole ratio $I_2:PhMe_2P = 1:1$. The above method was repeated using equimolar quantities of iodine and phosphine. The pale yellow solid, after filtration, was washed with ether to give a white solid which turned pale yellow on the surface even in the dry-box. M.p. 224-228°C. (Found: C, 24.32; H, 2.67; I, 61.90. $PhMe_2PI_2$ requires C, 24.52; H, 2.83; I, 64.75%.) UV spectrum shows traces of I_3^- ion ($\lambda_{max} = 293$ and 361 m μ).

Mole ratio $I_2:PhMe_2P = 2:1$. Iodine solution was added to the phosphine in the mole ratio $I_2:PhMe_2P = 2:1$ giving a reddish-black solution, but no precipitate, even on ether addition. The solution was freeze dried whereupon a dark brown solid was obtained. M.p. 75-80°C decomp. (Found: C, 14.54; H, 1.71; I, 77.13. $PhMe_2PI_4$ requires C, 14.88; H, 1.72; I, 78.61%.) UV spectrum showed I_3^- ions ($\lambda_{max} = 296$ and 361 m μ).

(iii) $IBr-PhMe_2P$

Mole ratio $IBr:PhMe_2P = 1:1$. On mixing equimolar solutions of phosphine and iodine monobromide in methyl cyanide dense yellow fumes were formed. These slowly disappeared on shaking to leave a pale yellow solid and a pale yellow solution. The precipitate was filtered off and washed with ether to give a pale yellow solid which turned orange due to decomposition. M.p. 205-207°C. (Found: C, 28.32; H, 3.31; I, 35.55; Br, 23.05. $PhMe_2PIBr$ requires C, 27.85; H, 3.21; I, 36.79; Br, 23.16%.) UV shows traces of I_3^- (peaks at $\lambda_{max} = 291$ and 361 m μ).

Mole ratio $IBr:PhMe_2P = 2:1$. When a solution of iodine monobromide was added to the phosphine in the mole ratio $IBr:PhMe_2P = 2:1$, a pale yellow solid was immediately precipitated and clouds of white and pale yellow fumes were formed. The solid was dissolved by shaking for one hour. Addition of ether failed to produce a precipitate and therefore the solution was freeze dried to give a

dark brown solid. M.p. 73-75°C. (Found: C, 17.87; H, 1.98; I, 40.37; Br, 31.72. $\text{PhMe}_2\text{PI}_2\text{Br}_2$ requires C, 17.41; H, 2.01; I, 46.00; Br, 28.96%.) Note: Co-precipitation of bromide and iodide occurred resulting in low iodine and high bromine percentages. UV spectrum shows I_2Br^- ions (peaks at $\lambda_{\text{max}} = 281$ and 350 m μ).

Part 1 : C. Trimethylphosphine adducts

(i) $\text{Br}_2\text{-Me}_3\text{P}$

Mole ratio $\text{Br}_2\text{:Me}_3\text{P} = 0.5\text{:}1$. Methyl cyanide solutions of bromine and trimethylphosphine in the mole ratio 0.5:1 were mixed. The reaction was exothermic and clouds of white fumes were evolved. A white precipitate was immediately formed along with a colourless solution. This solid was filtered off and washed with ether. (Found: C, 21.35; H, 6.37. $(\text{Me}_3\text{P})_2\text{Br}_2$ requires C, 23.10; H, 5.82%.) The filtrate was treated with an excess of ether to produce a white precipitate which was filtered and washed with ether. M.p. 159-160°C. (Found: C, 22.46; H, 6.67; Br, 50.39. $(\text{Me}_3\text{P})_2\text{Br}_2$ requires C, 23.10; H, 5.82; Br, 51.23%.)

Mole ratio $\text{Br}_2\text{:Me}_3\text{P} = 1\text{:}1$. When equimolar solutions of bromine and trimethylphosphine in methyl cyanide were mixed an exothermic reaction ensued accompanied by clouds of white fumes and a white solid was formed. After shaking overnight the white solid was filtered from the colourless mother liquor and washed with dry ether. M.p. 308-316°C decomp. (Found: C, 14.89; H, 3.90; Br, 66.01. Me_3PBr_2 requires C, 15.27; H, 3.85; Br, 67.75%.)

Mole ratio $\text{Br}_2\text{:Me}_3\text{P} = 2\text{:}1$. Bromine (1.0146 g) was added to a suspension of trimethylphosphine (0.2405 g) in methyl cyanide (10 ml). The resulting orange solution was freeze dried as

attempts to obtain precipitation using ether were unsuccessful. An orange solid remained and this was pumped on the vacuum line for forty-five minutes. M.p. 82-85°C decomp. (Found: C, 10.14; H, 2.74; Br, 79.08. Me_3PBr_4 requires C, 9.11; H, 2.29; Br, 80.77%.) UV shows strong Br_3^- ($\lambda_{\text{max}} = 270 \text{ m}\mu$).

Atmospheric Hydrolysis of the Bromides of Trimethylphosphine

$\text{Me}_3\text{P(OH)Br}$: During the preparation of Me_3PBr_2 the mother liquor left after obtaining Me_3PBr_2 was treated with a large excess of ether and allowed to stand in the dry-box. The resulting white precipitate was filtered off and allowed to sit in the filter for some time when it appeared to darken slightly, becoming off-white. M.p. 126-128°C decomp. (Found: C, 20.83; H, 5.83. $\text{Me}_3\text{P(OH)Br}$ requires C, 20.02; H, 5.76%.)

$\text{Me}_3\text{P(OH)Br}_3$: If minute traces of moisture were present during the preparation of Me_3PBr_4 then the compound $\text{Me}_3\text{P(OH)Br}_3$ was formed as an orange solid. UV studies showed Br_3^- ions ($\lambda_{\text{max}} = 269 \text{ m}\mu$) and infrared spectra indicated that the structure was $\text{Me}_3\text{POH}^+\text{Br}_3^-$. (Found: C, 10.24; H, 2.93. $\text{Me}_3\text{P(OH)Br}_3$ requires C, 10.83; H, 3.03%.)

(ii) $\text{HgBr}_2 \cdot \text{Me}_3\text{P}$

A solution of mercuric bromide (1.2294 g) in methyl cyanide (20 ml) was added to a suspension of trimethylphosphine (0.2587 g) in methyl cyanide (10 ml). A white precipitate was immediately formed leaving a colourless solution. The solid was filtered off and washed twice with ether before pumping on the vacuum line for four hours. M.p. 239-240°C. (Found: C, 7.72; H, 2.02; Br, 35.67. $\text{Me}_3\text{PHgBr}_2$ requires C, 8.25; H, 2.08; Br, 36.61%.)

(iii) Br₂-Me₃PHgBr₂-

Mole ratio Br₂:Me₃PHgBr₂ = 0.5:1. Bromine (0.027 g) dissolved in methyl cyanide (3.5 ml) was added to a suspension of Me₃PHgBr₂ (0.1484 g) in methyl cyanide (10 ml). The solid gradually dissolved on shaking and the bromine was decolourised. Addition of an excess of ether produced a white solid precipitate which was filtered off and washed with ether. M.p. 137-139°C.

(Found: C, 9.78; H, 2.83. (Me₃P)₂HgBr₄ requires C, 10.72; H, 2.70%.)

Mole ratio Br₂:Me₃PHgBr₂ = 1:1. Equimolar solutions of bromine and Me₃PHgBr₂ were mixed together and treated in the same way as above. The resulting white solid was filtered off and washed with ether. M.p. 143-144°C. (Found: C, 8.90; H, 2.51; Br, 56.16.

(Me₃P)₂HgBr₆ requires C, 8.66; H, 2.18; Br, 57.61%.)

(iv) I₂-Me₃P

Mole ratio I₂:Me₃P = 0.5:1. On mixing methyl cyanide solutions of the two reagents (in the 0.5:1 mole ratio), an exothermic reaction occurred producing white fumes and a white solid was precipitated. The solid was filtered off and washed twice with ether. M.p. 242-244°C. (Found: C, 18.01; H, 4.80; I, 62.82.

(Me₃P)₂I₂ requires C, 17.75; H, 4.47; I, 62.52%.)

Mole ratio I₂:Me₃P = 1:1. Direct mixing of methyl cyanide solutions of the reagents in the above mole ratio produced an exothermic reaction, with clouds of white fumes. These disappeared on shaking and a yellow precipitate was observed in an iodine coloured solution. The precipitate was filtered off and washed with dry ether to give a white solid which turned pale yellow due to decomposition. M.p. 305-306°C. (Found: C, 10.66; H, 2.75; I, 76.70. Me₃PI₂ requires C, 10.92; H, 2.75; I, 76.94%.) The

UV spectrum showed minute traces of I_3^- ($\lambda_{\max} = 292$ and 357 m μ).
Mole ratio $I_2:Me_3P = 2:1$. Iodine (1.2829 g) dissolved in methyl cyanide (14 ml) was added to trimethylphosphine (0.1889 g) in methyl cyanide (10 ml). The solution became warm and clouds of white fumes were evolved. The black solution was freeze dried as ether precipitation failed. Crystals with a reddish tinge were observed on the walls of the flask above the level of the solution during freeze drying, however, when the flask was allowed to attain room temperature these crystals went into an oil and joined the bulk of the solution. The remaining solvent was removed and the resulting product was pumped for two hours. A soft reddish-black crystalline solid was present. M.p. $28-34^\circ C$ decomp. (Found: C, 6.00; H, 1.69; I, 85.49. Me_3PI_4 requires C, 6.17; H, 1.55; I, 86.97%.) The UV spectrum showed I_3^- ions (peaks at $\lambda_{\max} = 292$ and 363 m μ).

(v) $I\text{Br}-Me_3P$

Mole ratio $I\text{Br}:Me_3P = 1:1$. Equimolar solutions of iodine monobromide and trimethylphosphine in methyl cyanide were mixed together. Clouds of white fumes were evolved and the solution became warm. After shaking, a deep red solution was observed along with a pale yellow precipitate. This precipitate was filtered off and discarded. An excess of ether was added to the mother liquor and a pale yellow solid was precipitated. This was filtered off and washed with ether. M.p. $288-289^\circ C$. (Found: C, 12.55; H, 3.48; I, 53.22; Br, 23.56, total halogen 1.01 moles. $Me_3PI\text{Br}$ requires C, 12.74; H, 3.21; I, 44.86; Br, 28.25%, total halogen 1.00 moles.) UV spectrum shows traces of I_3^- ($\lambda_{\max} = 292$ and 360 m μ).

Mole ratio IBr:Me₃P = 2:1. On mixing directly methyl cyanide solutions of the two reagents in the 2:1 mole ratio, no precipitate appeared. The solution became warm and clouds of white fumes were evolved. After preliminary degassing, the solvent was removed by vacuum distillation, leaving a reddish-brown soft solid. This solid was washed with ether and pumped for five hours on the vacuum line to give a viscous oily solid. (Found: C, 8.02; H, 2.21; N, 0.23; I, 47.73; Br, 32.70; total halogen 1.93 moles. Me₃PI₂Br₂ requires C, 7.36; H, 1.85; I, 51.83; Br, 32.64%, total halogen 2.00 moles.) UV spectrum indicates I₂Br⁻ ions ($\lambda_{\text{max}} = 271 \text{ m}\mu$).

(b) Part 2 : A. Methylene-bis-diphenylphosphine adducts

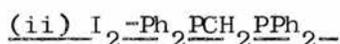
(i) Br₂-Ph₂PCH₂PPh₂-

Mole ratio Br₂:Ph₂PCH₂PPh₂ = 0.5:1. Addition of bromine dissolved in methyl cyanide to the phosphine in the mole ratio Br₂:Ph₂PCH₂PPh₂ = 0.5:1 produced a colourless solution. A white solid was obtained after freeze drying and this was pumped for forty-five minutes on the vacuum line. M.p. 74-76^oC. (Found: C, 62.80; H, 5.10; Br, 16.82. (Ph₂PCH₂PPh₂)₂Br₂ requires C, 64.67; H, 4.78; Br, 17.21%.)

Mole ratio Br₂:Ph₂PCH₂PPh₂ = 1:1. The procedure directly above was repeated, with the mole ratio Br₂:Ph₂PCH₂PPh₂ = 1:1. A hard white crystalline solid was formed when the solution was freeze dried to remove excess solvent. M.p. 82-84^oC. (Found: C, 55.10; H, 5.00; N, 2.04; Br, 29.80. Ph₂PCH₂PPh₂.Br₂ requires C, 55.18; H, 4.07; Br, 29.37%.)

Mole ratio Br₂:Ph₂PCH₂PPh₂ = 3:1. When a methyl cyanide solution of bromine was added to the phosphine in the mole ratio, 3:1, a

yellow solution was formed followed by the slow formation of a yellow precipitate. This was allowed to stand overnight before filtering off and washing the solid with a little methyl cyanide. M.p. 190-195°C. (Found: C, 45.72; H, 3.64; P, 9.38; Br, 34.27. $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2 \cdot 0.4 \cdot \text{Br}_6$ requires C, 45.77; H, 3.38; P, 9.44; Br, 36.54%.) UV spectrum shows Br_3^- ions ($\lambda_{\text{max}} = 270 \text{ m}\mu$).



Mole ratio $\text{I}_2:\text{Ph}_2\text{PCH}_2\text{PPh}_2 = 0.5:1$. Addition of iodine dissolved in methyl cyanide to the phosphine (mole ratio 0.5:1) produced a yellow solution along with precipitation of a yellow solid. On further shaking this solid disappeared and the solution became colourless. A pale greenish-yellow solid was produced when the solution was freeze dried. M.p. 71-73°C. (Found: C, 57.36; H, 4.55; N, 1.16. $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{I}_2$ requires C, 58.73; H, 4.34%.)

Mole ratio $\text{I}_2:\text{Ph}_2\text{PCH}_2\text{PPh}_2 = 1:1$. Direct mixing of the reagents in the 1:1 mole ratio using methyl cyanide as solvent produced a yellow precipitate. The solid was filtered off, washed with a little methyl cyanide and pumped on the vacuum line to remove traces of solvent. M.p. 151-153°C. (Found: C, 35.82; H, 2.83; I, 57.64. $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$ requires C, 33.66; H, 2.49; I, 56.91%.)

Mole ratio $\text{I}_2:\text{Ph}_2\text{PCH}_2\text{PPh}_2 = 2:1$. Behaviour exactly analogous to the 1:1 mole ratio case was observed. M.p. 178-180°C. (Found: C, 33.43; H, 2.57; I, 55.27. $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$ requires C, 33.66; H, 2.49; I, 56.91%.) UV shows traces of I_3^- ions ($\lambda_{\text{max}} = 292$ and $361 \text{ m}\mu$).

Mole ratio $\text{I}_2:\text{Ph}_2\text{PCH}_2\text{PPh}_2 = 3:1$. Again behaviour was exactly the same as the 1:1 mole ratio case. M.p. 187-188°C. (Found: C, 33.80;

H, 2.47; I, 55.97. $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$ requires C, 33.66; H, 2.49; I, 56.91%.) UV shows traces of I_3^- ($\lambda_{\text{max}} = 292$ and $363 \text{ m}\mu$).

Mole ratio $\text{I}_2:\text{Ph}_2\text{PCH}_2\text{PPh}_2 = 4:1$. When the reagents were mixed in the 4:1 mole ratio in methyl cyanide instant precipitation occurred.

The precipitate was yellow/brown and there was also some dark green compound present. The solution was shaken for ninety minutes whereupon most of the dark green precipitate redissolved and the remainder was separated as it was heavier than the other precipitate. The brown solid was filtered off and washed with a little methyl cyanide. M.p. 149-151. (Found: C, 30.89;

H, 2.24; N, 0.24; I, 56.85. $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_4$ requires C, 33.66; H, 2.49; I, 56.91%.) UV shows I_3^- ions ($\lambda_{\text{max}} = 292$ and $361 \text{ m}\mu$).

Mole ratio $\text{I}_2:\text{Ph}_2\text{PCH}_2\text{PPh}_2 = 6:1$. A dark green precipitate was formed when iodine and phosphine were mixed in the mole ratio 6:1 using methyl cyanide as solvent. The solid was filtered off and the resulting black crystals were washed with a little methyl cyanide and dried. M.p. $151-152^\circ\text{C}$. (Found: C, 17.83;

H, 1.31; I, 75.35. $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{I}_{10}$ requires C, 18.16; H, 1.34; I, 76.75%.) UV shows I_3^- ions ($\lambda_{\text{max}} = 290$ and $360 \text{ m}\mu$).

(iii) $\text{IBr} \cdot \text{Ph}_2\text{PCH}_2\text{PPh}_2$

Mole ratio $\text{IBr}:\text{Ph}_2\text{PCH}_2\text{PPh}_2 = 1:1$. Addition of an equimolar solution of iodine monobromide in methyl cyanide to the phosphine produced an orange-red solution and a dark yellow solid was precipitated. This solid was filtered off and washed with a little methyl cyanide and dried. M.p. $111-113^\circ\text{C}$. (Found: C, 48.08; H, 3.76; N, 1.58; I, 21.27; Br, 13.51. $\text{Ph}_2\text{PCH}_2\text{PPh}_2 \cdot \text{IBr}$ requires C, 50.79; H, 3.75; I, 21.46; Br, 13.52%.)

Mole ratio IBr:Ph₂PCH₂PPh₂ = 2:1. The above procedure was repeated using a 2:1 mole ratio of Br₂:Ph₂PCH₂PPh₂. A brownish-yellow solid was precipitated and after filtration this was washed with a little methyl cyanide before drying. M.p. 132-133°C.

(Found: C, 38.45; H, 3.09; N, 0.59; I, 29.65; Br, 19.05.

Ph₂PCH₂PPh₂.I₂.Br₂ requires C, 37.63; H, 2.78; I, 31.80, Br, 20.03%.)

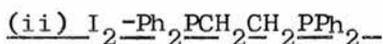
Mole ratio IBr:Ph₂PCH₂PPh₂ = 3:1. A yellow/brown solid was precipitated when iodine monobromide and phosphine (3:1 mole ratio) were mixed in methyl cyanide. The precipitate was treated in the same way as above. M.p. 132-133°C. (Found: C, 39.78; H, 3.37; I, 16.70; Br, 28.39. Ph₂PCH₂PPh₂.IBr₃ requires C, 39.98; H, 2.95; I, 16.90; Br, 31.93%.)

Part 2 : B. Ethylene-bis-diphenylphosphine adducts

(i) Br₂-Ph₂PCH₂CH₂PPh₂-

Mole ratio Br₂:Ph₂PCH₂CH₂PPh₂ = 1:1. On mixing Ph₂PCH₂CH₂PPh₂ and Br₂ in the 1:1 mole ratio in methyl cyanide, a white solid came down. The solid was filtered off and washed with a little methyl cyanide before drying. M.p. 206-208°C. (Found: C, 54.63; H, 4.69; Br, 29.84. Ph₂PCH₂CH₂PPh₂.Br₂ requires C, 55.94; H, 4.33; Br, 28.63%.)

Mole ratio Br₂:Ph₂PCH₂CH₂PPh₂ = 4:1. Addition of a methyl cyanide solution of bromine to Ph₂PCH₂CH₂PPh₂ (mole ratio 4:1), did not produce a solid precipitate. The solvent was reduced in volume whereupon orange crystals formed. These were filtered off and dried. M.p. 160-162°C. (Found: C, 44.65; H, 3.90; N, 0.74; Br, 44.34. Ph₂PCH₂CH₂PPh₂.Br₄ requires C, 43.49; H, 3.37; Br, 44.51%.)
UV shows tribromide ions ($\lambda_{\max} = 260 \text{ m}\mu$).



Mole ratio $\text{I}_2\text{:Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 = 1\text{:}1$. An equimolar solution of the above reagents was allowed to stand overnight. Yellow crystals were deposited from an orange/red solution and following filtration were pumped on the vacuum line. M.p. 159-161°C. (Found: C, 44.59; H, 3.93; I, 40.92; a trace of N was also detected. $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{I}_2$ requires C, 47.88; H, 3.71; I, 38.91%).

Mole ratio $\text{I}_2\text{:Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 = 2\text{:}1$. No solid was obtained when methyl cyanide solutions of the above reagents were mixed. The solvent volume was reduced whereupon a little brown solid was precipitated. This solid was filtered off, washed with methyl cyanide, and dried. M.p. 148-149°C. (Found: C, 34.87; H, 3.02; N, 0.92. $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{I}_4$ requires C, 34.47; H, 2.67%.) UV spectrum shows I_3^- ions ($\lambda_{\text{max}} = 291$ and $362 \text{ m}\mu$).

Mole ratio $\text{I}_2\text{:Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 = 4\text{:}1$. When methyl cyanide solutions of the above reagents were mixed, no solid precipitate was formed. The solution was freeze dried to give a reddish brown soft solid. The last traces of methyl cyanide could not be removed by pumping on the vacuum line. (Found: C, 24.10; H, 2.37; N, 2.63; I, 70.68. $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{I}_8$ requires C, 22.09; H, 1.71; I, 71.82%.) UV spectrum shows strong I_3^- absorption ($\lambda_{\text{max}} = 290$ and $359 \text{ m}\mu$).

Mole ratio $\text{I}_2\text{:Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 = 5\text{:}1$. Again no solid precipitate was obtained when methyl cyanide solutions were mixed. The solvent volume was reduced by vacuum distillation whereupon a reddish brown solid separated out. This was filtered off and pumped on the vacuum line, however, traces of methyl cyanide were present. M.p. 112-114°C. (Found: C, 23.32; H, 1.96; N, 0.42; I, 70.19. $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\cdot\text{I}_8$ requires C, 22.09; H, 1.71, I. 71.82%.) UV shows I_3^- ($\lambda_{\text{max}} = 291$ and $359 \text{ m}\mu$).

(iii) $\text{IBr} \cdot \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$

Mole ratio $\text{IBr}:\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 = 1:1$. A pale yellow solid was formed when equimolar solutions of the above reagents were mixed and allowed to stand overnight. The solid was filtered off and washed with methyl cyanide, leaving a white solid which was dried in the dry-box. M.p. 206-208°C. (Found: C, 54.19; H, 4.57; Br, 28.48. $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_2$ requires C, 54.63; H, 4.69; Br, 28.63%.)

Mole ratio $\text{IBr}:\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 = 2:1$. A 2:1 mole ratio mixture of IBr and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, using methyl cyanide as solvent, was allowed to stand for several days. Yellow crystals were formed, and after filtration they were washed with a little methyl cyanide before pumping on the vacuum line to remove the last traces of solvent. M.p. 198-199°C. (Found: C, 44.53; H, 3.77; Br, 43.72. $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \cdot \text{Br}_4$ requires C, 43.49; H, 3.37; Br, 44.51%.)

Mole ratio $\text{I}_2:\text{Ph}_2\text{MeP} = 2:1$. Iodine (0.7231 g) dissolved in methyl cyanide (12 ml) was added slowly to diphenylmethylphosphine (0.2806 g). After shaking a black solution resulted. Addition of ether and carbon tetrachloride produced no precipitation, however, black oils were observed. The solution was therefore freeze dried to give a black semi-crystalline solid, which was pumped for about six hours to remove the solvent.

(Found: C, 22.39; H, 1.96; N, 0.34; I, 68.47. Ph_2MePI_4 requires C, 22.06; H, 1.85; I, 71.71%.) UV spectrum shows strong triiodide ion absorption (peaks at $\lambda_{\text{max}} = 291$ and $363 \text{ m}\mu$).

4. Experimental Data

(a) Conductometric Titration Data of the Systems R_3P-X_2 in Various Solvents

Table 22 : Br_2-Ph_2MeP in Methyl Cyanide

Mole Ratio $Br_2: Ph_2MeP$	$K \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$	Mole Ratio $Br_2: Ph_2MeP$	$K \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$	Mole Ratio $Br_2: Ph_2MeP$	$K \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$	Mole Ratio $Br_2: Ph_2MeP$	$K \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$
0.000	0.007	1.063	11.24	2.048	15.78	2.981	22.03
0.039	2.31	1.140	11.21	2.125	16.63	3.085	22.26
0.130	5.64	1.218	11.10	2.229	17.50	3.162	22.37
0.246	8.54	1.335	11.13	2.320	18.47	3.240	22.49
0.324	10.33	1.426	11.27	2.424	19.29	3.305	22.60
0.428	10.56	1.516	11.70	2.514	20.00	3.396	22.72
0.518	10.51	1.620	12.19	2.566	20.28	3.499	22.84
0.583	10.51	1.685	12.65	2.644	20.67	3.564	22.96
0.674	10.61	1.776	13.23	2.722	21.17	3.629	22.96
0.778	10.82	1.866	14.00	2.799	21.48	3.707	23.08
0.881	11.10	1.944	14.86	2.903	21.81	3.784	23.08
0.972	11.30						

Table 23 : I_2-Ph_2MeP in Methyl Cyanide

Mole Ratio $I_2: Ph_2MeP$	$K \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$	Mole Ratio $I_2: Ph_2MeP$	$K \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$	Mole Ratio $I_2: Ph_2MeP$	$K \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$	Mole Ratio $I_2: Ph_2MeP$	$K \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$
0.000	0.005	1.122	15.61	2.155	22.03	3.099	22.03
0.118	4.77	1.210	16.07	2.243	22.37	3.188	21.92
0.221	9.31	1.299	16.69	2.332	22.37	3.276	21.81
0.339	13.44	1.387	17.29	2.435	22.49	3.365	21.70
0.472	13.82	1.476	18.16	2.509	22.49	3.438	21.59
0.590	13.78	1.564	18.95	2.612	22.49	3.527	21.48
0.679	13.78	1.653	19.64	2.686	22.26	3.616	21.38
0.753	14.00	1.741	20.00	2.774	22.26	3.704	21.17
0.856	14.37	1.800	20.28	2.863	22.26	3.778	21.17
0.944	14.71	1.904	20.76	2.937	22.26	3.866	21.07
1.048	15.12	1.977	21.27	3.011	22.14	3.970	20.97

Table 24 : IBr-Ph₂MeP in Methyl Cyanide

Mole Ratio IBr: Ph ₂ MeP	K 10 ⁴ x 10 ⁻¹ ohm ⁻¹ cm ⁻¹	Mole Ratio IBr: Ph ₂ MeP	K 10 ⁴ x 10 ⁻¹ ohm ⁻¹ cm ⁻¹	Mole Ratio IBr: Ph ₂ MeP	K 10 ⁴ x 10 ⁻¹ ohm ⁻¹ cm ⁻¹	Mole Ratio IBr: Ph ₂ MeP	K 10 ⁴ x 10 ⁻¹ ohm ⁻¹ cm ⁻¹
0.000	0.007	0.999	9.10	2.221	15.90	3.283	19.91
0.095	4.21	1.110	9.27	2.316	16.69	3.394	20.00
0.222	7.86	1.205	9.48	2.427	17.64	3.474	20.09
0.285	9.71	1.301	9.75	2.522	18.16	3.569	20.19
0.381	10.53	1.412	10.05	2.601	18.55	3.648	20.28
0.460	10.16	1.554	10.48	2.712	18.87	3.712	20.28
0.539	9.60	1.681	10.99	2.823	19.20	3.807	20.37
0.618	9.27	1.792	11.79	2.950	19.37	3.902	20.37
0.698	9.12	1.887	12.47	3.061	19.73	3.965	20.37
0.793	9.02	1.999	13.48	3.172	19.82	4.061	20.47
0.888	8.98	2.109	14.61				

Table 25 : Br₂-PhMe₂P in Methyl Cyanide - Graph 1

Mole Ratio IBr: PhMe ₂ P	K 10 ⁴ x 10 ⁻¹ ohm ⁻¹ cm ⁻¹	Mole Ratio IBr: PhMe ₂ P	K 10 ⁴ x 10 ⁻¹ ohm ⁻¹ cm ⁻¹	Mole Ratio IBr: PhMe ₂ P	K 10 ⁴ x 10 ⁻¹ ohm ⁻¹ cm ⁻¹	Mole Ratio IBr: PhMe ₂ P	K 10 ⁴ x 10 ⁻¹ ohm ⁻¹ cm ⁻¹
0.000	0.31	1.034	5.68	2.069	13.24	3.104	18.44
0.094	2.95	1.129	6.34	2.163	13.93	3.198	18.70
0.188	4.69	1.223	6.94	2.257	14.63	3.292	19.01
0.282	6.77	1.317	7.59	2.351	15.32	3.386	19.14
0.376	7.33	1.411	8.25	2.445	15.97	3.480	19.40
0.470	6.68	1.505	8.81	2.539	16.49	3.574	19.49
0.564	5.55	1.599	9.50	2.633	16.97	3.668	19.66
0.658	5.08	1.693	10.20	2.727	17.36	3.762	19.79
0.752	4.69	1.787	11.02	2.821	17.58	3.856	19.96
0.846	4.90	1.881	11.72	2.915	17.92	3.981	20.31
0.940	5.21	1.975	12.67	3.010	18.23		

Table 26 : Br₂-PhMe₂P in Methyl Cyanide - Graph 2

Mole Ratio Br ₂ : PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio Br ₂ : PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio Br ₂ : PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio Br ₂ : PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹
0.000	0.74	0.958	16.67	1.829	33.85	2.701	47.26
0.087	8.16	1.045	17.75	1.917	35.76	2.788	48.00
0.174	13.54	1.133	19.10	2.004	37.63	2.875	48.43
0.261	17.40	1.220	20.70	2.091	39.23	2.962	48.74
0.348	20.01	1.307	22.61	2.178	40.88	3.049	49.00
0.436	19.10	1.394	24.39	2.265	42.18	3.136	49.35
0.523	16.71	1.481	26.14	2.352	42.53	3.223	49.43
0.610	16.01	1.568	28.21	2.439	44.66	3.310	49.61
0.697	15.58	1.655	30.12	2.526	45.61	3.398	49.91
0.784	15.23	1.742	31.98	2.614	46.52	3.485	50.17
0.871	15.62						

Table 27 : I₂-PhMe₂P in Methyl Cyanide

Mole Ratio I ₂ : PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio I ₂ : PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio I ₂ : PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio I ₂ : PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹
0.000	0.52	1.104	17.79	2.108	26.82	3.112	25.78
0.100	6.16	1.205	18.66	2.208	26.69	3.212	25.61
0.201	9.94	1.305	19.57	2.309	26.56	3.312	25.43
0.301	13.15	1.405	20.48	2.409	26.56	3.413	25.30
0.401	15.45	1.506	21.61	2.509	26.39	3.513	25.26
0.502	14.45	1.606	23.09	2.610	26.26	3.614	25.13
0.602	14.71	1.706	24.65	2.710	26.17	3.714	25.08
0.703	15.23	1.807	26.04	2.811	26.00	3.814	24.91
0.803	15.80	1.907	26.47	2.911	25.87	3.915	24.82
0.903	16.36	2.008	26.78	3.011	25.78	4.015	24.69
1.004	17.06						

Table 28 : IBr-PhMe₂P in Methyl Cyanide

Mole Ratio IBr: PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio IBr: PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio IBr: PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio IBr: PhMe ₂ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹
0.000	0.06	1.098	9.59	2.195	18.79	3.193	21.01
0.100	3.37	1.197	9.85	2.295	19.18	3.293	21.14
0.200	6.73	1.297	10.59	2.395	19.57	3.393	21.22
0.299	9.55	1.397	11.41	2.495	19.79	3.492	21.27
0.399	10.89	1.497	12.24	2.594	20.09	3.592	21.35
0.499	10.11	1.596	13.45	2.694	20.27	3.692	21.35
0.599	9.72	1.696	14.41	2.794	20.48	3.792	21.40
0.698	9.68	1.796	15.45	2.894	20.61	3.891	21.40
0.798	9.64	1.896	16.45	2.993	20.79	3.991	21.40
0.898	9.55	1.996	17.40	3.093	20.92	4.091	21.40
0.998	9.55	2.095	18.14				

Table 29 : Br₂-Me₃P in Methyl Cyanide

Mole Ratio Br ₂ : Me ₃ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio Br ₂ : Me ₃ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio Br ₂ : Me ₃ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹	Mole Ratio Br ₂ : Me ₃ P	K 10 ⁴ x ohm ⁻¹ cm ⁻¹
0.000	0.08	1.078	15.91	2.058	29.08	3.038	31.82
0.098	5.77	1.176	17.20	2.156	29.71	3.136	32.00
0.196	9.69	1.274	18.46	2.254	30.15	3.234	32.15
0.294	13.13	1.372	20.05	2.352	30.52	3.332	32.30
0.392	15.80	1.470	21.50	2.450	30.78	3.430	32.45
0.490	15.10	1.568	23.09	2.548	31.04	3.528	32.52
0.588	12.84	1.666	24.49	2.646	31.23	3.724	32.74
0.686	13.06	1.764	25.64	2.744	31.41	3.920	32.97
0.784	13.58	1.862	27.12	2.842	31.56	4.116	33.30
0.882	14.10	1.960	28.23	2.940	31.75	4.312	33.60
0.980	14.98						

Table 30 : HgBr_2 - $(\text{Me}_3\text{P})_2\text{Br}_2$ in Methyl Cyanide

Mole Ratio HgBr_2 : $(\text{Me}_3\text{P})_2\text{Br}_2$	10^4 K ohm^{-1} cm^{-1}	Mole Ratio HgBr_2 : $(\text{Me}_3\text{P})_2\text{Br}_2$	10^4 K ohm^{-1} cm^{-1}	Mole Ratio HgBr_2 : $(\text{Me}_3\text{P})_2\text{Br}_2$	10^4 K ohm^{-1} cm^{-1}
0.000	9.96	1.780	17.85	3.382	19.72
0.178	9.45	1.958	19.33	3.560	19.63
0.356	9.62	2.136	20.10	3.738	19.46
0.534	10.47	2.314	20.27	3.916	19.38
0.712	11.49	2.492	20.22	4.094	19.29
0.890	12.80	2.670	20.18	4.272	19.12
1.068	13.99	2.848	20.10	4.450	19.04
1.246	15.05	3.026	19.97	4.628	18.95
1.424	16.11	3.204	19.89	4.806	18.78
1.602	17.13				

Table 31 : HgBr_2 - Me_3PBr_2 in Methyl Cyanide

Mole Ratio HgBr_2 : Me_3PBr_2	10^4 K ohm^{-1} cm^{-1}						
0.000	15.56	0.669	17.93	1.338	23.07	2.007	23.02
0.096	14.33	0.765	18.70	1.434	23.07	2.103	23.02
0.191	13.91	0.860	19.93	1.529	23.07	2.198	22.98
0.287	14.20	0.956	21.11	1.625	23.02	2.294	23.02
0.382	15.01	1.051	22.22	1.720	23.11	2.389	23.07
0.478	15.98	1.147	22.73	1.816	23.02	2.485	23.02
0.573	16.87	1.242	22.98	1.912	23.07	2.581	22.98

Table 32 : I_2 - Me_3P in Methyl Cyanide

Mole Ratio I_2 : Me_3P	$K \times 10^4$ ohm^{-1} cm						
0.000	0.01	0.812	21.54	1.624	29.85	2.639	27.90
0.101	7.08	0.913	22.13	1.725	29.93	2.842	27.35
0.203	13.19	1.015	22.90	1.827	29.76	3.045	26.97
0.304	17.43	1.116	23.74	1.928	29.55	3.248	26.50
0.406	21.24	1.218	24.59	2.030	29.34	3.451	26.16
0.507	20.56	1.319	25.52	2.131	29.17	3.654	25.69
0.609	20.52	1.421	26.46	2.233	28.87	3.857	25.35
0.710	20.90	1.522	27.69	2.436	28.41	4.060	24.97

Table 33 : Solid I_2 - Me_3P in Methyl Cyanide

Mole Ratio I_2 : Me_3P	$K \times 10^4$ ohm^{-1} cm						
0.000	0.02	1.007	24.27	1.640	32.45	2.064	32.52
0.214	13.06	1.213	26.68	1.755	32.45	2.374	32.30
0.436	20.91	1.318	28.08	1.872	32.52	2.570	32.19
0.685	21.35	1.429	29.75	1.945	32.60	3.169	31.71
0.803	22.27	1.536	32.08				

Table 34 : I_2 - Me_3P in Nitrobenzene

Mole Ratio I_2 : Me_3P	$K \times 10^4$ ohm^{-1} cm						
0.000	0.01	0.833	1.84	1.667	4.66	2.605	4.83
0.104	1.19	0.938	2.17	1.771	5.00	2.813	4.75
0.208	1.30	1.042	2.56	1.875	5.05	3.021	4.66
0.313	1.29	1.146	2.92	1.980	5.00	3.230	4.58
0.417	1.26	1.250	3.23	2.084	5.00	3.438	4.54
0.521	1.29	1.354	3.65	2.188	4.96	3.647	4.45
0.625	1.39	1.459	3.93	2.292	4.96	3.855	4.41
0.729	1.56	1.563	4.32	2.396	4.92		

Table 35 : Solid I_2 - Me_3P in Nitrobenzene

Mole Ratio I_2 : Me_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_2 : Me_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_2 : Me_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_2 : Me_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$
0.000	0.01	1.101	2.46	1.714	5.64	2.127	6.27
0.191	1.24	1.303	3.45	1.823	6.15	2.226	6.32
0.394	1.14	1.492	4.45	1.930	6.23	2.354	6.32
0.584	1.17	1.615	5.13	2.020	6.27	2.653	6.32
0.896	1.74						

Table 36 : I_{Br} - Me_3P in Methyl Cyanide

Mole Ratio I_{Br} : Me_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_{Br} : Me_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_{Br} : Me_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_{Br} : Me_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$
0.000	0.02	0.935	15.06	1.871	29.38	3.087	31.23
0.093	5.40	1.029	15.69	1.964	30.45	3.274	31.15
0.187	9.84	1.122	16.83	2.058	30.97	3.461	31.12
0.281	13.47	1.216	18.17	2.151	31.26	3.648	31.04
0.374	16.95	1.309	19.76	2.245	31.30	3.835	31.01
0.468	17.02	1.403	21.27	2.338	31.45	4.022	30.93
0.561	15.06	1.497	23.01	2.432	31.49	4.209	30.86
0.655	14.84	1.590	24.53	2.526	31.49	4.396	30.89
0.748	14.76	1.684	26.27	2.713	31.41	4.583	30.82
0.842	14.76	1.777	27.90	2.900	31.26		

Table 37 : I_2 - Ph_3P in Methyl Cyanide

Mole Ratio I_2 : Ph_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_2 : Ph_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_2 : Ph_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_2 : Ph_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$
0.000	0.02	0.986	15.52	1.874	23.11	2.762	33.92
0.099	5.34	1.085	16.03	2.006	24.68	2.860	34.56
0.197	8.61	1.184	16.54	2.071	25.48	2.959	34.81
0.296	11.87	1.282	17.30	2.170	27.14	3.058	34.89
0.395	14.63	1.381	18.06	2.269	28.36	3.189	34.89
0.493	14.63	1.480	18.96	2.367	29.26	3.288	34.73
0.592	14.59	1.578	20.05	2.466	30.19	3.387	34.56
0.690	14.63	1.677	21.03	2.565	31.12	3.485	34.30
0.789	14.84	1.775	22.13	2.663	32.10	3.584	34.09
0.888	15.14						

Table 38 : Solid I_2 - Ph_3P in Methyl Cyanide

Mole Ratio I_2 : Ph_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_2 : Ph_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_2 : Ph_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio I_2 : Ph_3P	$K \times 10^4$ $ohm^{-1} cm^{-1}$
0.000	0.02	1.812	24.80	2.694	37.48	3.145	39.73
0.512	14.29	2.022	27.77	2.802	38.33	3.286	40.03
0.827	15.26	2.477	34.13	2.908	39.09	3.684	40.07
1.042	16.37	2.581	35.87	3.020	39.64	4.044	40.03

(b) Conductometric Titration Data of the Systems $Ph_2PCH_2PPh_2-X_2$ and $Ph_2PCH_2CH_2PPh_2-X_2$ in Methyl Cyanide

Table 39 : Br_2 - $Ph_2PCH_2PPh_2$ in Methyl Cyanide

Mole Ratio Br_2 : $Ph_2PCH_2PPh_2$	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio Br_2 : $Ph_2PCH_2PPh_2$	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio Br_2 : $Ph_2PCH_2PPh_2$	$K \times 10^4$ $ohm^{-1} cm^{-1}$
0.000	0.03	1.573	4.07	3.228	6.53
0.110	1.26	1.655	4.09	3.394	6.93
0.165	1.81	1.738	4.14	3.559	7.19
0.248	2.48	1.821	4.17	3.725	7.60
0.331	3.23	1.904	4.23	3.890	8.01
0.414	3.77	1.986	4.27	4.056	8.47
0.497	3.98	2.069	4.32	4.221	8.80
0.579	4.04	2.152	4.37	4.387	9.16
0.662	4.02	2.235	4.45	4.552	9.52
0.745	4.00	2.318	4.60	4.718	9.93
0.828	3.97	2.400	4.77	5.049	10.60
0.910	3.97	2.483	4.92	5.380	11.39
0.993	3.96	2.566	5.07	5.711	12.18
1.076	3.96	2.649	5.26	6.042	12.86
1.159	3.96	2.731	5.44	6.373	13.34
1.241	3.97	2.814	5.60	6.704	14.03
1.324	3.99	2.897	5.79	7.035	14.70
1.407	4.01	2.980	5.96	7.366	15.23
1.490	4.04	3.062	6.17	7.698	15.79

Table 40 : Br₂-Compound A in Methyl Cyanide

Mole Ratio Br ₂ : Compound A	$K \times 10^4$ ohm^{-1} cm^{-1}	Mole Ratio Br ₂ : Compound A	$K \times 10^4$ ohm^{-1} cm^{-1}	Mole Ratio Br ₂ : Compound A	$K \times 10^4$ ohm^{-1} cm^{-1}
0.000	7.21	1.266	9.62	2.531	10.18
0.105	7.46	1.371	9.71	2.637	10.22
0.211	7.67	1.477	9.79	2.742	10.22
0.316	7.93	1.582	9.84	2.848	10.22
0.422	8.18	1.688	9.88	2.953	10.26
0.527	8.39	1.793	9.92	3.059	10.26
0.633	8.65	1.899	9.96	3.164	10.26
0.738	8.90	2.004	10.05	3.270	10.30
0.844	9.12	2.110	10.09	3.481	10.30
0.949	9.33	2.215	10.09	3.692	10.35
1.055	9.45	2.321	10.13	3.903	10.35
1.160	9.54	2.426	10.18		

Table 41 : I₂-Ph₂PCH₂PPh₂ in Methyl Cyanide

Mole Ratio I ₂ : Ph ₂ PCH ₂ PPh ₂	$K \times 10^4$ ohm^{-1} cm^{-1}	Mole Ratio I ₂ : Ph ₂ PCH ₂ PPh ₂	$K \times 10^4$ ohm^{-1} cm^{-1}	Mole Ratio I ₂ : Ph ₂ PCH ₂ PPh ₂	$K \times 10^4$ ohm^{-1} cm^{-1}
0.000	0.03	1.926	26.41	3.756	45.03
0.096	5.13	2.022	27.18	3.852	46.22
0.193	8.23	2.119	28.11	3.948	46.55
0.289	11.57	2.215	29.00	4.045	46.43
0.385	14.71	2.311	29.76	4.141	46.26
0.481	16.79	2.407	30.74	4.237	46.09
0.578	16.87	2.504	31.55	4.333	45.96
0.674	17.26	2.600	32.56	4.430	45.88
0.770	17.60	2.696	33.37	4.526	45.66
0.867	17.98	2.793	34.39	4.622	45.45
0.963	18.57	2.889	35.19	4.719	45.16
1.059	19.04	2.985	36.34	4.815	45.03
1.156	19.67	3.082	37.27	5.008	44.48
1.252	20.35	3.178	38.37	5.200	43.76
1.348	21.16	3.274	39.35	5.393	43.21
1.444	22.01	3.370	40.36	5.585	42.65
1.541	22.85	3.467	41.42	5.778	41.98
1.637	23.74	3.563	42.70	5.971	41.42
1.733	24.59	3.659	43.71	6.163	40.96
1.830	25.57				

Table 42 : $\text{IBr-Ph}_2\text{PCH}_2\text{PPh}_2$ in Methyl Cyanide

Mole Ratio $\text{IBr:Ph}_2\text{PCH}_2\text{PPh}_2$	$K \times 10^4$ $\text{ohm}^{-1}\text{cm}^{-1}$	Mole Ratio $\text{IBr:Ph}_2\text{PCH}_2\text{PPh}_2$	$K \times 10^4$ $\text{ohm}^{-1}\text{cm}^{-1}$
0.000	0.02	3.069	16.11
0.102	3.07	3.171	16.32
0.205	5.21	3.274	16.79
0.307	6.87	3.376	17.55
0.409	8.56	3.478	18.23
0.511	9.29	3.580	18.99
0.614	9.75	3.683	19.72
0.716	10.09	3.785	20.44
0.818	10.39	3.887	21.20
0.921	10.81	3.990	22.09
1.023	11.07	4.092	22.90
1.125	11.36	4.194	23.66
1.228	11.66	4.297	24.46
1.330	12.08	4.399	25.31
1.432	12.38	4.501	26.20
1.534	12.80	4.603	27.05
1.637	13.19	4.706	27.77
1.739	13.57	4.808	28.79
1.841	13.82	4.910	29.34
1.944	14.16	5.013	30.36
2.046	14.50	5.115	31.04
2.148	14.84	5.217	31.93
2.251	15.09	5.320	32.90
2.353	15.56	5.422	33.41
2.455	15.65	5.524	34.22
2.557	15.77	5.729	35.74
2.660	15.90	5.933	37.01
2.762	15.94	6.138	38.03
2.864	15.98	6.343	38.92
2.967	16.03	6.547	precipitation

Table 43 : Br_2 - $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ in Methyl Cyanide

Mole Ratio Br_2 : $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	$K \times 10^4$ ohm^{-1} cm^{-1}	Mole Ratio Br_2 : $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	$K \times 10^4$ ohm^{-1} cm^{-1}	Mole Ratio Br_2 : $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	$K \times 10^4$ ohm^{-1} cm^{-1}
0.000	0.07	1.745	12.17	4.516	33.75
0.103	3.76	1.847	12.13	4.721	35.95
0.205	6.36	1.950	12.25	4.926	38.20
0.308	8.61	2.053	11.91	5.131	40.19
0.410	10.26	2.155	11.83	5.337	42.31
0.513	11.49	2.258	12.42	5.542	44.22
0.616	11.66	2.360	13.27	5.747	45.83
0.718	11.45	2.463	14.08	5.952	47.06
0.821	11.24	2.668	15.81	6.158	48.34
0.924	11.07	2.874	17.51	6.363	49.61
1.026	10.98	3.079	19.38	6.568	50.46
1.129	11.02	3.284	21.16	6.774	50.88
1.232	11.24	3.489	23.23	6.979	51.52
1.334	11.53	3.695	25.18	7.184	51.98
1.437	11.83	3.900	27.26	7.389	52.19
1.539	12.00	4.105	29.47	7.595	52.41
1.642	12.13	4.310	31.59		

Table 44 : I_2 - $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ in Methyl Cyanide

Mole Ratio I_2 : $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	$K \times 10^4$ ohm^{-1} cm^{-1}	Mole Ratio I_2 : $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	$K \times 10^4$ ohm^{-1} cm^{-1}	Mole Ratio I_2 : $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	$K \times 10^4$ ohm^{-1} cm^{-1}
0.000	0.04	1.828	18.06	4.671	37.61
0.101	3.26	2.031	19.21	4.874	39.35
0.203	6.57	2.234	20.39	5.077	41.04
0.305	8.95	2.437	22.01	5.281	42.99
0.406	11.19	2.640	23.11	5.484	44.77
0.508	12.80	2.843	24.42	5.585	46.17
0.609	13.36	3.046	25.74	5.687	46.77
0.711	13.65	3.250	27.05	5.788	47.36
0.812	13.86	3.453	28.53	5.890	47.32
0.914	13.99	3.656	30.02	5.991	47.11
1.015	14.37	3.859	31.42	6.093	46.85
1.219	15.14	4.062	32.99	6.296	46.34
1.422	16.11	4.265	34.39	6.499	45.79
1.625	16.96	4.468	36.04	6.702	45.11

Table 45 : $\text{IBr} \cdot \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ in Methyl Cyanide

Mole Ratio $\text{IBr} : \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	$K \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$	Mole Ratio $\text{IBr} : \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	$K \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$
0.000	0.07	2.968	17.26
0.102	3.36	3.070	17.64
0.205	5.94	3.172	18.15
0.307	8.39	3.275	18.87
0.409	10.18	3.377	19.80
0.512	11.32	3.479	20.69
0.614	11.87	3.684	22.68
0.716	11.91	3.888	24.68
0.819	12.00	4.093	26.67
0.921	12.13	4.298	28.70
1.023	12.38	4.502	30.82
1.126	12.76	4.707	32.56
1.228	13.19	4.912	34.68
1.330	13.69	5.116	36.38
1.433	14.20	5.321	38.12
1.535	14.46	5.526	39.52
1.637	14.75	5.730	40.87
1.740	14.97	5.935	41.76
1.842	15.26	6.140	42.70
1.944	15.48	6.344	43.12
2.047	15.65	6.549	43.67
2.149	15.90	6.754	43.93
2.251	16.15	6.958	44.10
2.354	16.58	7.163	43.97
2.456	16.75	7.368	43.93
2.558	16.83	7.675	43.71
2.661	17.00	8.084	43.12
2.763	17.09	8.493	42.44
2.865	17.17	8.698	42.10

(c) Infrared Spectra

The infrared spectra of the phosphines and phosphine-halogen adducts studied in this thesis are recorded below. In many cases no value is given for the C-H stretching frequency in the region 2700-3100 cm^{-1} as this is often obscured by the nujol peaks.

Ph₂MeP : 3088 (m), 3070 (m), 2982 (m), 2918 (m), 1583 (m), 1479 (s), 1433 (s), 1420 (s), 1326 (w), 1303 (w), 1279 (w), 1181 (w), 1155 (w), 1098 (m), 1068 (w), 1025 (m), 998 (m), 878 (sb), 737 (s), 705 (s), 693 (s), 671 (w), 621 (w), 466 (s), 443 (m), 386 (m) cm^{-1} .

Ph₂MePBr₄ : 3085 (w), 3000 (m), 2920 (m), 1586 (m), 1484 (w), 1440 (s), 1394 (w), 1340 (w), 1315 (w), 1192 (w), 1164 (w), 1112 (s), 1107 (s), 1027 (vw), 999 (m), 902 (mb), 784 (m), 744 (s), 720 (m), 682 (s), 623 (vw) cm^{-1} .

Ph₂MePI₂ : 1581 (m), 1570 (m), 1480 (m), 1435 (s), 1395 (w), 1333 (m), 1309 (w), 1291 (m), 1155 (w), 1096 (s), 994 (m), 890 (s), 883 (s), 840 (w), 766 (w), 750 (s), 742 (s), 681 (s), 622 (w) cm^{-1} .

PhMe₂P : 3060 (w), 3045 (w), 2950 (m), 2895 (m), 2805 (vw), 1484 (w), 1433 (s), 1290 (vw), 1275 (vw), 1107 (w), 1070 (vw), 1028 (vw), 1000 (vw), 940 (m), 895 (s), 865 (w), 740 (s), 693 (s), 661 (w) cm^{-1} .

PhMe₂PBr₂ : 1443 (s), 1300 (m), 1134 (s), 1114 (m), 1010 (s), 1000 (m), 948 (sb), 880 (m), 870 (w), 780 (w), 743 (s), 687 (s) cm^{-1} .

PhMe₂PI₂ : 1440 (s), 1303 (w), 1118 (m), 970 (s), 930 (sb), 883 (s), 865 (s), 756 (s), 735 (s), 680 (s) cm^{-1} .

PhMe₂PBr : 1440 (s), 1342 (w), 1315 (w), 1290 (m), 1132 (m), 1113 (m), 1009 (m), 1000 (m), 962 (s), 933 (sb), 884 (m), 869 (w), 776 (w), 742 (s), 686 (s) cm^{-1} .

Me₃P (gas phase) : 3915 (vw), 3850 (vw), 3228 (w), 3152 (w), 2972 (s), 2960 (s), 2900 (s), 2835 (m), 2820 (m), 1445 (s), 1433 (s),

1317 (m), 1303 (s), 1288 (s), 1070 (wb), 950 (sb), 945 (sb), 830 (vwb), 710 (sb) cm^{-1} .

$\underline{\text{Me}}_3\underline{\text{PO}}$: 1455 (s), 1330 (w), 1300 (s), 1285 (s), 1168 (sb), 1040 (w), 950 (sb), 877 (s), 870 (s), 750 (s) cm^{-1} .

$\underline{\text{Me}}_3\underline{\text{PBr}}_2$: 1630 (wb), 1428 (w), 1420 (m), 1398 (vw), 1378 (m), 1318 (m), 1297 (m), 1288 (s), 1160 (vwb), 994 (sb), 960 (sb), 882 (s), 874 (vw), 773 (s), 722 (w), 678 (s), 412 (s), 270 (w), 243 (m) cm^{-1} .

$\underline{\text{Me}}_3\underline{\text{PBr}}_4$: 2980 (wb), 2965 (wb), 2890 (w), 1400 (wb), 1384 (w), 1284 (s), 1155 (wb), 950 (sb), 880 (m), 862 (s), 767 (m), 720 (w), 673 (s), 426 (m), 415 (s) cm^{-1} .

$\underline{\text{Me}}_3\underline{\text{P(OH)Br}}$: 2700-2000 (OH hydrogen bonded), 1400 (m), 1295 (s), 1160 (m), 1015 (sb), 995 (s), 960 (sb), 882 (m), 877 (m), 870 (s), 775 (w), 765 (w), 721 (vw), 690 (vw), 678 (w) cm^{-1}

$\underline{\text{Me}}_3\underline{\text{PHgBr}}_2$: 1425 (w), 1419 (m), 1412 (m), 1309(vw), 1298 (m), 1289 (m), 978 (s), 964 (s), 863 (m), 762 (m), 678 (w) cm^{-1} .

$(\underline{\text{Me}}_3\underline{\text{P}})_2\underline{\text{I}}_2$: 1419 (m), 1412 (m), 1312 (m), 1307 (m), 1109 (wb), 1010 (wb), 979 (s), 950 (sb), 890 (w), 858 (m), 779 (m), 726 (wb), 657 (m) cm^{-1} .

$\underline{\text{Me}}_3\underline{\text{PI}}_4$: 1400 (sb), 1300 (s), 1290 (s), 1000 (sb), 958 (sb), 861 (m), 767 (m), 670 (s), 365 (s) cm^{-1} .

$\underline{\text{Me}}_3\underline{\text{PIBr}}$: 1410 (w), 1290 (m), 1283 (s), 1155 (wb), 1121 (wb), 1024 (wb), 956 (sb), 868 (m), 859 (m), 770 (wb), 721 (wb), 681 (m), 418 (m) cm^{-1} .

$\underline{\text{Ph}}_2\underline{\text{PCH}}_2\underline{\text{PPh}}_2$: 3040 (m), 1948 (w), 1875 (w), 1812 (w), 1755 (vw), 1580 (m), 1478 (s), 1431 (s), 1379 (m), 1330 (w), 1308 (w), 1272 (w), 1187 (w), 1158 (w), 1095 (m), 1070 (w), 1040 (w), 1028 (s), 1002 (m), 970 (w), 918 (w), 782 (s), 746 (s), 719 (s), 693 (s), 512 (s), 501 (s), 482 (s), 473 (m), 439 (w), 423 (m), 388 (w), 348 (m) cm^{-1} .

Compound A: 2862 (m), 2821 (w), 1583 (w), 1571 (w), 1475 (wb),
1433 (s), 1380 (mb), 1339 (w), 1312 (vw), 1232 (wb), 1204 (w),
1168 (m), 1128 (s), 1111 (s), 1032 (m), 1003 (s), 1000-830 (sb),
813 (s), 764 (w), 748 (s), 737 (s), 723 (s), 688 (s), 551 (s),
507 (s), 460 (m), 425 (wb), 402 (w), 353 (mb), 300 (w) cm^{-1} .

Ph₂PCH₂PPh₂.I₄: 2791 (m), 1580 (w), 1571 (w), 1480 (m), 1437 (s),
1320 (w), 1182 (w), 1168 (m), 1127 (w), 1096 (s), 999 (m), 790 (m),
772 (m), 742 (s), 729 (m), 687 (s), 551 (w), 520 (m), 505 (w),
496 (m), 478 (s), 452 (wb), 356 (wb) cm^{-1} .

Ph₂PCH₂PPh₂.I₁₀: 1568 (wb), 1432 (s), 1333 (wb), 1305 (vw), 1115
(m), 1091 (mb), 997 (m), 795 (w), 764 (m), 741 (m), 732 (s), 712
(w), 676 (m), 517 (w), 494 (s), 468 (m), 454 (w), 362 (w) cm^{-1} .

Ph₂PCH₂PPh₂.I₂.Br₂: 1690 (wb), 1580 (w), 1478 (m), 1437 (s),
1320 (w), 1188 (w), 1161 (w), 1122 (m), 1098 (s), 997 (m), 780 (sb),
742 (s), 687 (s), 519 (w), 506 (m), 495 (m), 480 (m), 450 (wb),
354 (w) cm^{-1} .

Ph₂PCH₂CH₂PPh₂: 3060 (m), 3038 (w), 3010 (wb), 2990 (w), 2923 (w),
2891 (vw), 1950 (wb), 1882 (w), 1800 (wb), 1762 (vw), 1582 (w),
1481 (s), 1437 (s), 1431 (s), 1335 (vw), 1310 (w), 1190 (vw), 1167
(m), 1159 (m), 1100 (mb), 1087 (m), 1070 (m), 1031 (m), 1007 (m),
1002 (m), 759 (s), 751 (s), 732 (s), 710 (s), 697 (s), 678 (w),
513 (s), 480 (s), 445 (s), 402 (w), 341 (w) cm^{-1} .

Ph₂PCH₂CH₂PPh₂.Br₂: 1440 (s), 1378 (sb), 1216 (m), 1140 (m), 1118
(mb), 1005 (wb), 993 (m), 748 (s), 742 (s), 728 (m), 718 (m),
689 (s), 532 (w), 510 (m), 500 (s), 483 (m), 408 (wb), 337 (w) cm^{-1} .

Ph₂PCH₂CH₂PPh₂.I₂: 1586 (w), 1441 (s), 1342 (vw), 1217 (w), 1165
(wb), 1142 (m), 1119 (mb), 1000 (w), 840 (w), 742 (s), 730 (s),
690 (s), 560 (m), 530 (vw), 500 (w), 480 (w), 405 (vwb), 337 (w)
 cm^{-1} .

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