

University of St Andrews



Full metadata for this thesis is available in
St Andrews Research Repository
at:

<http://research-repository.st-andrews.ac.uk/>

This thesis is protected by original copyright

SOME ASPECTS OF
PHOSPHORUS HALIDE CHEMISTRY

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

by

Angus Iain Thomson MacPherson, B.Sc.

September 1970

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 1967, under the supervision of Dr. G.S. Harris.

Certification

I hereby certify that

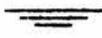
..... Angus Iain Thomson MacPherson

has spent eleven terms at research work under my supervision, has fulfilled the conditions of Ordinance 16 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research

LIST OF CONTENTS

	Page
LIST OF FIGURES	i
LIST OF TABLES	iii
ACKNOWLEDGEMENTS	vi
GENERAL INTRODUCTION	1
PART I : Some Reactions of Phenylchlorophosphine and Diphenylchlorophosphine with Halogens .. .	41
PART II : Some Reactions of Phenylbis(pentafluorophenyl)- phosphine and Bis(phenyl)pentafluorophenyl- phosphine with Halogens	91
PART III : Some Reactions of Tri(<u>p</u> -tolyl)phosphine with Halogens	117
APPENDIX: Some Halogen Adducts of Phenylchlorophosphine	142
EXPERIMENTAL	149
REFERENCES	181



LIST OF FIGURES

		Page
Figure 1:	The possible configurations for ML_5	9
" 2:	Non-equivalence of ligands	9
" 3:	ML_4X structures	11
" 4:	ML_3X_2 structures	11
" 5:	Pseudo-rotation	13
" 6:	Possible mechanism for intramolecular exchange of ligands in a five-coordinate structure .. .	13
" 7:	Sp^3d hybridisation of phosphorus	16
" 8:	Cotton's suggested structure for PCl_5	16
" 9:	Wells' resonance hybrids for Me_3SbHal_2	16
" 10:	Molecular orbital description of the bonding in I_3^-	34
" 11:	Conductometric analysis of the systems $PhPCl_2-Cl_2$; $PhPCl_2-I_2$	44
" 12:	Conductometric analysis of the system $PhPCl_2-Br_2$.	48
" 13:	Conductometric analysis of the systems $PhPCl_2-ICl$; $PhPCl_2-IBr$; $PhPCl_2-ICl_3$	58
" 14:	Conductometric analysis of the systems $PhPCl_4-ICl$; $PhPCl_4-IBr$	63
" 15:	Conductometric analysis of the systems $Ph_2PCl-Cl_3$; $Ph_2PCl-Br_2$; Ph_2PCl-I_2	68
" 16:	Conductometric analysis of the systems $Ph_2PCl-ICl$; $Ph_2PCl-IBr$; $Ph_2PCl-ICl_3$	75
" 17:	Conductometric Analysis of the systems Ph_2PCl_3-ICl ; PCl_3-ICl ; PCl_3-ICl_3	82
" 18:	Conductometric analysis of the systems $PhP(C_6F_5)_2-Cl_2$; $PhP(C_6F_5)_2-Br_2$	94
" 19:	Conductometric analysis of the systems $PhP(C_6F_5)_2-I_2$; $PhP(C_6F_5)_2-IBr$	103

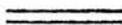
	Page
Figure 21: Conductometric analysis of the systems $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-I}_2$; $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-IBr}$	107
" 22: Conductometric analysis of the systems $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\cdot\text{Br}_2\text{-IBr}$; $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\cdot\text{I}_2\text{-IBr}$..	111
" 23: Conductometric analysis of the systems $(\underline{\text{p-tol}})_3\text{P-Cl}_2$; $(\underline{\text{p-tol}})_3\text{P-Br}_2$	120
" 24: Vapour pressure study of the system $(\underline{\text{p-tol}})_3\text{P-Br}_2$ at 15°C	126
" 25: Conductometric analysis of the systems $(\underline{\text{p-tol}})_3\text{P-I}_2$; $(\underline{\text{p-tol}})_3\text{P-IBr}$	128
" 26: Conductometric analysis of the systems $(\underline{\text{p-tol}})_3\text{P}\cdot\text{Br}_2\text{-I}_2$; $(\underline{\text{p-tol}})_3\text{P}\cdot\text{Br}_2\text{-IBr}$; $(\underline{\text{p-tol}})_3\cdot\text{IBr-I}_2$	134
" 27: Conductometric analysis of the system $\text{PhPBr}_2\text{-Br}_2$	143
" 28: Vacuum system for vapour pressure study ..	151
" 29: Vacuum system for conductometric titrations using chlorine	154
" 30: Conductance cell for chlorine titrations ..	154

LIST OF TABLES

Table No.		Page
I:	The trihalides of P, As, Sb and Bi .. .	3
" "	II: The pentahalides of P, As, Sb and Bi .. .	5
" "	III: The phosphorus (V) chlorofluorides (Cl _n PF _(5-n))	19
" "	IV: The fluorophosphoranes (R _n PF _(5-n)) .. .	20
" "	V: Polyhalide complex ions in crystalline salts	32
" "	VI: Order of decreasing stability for trihalides of the same cation	36
" "	VII: Conductometric analysis of the system PhPCl ₂ -Cl ₂	45
" "	VIII: Conductometric analyses of the system PhPCl ₂ -Br ₂	49
" "	IX: Conductometric analysis of the system PhPCl ₂ -I ₂	52
" "	X: Conductometric analysis of the system PhPCl ₂ -ICl	54
" "	XI: Conductometric analysis of the system PhPCl ₂ -IBr	59
" "	XII: Conductometric analysis of the system PhPCl ₂ -ICl ₃	61
" "	XIII: Conductometric analysis of the system PhPCl ₄ -ICl	64
" "	XIV: Conductometric analysis of the system PhPCl ₄ -IBr	65
" "	XV: Conductometric analysis of the system Ph ₂ PCl-Cl ₂	69
" "	XVI: Conductometric analysis of the system Ph ₂ PCl-Br ₂	70
" "	XVII: Conductometric analysis of the system Ph ₂ PCl-I ₂	72
" "	XVIII: Conductometric analysis of the system Ph ₂ PCl-ICl	74

Table No.		Page
XIX:	Conductometric analysis of the system $\text{Ph}_2\text{PCl-IBr}$	78
" "	XX: Conductometric analysis of the system $\text{Ph}_2\text{PCl-ICl}_3$	80
" "	XXI: Conductometric analysis of the system $\text{Ph}_2\text{PCl}_3\text{-ICl}$	83
" "	XXII: Conductometric analysis of the system $\text{PCl}_3\text{-ICl}$	85
" "	XXIII: Conductometric analysis of the system $\text{PCl}_3\text{-ICl}_3$	87
" "	XXIV: Conductometric analysis of the system $\text{PhP}(\text{C}_6\text{F}_5)_2\text{-Cl}_2$	95
" "	XXV: Conductometric analysis of the system $\text{PhP}(\text{C}_6\text{F}_5)_2\text{-Br}_2$	96
" "	XXVI: Conductometric analysis of the system $\text{PhP}(\text{C}_6\text{F}_5)_2\text{-I}_2$	99
" "	XXVII: Conductometric analysis of the system $\text{PhP}(\text{C}_6\text{F}_5)_2\text{-IBr}$	100
" "	XXVIII: Conductometric analysis of the system $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-Cl}_2$	102
" "	XXIX: Conductometric analysis of the system $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-Br}_2$	105
" "	XXX: Conductometric analysis of the system $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-I}_2$	106
" "	XXXI: Conductometric analysis of the system $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-IBr}$	109
" "	XXXII: Conductometric analysis of the system $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-Br}_2\text{-IBr}$	112
" "	XXXIII: Conductometric analysis of the system $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{I}_2\text{-IBr}$	113
" "	XXXIV: Conductometric analysis of the system $(\underline{p}\text{-tol})_3\text{P-Cl}_2$	119
" "	XXXV: Conductometric analysis of the system $(\underline{p}\text{-tol})_3\text{P-Br}_2$	122
" "	XXXVI: Vapour pressure study of the system $(\underline{p}\text{-tol})_3\text{P-Br}_2$ at 15°C	125
" "	XXXVII: Conductometric analysis of the system $(\underline{p}\text{-tol})_3\text{P-I}_2$	129

		Page
Table No. XXXVIII:	Conductometric analysis of the system (<u>p</u> -tol) ₃ P-IBr 131
" "	XXXIX: Conductometric analysis of the system (<u>p</u> -tol) ₃ P·Br ₂ -I ₂ 135
" "	XL: Conductometric analysis of the system (<u>p</u> -tol) ₃ P·Br ₂ -IBr 136
" "	XLI: Conductometric analysis of the system (<u>p</u> -tol) ₃ P·IBr-I ₂ 138
" "	XLII: Conductometric analysis of the system PhPBr ₂ -Br ₂ 144



Summary Chart 1: Conductometric Analyses of Hal₂ with PhPCl₂,
Ph₂PCl and PCl₃ in Acetonitrile .. . 90

Summary Chart 2: Conductometric Analyses of Hal₂ with
PhP(C₆F₅)₂ and Ph₂P(C₆F₅) in Aceto-
nitrile 116

Summary Chart 3: Conductometric Analyses of Hal₂ with
(p-tol)₃P in Acetonitrile 141

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Dr. G.S. Harris for the kindness, encouragement and ready guidance received over the three years in which this work was carried out.

Thanks are also due to my departmental colleagues Mr. J.S. McKechnie for many helpful discussions and Mr. J. Bews for many readily- and efficiently-performed analyses.

Receipt of a maintenance allowance from the Science Research Council is most gratefully acknowledged.

GENERAL INTRODUCTION

GENERAL INTRODUCTION

The halides of the Group V(b) elements - in particular phosphorus - were among the earliest of the non-metallic halides to be studied by chemists. The tri- and pentahalides of phosphorus with chlorine and bromine, for example, could be easily prepared from such basic starting materials as yellow and red phosphorus and the appropriate elemental halogen. In addition, the high reactivity of these halides with hydroxyl compounds enabled analysis to be undertaken readily and formulas to be firmly established. Many famous investigators - including Gay-Lussac and Davy - were involved in this early work, which began in the early years of the nineteenth century and was pursued until late in that century. One of the features of great interest to these early experimenters was the existence of two well-defined series of compounds, an aspect of the chemistry of the phosphorus halides which was to continue to be - and remains - of prime interest. By virtue of its position in the Periodic Table (electronic configuration $1s^2; 2s^2, 2p^6; 3s^2, 3p^3$) phosphorus - in forming pentahalides - became a point of controversy in the development of valency theory. In fact, it still remains an exacting test for the applicability of any system of bond description.

Much of the early work done on the Group V(b) halides was preparative: e.g. Boyle¹ prepared bismuth trichloride in 1664, whilst antimony trichloride was first correctly identified by Glauber in 1648. Indeed, the synthetic routes required to produce the simple halides are limited, and it appears to be a lack of an adequate purpose, rather than any inherent difficulty, which has led to the relatively small number of compounds prepared. The published work on the halides in question stretches over a very long period, and while some of the early results must be considered of dubious validity, it is of the greatest credit to the early chemists that they obtained, with the limited apparatus at their disposal, so much correct and valuable information on these very reactive materials. Many early results can now be interpreted in modern chemical terms, and in fact add significantly to our present picture of the Group V(b) halides.

The Trihalides

The Group V(b) trihalides which have been isolated and whose individual properties have been recognised are set out in Table I (below). As is seen from the table, all possible simple halides are known. However, although the number of mixed trihalides theoretically possible is large, only a few have as yet been prepared and characterised. Others have so far only been identified in the course of ebullioscopic,⁵ Raman spectra.^{6,7} and nuclear

TABLE I : The Trihalides of P, As, Sb and Bi

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
PF ₂ Cl ²		SbBrI ₂ ⁴	
PFCl ₂ ²			
PF ₂ Br ³			
PBr ₂ ³			

magnetic resonance⁸ studies. Van Wazer and co-workers showed that mixtures of phosphorus (III) chloride and phosphorus (III) bromide reorganise slowly at room temperature to produce both PCl₂Br and PClBr₂ in equilibrium with the original halides;⁸ analogously, the PBr₃-PI₃ system gives evidence of PBr₂I and PBrI₂ in an equilibrium mixture.⁹ Evidence has also been offered for a chlorobromofluoride of phosphorus PFClBr, based on the Raman spectrum of a mixture of PFCl₂ and PFBr₂.¹⁰ In no case above is equilibrium established instantaneously, the reaction being considerably slower when fluoride is present in one of the molecules involved;⁸ hence the isolation of some of the possible mixed fluorophosphines.

To date, attempts to prepare arsenic fluorochlorides by partial fluorination have not been successful,¹¹ although ^{19}F nuclear magnetic resonance studies have established the formation of AsF_2Cl and AsFCl_2 in exchange equilibria set up by AsF_3 and AsCl_3 . Little work has been done regarding mixed trihalides of arsenic and antimony and bismuth, although general considerations on complexes with mixed ligands have been made by Preetz and Blasius.¹² Thus it can be seen that re-organisation reactions are a feature of the chemistry of the phosphorus (III) halides, and in fact it appears likely that this type of reaction is general to the group. It would appear, however, that the composition of any equilibrium mixture will not necessarily include appreciable amounts of mixed halides, unless there is some particular feature favouring their stability.

In conclusion, therefore, it can fairly be said that the numerous reactions involving interchange of halogens are far from being understood, and a thorough re-investigation employing modern techniques would be most welcome. There is also a good deal to be elucidated concerning the stabilities of mixed halogen compounds when in complexes, as well as the reactions of these mixed compounds.

The Pentahalides

The Group V(b) pentahalides which have been isolated and whose individual properties have been recognised are:-

TABLE II: The Pentahalides of P, As, Sb and Bi

Phosphorus	Arsenic	Antimony	Bismuth
PF_5 PCl_5 PBr_5	AsF_5	SbF_5 SbCl_5	BiF_5
PF_4Cl 21 PF_3Cl_2 14,15 PF_2Cl_3 16 PFCl_4 16 PF_3Br_2 17 PF_2Br_3 4 PBr_4 4,18		SbF_3Cl_2 19 SbFCl_4 20	

It should immediately be noted that while it is common to talk of specific pentahalides, this is in many cases merely a reference to the stoichiometric composition and in no way reflects the structural state of the species concerned.

While all the simple trihalides of phosphorus, arsenic, antimony and bismuth are known, it can be seen from Table II that the same cannot be said regarding the simple pentahalides. Although certain of this class of compound have been known for a long

time (e.g. phosphorus pentachloride, which has long been used as a "classic" example of equilibrium in thermal dissociation), some are of relatively recent preparation - the most recent being that of BiF_5 .¹³ It would appear that the occurrence of pentahalides of these elements is governed by three factors: (i) the increasingly favourable steric factor (i.e. size of Group V(b) atom relative to the halogen ligands) in the direction P-As-Sb-Bi; (ii) the increasing oxidising power of M(V) in this series; (iii) the large promotion energies required to uncouple the 's' pair of electrons in the case of As and Bi.¹³² Although arsenic pentachloride can be found described as "Unstable at 25°C",²² it seems fairly certain that this species is entirely unknown^{23,24} at such a temperature, if known at all. The number of possible species - even excluding stereoisomers - which might be obtained by allowing for simple and mixed fluorides, chlorides, bromides and iodides of phosphorus, arsenic, antimony and bismuth is over 200, less than a tenth having so far been recognised, due partly to the fairly superficial investigation accorded this type of compound.

With regard to the mixed pentahalides, again the bulk of the work done has been concerned with phosphorus, yet even here only the fluorochlorides can be said to be well known, largely due to American work within the last decade or so.^{25,26} As in the trihalide case, again several species have been detected as having transitory existence or as being present in equilibria, without

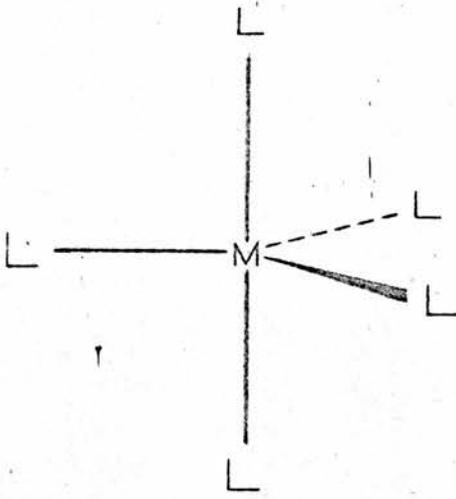
allowing isolation. Mention of compounds involving phosphorus (V), bromine and chlorine is widespread in the literature, but there is little agreement on the composition of these substances. This particular system will be dealt with in considerably more detail below (pp. 37 ff). Although the arsenic trifluoride-chlorine system does give a "chlorofluoride" product, this is thought to exist solely as $[\text{AsCl}_4^+][\text{AsF}_6^-]$ ^{27,28} and never 'AsCl₂F₃'; hence its omission from Table II. In fact, in anhydrous conditions, AsF₃ simply does not react with Cl₂. Attempts to add Br₂ or I₂ to AsF₃ were unsuccessful.²⁹ The antimony pentafluoride-antimony pentachloride system is extremely complex, and although SbCl₄F²⁰ and SbCl₂F₃¹⁹ are well established, claims for other species, while appearing dubious at present, may yet be substantiated. This system was studied in the early years of this century,³⁰ and the investigators found evidence for many species, including (SbF₅)₂·(SbCl₅)₃ which is, of course, 'SbCl₃F₂'. A recent reinvestigation³¹ found this system "too complicated to interpret in the desired quantitative manner". Although exchanging to give SbCl₂F₃ and SbF₅, it appears that SbF₄Cl is formed in the reaction between antimony pentafluoride and potassium chloride.³² No mixed pentahalides of bismuth have been reported.

Pentacoordinate Structures

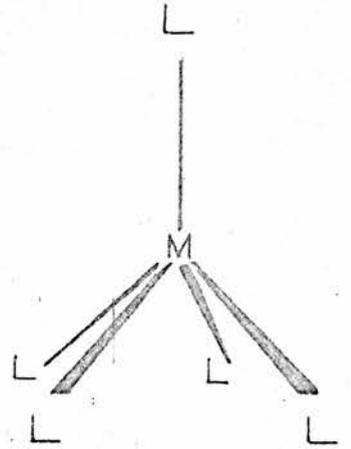
It is obvious from the preceding few paragraphs that pentahalide chemistry is extremely complex: although due in no small

measure to the natural "reactivity" and lability of the halogen atoms themselves, it is also partly due to the inherent nature of pentacoordination. Before proceeding with any more detailed discussion on the Group V(b) pentahalides, therefore, it will be necessary to examine the nature of pentacoordination. The Sidgwick-Powell³³ theory, developed further by Gillespie and Nyholm,³⁴ accounts well in a qualitative manner for the general shapes and bond angles of most inorganic molecules. In essence, repulsions between electron pairs in the valence shell determine any given molecule's stereochemistry. (It appears that this theory is usually now referred to as the V.S.E.P.R. Theory ("Valence-Shell Electron-Pair Repulsion"), and it has been widely publicised by Gillespie.)^{35,36,37,38,39,40}

Making use of the familiar "sphere" model, it immediately becomes obvious that while systems of four or six electron pairs can be dealt with very easily (leading, of course, to the familiar tetrahedron and octohedron, respectively), five electron pairs present a problem: it is not possible to maximise the least distance between any two of the five particles on the surface of a sphere. (This discounts trivial solutions such as five particles all on a given circle in the sphere.) In fact, the two most favourable configurations for five particles are the trigonal bipyramid and the tetragonal pyramid; moreover, the energy difference between these two configurations is usually small, although



(a) Trigonal bipyramid



(b) Tetragonal pyramid

FIGURE 1: The two possible configurations for ML_5

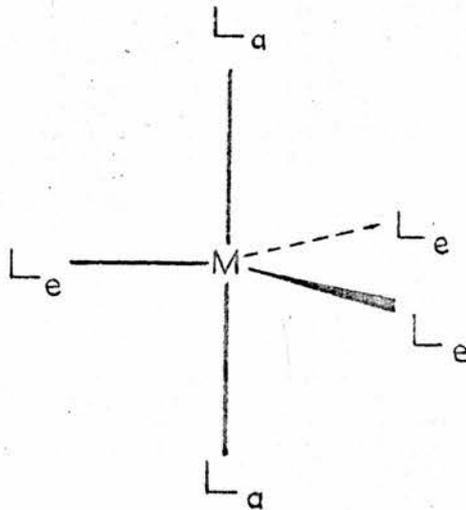


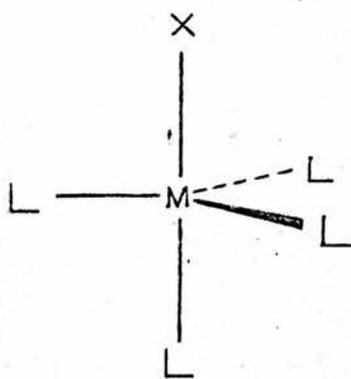
FIGURE 2: Non-equivalence of ligands

the former will very probably prove to be the most common ground-state structure.⁴¹ The two configurations in question may be represented as in Figure 1.

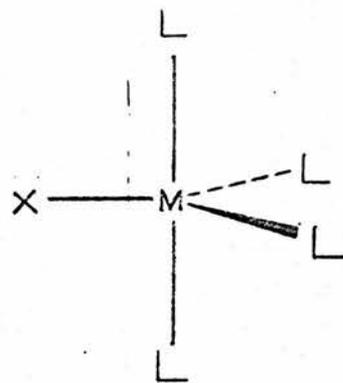
Concentrating on Figure 1(a), the more common configuration, it is at once obvious that all 'L' positions are not the same: in other words, the ligands will not all be equivalent. There are, indeed, two different types of ligand - axial (denoted 'La' in Figure 2) and equatorial (denoted 'Le').

The two axial bond electron-pairs each have three equatorial bonding pairs at 90° as nearest neighbours, while the equatorial bonding pairs have only two axial pairs at 90° as nearest neighbours. Hence the total repulsion exerted on the axial-bond electron pairs is greater than that exerted on the equatorial-bond electron pairs. Thus if all the bonding electrons were at the same distance from 'M', the system would not be in equilibrium: consequently the electron pairs bonding the ligands to M will adjust so as to equalise the repulsions between any pair of electrons. Thus the electron pairs in the axial-ligand bonds will settle at a greater distance from M than the equatorial electron pairs: this simply means that the axial bonds will be longer than the equatorial bonds (e.g. $\text{PF}_5(\text{g})$ has axial bonds 1.577\AA , and equatorial bonds 1.534\AA).

While the non-equivalence of bonds may not be of much apparent

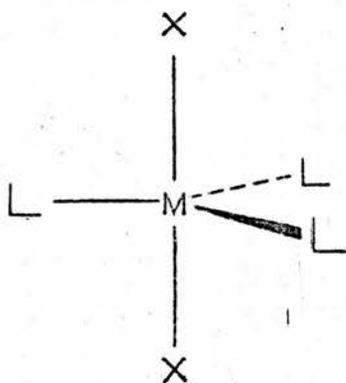


(a) C_{3v}

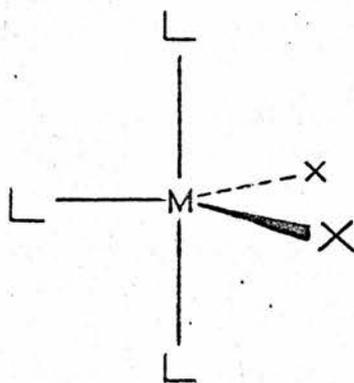


(b) C_{2v}

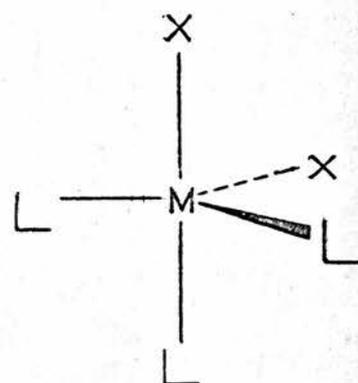
FIGURE 3: ML_4X structures



(a) D_{3h}



(b) C_{2v}



(c) C_s

FIGURE 4: ML_3X_2 structures

concern in the ML_5 case considered above, it very much matters if we have more than one type of ligand attached to 'M'. Thus, with one "odd" ligand (X, say), we get two different molecular symmetries:^{42,43} Figure 3(a) is of C_{3v} symmetry and 3(b) of C_{2v} symmetry, as opposed to the ML_5 case where the symmetry is D_{3h} .

If, again, we have more than one type of ligand, but now in the ratio of 3:2 (ML_3X_2 in this case) we have the possibilities set out in Figure 4. Figure 4 shows that we have three different symmetries for this class of compound: (a) D_{3h} , (b) C_{2v} and (c) C_s . It must be borne in mind that molecule 3(a) is non-equivalent to molecule 3(b); likewise, 4(a), 4(b) and 4(c) are all different. Using modern spectroscopic techniques, however (infra-red, Raman, nuclear magnetic resonance, etc.), identification of symmetry-type is quite feasible.

If we were to consider more complex five-ligand systems (e.g. ML_2XYZ) obviously the number of possible permutations would increase rapidly. However, by considering ML_5 , ML_4X and ML_3X_2 , we have covered all the cases $M(\text{Hal})_n(\text{Hal}')_{(5-n)}$ where $M = P, As, Sb$ or Bi and $\text{Hal}, \text{Hal}' = F, Cl, Br$ or I , which are actually known. The above theory will be employed below in the section devoted to phosphorus.

To complicate things further, however, a particularly interesting feature of trigonal-bipyramidal molecules is the possibility of internal exchange of atoms, or "pseudorotation", as

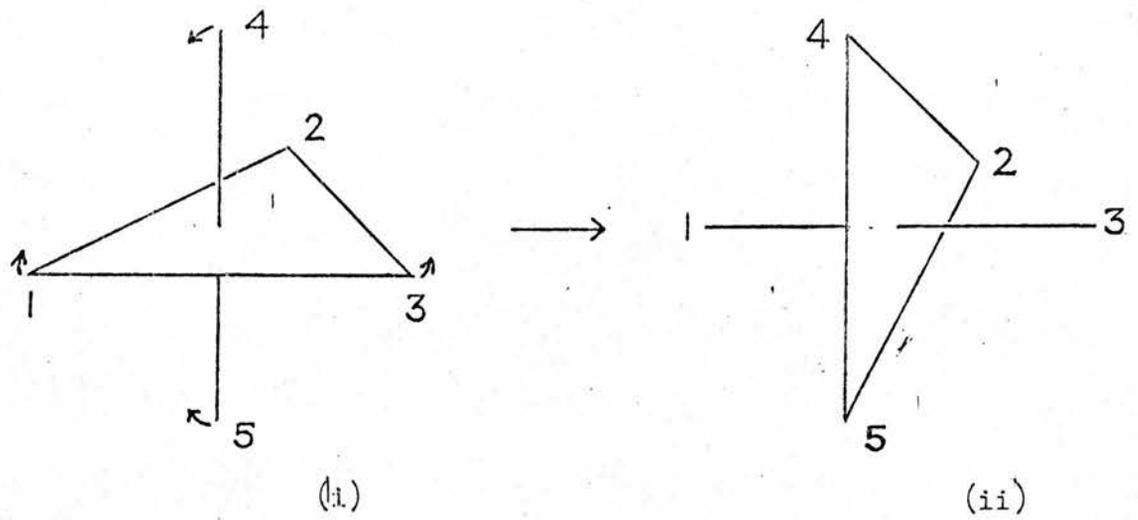


FIGURE 5: "Pseudorotation"

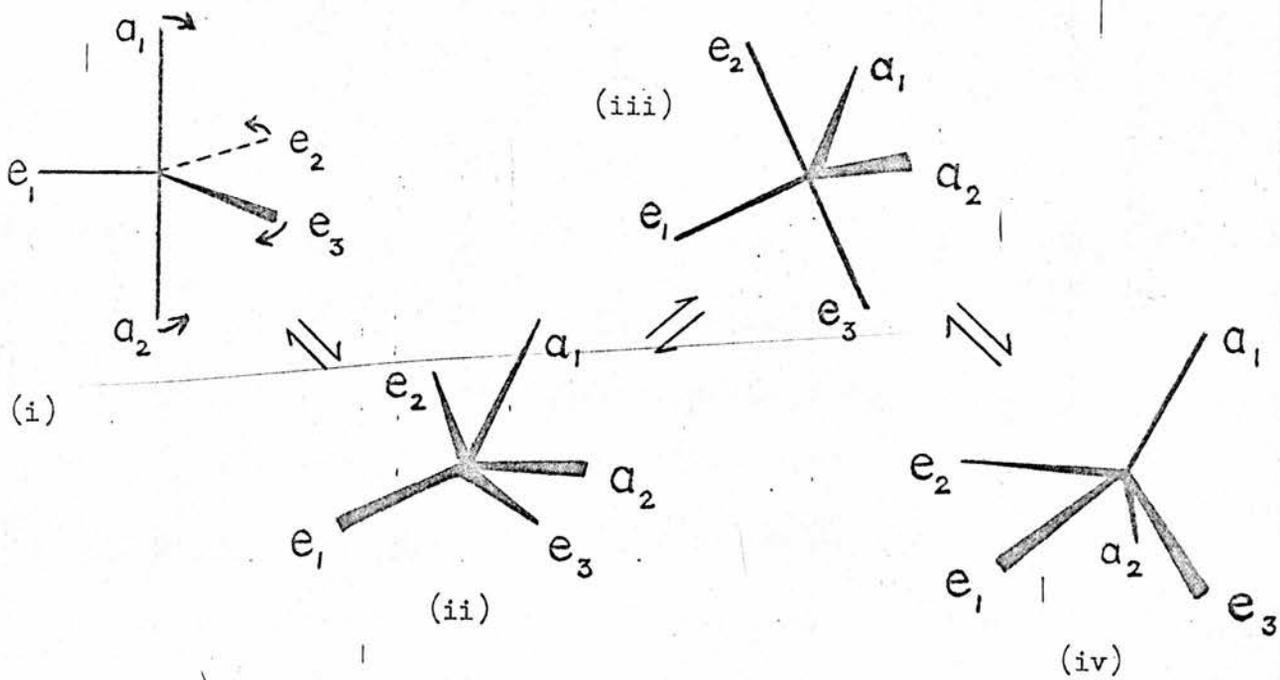


FIGURE 6: Possible mechanism for intramolecular exchange of ligands in a five-coordinate structure

described by Berry,⁴⁴ and depicted in Figure 5. Thus the two original axial ligands have both become equatorial, while two of the original equatorial ligands assume the axial positions. There is therefore a possibility that the life-time of the ground-state geometry for a pentacoordinate compound or ion is short.^{44,45}

Moreover, although the tetragonal pyramid and the trigonal bipyramid may appear at first glance to be grossly different, they are quite closely related, and concerted (M-L) vibrations may well be sufficient to cause interconversion of the two configurations in question. Figure 6 demonstrates the close relationship of these two structures, by (i) \rightleftharpoons (iv). It can be seen that (i) \rightleftharpoons (iii) is, in fact, pseudorotation. In such dynamic systems, the molecule may either spend most of its time in one configuration, or equally in the two geometric configurations.

Before dealing more thoroughly with Group V(b) pentahalide chemistry - in particular some aspects of phosphorus (V) chemistry which are relevant to the subject matter of this thesis - it might be appropriate to deal briefly and in a qualitative manner with the actual bonding schemes which have been proposed for pentacoordinate structures.

Bonding Schemes for Pentacoordination

The formal valence-bond approach developed along Sidgwick-Powell lines (see, for example, the review by Gillespie and Nyholm)³⁴

simply quotes 5 coordinate species as most probably being formed by " sp^3d hybridisation". This involves, of course, the promotion of an 's' electron into the empty 'd' shell. If we take phosphorus as our example, we have the situation where ground-state P ($1s^2; 2s^2, 2p^6; 3s^2, 3p^3$) is converted to higher-energy state P ($1s^2; 2s^2, 2p^6; 3s^1, 3p^3; 3d^1$) and then hybridisation (or "mixing") of the 3s, 3p and 3d orbitals takes place. This may be conveniently described by Figure 7 (p. 16).

Now if 5 electrons were to be provided by 5 ligands to the P atom in 7(ii) - as shown by 'x's - we would obviously have sp^3d bonding. It will not be appropriate to deal with the mechanics of bond hybridisation here: it may be said that the configuration assumed by the " sp^3d " bonds is dependent on which d orbital is entered by the promoted 's' electron. Entering ' d_{z^2} ' leads to ' $sp^3d_{z^2}$ ' hybridisation and a trigonal bipyramidal arrangement of bonds; entering ' $d_{x^2-y^2}$ ' leads to ' $sp^3d_{x^2-y^2}$ ' and a consequent tetragonal pyramidal configuration.⁴⁶ The topic of pentacoordination and possible bonding schemes was considered in some detail by Kimball:⁴⁷ he concluded that for phosphorus pentachloride and other molecules "of this type" the trigonal bipyramid was the configuration assumed. Later examination demanded virtually 100% 'sp' character for axial bonds if observations on relative bond strengths were to be justified.⁴⁸ Moreover, two of the remaining d orbitals could form strong π bonds (as depicted in Figure 8),

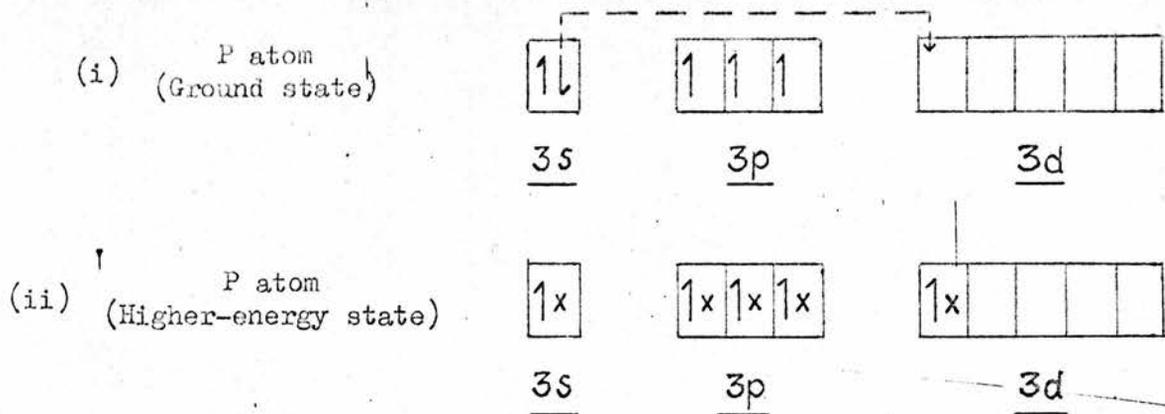


FIGURE 7: sp^3d hybridisation of phosphorus (outer-shell electrons only shown)

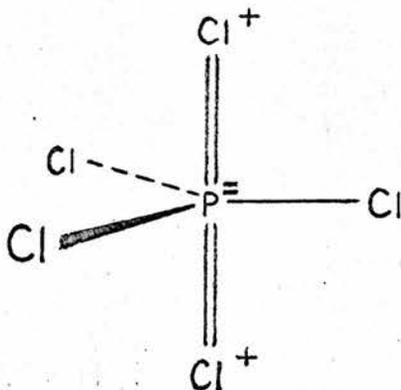


FIGURE 8: Cotton's suggested structure for PCl_5

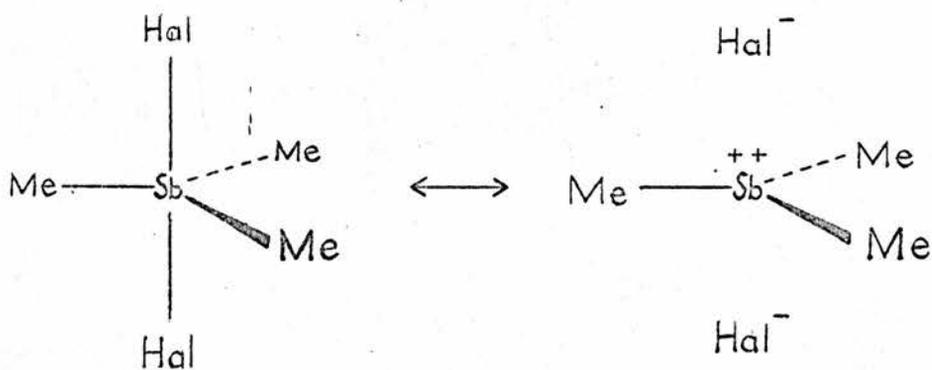


FIGURE 9: Wells' resonance hybrids for Me_3SbHal_2

a view unfortunately incompatible with modern bond-length data.

A simple semi-quantitative scheme to represent the bonding situation in pentacoordinated compounds has been proposed by Rundle,⁴⁹ which in fact is a development from an original idea of Pimentel,⁵⁰ previously applied with much success to other structures such as the polyhalide ions by Dutch workers.^{51,52} This scheme will be considered at greater length below (pp. 29 ff), but the basic ideas are as follows. No violation of the "Octet Rule" (as in the sp^3d approach) is required by picturing the axial bonds as three-centre, four-electron bonds constructed primarily from p-orbitals. Thus, it assumes an insignificant amount of s- and d-character in the axial bond: the three relevant atoms provide three atomic orbitals which lead to three molecular orbitals - these being bonding, non-bonding and anti-bonding respectively. Since the four bonding electrons naturally will fill the bonding and non-bonding orbitals (being of lowest energy), we have only two bonding electrons for two bonds. Hence the axial bonds are essentially "half-bonds" as opposed to the equatorial bonds which are regarded as normal two-electron bonds. The nature of the non-bonding contribution leads to an accumulation of charge on the extreme atoms of the three-centre bond. Consequently, axial bonds are both more polar and longer than equatorial bonds: it also follows that more electronegative substituents tend to occupy axial positions.

Rundle's predictions have been found valid in all structural studies on PF_5 , the mixed fluorochalides of phosphorus (V), and the fluorophosphoranes.^{53,54} Although not new, and not without publicity,^{49,52,55,56,57,58} the Rundle scheme has not had the general acceptance and acclaim it might deserve on the basis of its results so far. Pentacoordinate bonding has prompted several interesting exchanges,^{59,60} and indeed this fascinating subject is still very much at issue,^{61,62} Bartell being currently the most prominent champion of the Rundle cause.^{53,54,60} (A fine and thoroughly fitting epitaph to Rundle is to be found in one of his 1965 papers.)⁵⁴

The Fluorophosphoranes and the Phosphorus (V) Chlorofluorides

Any system of bonding (with its consequent stereochemical implications) can be - and almost certainly has been - fairly tested by attempted application to two groups of compounds, the fluorophosphoranes and the phosphorus (V) chlorofluorides. These series are somewhat analogous, as can be seen from the respective generalised formulae: $\text{R}_n\text{PF}_{(5-n)}$ and $\text{Cl}_n\text{PF}_{(5-n)}$ (R = alkyl or aryl group). Some of the structural work done on elucidating structures in the above series (considering R = Me only for brevity, being in any case a typical member of $\text{R}_n\text{PF}_{(5-n)}$) is summarised in Tables III and IV:-

TABLE III: The Phosphorus (V) Chlorofluorides ($\text{Cl}_n\text{PF}_{(5-n)}$)

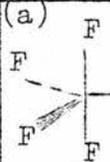
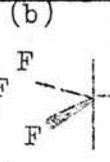
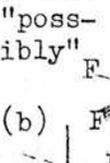
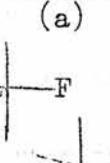
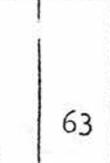
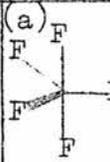
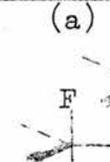
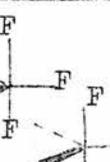
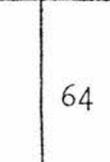
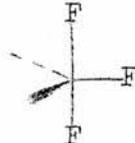
Year	Species investigated	Spectroscopic methods	Formulae proposed	Ref.
1938	(a) PF_5 (b) PF_3Cl_2	electron diffusion	(a)  (b) 	73
1963	(a) PF_3Cl_2 (b) PF_2Cl_3 (c) PFCl_4	^{19}F n.m.r.	"possibly" (a)  (b)  (c) 	63
1964	(a) PF_5 (b) PF_3Cl_2 (c) PF_2Cl_3 (d) PFCl_4	I.R.; Raman	(a)  (b)  (c)  (d) 	25
1964	(a) PF_3Cl_2 (b) PF_2Cl_3 (c) PFCl_4	^{35}Cl n.q.r.; ^{19}F n.m.r.	(a)  (b)  (c) 	64
1964	PF_3Cl_2	^{19}F n.m.r.		45
1965	PF_4Cl	I.R.; ^{19}F n.m.r.	no proposal	21
[continued]				

TABLE III (continued)

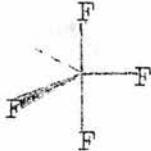
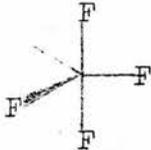
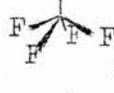
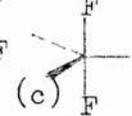
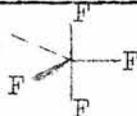
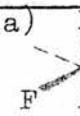
Year	Species investigated	Spectroscopic methods	Formulae proposed	Ref.
1967	PF_4Cl	I.R.; Raman; ^{35}Cl n.q.r.		65
1968	PF_4Cl	I.R.; ^{19}F n.m.r.; ^{31}P n.m.r.		66

TABLE IV: The Fluorophosphoranes ($\text{R}_n\text{PF}_{(5-n)}$)

Year	Species investigated	Spectroscopic methods	Formulae proposed	Ref.
1963	(a) PF_4Me (b) PF_3Me_2 (c) PF_2Me_3	I.R.; ^{19}F n.m.r.	(a)  <u>or</u>  (b)  (c)	67
1965	PF_4Me	I.R.; Raman		68
1965	(a) PF_4Me (b) PF_3Me_2	electron diffraction	(a)  (b) 	54
1967	(a) PF_3Me_2 (b) PF_2Me_3	I.R.; Raman; ^1H n.m.r.; ^{19}F n.m.r.; ^{31}P n.m.r.	(a)  (b) 	69

(Abbreviations:- The abbreviations used in the above tables are as follows: I.R. = infra-red spectroscopy; n.m.r. = nuclear magnetic resonance spectroscopy; n.q.r. = nuclear quadrupole resonance spectroscopy.)

Thus in spite of early uncertainties and apparent contradictions, a clear pattern can be seen to emerge with regard to the stereochemistry of these two families, both of which have been deemed worthy of considerable attention⁷⁰ over the last decade or so. (It will be noted that no mention of PMe_4 appears in the appropriate table above: in fact this compound as such has not yet been reported. There is no overriding reason why it should not exist, but it would very probably be in the ionic form $[\text{Me}_4\text{P}^+][\text{F}^-]$,⁶⁹ as would be deduced from below.)

It would appear that the general "rule" is that for the trigonal bipyramidal configuration the most electronegative ligands always tend to occupy the axial positions preferentially.^{54,69,70} This would, of course, be just as expected from Gillespie's V.S.E.P.R. Theory: space occupied by bonding electron pairs being all-important, it would seem only reasonable that the less electronegative ligands (and hence "bulkier" bonding electron-pairs) should assume the "less crowded" equatorial positions.^{38,39,40} This tendency would, however, also make good sense from the Rundle viewpoint:⁴⁹ the apical ligands are in fact occupying the extreme positions of the proposed 3-centre bond which - as explained earlier - would be expected to claim the most electronegative substituents, due to the nature of the non-bonding orbital involved. However, it is said that rules are made to be broken, and - just as the PF_3 bond angle⁷¹ caused some hasty re-thinking

in the Gillespie "rules" for bond lengths and bond angles - so, it would appear, the species $(\text{CF}_3)\text{PF}_4$ ⁷² must, for the present at any rate, be regarded as an exception to our above "rule".

A most intriguing facet of phosphorus (V) chemistry arising out of the general spectroscopic work done on structure determination is the observation that the difference (axial bond length - equatorial bond length) increases with number of less electronegative substituents present, i.e. in the series $\text{Me}_n\text{PF}_{5-n}$, say, $(r_{\text{ax}} - r_{\text{eq}})$ increases as n increases. This, of course, demands justification by any scheme of bonding which demands recognition as feasible. The Gillespie (V.S.E.P.R.) and Rundle (delocalisation) approaches "solve" this problem in different manners. Gillespie suggests⁵⁹ that Me substitution for F (effectively decreasing the electronegativity of P) will increase all bond lengths. But the axial fluorine bonds - being closer to the bulky (Me—P) bonds than their equatorial counterparts - will suffer a greater repulsion, and so increase more in length than the equatorial bonds. On the other hand, Bartell and Hansen⁵⁴ (using the Rundle approach) emphasise the analogy between the PF_5 , MePF_4 , Me_2PF_3 series and the PF_5 , SF_4 , ClF_3 series. However, use must be made of the 's' orbital now: in comparison with (P—F), a (P—C) bond orbital will have greater 's' character,⁷⁴ and in that respect will have closer affinity to a pair of non-bonding electrons. Hence, after the PF_5 , SF_4 , ClF_3 series, we can expect larger

($r_{ax} - r_{eq}$) values for increasing number of (P—C) bonds. Although taking care to avoid the use of 'd' orbitals, Bartell and Hansen really deviate from the original Rundle scheme by including 's' orbitals. An attractive picture is presented, however, by Downs and Schmutzler⁶⁹ who still support phosphorus 3d-orbital participation. Equatorial bonds are held to be largely 'sp' in character, while axial bonds have 'pd_z²' character. An increasing number of Me substituents would cause a steadily diminishing electrostatic field around P, with resultant increasing energy of the 'pd' combination. Ultimately the trigonal bipyramidal arrangement will cease to be energetically favourable, and compounds of predominantly ionic constitution can be expected (cf. reference to $[Me_4P^+][F^-]$ above).

In conclusion, it may be said that the subject of bonding in pentacoordinate phosphorus species is both fascinating and extremely complex. It seems certain that many years will pass before the topic will be classed as fully understood and rationalised.

Some Other Coordination Numbers of Phosphorus

It may be remembered that earlier reference was made to the "pentahalides" of the Group V(b) elements as being merely a formal stoichiometric term. The above section leads us to believe that the R_4MHal species will not, in fact, contain phosphorus with a coordination number of five. Indeed if we survey the series

PHal_5 , RPHal_4 , R_2PHal_3 , R_3PHal_2 , R_4PHal , R_5P , we will find that in many cases phosphorus does not have a coordination number of five: very often (as in $[\text{Me}_4\text{P}^+][\text{F}^-]$) it assumes a coordination number of four. Some of the pentahalides of phosphorus are found to be capable of existing in two different structural forms (e.g. $\text{PCl}_{5(s)}$ is $[\text{PCl}_4^+][\text{PCl}_6^-]$ ⁷⁵ while $\text{PBr}_{5(s)}$ is $[\text{PBr}_4^+][\text{Br}^-]$).⁷⁶ In fact, the structure assumed by any member of the $\text{R}_n\text{PHal}_{(5-n)}$ series is liable to be very dependent on the physical state of that compound (solid, liquid, vapour, solvent, etc.) and hence conditions should be carefully specified before quoting any structure. Thus $[\text{PCl}_4^+][\text{PCl}_6^-]$ of the solid state becomes, on melting, molecular $\text{PCl}_{5(l)}$ - i.e. the familiar trigonal bipyramid. At the other end of the series, R_5P is not a common species, the most simple existing case being $\text{R} = \text{Ph}$.⁷⁷ Pentaphenyl phosphorus was shown by X-ray analysis to have the trigonal bipyramid structure.⁷⁸ (It is interesting to note that while $\text{Ph}_5\text{As}_{(s)}$ ⁷⁹ is isomorphous with $\text{Ph}_5\text{P}_{(s)}$, Ph_5Sb has - anomalously - tetragonal pyramidal geometry⁸⁰ - although this seems to be the only well-established example of this stereochemistry in a five-coordinate compound of a Group V element.

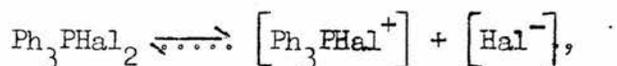
Many examples, however, of R_4PHal are known. They tend to be high-melting, crystalline solids, soluble in polar solvents in which they give highly-conducting solutions; this would suggest that they are ionic, both in the solid state and in solution.

Indeed there is no evidence of any $R_4\text{PHal}$ type of compound exhibiting a covalent structure.

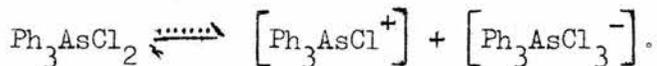
As might be expected, the picture concerning the intermediate members of our series, viz., RPHal_4 , R_2PHal_3 and R_3PHal_2 , is not so clearly established, and conflicting ideas were put forward by Rochow and Van Wazer.⁸² However, there now appears to be fairly firm evidence for both ionic and covalent forms in the RPHal_4 and R_2PHal_3 groups of compounds. Chloro-organo-phosphonium cations (of the type expected for the ionic forms of RPHal_4 and R_2PHal_3) have been demonstrated by ^{31}P n.m.r. to be present in $[\text{Ph}_4\text{PCl}_{4-n}]^+$ $[\text{ClO}_4]^-$ and $[\text{Ph}_n\text{PCl}_{4-n}]^+ [\text{SbCl}_6]^-$.⁸³ Also, recent ^{19}F n.m.r. investigations of a number of fluorophosphoranes (e.g. RPF_4 ; $\text{R} = \text{Me}$; Ph) suggest trigonal bipyramidal structure for these compounds.^{45,67}

The structure of the derivatives R_3PHal_2 has been discussed from time to time by various authors. The trimethylphosphine dihalides (i.e. $\text{R} = \text{Me}$; $\text{Hal} = \text{Cl}$, Br , or I) have been the subject of spectroscopic studies from which it has been shown that in the solid state ionic structures of the type $[\text{Me}_3\text{PHal}]^+ [\text{Hal}]^-$ are adopted.⁸⁴ It is interesting to note here that Wells, in 1938, having used X-ray diffraction methods to establish the trigonal bipyramidal structure of $\text{Me}_3\text{SbHal}_2$ ($\text{Hal} = \text{Cl}$, Br , I), proposed - with respect to bonding - the hybrids shown in Figure 9 (p. 16 supra). It can be seen that in Figure 9(ii) the Group V element in question has a coordination number of three. More recently,

however, trigonal bipyramidal structures have been confirmed for the trimethyl antimony dihalides.⁸⁵ The existence of the halo-triphenylphosphonium cation $[\text{Ph}_3\text{PHal}^+]$ in the tertiary phosphorus dihalides has been inferred from their high decomposition temperatures, solubility behaviour, and the electrical conductivities of their nitrobenzene solutions.⁸⁶ An extensive study of halogen adducts of the triaryl derivatives of the Group V(b) elements has been made by Harris and co-workers.^{87,88,89} The triarylphosphorus dihalides have been shown to be strong electrolytes in methylene cyanide solution, which again would suggest the corresponding solids to be ionic. The mode of ionisation in triphenylphosphorus dihalides has recently been shown by ^{31}P n.m.r. study,⁹⁰ and reaction with the strong chloride ion donor $\text{Et}_4\text{N}^+\text{Cl}^-$,⁹¹ to be



ionisation being complete. It is interesting to note that this mode of ionisation is not followed by the dichloride of triphenylarsenic. Although triphenylarsenicdibromide does ionise according to the above equation, the dichloride follows the scheme⁸⁸



However, if we consider the pentahalides of phosphorus, we see that the behaviour of the dichloride of triphenylarsenic has a parallel in the ionisations of the pentachloride and pentabromide

of phosphorus in methyl cyanide. Thus we get



It is clear, especially from fluorochloride studies, that many of the five-valent phosphorus compounds (with the notable exception of molecular PF_5) can exist in ionic as well as molecular forms. This adds, of course, to the number of compounds based on phosphorus (V) which can be encountered. A rich source of examples of bond isomerism is, indeed, the mixed pentahalide family of phosphorus. On preparation, the fluorochlorides of phosphorus usually form as molecular liquids. On standing they transform - generally over a period of days - to solid ionic modifications, both forms being moisture-sensitive. Taking PF_3Cl_2 as an example, the gaseous covalent molecule is formed when PF_3 and Cl_2 (gas or liquid) react,⁹⁴ but a white hygroscopic solid of this same composition - clearly ionic in nature - results when PCl_5 is treated with AsF_3 .⁹⁵ Transformation of the covalent to the ionic form has been reported to occur in acetonitrile.¹⁴ Closely paralleling the dimorphic character of PF_3Cl_2 is the behaviour of PF_3Br_2 . The ionic forms of these two molecules are, respectively, $[\text{PCl}_4^+][\text{PF}_6^-]$ and $[\text{PBr}_4^+][\text{PF}_6^-]$, while on the other hand the ionic forms of PCl_4F and PBr_4F are, respectively, $[\text{PCl}_4^+][\text{F}^-]$ ⁹⁶ and $[\text{PBr}_4^+][\text{F}^-]$,¹⁸ so that while the anionic form is often six-coordinate, it is by no means invariably so. It is perhaps relevant to note here that the $\text{AsF}_3\text{-Cl}_2$ reaction²⁸ yields $[\text{AsCl}_4^+][\text{AsF}_6^-]$ directly, and no

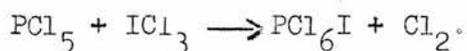
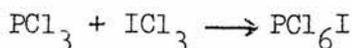
evidence can be found for molecular 'AsCl₂F₃', in contrast to the analogous phosphorus reaction. This reflects the instability of the pentavalent state for arsenic.

One example of a six-coordinate anion quoted above (in connection with the form assumed by PCl₅ in acetonitrile) was that of [PCl₆⁻]: in fact, as yet, phosphorus pentachloride is the only compound containing the [PCl₆⁻] ion. The relative instability of this ion - presumably on steric grounds, as examples of species containing [PF₆⁻] are numerous - is demonstrated by the reaction of AsF₃ on a solution of phosphorus pentachloride in arsenic trichloride, which produces [PCl₄⁺][PF₆⁻]. Thus the anion originally present (i.e. [PCl₆⁻]) is much less resistant to fluorination than the cation. By contrast, the cation present in the ionic form of phosphorus pentachloride, viz., [PCl₄⁺], is a much more stable entity. As a result, a large number of complexes based on the tetrachlorophosphonium ion, [PCl₄⁺], have been prepared, and have been covered fairly thoroughly in recent reviews.^{97,98,99,100} Some species formed (referred to in the above reviews) are: [PCl₄⁺][MoCl₆⁻]; [PCl₄⁺][SnCl₅⁻]; [PCl₄⁺][BCl₄⁻]. The apparently favourable stability of these complexes no doubt arises from the comparable size of the [PCl₄⁺] ion and the chloro-anions, resulting in favourable lattice energies.

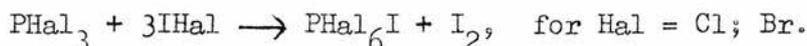
The Higher Halides of Phosphorus

Various polyhalides of the halo- and organohalophosphonium ions are known; their chemistry is more the chemistry of the polyhalide ions than that of the phosphonium ions which they contain. Clearly the halo- and organohalophosphonium ions in question are well suited to form stable lattices with ions of this type and size. While compounds of the form $[\text{P}\text{Hal}_4^+][\text{Hal}_3^-]$; $[\text{R}_n\text{P}\text{Hal}_{4-n}^+][\text{Hal}_3^-]$ or even $[\text{P}\text{Hal}_4^+][\text{Hal}_5^-]$; $[\text{R}_n\text{P}\text{Hal}_{4-n}^+][\text{Hal}_5^-]$ might be expected, some of the species encountered, e.g. the molecular PBr_7 , would involve an acceptor-donor system either monomerically or as a polymer and their bonding is an open question. However, in view of the orbitals available both to the phosphorus and the halogen, addition complexes of various kinds are possible, and halogen molecules may be able to interact to give complexes with high halogen to phosphorus ratios.

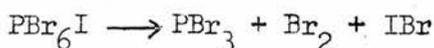
The first polyhalide complex, PCl_6I , was prepared more than a century ago by Baudrimont by several different techniques, including the following:-



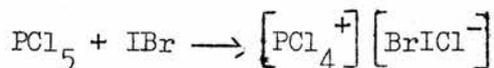
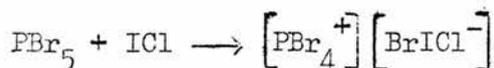
Much more recently, however, Fialkov and Kuz'menko prepared PCl_6I and PBr_6I by means of:



These crystalline compounds, stable at room temperature and readily soluble in polar organic solvents, have been shown to be ionic by the conductance of their solutions in nitrobenzene, acetonitrile and chloroform, by the conducting properties of their melts, and by cryoscopic studies.¹⁰¹ The structure $[\text{PHal}_4^+][\text{IHal}_2^-]$ postulated by Fialkov and co-workers for the above heptahalides was confirmed by spectrophotometric measurements in acetonitrile solution,¹⁰² and by X-ray study of the PCl_6I .¹⁰³ It should be noted, however, that in carbon tetrachloride solutions, phosphorus heptahalides dissociate molecularly rather than ionically,¹⁰² thus:-



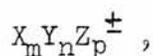
Finally, two compounds containing chlorine, bromine and iodine have been reported as the product of the following reactions in carbon tetrachloride solution:-



the ionic formulation¹⁰⁴ being suggested by electrical conductivity in nitrobenzene. (Phosphorus polyhalides containing chlorine and bromine have been reported, but these will be dealt with in a separate section, below.)

It should be pointed out that in spite of the large volume of written material on the polyhalide ions, both the data and the

interpretations are contradictory at times (e.g. the reasons behind the symmetry or asymmetry of the tri-iodide ion), and the chemistry of polyhalogen ions still presents many problems awaiting solution. This fact is due in no small measure to the inherent instability of polyhalogen compounds and polyhalide ions, which tend to lose halogen until a stable entity is formed. Polyhalide ions can be represented by a generalised formula:



where X, Y and Z represent either an identical, two different or, in the case of the anions, three different halogen atoms. The sum ($m + n + p$) is usually an odd number which can be 3, 5, 7 or 9. Although other types of anion have been reported, experimental evidence is not unambiguously convincing. The polyhalide ions identified more or less convincingly as anions or cations of electrovalent salts are listed in Table V (p. 32).

The crystal structures of compounds containing polyhalide ions have been studied quite intensively by a number of investigators, although their results have not always agreed. Even the ions which might appear most simple have been the subject of some controversy: thus the tri-iodide ion has been found to be both linear-symmetric and linear-asymmetric, an example of the former being the tri-iodide ion in $[\text{Ph}_4\text{As}^+][\text{I}_3^-]$ and of the latter being the anion in $[\text{Cs}^+][\text{I}_3^-]$. Different viewpoints have been put forward to explain this phenomenon,^{105,106} and further crystallo-

ographic and infra-red studies to attempt a rational explanation would be most welcome. Nor can it be said that the structures of the pentahalides and higher aggregates show great regularity. The

TABLE V: Polyhalide Complex Ions in Crystalline Salts

X_3^-	X_5^-	X_7^-	X_9^-	X_n^-	X_n^+
I_3^-	I_5^-	I_7^-	I_9^-	I_4^-	ICl_2^+
I_2Br^-	I_4Br^-	I_6Br^-			IF_4^+
I_2Cl^-	I_4Cl^-	IF_6^-			BrF_2^+
IBr_2^-	$I_2Br_3^-$	Br_6Cl^-			ClF_2^+
ICl_2^-	$I_2Br_2Cl^-$				
$IBrCl^-$	$I_2BrCl_2^-$				
$IBrF^-$	$I_2Cl_3^-$				
Br_3^-	$IBrCl_3^-$				
Br_2Cl^-	ICl_4^-				
$BrCl_2^-$	ICl_3F^-				
Cl_3^-	IF_4^-				
ClF_2^-	BrF_4^-				
	ClF_4^-				

pentahalides so far examined in detail fall into two classes:-

(a) the tetrachloroiodate ion^{107,108} (in $[K^+][ICl_4^-]$) and the tetrafluorobromate ion¹⁰⁹ (in $[K^+][BrF_4^-]$) both have the heavier halogen atom at the centre and four coplanar bonds to the lighter atoms, the angles between these bonds all being approximately 90° ;

(b) the pentaiodide ion⁵⁶ (in $[Me_4N^+][I_5^-]$) on the other hand has an entirely different structure, viz., V-shaped. Three higher polyhalide ions - all of iodine - investigated by X-ray diffraction, viz., I_7^- ,¹¹⁰ I_9^- ,¹¹¹ and I_4^- ,¹¹² have all been shown as built up from lower polyhalide ions (e.g. I_3^- ; I_5^-) and iodine molecules. The " I_4^- " ion is, in fact, octaiodide with double negative charge, i.e. $I_8^{=}$, and contains asymmetric I_3^- ions in the arms of its 'Z' configuration.

From the structural work done on the polyhalides, two significant themes emerge: (i) interatomic distances are usually larger than those found in the simple halogen molecules; (ii) the vast majority of bond angles are close to 90° or 180° (although there are a few exceptions, e.g. I_5^- has one angle of 156°). Hence an adequate theory of bonding in polyhalogen complexes will have to explain these two striking characteristics. Over the years, three types of interpretation have been put forward.

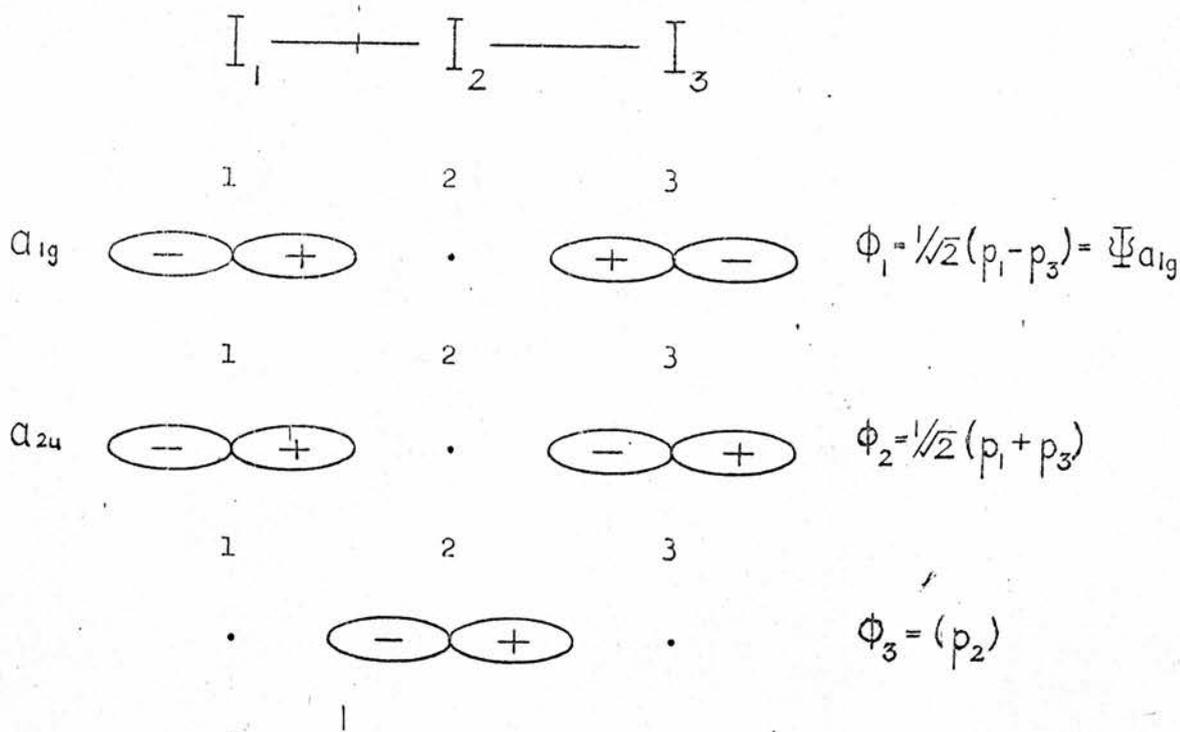
The first attempt was made on a non-quantum-mechanical basis and may be termed the "electrostatic" approach:¹¹⁴ bonding in the ions involved was described as an ion-dipole interaction between a given halide ion and a point dipole induced by it in an associated

halogen molecule. This approach, however, could not explain the symmetric tri-iodide ion or other symmetrical polyhalide ions, the interhalogens or the $[\text{ICl}_2^+]$ ion. In fact, its use was severely limited.

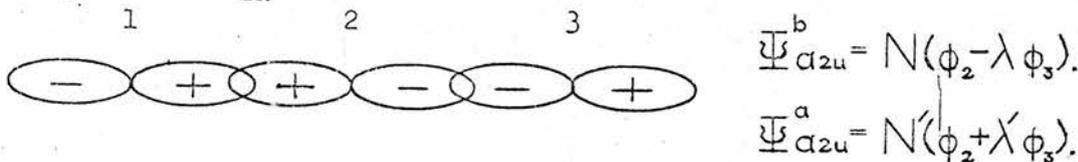
The second approach used localised covalent bonds: here, any increase in the valency of the central atom was achieved by promotion of 's' and 'p' electrons to 'd' orbitals. This theory was put forward by Kimball,⁴⁷ and has subsequently been accepted by many investigators. It has been referred to above and will not therefore be expanded here, except to mention that it has difficulty in justifying the structures of solid ICl and I_2Cl_6 and also those of I_5^- ; I_7^- ; I_9^- ; and I_8^- .

The third theory propounded was that of non-localised orbitals, first used for the case of I_3^- by Pimentel, and also referred to earlier.⁵⁰ The use of 'd' orbitals in the bonding was deemed unnecessary, tri-iodide formation being ascribed to delocalisation of the '5p' electron of the iodine atoms. Taking the classic case (I_3^-), the approach of Pimentel would be as in Figure 10 (p. 34).

The analogy with the apical (Hal—P—Hal) bonds in the trigonal bipyramid can be clearly seen from Figure 10. Without expanding on it here,⁴⁹ this figure also gives a justification for elongation of bond lengths (2 bonding electrons for 2 bonds) and angles of approximately 90° or 180° (p orbitals only in use). This



Hence we get from a_{2u} :-



And so the bonding scheme is:-

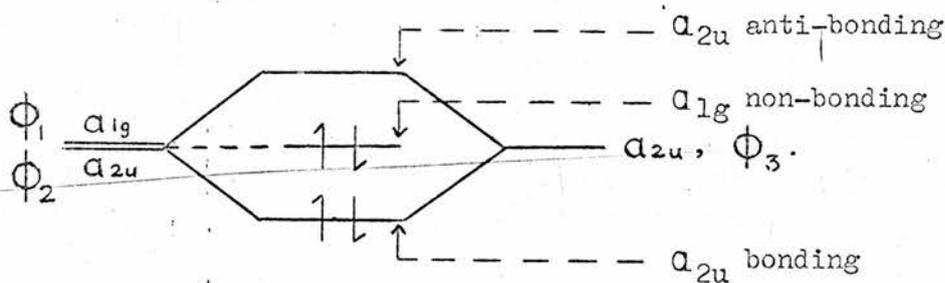


FIGURE 10: Molecular Orbital Description of the Bonding in I_3^-

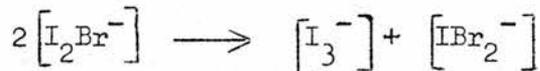
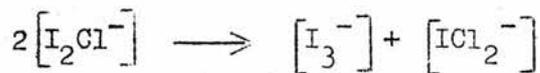
"molecular-orbital" method has been taken up and publicised^{51,52,115} by Havinga, Wiebenga and co-workers in Holland and, indeed, they have found it possible to give a consistent qualitative explanation⁵¹ of the bond angles, atomic configurations, and bond lengths in all polyhalogen complexes by means of it. Strong support for the above reliance on 'p' electrons was obtained after nuclear quadrupole resonance studies¹¹⁶ showed the bonds in chloriodides to have negligible 's' and 'd' character. A limitation of this general method, however, is the well-known difficulty connected with the crude "Linear Combination of Atomic Orbitals" method, viz., the extra stability obtained when more atoms are added to a complex. Thus, one cannot predict, by this method, the number of atoms in a complex, but only the configuration of a given number of atoms.

It can also be seen that this scheme is in accord with the general stability trends observed. By the nature of the non-bonding contribution, the most electronegative atoms would be at the extremities of any trihalide ion: in fact the heaviest halogen atom in the given ion has always been observed to occupy the central position. Thus $[I_2Cl]^-$ is $[I-I-Cl]^-$ and not $[I-Cl-I]^-$. Similarly, symmetry will be important, and it is found that ICl_2^- which of course will be $[Cl-I-Cl]^-$ is indeed more stable than $[I-I-Cl]^-$. The order of stabilities has been determined by three different methods, and the results for trihalides of the same cation are shown in Table VI:-

TABLE VI: Order of Decreasing Stability for Trihalides of the Same Cation

Dissociation pressure ¹¹⁷	CCl ₄ method ¹¹⁸	Dissociation in H ₂ O ¹¹⁹
I ₃ ⁻	ICl ₂ ⁻	I ₃ ⁻
IBr ₂ ⁻	IBr ₂ ⁻	IBr ₂ ⁻
ICl ₂ ⁻	I ₃ ⁻	BrCl ₂ ⁻
I ₂ Br ⁻	IBrCl ⁻	ICl ₂ ⁻
Br ₃ ⁻		Br ₃ ⁻
BrCl ₂ ⁻		I ₂ Br ⁻
Br ₂ Cl ⁻		I ₂ Cl ⁻
		Cl ₃ ⁻

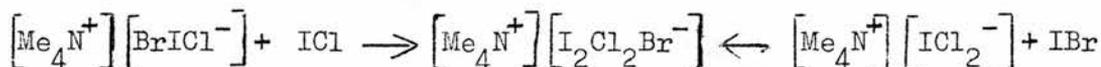
Thus, the trihalide ions, I₂Cl⁻; I₂Br⁻; and IBrCl⁻ are found to dissociate:-



As mentioned earlier, polyhalides are not stable with respect to dissociation, and this dissociation always takes place in such a way that the halogen or interhalogen molecules formed contain the heaviest halogen atoms. Thus we get $[Cs^+][ICl_2]^- \longrightarrow [Cs^+][Cl]^- + [ICl]$ and not $[Cs^+][ICl_2]^- \longrightarrow [Cs^+][I]^- + Cl_2$. Similarly, in

solution we get $[\text{ICl}_4^-] \rightarrow [\text{ICl}_2^-] + \text{Cl}_2$, and $[\text{ICl}_2^-] \rightarrow [\text{Cl}^-] + \text{ICl}$.

Considering briefly the reverse process, Cremer and Duncan¹²⁰ observed that while it was possible to add a halogen molecule to a polyhalide ion, such as $\text{ICl}_2^- + \text{Cl}_2 \rightarrow \text{ICl}_4^-$, their attempts to add an interhalogen molecule to a polyhalide ion were unsuccessful, i.e. $[\text{ICl}_2^-] + \text{ICl} \not\rightarrow [\text{I}_2\text{Cl}_3^-]$. Recently, however, it has been shown that this generalisation is incorrect,¹²¹ and the following reactions have been successfully performed:-



The Phosphorus Trichloride-Bromine Reaction

The expected reaction of phosphorus trichloride and bromine in the 1:1 ratio, although exothermic, does not yield a simple product. The study of this complex system has been attempted using the $\text{PCl}_3\text{-Br}_2$; $\text{PCl}_5\text{-PBr}_5$; $\text{PCl}_5\text{-PBr}_3$; and $\text{PCl}_3\text{-PBr}_5$ systems. It is, however, true to say that no really clear understanding has yet been achieved. The investigations can be divided chronologically into three groups: 1847-1886 and 1928-1934, concerned primarily with synthesis of definite chlorobromides, while the third group (1951 onwards) has been primarily interested in re-investigating the system with more modern techniques.

Although claims for PCl_3Br have been made,^{122,123} no compound of this stoichiometry has ever been isolated.^{124,125} Solids with

a variety of composition, e.g. PCl_2Br_7 , PCl_4Br , and PCl_3Br_n (where $n = 4 - 10$)¹²⁶ have been mentioned as being obtained from this ratio of $\text{PCl}_3:\text{Br}_2$. In arsenic trichloride the reaction is simpler, the two components giving a solid of composition $\text{PCl}_{4.5}\text{Br}_{0.5}$ which is assumed to be $[\text{PCl}_4^+][\text{PCl}_5\text{Br}^-]$: on heating this solid, PCl_5 remains.¹²⁷ The cryoscopic behaviour of $\text{PCl}_3\text{-Br}_2$ mixtures in nitrobenzene can be explained in terms of PAl_5 and PAl_7 species, but no isolation has been attempted.¹²⁸ Fialkov and Kuz'menko studied the temperature-composition relationship, the specific conductance and the viscosity of this system. On the basis of their results they reported the formation of definite compounds with the composition of PCl_3Br_4 , PCl_3Br_8 and $\text{PCl}_3\text{Br}_{18}$.^{129,130} From these data as well as from ion-transference measurements, the authors suggested that these compounds are ionic and that their structure can be represented by $[\text{PCl}_3\text{Br}^+].[\text{Br}(\text{Br}_2)_n^-]$.

Some of the above results, however, could not be reproduced experimentally in a later study.¹³¹ An addition of an excess of bromine to PCl_3 yielded a solid compound with a variable composition $\text{PCl}_3\text{Br}_{5.1-5.7}$, which was unstable at room temperature, losing bromine readily. When kept under vacuum, it continued to lose bromine until it attained the composition $\text{PCl}_{4.67}\text{Br}_{0.33}$. The latter compound was characterised unambiguously by X-ray powder studies and was shown to be a unique single phase with the composition $\text{P}_{12}\text{Cl}_{56}\text{Br}_4$, consisting of an arrangement of 8 $[\text{PCl}_4^+]$ ions, 4

$[\text{PCl}_6^-]$ ions and 4 $[\text{Br}^-]$ ions in the unit cell. It appears, therefore, that the presence of polybromide ions in the $\text{PCl}_3\text{-Br}_2$ system is still largely problematical. This system is the more interesting since the first reactions studied in this thesis will be those between PhPCl_2 and the halogens, including bromine, and between Ph_2PCl and the same halogens.

Related Systems Previously Studied

As mentioned earlier, an extensive survey of the halogen adducts of triaryl derivatives of the Group V(b) elements has been made by Harris and co-workers. Having mentioned the series $\text{Ph}_n\text{PCl}_{(3-n)}$ above (for $n = 0, 1, 2$), it is worth noting that the remaining member of the series (*i.e.* Ph_3P , for $n = 3$) has already been thoroughly studied with respect to its reactions with halogens. In fact, Beveridge studied the family $\text{Ph}_3\text{M} + \text{Halogens}$, where $\text{M} = \text{P}$, As , or Sb . This line of work was carried on by Inglis, who studied the systems $\text{Ph}_3\text{Bi} + \text{Halogens}$, and also $(\text{p-Me-C}_6\text{H}_4)_3\text{As} + \text{Halogens}$ and $(\text{p-Cl-C}_6\text{H}_4)_3\text{As} + \text{Halogens}$. Finally, Ali introduced ICl and ICl_3 into the scheme, reacting them with Ph_3M , for $\text{M} = \text{P}$, As and Sb . Following the pattern of Inglis, he then introduced groups of differing electronegativities to the Group V(b) elements in question, allowing study of the $(\text{C}_6\text{F}_5)_3\text{M}$ and $(\text{Me}_2\text{N})_3\text{M}$ (for $\text{M} = \text{P}$ and As) systems with halogens.

As well as venturing down the $\text{Ph}_n\text{PCl}_{(3-n)}$ series by using

PhPCl_2 and Ph_2PCl , the work of this thesis also probes further into the series $(\text{C}_6\text{F}_5)_n\text{PPh}_{(3-n)}$ - started by Ali (for $n = 3$) - by considering the systems $(\text{C}_6\text{F}_5)_n\text{PPh}_{(3-n)}$ for $n = 2, 1$ with halogens. Finally, the more electropositive p-tolyl group is introduced on to phosphorus, and the $(\text{p-Me-C}_6\text{H}_4)_3\text{P}$ - Halogen systems studied.

PART I

PART I:

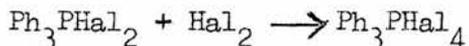
SOME REACTIONS OF PHENYLDICHLOROPHOSPHINE
AND DIPHENYLCHLOROPHOSPHINE WITH HALOGENS

	Page
1. <u>Introduction</u>	42
2. <u>Results and Discussion</u>	43
(a) Reactions of PhPCl_2 with Halogens	43
(i) Reaction of PhPCl_2 with chlorine	43
(ii) Reaction of PhPCl_2 with bromine	47
(iii) Reaction of PhPCl_2 with iodine	47
(iv) Reaction of PhPCl_2 with iodine chloride	53
(v) Reaction of PhPCl_2 with iodine bromide	57
(vi) Reaction of PhPCl_2 with iodine tri- chloride	60
(vii) Reaction of $\text{PhPCl}_2 \cdot \text{Cl}_2$ with iodine chloride	62
(viii) Reaction of $\text{PhPCl}_2 \cdot \text{Cl}_2$ with iodine bromide	65
(b) Reactions of Ph_2PCl with Halogens	67
(i) Reaction of Ph_2PCl with chlorine	67
(ii) Reaction of Ph_2PCl with bromine	70
(iii) Reaction of Ph_2PCl with iodine	71
(iv) Reaction of Ph_2PCl with iodine chloride	74
(v) Reaction of Ph_2PCl with iodine bromide	75
(vi) Reaction of Ph_2PCl with iodine tri- chloride	80
(vii) Reaction of $\text{Ph}_2\text{PCl} \cdot \text{Cl}_2$ with iodine chloride	81
(c) Reactions of PCl_3 with Iodine Chloride and Iodine Trichloride	84
(i) Reaction of PCl_3 with iodine chloride	85
(ii) Reaction of PCl_3 with iodine trichloride	86
3. <u>Summary</u>	88

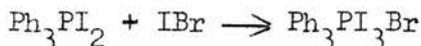
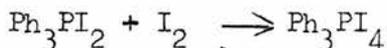
1. Introduction

As explained earlier, much work has been done on the Ph_3P - Halogen systems, and also on the PCl_3 - Halogen systems. Relatively little, however, is known of the reactions of halogens with PhPCl_2 and Ph_2PCl .

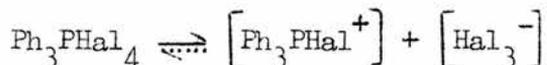
Conductometric studies have shown that the triphenylphosphorus dihalides are strong electrolytes in acetonitrile. The tetrahalides (Ph_3PHal_4) have been obtained as crystalline solids by the addition of halogen to the dihalides in acetonitrile:



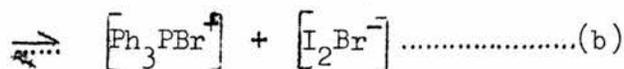
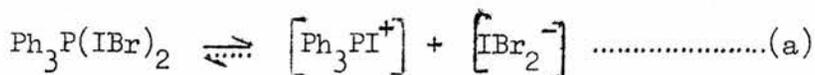
It has been found possible to prepare both simple and mixed tetrahalides, e.g.:



With regard to tetrahalides containing only one kind of halogen atom, it has been shown by conductance measurements and the ultraviolet spectra of their methyl cyanide solutions that trihalide ions are present, arising from the ionisation:⁸⁸



With mixed tetrahalides, of course, two ionisation schemes are theoretically possible, viz.:



Ultraviolet examination of MeCN solutions shows mode (b) to occur, and the general rule - as yet without exception - appears to be that in the mixed tetrahalides, the cation contains the halogen of lower atomic number.

It should be added that although many of the adducts indicated by conductometric titrations have been isolated as crystalline solids, several could not be obtained as pure solids, particularly when chlorine was involved, as opposed to the heavier halogen atoms, Br and I. This instability as solids may be attributed to two factors: first, the ready dissociation of the unsymmetrical trihalide ions, e.g. I_2Cl^- , and second, the great moisture sensitivity of (M—Hal) bonds, especially on passing to the most electronegative halogen used, viz., chlorine.

2. Results and Discussion

(a) The Reactions of Phenyldichlorophosphine with Halogens

(i) The PhPCl_2 -chlorine system

The results of the conductometric titration of phenyldichlorophosphine with chlorine in acetonitrile are recorded in Table VII and illustrated graphically in Figure 11:-

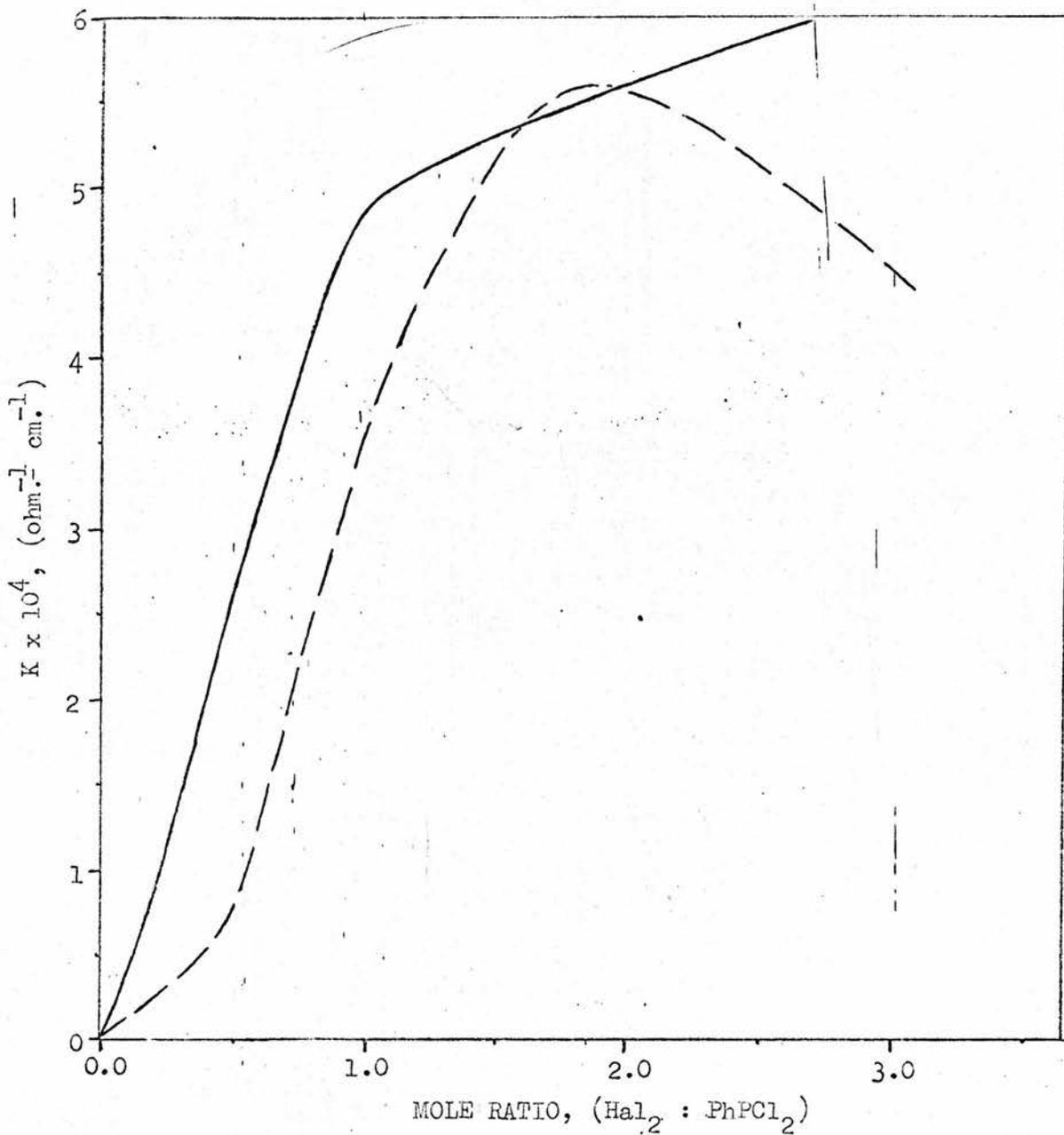


FIGURE 11: Conductometric Analysis of the Systems:

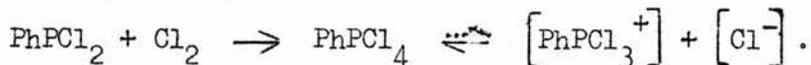
PhPCl₂-Cl₂: 
PhPCl₂-I₂: 

TABLE VII: Conductometric Analysis of the System PhPCl₂-Cl₂

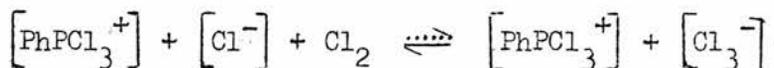
<u>Mole ratio</u> (Cl ₂ : PhPCl ₂)	<u>K x 10⁴</u> (ohm. ⁻¹ cm. ⁻¹)
0.000	0.0548
0.108	0.0598
0.216	1.177
0.324	2.223
0.432	2.842
0.540	3.466
0.648	4.056
0.757	4.338
0.865	4.700
0.972	4.829
1.080	4.928
1.189	5.136
1.404	5.332
1.621	5.490
1.838	5.650
2.054	5.813
2.266	5.979
2.483	6.061
2.700	6.150

The graph shows a distinct inflection at the 1:1 mole ratio, indicating formation of the 1:1 adduct, PhPCl₄, in acetonitrile solution. Although the value of specific conductance rises steadily up to the 1:1 ratio, the molar conductance value for the 1:1 mixture, i.e. PhPCl₄, in acetonitrile is very low ($\Delta_m = 16.88$ ohm.⁻¹ cm.² mole⁻¹; $c_m = 0.02884$ mole/l.) thus indicating PhPCl₄ to

be a weak electrolyte in the given solvent. Thus, for the reaction up to the 1:1 mole ratio in acetonitrile (during which time the solution remained colourless), we may write:



At higher (Halogen:Phosphine) ratios, the solution exhibits a yellow-green colour, i.e. the colour of Cl_2 solution in MeCN, the colour becoming progressively more intense with higher ($\text{Cl}_2:\text{PhPCl}_2$) ratio. Even beyond the 1:1 mole ratio, however, the conductance continues to increase, albeit much less rapidly than previously. This increase is probably due to a small amount of trichloride ion formed in solution by the equilibrium reaction:



the equilibrium lying well to the left-hand side. The trichloride ion has, indeed, been postulated in acetonitrile in the $(\text{Me}_2\text{N})_3\text{P}-\text{Cl}_2$ reaction (by Ali), the species $[(\text{Me}_2\text{N})_3\text{PCl}^+][\text{Cl}^-]$ actually being isolated, and having a molar conductance value in acetonitrile $\Lambda_m = 78.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ($c_m = 0.022 \text{ mole/l}$). However, the low value of Λ_m found in the present system at 2:1 ratio, viz., $\Lambda_m = 19.58 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ($c_m = 0.02884 \text{ mole/l}$), ties in with the fact that no solid species "PhPCl₆" or "[PhPCl₃⁺][Cl₃⁻]" could be isolated from acetonitrile solution, even on adding chlorine beyond the 2:1 mole ratio. The 1:1 adduct, PhPCl₄, was, however, isolated on slowly passing a $\text{Cl}_2(\text{g})$ mixture through cool PhPCl₂/MeCN solution.

(The PhPCl_4 so prepared was carefully stored and used in later conductometric work with iodine chloride and iodine bromide.)

(ii) The PhPCl_2 -bromine system

The background to this system is most interesting in view of the complexity of the closely-related PCl_3 - Br_2 reaction, particularly in that Harris found the PCl_3 - Br_2 -MeCN system totally unsuitable for conductometric analysis. Fortunately, it was found that the replacement of one chlorine atom by a phenyl group gave a system PhPCl_2 - Br_2 -MeCN which could lend itself to conductometric analysis. The titration figures are to be found in Table VIII(a) and (b), and the conductance-composition graphs are reproduced in Figure 12 (pages 49 and 48 respectively). Two complete sets of titration data have been included to demonstrate the sizeable effect of concentration on conductometric results. The repeat titration (Table VIII(b) and Figure 12(b)) was performed at higher concentration (ca.2.5 X) than the original run, and precipitation was found to occur in the conductometric flask: this produced a marked change in conductance-composition graph, the arrows in Figure 12(b) signifying the onset and cessation of precipitation. It is postulated that the course of titration (b) would follow path (-·-·-·-·-) between the precipitation limits had no precipitation occurred: this would give curves (a) and (b) similar character, viz., a smooth "rounded" curve, with no inflections below the

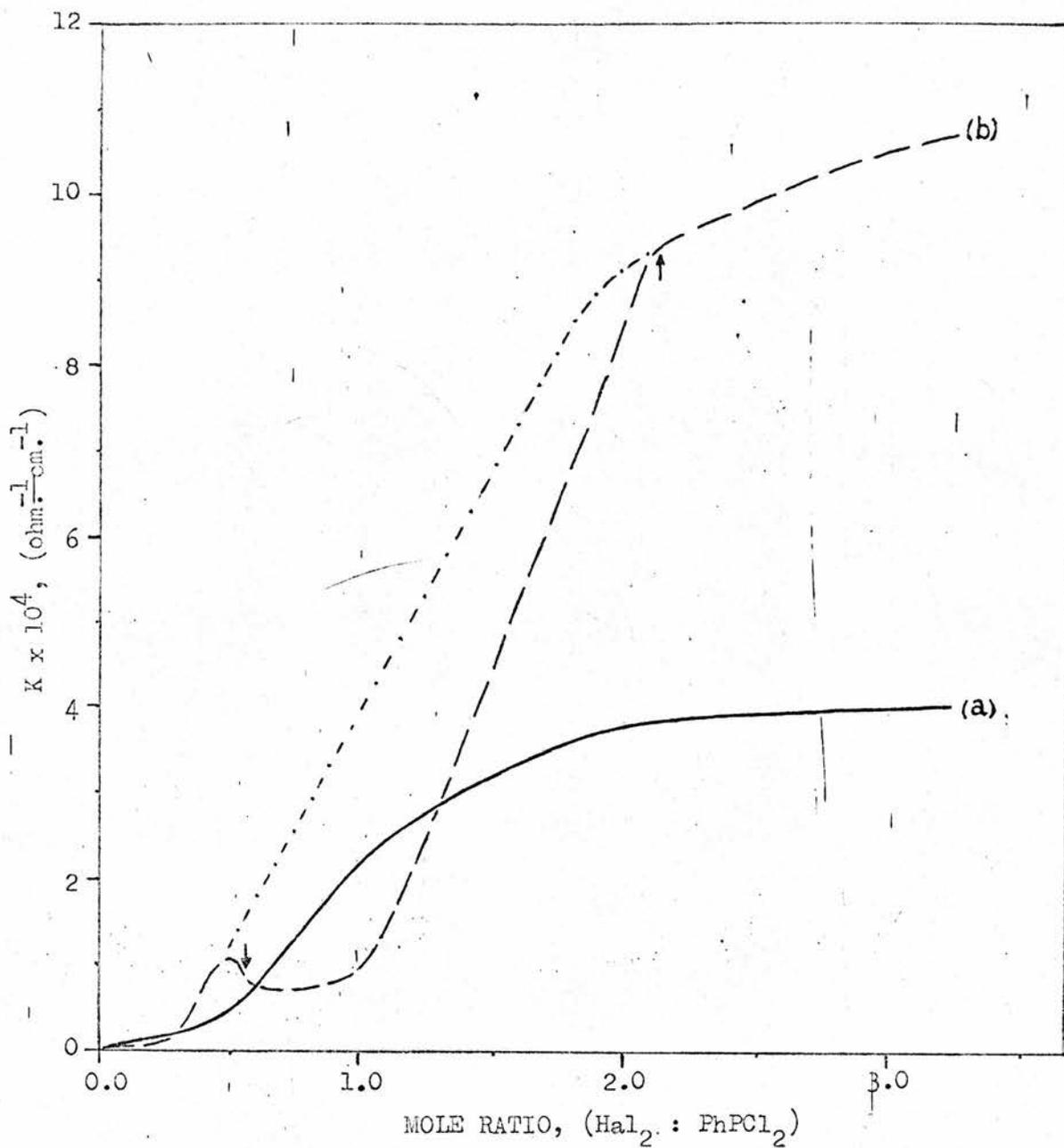


FIGURE 12: Conductometric Analysis of the System $\text{PhPCl}_2\text{-Br}_2$

(a) ————— with non-occurrence of precipitate

(b) - - - - - with occurrence of precipitate
(arrows show limits of precipitation)

TABLE VIII: Conductometric Analyses of the System $\text{PhPCL}_2\text{Br}_2$

(a)

Mole ratio $\frac{\text{Mole ratio}}{(\text{Br}_2:\text{PhPCL}_2)}$	$\frac{\text{K} \times 10^4}{(\text{ohm} \cdot \text{cm}^{-1})}$	Mole ratio $\frac{\text{Mole ratio}}{(\text{Br}_2:\text{PhPCL}_2)}$	$\frac{\text{K} \times 10^4}{(\text{ohm} \cdot \text{cm}^{-1})}$	Mole ratio $\frac{\text{Mole ratio}}{(\text{Br}_2:\text{PhPCL}_2)}$	$\frac{\text{K} \times 10^4}{(\text{ohm} \cdot \text{cm}^{-1})}$
0.000	0.0364	1.236	3.041	2.433	3.797
0.140	0.0639	1.335	3.133	2.531	3.824
0.259	0.0935	1.435	3.190	2.632	3.854
0.339	0.118	1.535	3.251	2.733	3.881
0.439	0.126	1.635	3.378	2.830	3.910
0.539	0.265	1.735	3.491	2.930	3.940
0.639	0.635	1.835	3.563	3.031	3.971
0.738	1.126	1.934	3.612	3.130	4.000
0.838	1.721	2.034	3.662	3.229	4.032
0.938	2.280	2.134	3.714	3.310	4.064
1.038	2.652	2.252	3.750	3.430	4.097
1.137	2.921	2.331	3.770		

(b)

Mole ratio $\frac{\text{Mole ratio}}{(\text{Br}_2:\text{PhPCL}_2)}$	$\frac{\text{K} \times 10^4}{(\text{ohm} \cdot \text{cm}^{-1})}$	Mole ratio $\frac{\text{Mole ratio}}{(\text{Br}_2:\text{PhPCL}_2)}$	$\frac{\text{K} \times 10^4}{(\text{ohm} \cdot \text{cm}^{-1})}$	Mole ratio $\frac{\text{Mole ratio}}{(\text{Br}_2:\text{PhPCL}_2)}$	$\frac{\text{K} \times 10^4}{(\text{ohm} \cdot \text{cm}^{-1})}$
0.000	0.0173	1.310	4.062	2.642	10.200
0.097	0.0418	1.429	5.502	2.764	10.310
0.238	0.0669	1.556	6.700	2.885	10.450
0.361	0.0903	1.672	7.643	3.004	10.570
0.460	1.040	1.794	8.475	3.126	10.600
0.584 *	0.771	1.915 *	9.128	2.246	10.600
0.703	0.758	2.036	9.630	3.373	10.600
0.836	0.847	2.156	9.735	3.490	10.520
0.945	0.910	2.280	9.849		
1.067	1.220	2.400	9.960		
1.188	2.203	2.522	10.080		

(asterisks denote limits of precipitation)

2:1 mole ratio, thereafter approaching the horizontal. (A third titration, performed with the sole purpose of establishing onset of precipitation, started to throw down precipitate at ca.0.9:1 mole ratio ($\text{Br}_2:\text{PhPCl}_2$), showing the 0.5:1 precipitation - and hence also, presumably, the "humped" graph (b) - to be entirely fortuitous. The conductance-composition graph is therefore taken to be of similar shape to that obtained for the $\text{PhPCl}_2\text{-I}_2$ system (directly below), showing no marked inflections - the typical behaviour of an equilibrium system.

Molar conductance values were calculated for titration (a) and titration (b) at both the 1:1 and the 2:1 mole ratios. The values obtained were:-

Titration (a):

$$1:1; \quad \Lambda_m = 21.15 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.01216 \text{ mole/l.})$$

$$2:1; \quad \Lambda_m = 37.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.00974 \text{ mole/l.})$$

Titration (b):

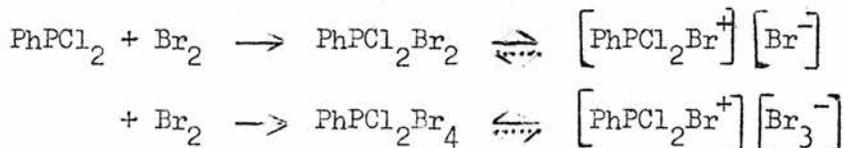
$$1:1; \quad \Lambda_m = 3.40* \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.02971 \text{ mole/l.})$$

$$2:1; \quad \Lambda_m = 37.10 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0256 \text{ mole/l.})$$

(*Note anomalously low value due to precipitation effect: the Λ_m 's measured at the 2:1 ratio agree rather well.)

The reaction solution was colourless until the 1:1 mole ratio was approached, when it assumed a yellow colouration. This change of colour could be monitored on the ultraviolet spectrum, the appearance of yellow colouration coinciding with the appearance of tribromide ion (Br_3^-) giving the absorption $\lambda_{\text{max.}} = 269 \text{ m}\mu$. The

appearance of Br_3^- at slightly less than 1:1 ratio, coupled with the lack of inflection in the titration graph, could well mean that the equilibria present overlap slightly, the second beginning to be set up before the completion of the first:-



The fairly low Λ_m values indicate weak electrolyte behaviour for both the 1:1 and the 2:1 adduct, hence the equilibria signs.

Two (yellow) solids were isolated from the system, viz., $\text{PhPCl}_2\text{Br}_2$ and $\text{PhPCl}_2\text{Br}_4$ at mole ratios (0.5:1) and (2:1) respectively, the former again demonstrating the point frequently found in past investigations of P(III) \rightarrow (P(V)) systems that the composition of the compound which crystallises from solution at a stoichiometric mole ratio need not reflect the composition of the solution. Thus the species precipitated during the conductometric analysis (b) must have been $\text{PhPCl}_2\text{Br}_2$. On dissolving solid $\text{PhPCl}_2\text{Br}_2$ in acetonitrile at molar concentration $c_m = 0.0129$ mole/l. the molar conductance at 25°C was found to be $\Lambda_m = 12.71$ ohm $^{-1}$ cm 2 mole $^{-1}$. It was found that on adding bromine directly to the above solution, the conductance steadily rose with each successive bromine addition.

(iii) The PhPCl_2 -iodine system

Conductometric analysis of the PhPCl_2 - I_2 system gave the

results laid out in Table IX and illustrated graphically in Figure 11 (p. 44 supra).

TABLE IX: Conductometric Analysis of the System $\text{PhPCl}_2\text{-I}_2$

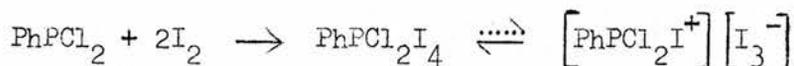
Mole ratio $\left(\frac{\text{I}_2}{\text{PhPCl}_2}\right)$	$\frac{\text{K} \times 10^4}{(\text{Ohm}^{-1} \text{ cm.}^{-1})}$	Mole ratio $\left(\frac{\text{I}_2}{\text{PhPCl}_2}\right)$	$\frac{\text{K} \times 10^4}{(\text{Ohm}^{-1} \text{ cm.}^{-1})}$	Mole ratio $\left(\frac{\text{I}_2}{\text{PhPCl}_2}\right)$	$\frac{\text{K} \times 10^4}{(\text{Ohm}^{-1} \text{ cm.}^{-1})}$
0.000	0.0173	1.225	4.860	2.450	5.067
0.214	0.108	1.379	5.180	2.600	4.991
0.306	0.211	1.531	5.316	2.754	4.922
0.478	0.800	1.684	5.430	2.910	4.839
0.612	1.941	1.837	5.442	3.060	4.708
0.765	2.938	1.990	5.295	3.215	4.603
0.918	3.797	2.144	5.192	3.370	4.490
1.071	4.565	2.294	5.118		

Both the conductance-composition graph and the ultraviolet examination show the reaction to produce the tetrahalide, PhPCl_2I_4 , from the start. The characteristic 291 μ . and 360 μ . absorptions of triiodide ion are present in the ultraviolet spectrum from the first trace of iodine added: the titration graph shows no inflections, but attains a maximum value near the 2:1 iodine:phosphine mole ratio and thereafter 'K' decreases, due to lack of further ion formation in a solution of increasing volume. The form of the curve (cf. $\text{Br}_2\text{-PhPCl}_2$ system above) suggests an equilibrium system, and the molar conductance values for the solution at 1:1 at 2:1 ratios suggest weak electrolyte behaviour:-

$$1:1; \Lambda_m = 30.80 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} (c_m = 0.0138 \text{ mole/l.})$$

$$2:1; \Lambda_m = 45.70 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} (c_m = 0.0116 \text{ mole/l.})$$

Thus we may write the reaction as follows:-



Neither the dihalide adduct (with no evidence for its formation in solution) nor the tetrahalide (apparently formed in acetonitrile solution) could be isolated as stable solids. Attempts to prepare solid adducts, using mole ratios of halogen:phosphine near 1:1 and 2:1, yielded oils in both cases so extremely unstable as to render analysis meaningless. This outcome is quite in accord with previous research on such classes of compound, where much evidence points to general lack of interaction between iodine and phosphorus (III) halides to produce a phosphorus (V) halide. This situation is partly due to the steric effect of the large iodine atoms and partly due to the low electronegativity of iodine which operates against its presence in compounds containing a phosphorus atom in its higher oxidation state. Many of such adducts identified in the past have been found to be stable only at low temperatures, if at all.¹³³

(iv) The PhPCl₂-iodine chloride system

As can be seen from Figure 13 (p. 58), the conductance-composition graph for the PhPCl₂-ICl system is rather complicated, showing a maximum just beyond the 1:1 mole ratio, and a minimum

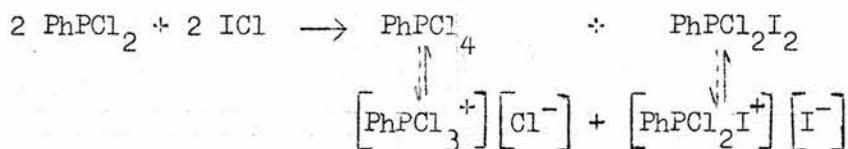
near $\text{ICl}:\text{PhPCl}_2::1.5:1$. The relevant statistics are listed in Table X:-

TABLE X: Conductometric Analysis of the System $\text{PhPCl}_2\text{-ICl}$

Mole ratio ($\text{ICl}:\text{PhPCl}_2$)	$\frac{K \times 10^4}{(\text{Ohm}^{-1} \text{ cm.}^{-1})}$	Mole ratio ($\text{ICl}:\text{PhPCl}_2$)	$\frac{K \times 10^4}{(\text{Ohm}^{-1} \text{ cm.}^{-1})}$	Mole ratio ($\text{ICl}:\text{PhPCl}_2$)	$\frac{K \times 10^4}{(\text{Ohm}^{-1} \text{ cm.}^{-1})}$
0.000	0.0174	1.313	1.348	2.542	2.989
0.102	0.122	1.424	0.913	2.643	3.133
0.204	0.182	1.527	0.841	2.749	3.290
0.306	0.252	1.628	0.859	2.852	3.463
0.408	0.320	1.730	0.963	2.953	3.610
0.509	0.439	1.831	1.178	3.952	3.661
0.610	0.517	1.932	1.539	3.154	3.717
0.713	0.655	2.034	1.882	3.258	3.797
0.815	0.867	2.137	2.182	3.359	3.880
0.917	1.221	2.239	2.407	3.460	3.973
1.019	1.627	2.340	2.626		
1.180	1.733	2.440	2.857		

This rather complex type of conductance behaviour is not altogether unexpected, however, as Ali obtained a graph of the same form for the system $\text{Ph}_3\text{P-ICl}$: in the latter case, though, the maximum and minimum were found to occur at the Halogen:Phosphine ratios of 0.67:1 and 1.33:1 respectively. Moreover, for the $\text{Ph}_3\text{P-ICl}$ system, Ali found no evidence of trihalide ion absorption in the ultra-violet region below the 0.67:1 maximum, whereas triiodide ion absorption ($\lambda_{\text{max.}} = 360, 291 \text{ m}\mu$) is present in the $\text{PhPCl}_2\text{-ICl}$ system from the beginning.

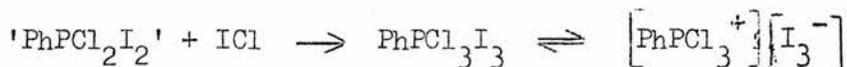
The picture painted by the ultraviolet spectra for this system is indeed complex, the pattern being a steady change in the nature of trihalide ion present, with I_3^- giving way to I_2Cl^- and finally ICl_2^- beyond the 1:1 ratio - often two or more of the above ions coexisting. At high ratios (viz., $ICl:PhPCl_2 > 2:1$), molecular iodine is present alongside ICl_2^- , whereas ultraviolet/visible examination at 1.2:1 mole ratio shows a trace of iodine initially present, but absent after ca.90 minutes. Thus the system is extremely complex, with several reactions overlapping. However, a plausible scheme for the overall reaction may be propounded:-



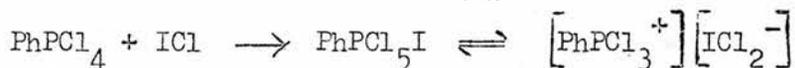
The slight rise in conductance from 0:1 to 1:1 mole ratio can thus be explained by the presence of Cl^- and I^- . The fact that these are only present to a small extent is shown by the low value of the molar conductance at the 1:1 mole ratio:-

$$1:1; \Lambda_m = 11.24 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} (c_m = 0.0146 \text{ mole/l.})$$

However, from the $PhPCl_2-I_2$ study above, we see that ' $PhPCl_2I_2$ ' is not stable in acetonitrile solution, and it can thus be expected that this species reacts immediately upon formation with more ICl : hence, from the lowest mole ratio, we might expect:-

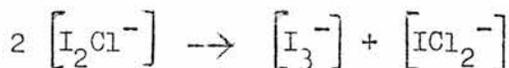


giving rise to triiodide absorption in the ultraviolet. In addition, we might expect the PhPCl_4 to react with the added ICl , thus:-

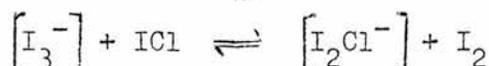


and, indeed, the solid adduct isolated at 1:1 mole ratio is found to be PhPCl_5I . (Found: C, 17.48; H, 1.24; I, 31.0; Cl, 48.5; PhPCl_5I requires C, 17.46; H, 1.21; I, 30.8; Cl, 43.0%).

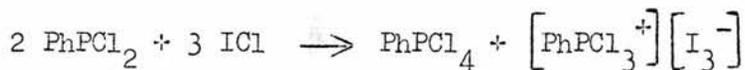
Just as Ali explains the decrease in conductance between 0.66:1 and 1.33:1 mole ratios in the $\text{Ph}_3\text{P-ICl}$ system by the conversion of simple halide ions to trihalide ions (with no net increase), we can do likewise, for we can regard ' PhPCl_2I_2 ' as to a small extent dissociated into $[\text{PhPCl}_2\text{I}^+]$ and $[\text{I}^-]$ - similarly $\text{PhPCl}_4 \rightleftharpoons [\text{PhPCl}_3^+][\text{Cl}^-]$. Addition of ICl to the "molecular" PhPCl_2I_2 , yielding PhPCl_3I_3 gives $[\text{PhPCl}_3^+][\text{I}_3^-]$, whereas addition to the $[\text{PhPCl}_2\text{I}^+][\text{I}^-]$ form gives, of course, $[\text{PhPCl}_2\text{I}^+][\text{I}_2\text{Cl}^-]$, although the unsymmetrical $[\text{I}_2\text{Cl}^-]$ ion is unstable in acetonitrile, dissociating thus:-



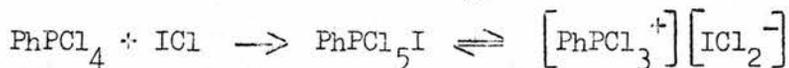
giving a possible explanation for the complicated ultraviolet spectra. The trace of molecular iodine detected by U.V./visible spectrophotometry might well be due to an overlapping equilibrium (known to occur):-



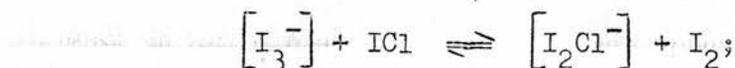
Perhaps the best overall "equation", to represent the overall reaction up to the 1.5:1 mole ratio, formally at least, is:-



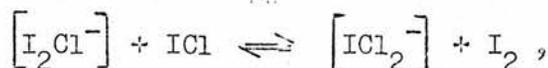
Beyond that stage, of course, further reaction with ICl will occur, to give:-



and also:-



then:-



so that eventually the trihalide species present will be the symmetrical, and stable $\left[\text{ ICl}_2^- \right]$, accompanied by molecular iodine.

(v) The PhPCl₂-iodine bromide system

Table XI and Figure 13 (pp. 59,58) contain the results of the conductometric analysis of the PhPCl₂-IBr system. As in the cases PhPCl₂-Hal₂, where Hal₂ = Br₂;I₂, the graph once again contains no sharp inflection, the conductance rising gradually but steadily until just after the 2:1 Halogen:Phosphine ratio, when the slope becomes less steep. Once again, therefore, it appears that the reaction does not occur in distinct stoichiometric stages, but rather that an equilibrium system is set up, the more complicated as chlorine, bromine and iodine are all present simultaneously.

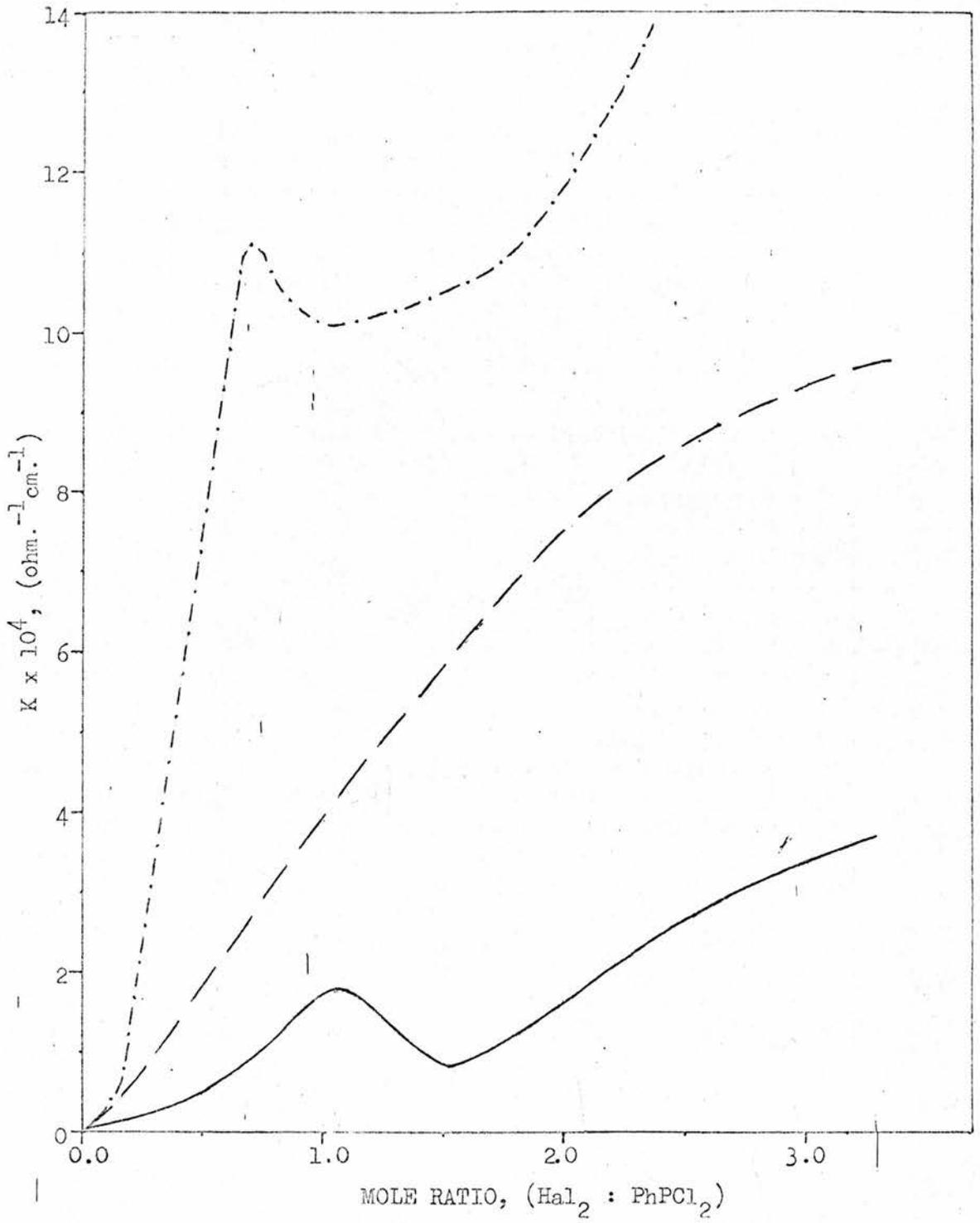


FIGURE 13: Conductometric Analysis of the systems:

- PhPCl₂ - ICl: —————
- PhPCl₂ - IBr: - - - - -
- PhPCl₂ - ICl₃: - · - · - ·

TABLE XI: Conductometric Analysis of the System $\text{PhPCl}_2 - \text{IBr}$

Mole ratio (IBr:PhPCl ₂)	$\frac{K \times 10^4}{(\text{ohm. cm.}^{-1})}$	Mole ratio (IBr:PhPCl ₂)	$\frac{K \times 10^4}{(\text{ohm. cm.}^{-1})}$	Mole ratio (IBr:PhPCl ₂)	$\frac{K \times 10^4}{(\text{ohm. cm.}^{-1})}$
0.000	0.0188	1.165	4.767	2.392	8.664
0.123	0.109	1.319	5.532	2.545	8.998
0.245	0.684	1.471	6.080	2.700	9.285
0.399	1.203	1.626	6.735	2.852	9.385
0.552	1.502	1.778	7.200	3.007	5.385
0.699	2.406	1.931	7.628	3.160	9.385
0.859	3.168	2.084	8.075	3.307	9.385
1.011	4.061	2.239	8.398		

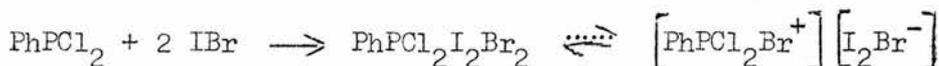
The molar conductance values, calculated at the 1:1 and 2:1 Halogen:Phosphine mole ratios, are again relatively small:-

$$1:1; \Delta m = 16.53 \text{ ohm.}^{-1} \text{ cm.}^2 \text{ mole}^{-1} (c_m = 0.0242 \text{ mole/l.})$$

$$2:1; \Delta m = 38.70 \text{ ohm.}^{-1} \text{ cm.}^2 \text{ mole}^{-1} (c_m = 0.0203 \text{ mole/l.})$$

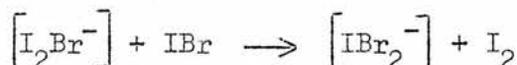
A highly unstable solid adduct was obtained from the reagents taken in 1:1 mole ratio: its analysis was near that required for PhPCl_2IBr , although this does not unambiguously confirm this composition for the reactive species in solution at that ratio.

However, reaction via " PhPCl_2IBr ", which would give the overall 2:1 reaction:-

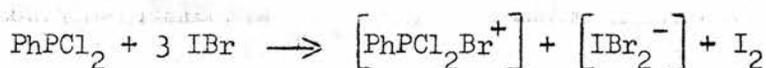


certainly appears feasible from the ultraviolet examination, where a mixture of $[\text{I}_3^-]$ and $[\text{I}_2\text{Br}^-]$ ions appears to be present at mole ratios below 2:1, thereafter giving way to $[\text{IBr}_2^-]$ together

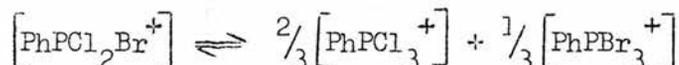
with molecular iodine. Of course, the asymmetric I_2Br^- ion is known to dissociate in acetonitrile, $2 [I_2Br^-] \rightleftharpoons [I_3^-] + [IBr_2^-]$ justifying the triiodide absorption. Addition of further iodine bromide to the 2:1 "adduct" quoted above would also be expected to give:-



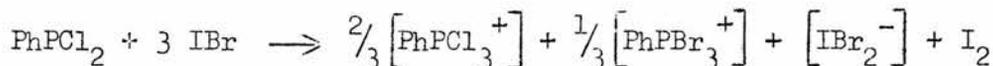
hence the molecular iodine eventually detected. While the overall reaction:-



looks perfectly reasonable, it is very probable that an equilibrium is also in play affecting the mixed cation. Behaviour of other mixed chloro-bromo phosphorus compounds (e.g. PCl_2Br) leads us to expect a rearrangement to yield single-halogen cations of somewhat higher stability: thus we may expect

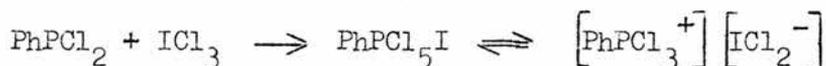


and so the proposed overall reaction for the given system is:-



(vi) The $PhPCl_2$ -iodine trichloride system

The data and graph for the conductometric analysis of the $PhPCl_2 - ICl_3$ system are contained in Table XII and Figure 13 respectively. This system might well be expected to give a simple straight 1:1 reaction:-



as both the cation and anion formed are stable entities in their own right. Indeed, the solid adduct isolated at the 1:1 mole ratio is PhPCl_5I (analysis shows relative number of halogen atoms Cl:I::4.9:1), but both the conductance-composition graph and the ultraviolet spectra recorded show the reaction not to be so straightforward as might be presumed. Again, comparison with Ali's work

TABLE XII: Conductometric Analysis of the System $\text{PhPCl}_2 - \text{ICl}_3$

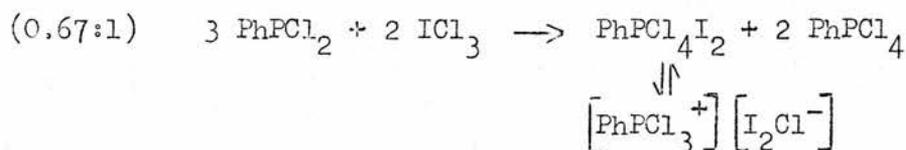
Molar ratio ($\text{ICl}_3:\text{PhPCl}_2$)	$\frac{\kappa \times 10^4}{(\text{ohm.}^{-1} \text{cm.}^{-1})}$	Molar ratio ($\text{ICl}_3:\text{PhPCl}_2$)	$\frac{\kappa \times 10^4}{(\text{ohm.}^{-1} \text{cm.}^{-1})}$	Molar ratio ($\text{ICl}_3:\text{PhPCl}_2$)	$\frac{\kappa \times 10^4}{(\text{ohm.}^{-1} \text{cm.}^{-1})}$
0.000	0.0659	0.869	10.780	1.703	11.140
0.178	2.14	0.991	10.360	1.805	11.480
0.279	4.145	1.092	10.180	1.906	11.850
0.381	6.112	1.194	10.210	2.009	12.260
0.483	7.792	1.296	10.280	2.110	12.700
0.585	9.450	1.398	10.340	2.213	13.080
0.686	11.090	1.499	10.400	2.315	13.480
0.788	10.970	1.601	10.790	2.417	13.890

shows the $\text{Ph}_3\text{P} - \text{ICl}_3$ system also to be complex, giving a peak/trough graph - as here - but with peak and trough more pronounced than here and at 0.5:1 and 1:1 mole ratios respectively, whereas the present system exhibits its maximum at 0.67:1 (the shallow minimum occurring at 1:1 mole ratio). Molar conductance values, calculated at the maximum and minimum, are:-

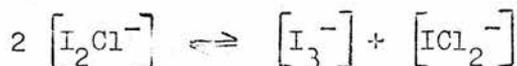
$$0.67:1; \Lambda_m = 52.52 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1} \text{ (} c_m = 0.0211 \text{ mole/l.)}$$

$$1:1; \Lambda_m = 51.50 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1} \text{ (} c_m = 0.0198 \text{ mole/l.)}$$

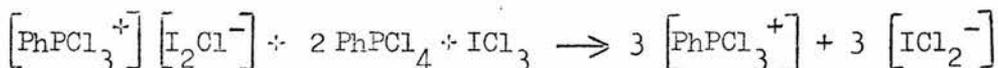
While, again, Ali finds no trihalide ion absorption in the initial steeply-rising portion of his graph, the present system does show $[\text{I}_2\text{Cl}^-]$ and also possibly $[\text{I}_3^-]$ to be present from the 0:1 ratio up to the maximum. Beyond the 0.67:1 ratio, the only trihalide absorption present is that of the stable $[\text{ICl}_2^-]$ ion, with $\lambda_{\text{max.}} = 227, 336 \text{ m}\mu$. Thus, for this system we can write two equations:-



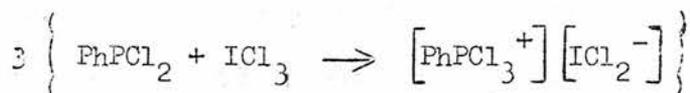
again, triiodide presence being justifiable through the disproportionation:-



Addition of one mole of ICl_3 (thus attaining 1:1 mole ratio overall) gives:-



which is, of course, equivalent to:-



(vii) The $\text{PhPCl}_2 \cdot \text{Cl}_2$ - iodine chloride system

The conductometric data and graph for the PhPCl_4 - ICl system are contained in Table XIII and Figure 14 respectively:-

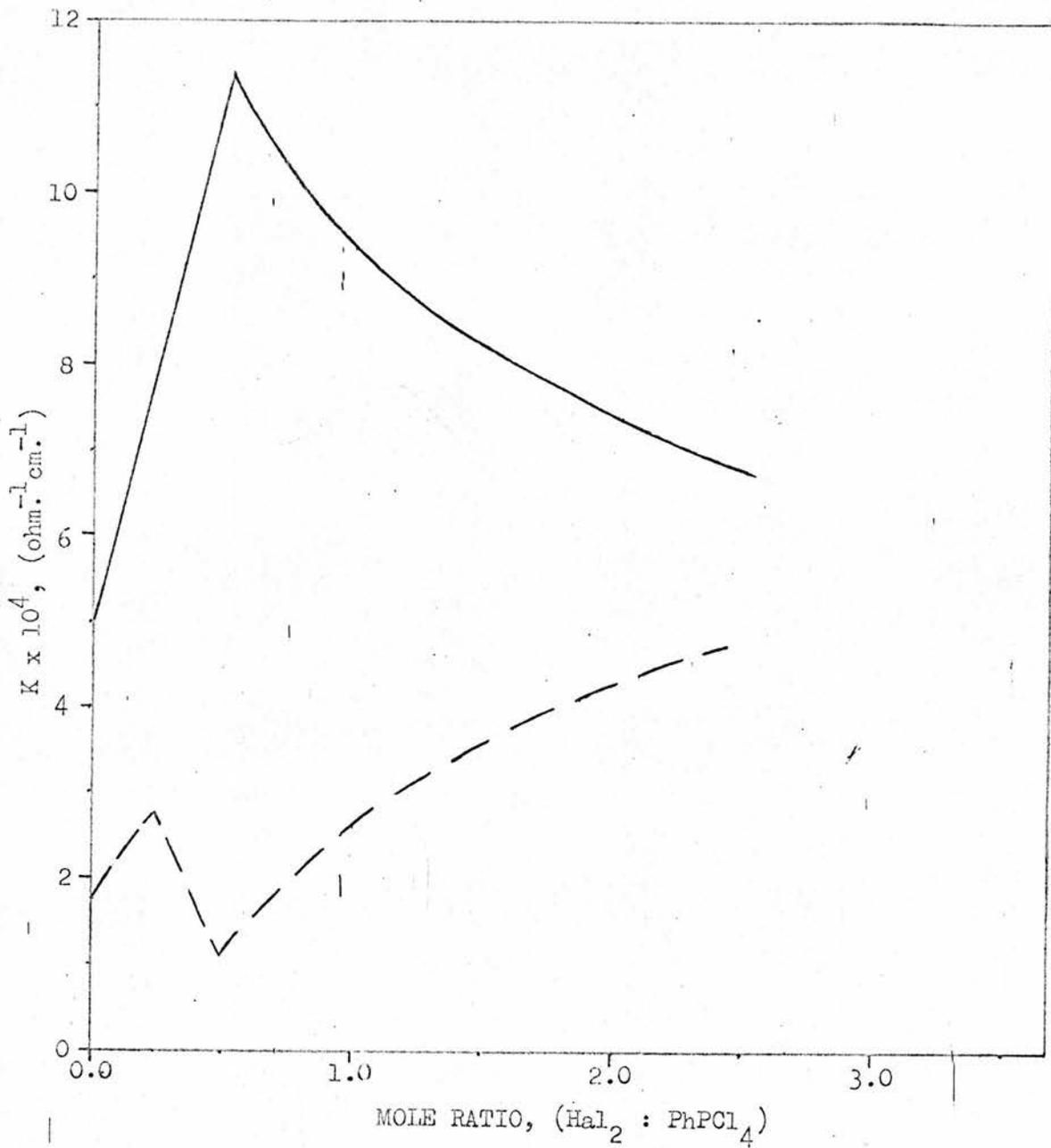


FIGURE 14: Conductometric Analysis of the Systems:

PhPCl₄-ICl: —————

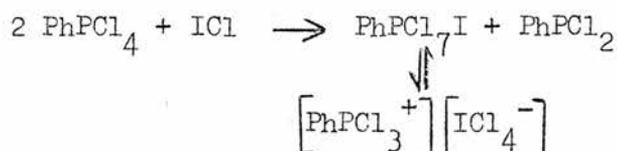
PhPCl₄-IBr: - - - - -

TABLE XIII: Conductometric Analysis of the System $\text{PhPCl}_4\text{-ICl}$

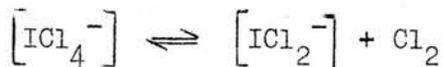
Mole ratio (ICl : PhPCl_4)	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)	Mole ratio (ICl : PhPCl_4)	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)
0.000	5.113	1.218	8.620
0.174	7.958	1.392	8.230
0.348	10.520	1.566	7.870
0.522	11.560	1.740	7.640
0.696	10.560	1.914	7.456
0.870	9.710	2.088	7.290
1.044	9.205	2.262	7.140

On this occasion, although the U.V. spectra lead one on to the expected simple 1:1 mole ratio reaction, the conductance-composition graph (with a sharp break at 0.5:1 Halogen:Phosphine ratio) and the analysis of the adduct isolated at that same mole ratio (showing relative number of halogen atoms Cl:I :: 7.18:1) show the mechanism to be other than simple. However, titration graph, U.V. spectra, Λ_m value at 0.5:1 ratio and adduct obtained at that same ratio are all mutually compatible.

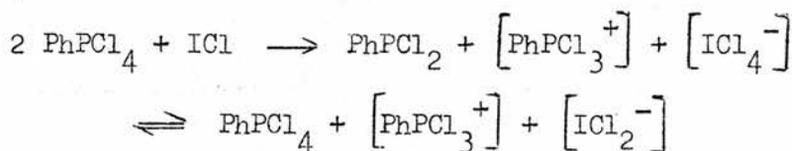
The molar conductance at 0.5:1 ratio ($\Lambda_m = 55.00 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1}$, $c_{11} = 0.0212 \text{ mole/l.}$, if it is assumed that only one P-containing species forms) becomes $\Lambda_m = 110.00 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1}$, $c_m = 0.0106 \text{ mole/l.}$ - typical of strong electrolyte behaviour - if only half the phosphorus originally present transforms to give an electrolytically-conducting product. Thus we can write:-



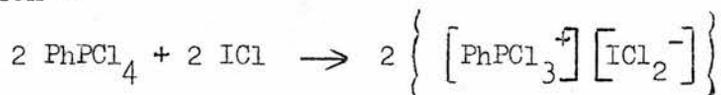
the tetrachloriodate (III) ion ICl_4^- dissociating in acetonitrile:-¹³⁴



and hence explaining the $[\text{ICl}_2^-]$ absorption present in the U.V. spectrum from start to finish. The chlorine evolved by the dissociation of $[\text{ICl}_4^-]$ can be expected to chlorinate the PhPCl_2 in solution, so we can write:-



and addition of ICl to reach the 1:1 mole ratio gives the expected equation:-



(viii) The $\text{PhPCl}_2 \cdot \text{Cl}_2$ - iodine bromide system

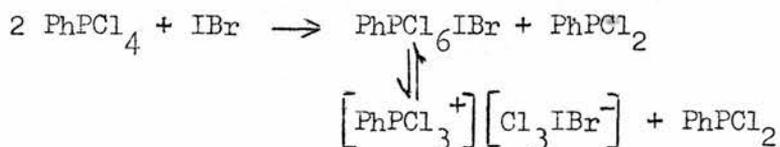
Once again, the conductometric graph shown in Figure 14 (the relevant data being listed in Table XIV) shows this to be a rather

TABLE XIV: Conductometric Analysis of the System PhPCl_4 -IBr

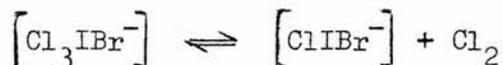
<u>Mole ratio</u> (IBr : PhPCl_4)	<u>$K \times 10^4$</u> ($\text{ohm}^{-1} \text{cm}^{-1}$)	<u>Mole ratio</u> (IBr : PhPCl_4)	<u>$K \times 10^4$</u> ($\text{ohm}^{-1} \text{cm}^{-1}$)
0.000	1.829	1.520	3.683
0.253	2.740	1.773	4.114
0.507	1.091	2.026	4.530
0.760	2.066	2.280	4.889
1.013	2.611	2.533	5.250
1.267	3.247		

complex system, as might be expected since Cl, Br, and I are all present. Unfortunately, the solid adduct isolated gives little aid in proposing a possible scheme, as its analysis is somewhat dubious: this may well be due to its being a mixture.

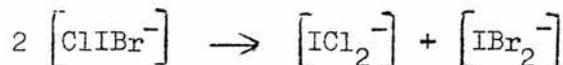
The ultraviolet examination showed a mixture of $[\text{ICl}_2^-]$, $\lambda_{\text{max.}} = 227, 336 \text{ m}\mu$; and $[\text{IBr}_2^-]$, $\lambda_{\text{max.}} = 256, 370 \text{ m}\mu$, to be present at all mole ratios. It is difficult to explain the 0.25:1 maximum, although the break at the $\text{IBr}:\text{PhPCl}_4 :: 1:2$ ratio could be explained in a manner analogous to that used for the $\text{PhPCl}_4\text{-ICl}$ system:-



And we would naturally expect the $[\text{Cl}_3\text{IBr}^-]$ to behave in acetonitrile in a manner similar to that of $[\text{ICl}_4^-]$, thus:-

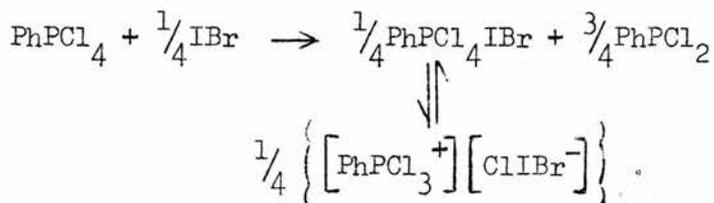


and the $[\text{ClIBr}^-]$ ion is known to disproportionate in acetonitrile to yield more stable trihalide ions:-

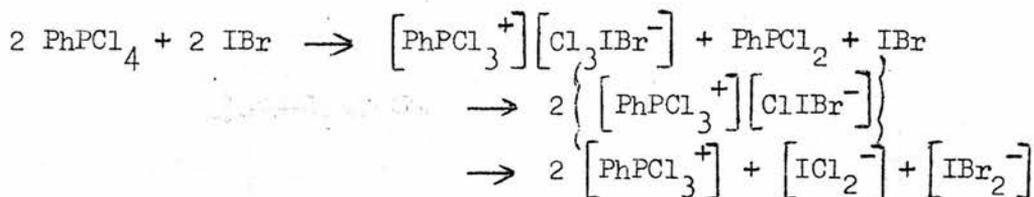


justifying the ultraviolet absorptions observed.

It could well be that the discontinuity at the 0.25:1 ratio is caused by an initial reaction of the added IBr to give:-



At any rate, it may be expected that after the 0.5:1 minimum, more iodine bromine will be absorbed to give for the 1:1 reaction:-



Assuming the reaction proposed above for the 0.5:1 mole ratio is correct, i.e. one half of the original P present is converted into a conducting species, we get, at 0.5:1:-

$$\Lambda_m = 31.80 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.00344 \text{ mole/l.})$$

However, c_m here is very low, and on doubling the concentration it is found that

$$\Lambda_m = 64.40 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.00766 \text{ mole/l.})$$

which is in reasonable agreement with the value expected for $\left[\text{PhPCl}_3^+ \right] \left[\text{Cl}_3\text{IBr}^- \right]$.

(b) The Reactions of Diphenylchlorophosphine with Halogens

(i) The Ph₂PCl - chlorine system

The rather featureless conductometric titration graph for the

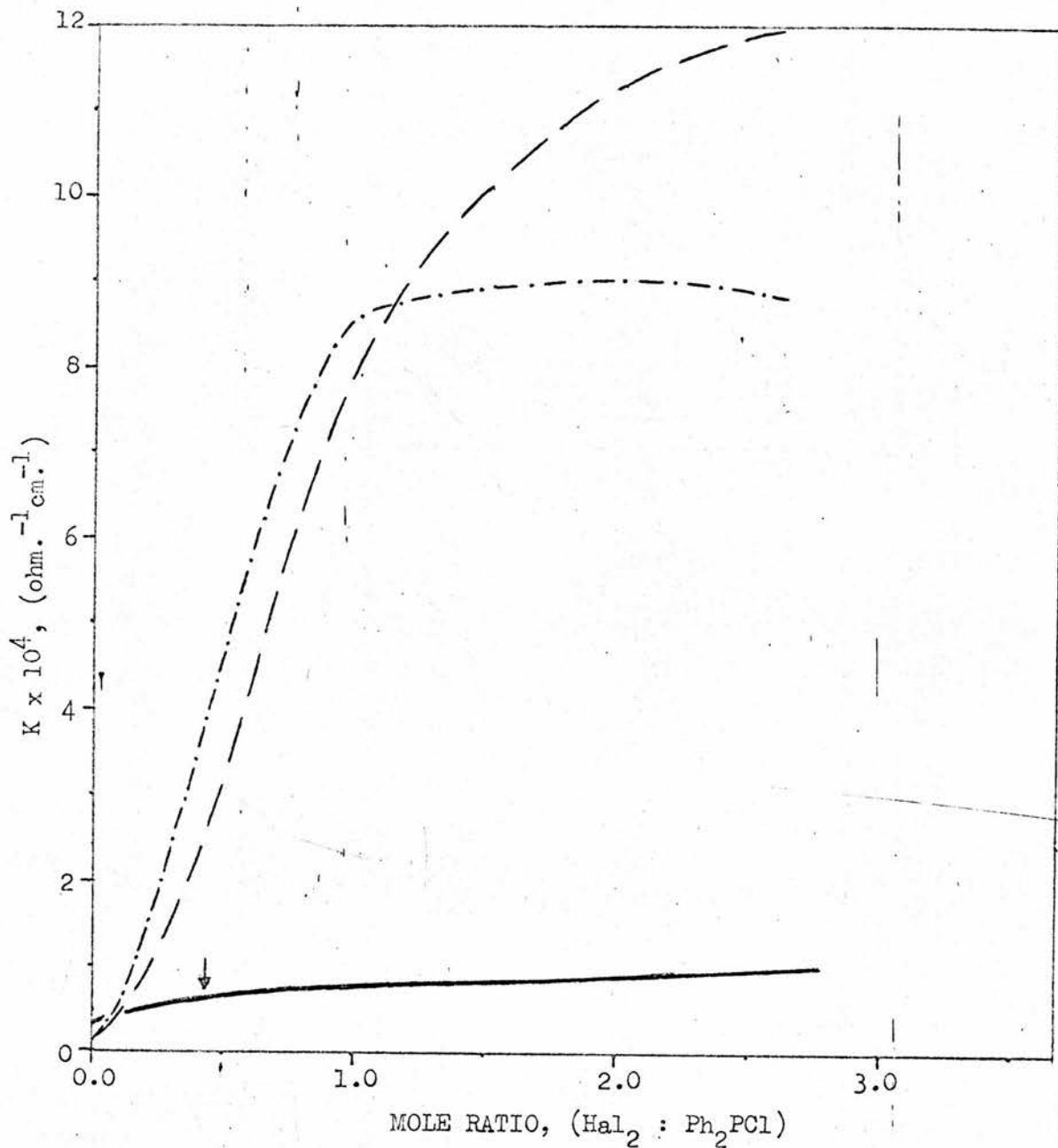


FIGURE 15: Conductometric Analysis of the Systems:

Ph₂PCl-Cl₂: _____
(arrow denotes appearance of precipitate)

Ph₂PCl-Br₂: - - - - -

Ph₂PCl-I₂: - · - · - · -

Ph₂PCl-Cl₂ system is shown in Figure 15, the relevant data being listed in Table XV:-

TABLE XV: Conductometric Analysis of the System Ph₂PCl - Cl₂

<u>Mole ratio</u> (Cl ₂ : Ph ₂ PCl)	<u>K x 10⁴</u> (ohm. ⁻¹ cm. ⁻¹)
0.000	0.274
0.147	0.484
0.294	0.552
0.440 *	0.568
0.587	0.568
0.734	0.574
0.881	0.581
1.028	0.588
1.174	0.602
1.393	0.625
1.613	0.663
1.835	0.681
2.058	0.698
2.278	0.706

(asterisk denotes first appearance of white precipitate, which remains throughout.)

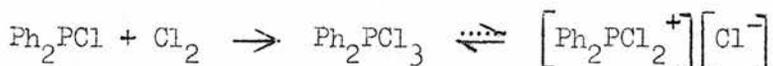
The conductance does rise during the titration, but only very slightly, and there is no suggestion of any break in the graph. Once again, precipitation was found to occur in the titration vessel; however a repeat titration at higher dilution (avoiding any precipitation) gave an exactly similar curve.

The molar conductance (measured at 1:1 mole ratio) is:-

$$\Lambda_m = 2.54 \text{ ohm.}^{-1} \text{ cm.}^2 \text{ mole}^{-1} \quad (c_m = 0.0231 \text{ mole/l.}),$$

suggesting a very weak electrolyte in solution, as expected from

the graph. The reaction therefore is:-



and there is no evidence for further reaction beyond the 1:1 mole ratio.

White solid adduct - giving excellent analysis for Ph_2PCl_3 - is easily obtained on passing $\text{N}_2(\text{g})/\text{Cl}_2(\text{g})$ mixture into diphenylchlorophosphine in acetonitrile, identifying the titration precipitate unambiguously.

(ii) The Ph_2PCl - bromine system

Table XVI and Figure 15 contain the relevant conductometric data for the $\text{Ph}_2\text{PCl}-\text{Br}_2$ system:-

TABLE XVI: Conductometric Analysis of the System $\text{Ph}_2\text{PCl}-\text{Br}_2$

Mole ratio ($\text{Br}_2:\text{Ph}_2\text{PCl}$)	$\frac{K \times 10^4}{(\text{ohm} \cdot \text{cm} \cdot \text{l}^{-1})}$	Mole ratio ($\text{Br}_2:\text{Ph}_2\text{PCl}$)	$\frac{K \times 10^4}{(\text{ohm} \cdot \text{cm} \cdot \text{l}^{-1})}$	Mole ratio ($\text{Br}_2:\text{Ph}_2\text{PCl}$)	$\frac{K \times 10^4}{(\text{ohm} \cdot \text{cm} \cdot \text{l}^{-1})}$
0.000	0.308	0.987	8.509	1.974	11.422
0.141	1.247	1.128	9.200	2.115	11.700
0.282	1.761	1.269	9.750	2.256	11.861
0.423	2.623	1.410	10.175	2.397	11.991
0.564	4.792	1.551	10.500	2.538	12.100
0.705	6.330	1.692	10.972		
0.846	7.513	1.833	11.181		

The graph is obviously of similar form to that obtained for the $\text{PhPCl}_2-\text{Br}_2$ reaction (although no precipitation occurs in the

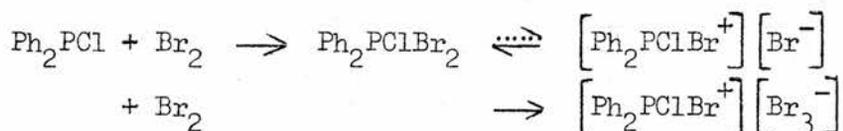
present system) and so the reaction can be expected to be somewhat analogous. Once again the "smooth" curve with no inflections suggests an equilibrium system, and once again ultraviolet examination shows the 269 m μ absorption of the tribromide ion at all ratios beyond 1:1, it having been absent before that point.

The molar conductances at the 1:1 and 2:1 Halogen:Phosphine mole ratios are:-

$$1:1; \Lambda_m = 55.41 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}, (c_m = 0.0156 \text{ mole/l.})$$

$$2:1; \Lambda_m = 93.20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}, (c_m = 0.0124 \text{ mole/l.})$$

-higher in both cases than the corresponding values for the PhPCl₂-Br₂ system. In fact, the 2:1 value in the present case is that of a strong electrolyte in acetonitrile. We may therefore write the reaction scheme:-



The solid adducts Ph₂PClBr₂ and Ph₂PClBr₄ can be obtained from the reagents in the appropriate mole ratios, the latter by ether precipitation technique as might be expected for a strong electrolyte which would tend to be soluble in acetonitrile.

(iii) The Ph₂PCl - iodine system

Conductometric analysis of the Ph₂PCl-I₂ system gave the results listed in Table XVII:-

TABLE XVII: Conductometric Analysis of the System $\text{Ph}_2\text{PCl-I}_2$

Mole ratio ($\text{I}_2 : \text{Ph}_2\text{PCl}$)	$\frac{\kappa \times 10^4}{(\text{ohm.}^{-1} \text{cm.}^{-1})}$	Mole ratio ($\text{I}_2 : \text{Ph}_2\text{PCl}$)	$\frac{\kappa \times 10^4}{(\text{ohm.}^{-1} \text{cm.}^{-1})}$	Mole ratio ($\text{I}_2 : \text{Ph}_2\text{PCl}$)	$\frac{\kappa \times 10^4}{(\text{ohm.}^{-1} \text{cm.}^{-1})}$
0.000	0.0681	0.921	8.330	1.729	9.020
0.144	1.140	0.979	8.606	1.872	9.035
0.288	3.143	1.038	8.703	1.945	9.047
0.389	4.491	1.152	8.776	2.016	9.000
0.461	5.225	1.296	8.838	2.088	8.980
0.533	5.810	1.414	8.900	2.160	8.940
0.605	6.629	1.512	8.930	2.305	8.920
0.720	7.454	1.583	8.980	2.450	8.880
0.864	8.100	1.657	9.000		

and depicted graphically in Figure 15 (p. 68 supra). The curve shows a distinct inflection at the 1:1 mole ratio, in contrast to the $\text{PhPCl}_2\text{-I}_2$ case where there was no indication for the existence of a 1:1 adduct either in the solid state or in solution. The value of the molar conductance at the $\text{I}_2:\text{Ph}_2\text{PCl} :: 1:1$ ratio is:-

$$\Lambda_m = 61.10 \text{ ohm.}^{-1} \text{cm.}^2 \text{ mole}^{-1} \quad (c_m = 0.0142 \text{ mole/l.})$$

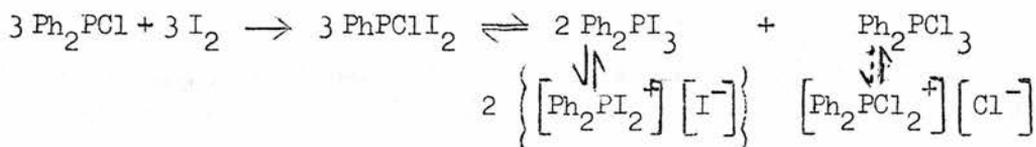
Although this might therefore appear a straightforward 1:1 reaction, proceeding



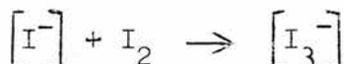
which then absorbs more iodine, both the ultraviolet spectrum (which shows $\lambda_{\text{max.}} = 291, 360 \text{ m}\mu$ typical of I_3^- from the beginning) and the solid isolated at the 1:1 ratio (with analysis near Ph_2PI_3) show this not to be the case.

To reinforce the quantitative analysis performed on the solid adduct obtained (Found: C, 25.94; H, 1.73; Hal, 65.61; Ph_2PI_3 requires C, 25.43; H, 1.79; Hal, 67.21%), the qualitative test for chloride - using potassium dichromate and concentrated sulphuric acid - was performed, giving a negative result.

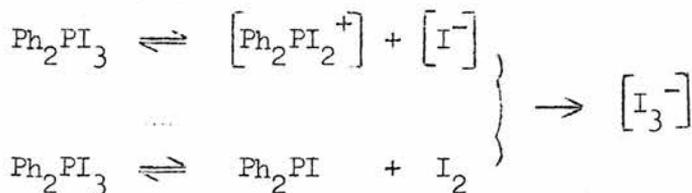
The probable course of the reaction is therefore one involving disproportionation:-



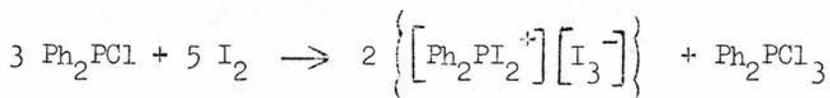
This proposal is entirely reasonable in view of the earlier generalisation about the instability of P(V) compounds containing iodine: also, species containing only one kind of halogen atom would be expected to be of higher stability than mixed halides. The I_3^- observed by U.V. may be formed by the immediate reaction of the $\left[\text{I}^- \right]$ formed with the iodine titrant



or it may be due to the existence of both molecular and ionic dissociation of Ph_2PI_3 :-



Beyond the 1:1 mole ratio, the expected reaction is:-



with no significant increase in conductance, as the process is one of ion transformation, $[\text{Hal}^-] + \text{Hal}_2 \longrightarrow [\text{Hal}_3^-]$, no net addition of ions occurring. (As seen from the $\text{Ph}_2\text{PCl}-\text{Cl}_2$ case, Ph_2PCl_3 is almost a non-electrolyte in acetonitrile, and its ionic dissociation is therefore negligible.)

(iv) The Ph_2PCl - iodine chloride system

Figure 16 (p. 75) shows once again the complications introduced when the halogen titrant is iodine chloride: the relevant data are listed in Table XVIII:-

TABLE XVIII: Conductometric Analysis of the System $\text{Ph}_2\text{PCl}-\text{ICl}$

<u>Mole ratio</u> (ICl : Ph_2PCl)	<u>$K \times 10^4$</u> ($\text{ohm}^{-1}\text{cm}^{-1}$)	<u>Mole ratio</u> (ICl : Ph_2PCl)	<u>$K \times 10^4$</u> ($\text{ohm}^{-1}\text{cm}^{-1}$)
0.000	0.058	2.303	3.742
0.121	0.825	2.424	3.687
0.242	2.330	2.545	3.659
0.364	3.829	2.666	3.659
0.485	5.103	2.788	3.742
0.606	5.938	2.909	3.829
0.727	5.639	3.030	3.921
0.848	5.255	3.151	4.049
0.970	4.965	3.272	4.151
1.091	4.750	3.394	4.259
1.212	4.617	3.515	4.411
1.333	4.491	3.636	4.532
1.454	4.372	3.757	4.660
1.576	4.259	3.878	4.796
1.697	4.151	4.000	4.940
1.818	4.049	4.121	5.093
1.939	3.952	4.242	5.200
2.060	3.890	4.363	5.341
2.182	3.771	4.484	5.429

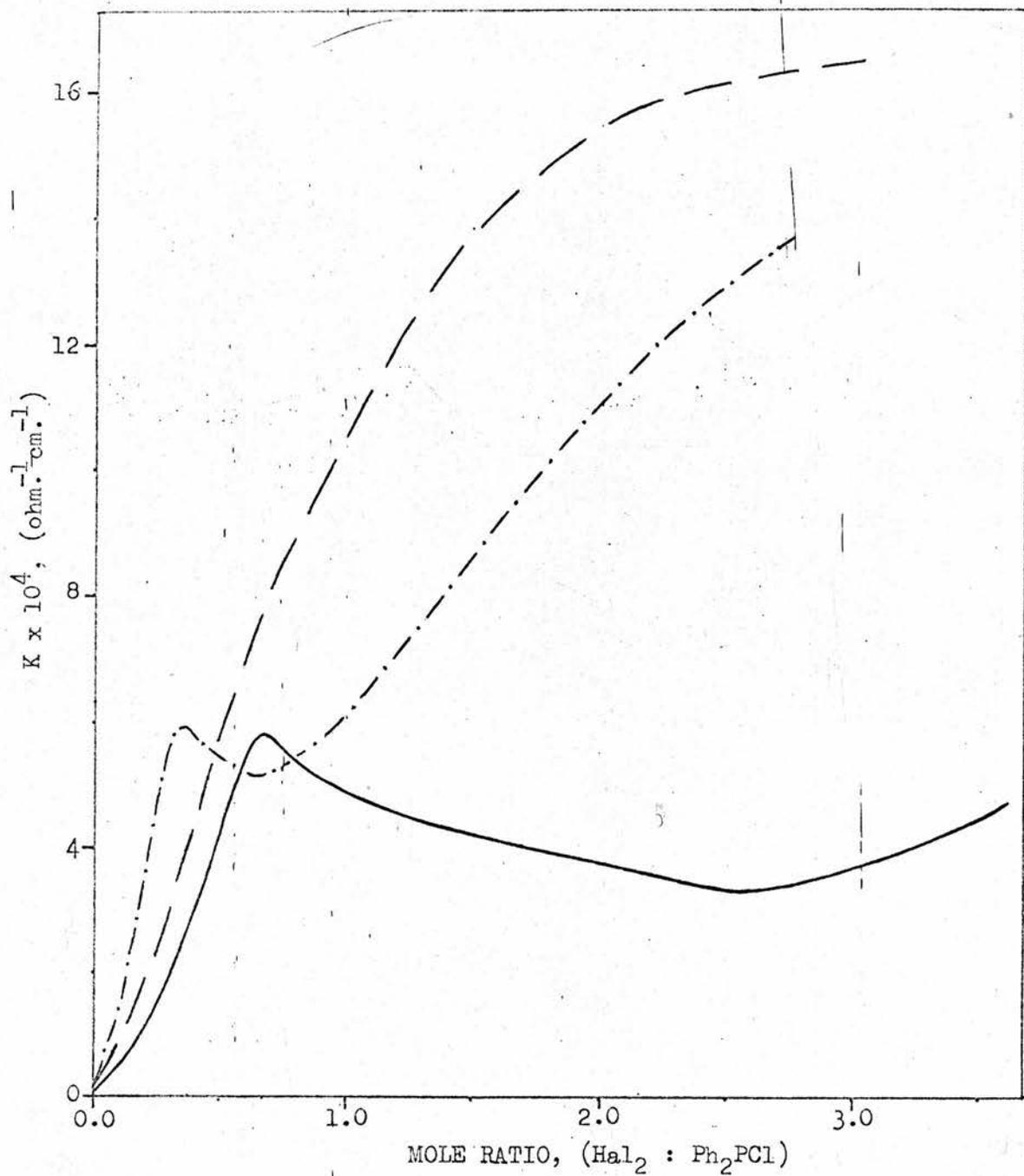
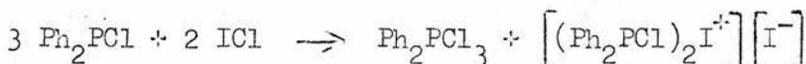


FIGURE 16: Conductometric Analysis of the Systems:

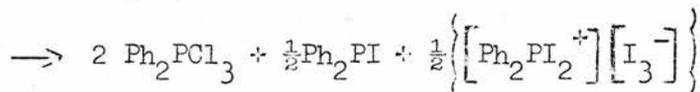
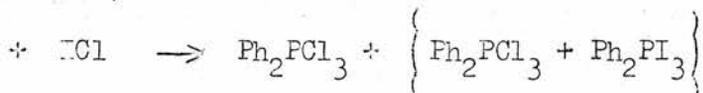
Ph₂PCl-ICl: —————
Ph₂PCl-IBr: - - - - -
Ph₂PCl-ICl₃: - · - - -

Again the titration graph is of the maximum/minimum variety, although in this case the minimum is very shallow. It is interesting to note that the maximum here occurs at the 0.67:1 mole ratio as did that of Ali in the $\text{Ph}_3\text{P-ICl}$ system: in addition, the ultraviolet scheme is somewhat similar to that of the $\text{Ph}_3\text{P-ICl}$ case, viz., no trihalide absorption until the maximum is attained, then a progression from I_3^- through I_2Cl^- to ICl_2^- , molecular iodine also being present after the 1:1 ratio. A similar scheme to that proposed for the $\text{Ph}_3\text{P-ICl}$ system is thus suggested:-

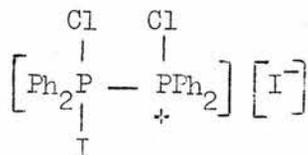
(0:1 \rightarrow 0.67:1):



(0.67:1 \rightarrow 1:1):



The $[(\text{Ph}_2\text{PCl})_2\text{I}^+][\text{I}^-]$ would be expected to have a structure analogous to the $[(\text{Ph}_3\text{P})_2\text{Cl}^+][\text{Cl}^-]$ of Ali, viz.:-



the $\left[\begin{array}{c} \text{Ph}_3\text{P} \\ | \\ \text{Cl} \end{array} - \begin{array}{c} \text{PPh}_3 \\ + \end{array} \right] [\text{Cl}^-]$ structure of Ali having been supported

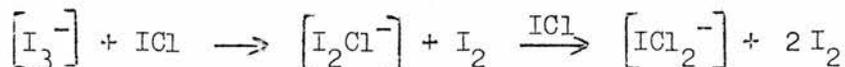
against the $[\text{Ph}_3\text{P} \rightarrow \text{Cl} \leftarrow \text{PPh}_3]^+ [\text{Cl}^-]$ possibility by infra-red spectroscopic methods. The other entity formed at the

0.67:1 ratio is the well-known and very stable Ph_2PCl_3 . The Ph_2PI_3 formed in the ensuing addition of iodine chloride to reach the 1:1 ratio may be expected to be unstable in acetonitrile solution in the light of previous findings from P(V)-iodine compounds. The most probable disproportionation scheme (shown) would yield triiodide ion - whose absorption is monitored by U.V. at this ratio. The proposed scheme is lent further credence by the fact that the solid isolated from solution at the 1:1 mole ratio is Ph_2PCl_3 .

If it is assumed that all the conductance at the 1:1 mole ratio is due to ' Ph_2PI_3 ' in some form (i.e. from one-third of the total P in the system), then at that ratio the molar conductance is:-

$$\Lambda_m = 81.81 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0060 \text{ mole/l.})$$

typical of strong electrolyte behaviour, and therefore appropriate. The trihalide ion progression (accompanied by molecular iodine) can be readily explained by:-



(v) The Ph_2PCl - iodine bromide system

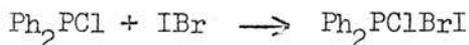
Again, the graph (Figure 16) of the conductometric titration data (listed in Table XIX) shows the smooth, unbroken form of an equilibrium system. In addition, since all three halogens are

present, the system is sure to be very complex, with overlapping equilibria and rearrangement reactions in no small number.

TABLE XIX: Conductometric Analysis of the System $\text{Ph}_2\text{PCl-IBr}$

<u>Mole ratio</u> (IBr : Ph_2PCl)	$K \times 10^4$ (ohm. ⁻¹ cm. ⁻¹)	<u>Mole ratio</u> (IBr : Ph_2PCl)	$K \times 10^4$ (ohm. ⁻¹ cm. ⁻¹)
0.000	0.247	1.398	14.012
0.155	1.968	1.522	14.560
0.280	3.312	1.648	15.000
0.404	4.890	1.770	15.410
0.529	6.017	1.896	15.591
0.652	7.838	2.020	15.712
0.777	8.654	2.145	15.878
0.901	10.150	2.270	15.972
1.025	11.209	2.395	16.071
1.149	12.330	2.520	16.190
1.273	13.382		

Attempted preparation of adducts at the Halogen:Phosphine mole ratios of 1:1 and 2:1 yielded the same red-brown unstable solid in each case, with analysis close to that required for Ph_2PClBrI . Although suggesting the feasibility of the reaction



in solution, the adduct isolation does not (as earlier explained) demand it.

Indeed, ultraviolet examination shows the presence of trihalide ions from the very start of the reaction (I_3^- and Br_3^- being present at or below the 1:1 ratio, and being converted to IBr_2^- after the 2:1 stage); this would of course, suggest immediate formation of the "tetrahalide" species $\text{Ph}_2\text{PCl} \cdot \text{Hal}_4$ in solution,

(vi) The Ph₂PCl - iodine trichloride system

The results of the conductometric analysis of the Ph₂PCl-ICl₃ system are contained in Table XX and Figure 16 (p. 75 supra):-

TABLE XX: Conductometric Analysis of the System Ph₂PCl-ICl₃

<u>Mole ratio</u> (ICl ₃ : Ph ₂ PCl)	<u>K x 10⁴</u> (ohm. ⁻¹ cm. ⁻¹)	<u>Mole ratio</u> (ICl ₃ : Ph ₂ PCl)	<u>K x 10⁴</u> (ohm. ⁻¹ cm. ⁻¹)
0.000	0.0705	0.733	8.700
0.177	2.175	0.843	8.942
0.310	6.173	0.975	9.105
0.443	8.400	1.108	9.202
0.577	8.250	1.241	9.281

The graph is of similar form to that obtained from the PhPCl₂-ICl₃ system, hence we might expect a reasonably similar reaction scheme.

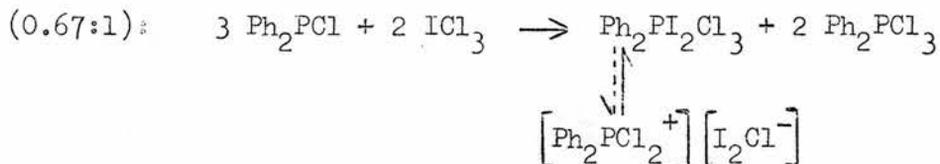
In this case, however, there is no inflection or turning value at the 1:1 ratio, and the (shallow) minimum occurs at the ratio containing the maximum turning-point in the PhPCl₂-ICl₃ case, viz., 0.67:1. In addition, while trihalide ion presence was detected throughout the PhPCl₂-ICl₃ titration, U.V. shows no trace of trihalide ions in this system until the maximum is reached.

A mixture of I₃⁻ and ICl₂⁻ appears to be present between the maximum and minimum, whereas beyond the minimum the only trihalide ion evident is ICl₂⁻.

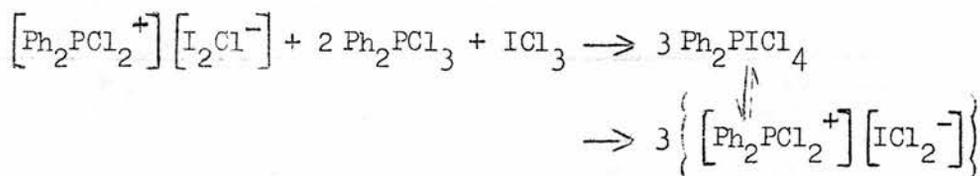
No stable solid adduct could be isolated; however an unstable viscous dark oil was obtained from the reagents in 1:1 mole ratio; the analysis of this oil approached that of the formal 1:1 adduct,

viz., Ph_2PICl_4 .

A possible scheme, therefore, and in accord with U.V. absorptions, titration graph and adduct isolated, is:-



(0.67:1 \rightarrow 1:1):



the triiodide absorption being justified by the familiar disproportionation of $\left[\text{I}_2\text{Cl}^- \right]$ in acetonitrile. Assuming the above scheme to be correct, then at the minimum:-

$$\Lambda_m = 27.03 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0015 \text{ mole/l.})$$

suggesting weak electrolyte behaviour for $\text{Ph}_2\text{PI}_2\text{Cl}_3$, it being assumed that Ph_2PCl_3 contributes negligibly to the conductance.

(vii) The $\text{Ph}_2\text{PCl} \cdot \text{Cl}_2$ - iodine chloride system

In view of the negative evidence for the 1:1 $\text{Ph}_2\text{PCl} \cdot \text{ICl}_3$ adduct in solution and instability of adduct obtained from that system, it was decided to study the related system $\text{Ph}_2\text{PCl}_3 \cdot \text{ICl}$, with especial interest attaching to the presence or absence of a 1:1 ratio inflection in the conductance-composition graph and

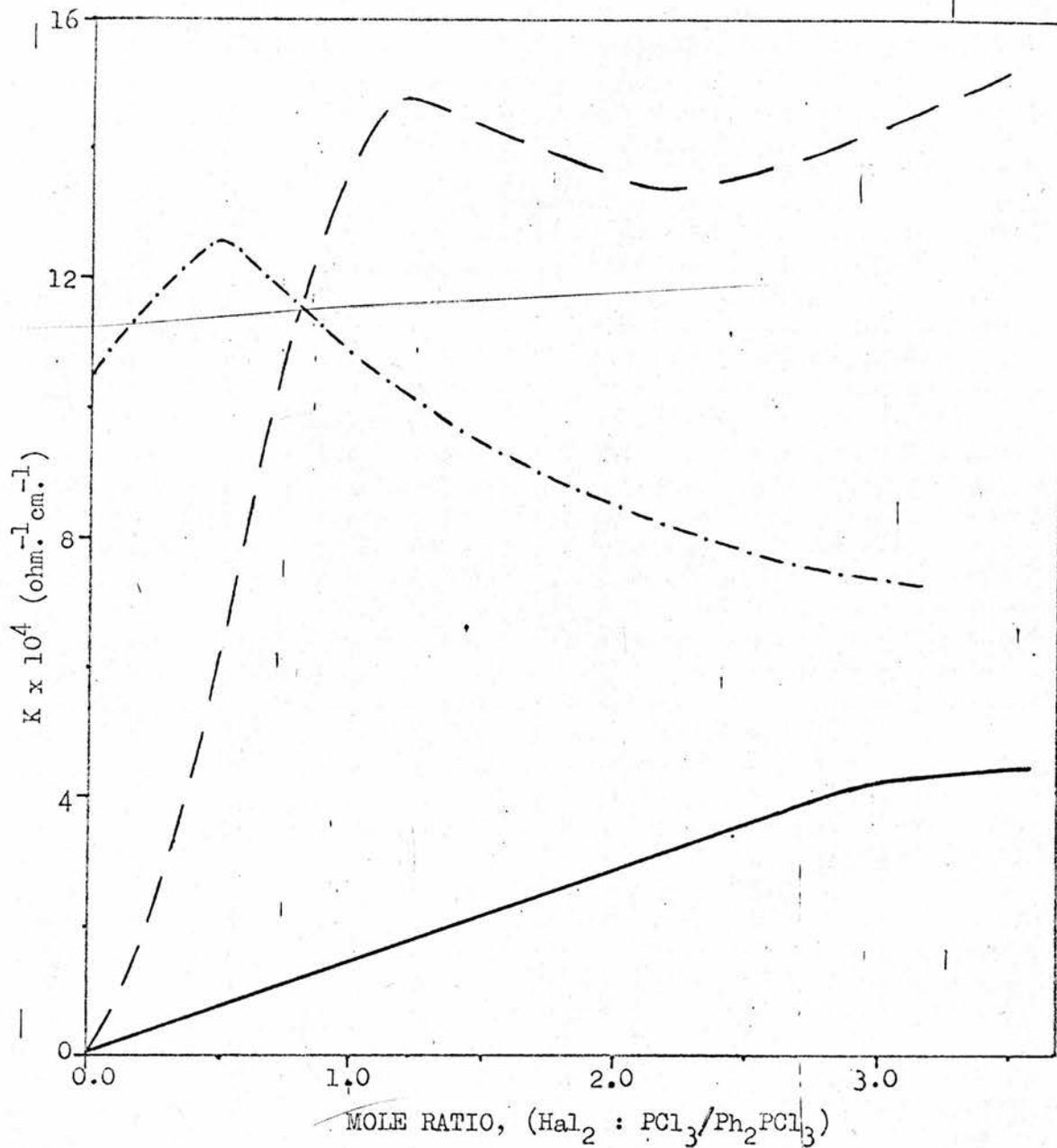


FIGURE 17: Conductometric Analysis of the Systems:

Ph₂PCl₃-ICl: - · - - - -

PCl₃-ICl: —————

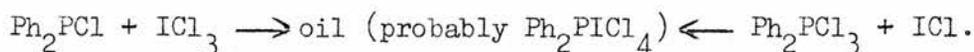
PCl₃-ICl₃: - - - - -

the nature of adduct isolated. The relevant data are listed in Table XXI; the graph is contained in Figure 17.

TABLE XXI: Conductometric Analysis of the System $\text{Ph}_2\text{PCl}_3\text{-ICl}$

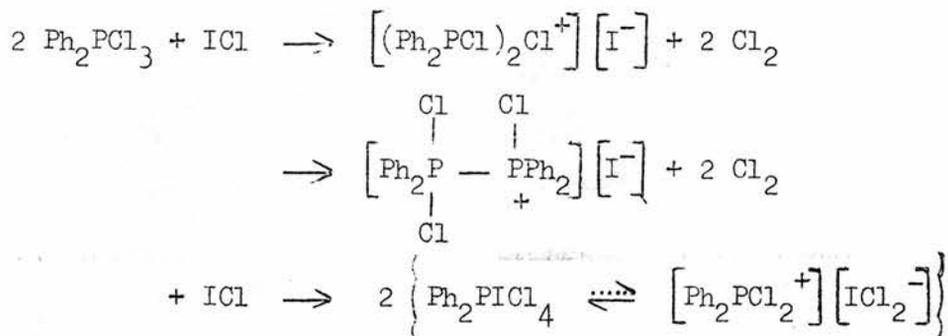
<u>Mole ratio</u> (ICl: Ph_2PCl_3)	$K \times 10^4$ (ohm. ⁻¹ cm. ⁻¹)	<u>Mole ratio</u> (ICl: Ph_2PCl_3)	$K \times 10^4$ (ohm. ⁻¹ cm. ⁻¹)
0.000	10.500	1.852	8.850
0.117	11.140	1.979	8.620
0.234	11.790	2.106	8.410
0.351	12.340	2.223	8.200
0.468	12.560	2.340	7.980
0.585	12.120	2.457	7.830
0.702	11.850	2.574	7.620
0.819	11.280	2.691	7.450
0.926	11.170	2.825	7.250
1.053	10.770	2.925	7.080
1.170	10.500	3.042	6.930
1.287	10.280	3.159	6.800
1.404	10.070	3.276	6.680
1.521	9.550	3.383	6.540
1.638	9.340	3.490	6.400
1.745	9.100		

It is immediately obvious that this system reinforces the negative evidence for Ph_2PICl_4 in acetonitrile solution obtained from the previous reaction. A sharp break is indeed present in the curve, but occurs at the Halogen:Phosphine :: 0.5:1 ratio, and not the 1:1 ratio. Moreover, direct addition of concentrated solutions of the reagents in the 1:1 ratio again yielded an unstable, dark, viscous oil whose analysis approximated that required by Ph_2PICl_4 , i.e.:-



The molar conductance value calculated at the 0.5:1 ratio (i.e. at the maximum) is $\Lambda_m = 103.90 \text{ ohm.}^2 \text{ cm.}^{-1} \text{ mole}^{-1}$ ($c_m = 0.0121 \text{ mole/l.}$), suggesting a strong electrolyte present.

All the above observations probably fit best into a scheme incorporating the $[(R_3P)_2Hal^+]$ -type cation already proposed in the Ph_3P-ICl reaction (by Ali) and in the $Ph_2PCl-ICl$ reaction (in this thesis). Thus we have:-



Thus, although this system is complex and not well understood, initial observations appear to be compatible with results from the $Ph_2PCl-ICl_3$ reaction.

(c) The Reactions of Phosphorus Trichloride with Iodine Chloride and Iodine Trichloride

Since the reactions of ICl and ICl_3 on Ph_3P (by Ali) and on Ph_2PCl and $PhPCl_2$ (in the present thesis) have received some attention, but the corresponding reactions with PCl_3 have so far been ignored, it was decided to rectify this omission. As, in the foregoing reactions, the systems involving ICl and ICl_3 have figured prominently among the more complex members, the author was not expecting these "straightforward" reactions (on paper, at least) to materialise as such: he was not disappointed!

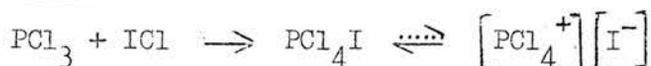
(i) The PCl₃-iodine chloride system

Table XXII and Figure 17 (p. 82 supra) contain the relevant conductometric data and graph from the PCl₃-ICl system. While at

TABLE XXII: Conductometric Analysis of the System PCl₃-ICl

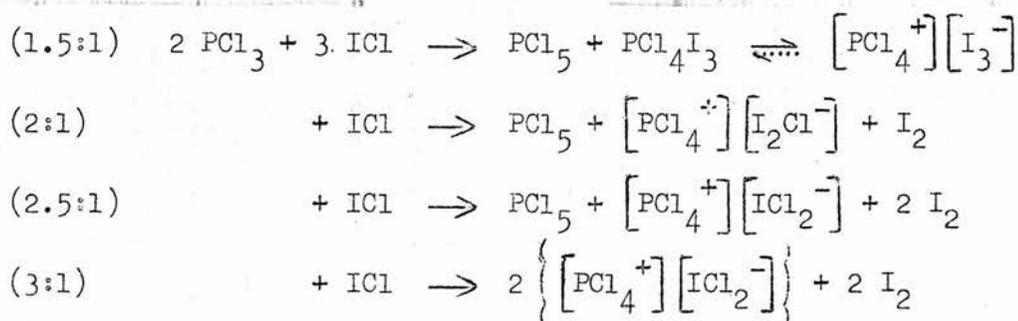
Mole ratio (ICl:PCl ₃)	$\frac{K \times 10^4}{\text{ohm}^{-1} \text{cm}^{-1}}$	Mole ratio (ICl:PCl ₃)	$\frac{K \times 10^4}{\text{ohm}^{-1} \text{cm}^{-1}}$	Mole ratio (ICl:PCl ₃)	$\frac{K \times 10^4}{\text{ohm}^{-1} \text{cm}^{-1}}$
0.000	0.031	1.219	1.973	2.411	3.526
0.136	0.241	1.328	2.127	2.520	3.657
0.244	0.436	1.436	2.254	2.628	3.796
0.352	0.680	1.544	2.432	2.737	3.918
0.461	0.806	1.652	2.597	2.844	3.987
0.569	1.025	1.760	2.724	2.973	4.081
0.678	1.130	1.869	2.870	3.061	4.110
0.786	1.360	1.978	2.990	3.169	4.146
0.894	1.469	2.087	3.121	3.279	4.183
1.003	1.668	2.195	3.268	3.386	4.251
1.110	1.827	2.302	3.380	3.495	4.329

a first glance one might expect the straightforward 1:1 reaction to occur, viz.:-



both the conductometric titration graph and the U.V. spectra show this not to be the case. The gently-rising graph shows a small inflection near the 3:1 Halogen:Phosphine ratio (as might be expected from the known existence of PCl₆I); however, the absence of 1:1 and 2:1 ratio breaks indicates the reaction not to occur in distinct stages. Ultraviolet examination shows [I₃⁻] to be present

initially, a regular feature - it would appear - of the titrations involving iodine chloride (and also iodine trichloride, which might be considered as $(ICl + Cl_2)$ in acetonitrile) as titrant. Between the 1:1 and 2:1 ratios I_3^- gives way to I_2Cl^- together with iodine, and beyond the 2:1 ratio ICl_2^- is the trihalide ion present. This trihalide ion progression thus lends weight to the titration graph's indication of a system involving overlapping equilibria, a plausible scheme being:-



The molar conductance at the 3:1 mole ratio is:-

$$3:1; \quad \Lambda_m = 31.68 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} \quad (c_n = 0.0129 \text{ mole/l.})$$

suggesting PCl_6I to be a weak electrolyte in acetonitrile (but see $\text{PCl}_3\text{-ICl}_3$ below).

(ii) The PCl_3 -iodine trichloride system

Although the conductance-composition graph for the $\text{PCl}_3\text{-ICl}_3$ system is relatively simple, showing a marked 1:1 inflection (see Table XXIII; Figure 17, p. 82), the U.V. spectra again show this not to be the straightforward equimolar reaction, viz.:-

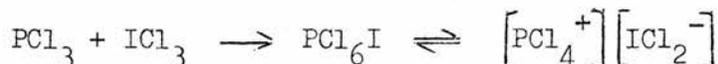


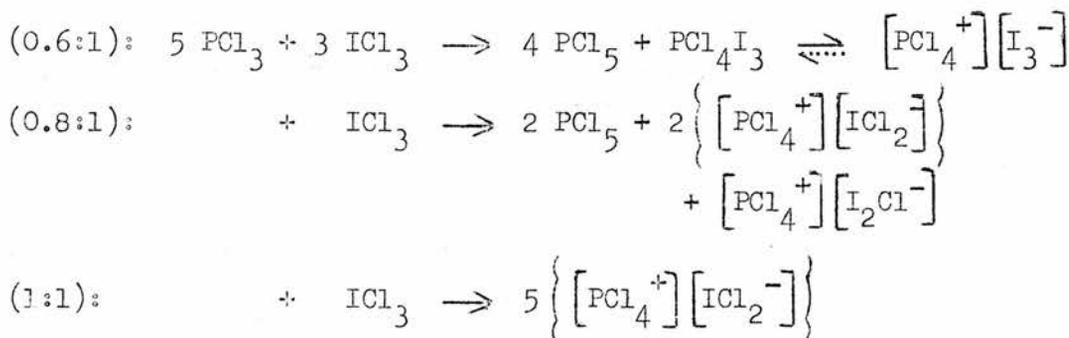
TABLE XXIII: Conductometric Analysis of the System $\text{PCl}_3\text{-ICl}_3$

Mole ratio ($\text{ICl}_3 : \text{PCl}_3$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm.}^{-1}$)	Mole ratio ($\text{ICl}_3 : \text{PCl}_3$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm.}^{-1}$)	Mole ratio ($\text{ICl}_3 : \text{PCl}_3$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm.}^{-1}$)
0.000	0.025	1.215	14.650	2.430	13.600
0.135	1.196	1.323	14.870	2.538	13.780
0.243	3.121	1.431	14.650	2.646	14.010
0.351	4.840	1.539	14.410	2.754	14.060
0.459	6.475	1.647	14.210	2.862	14.130
0.567	7.979	1.782	14.010	2.970	14.300
0.675	9.350	1.890	13.810	3.078	14.500
0.783	10.680	1.998	13.600	3.186	14.950
0.891	11.860	2.106	13.600	3.294	15.190
0.999	13.010	2.214	13.560	3.402	15.430
1.107	14.100	2.322	13.520	3.510	15.680

since once more the trihalide ion progression, is $\text{I}_3^- \rightarrow \text{I}_2\text{Cl}^-$ (below 1:1 ratio), followed by $\text{I}_2\text{Cl}^- \rightarrow \text{ICl}_2^-$ after the 1:1 ratio. In this case, the molar conductance value at the 1:1 ratio suggests strong electrolyte behaviour for ' PCl_6I ' as would be expected:-

$$1:1; \quad \Lambda_m = 90.60 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} (c_m = 0.0164 \text{ mole/l.})$$

The probable reaction scheme would therefore appear to be:-



There is no evidence for further reaction beyond the 1:1 mole ratio.

3. Summary

It is virtually impossible to see any general pattern emerging from the results obtained for the $\text{PhPCl}_2\text{-Hal}_2$ and $\text{Ph}_2\text{PCl-Hal}_2$ systems; they are certainly much more complex than the related $\text{Ph}_3\text{P-Hal}_2$ and $\text{PCl}_3\text{-Hal}_2$ cases. In particular, the reactions involving ICl and ICl_3 yield most complicated conductance-composition graphs (e.g. breaks at mole ratio Halogen:Phosphine :: 0.67:1), the complexity of the systems involved being monitored by the mixture of trihalide ions detected by ultraviolet spectrophotometry, and by the "unexpected" solid adducts isolated. Such results do, however, reinforce the general findings of Ali on the reactions of triaryl phosphines with ICl and ICl_3 .

The presence of two - and even more so three - halogens in the given systems not only increases the probability of exchange reactions and overlapping equilibria, but also aggravates analytical difficulties, already substantial on account of the extremely unstable nature of the species involved; thus the analysis of the solid adduct formed from PhPCl_4 and IBr does not fit the requirements of any single feasible product - it may well be a mixture.

In the case of $\text{PhPCl}_2\text{-Hal}_2$ systems, molar conductances were virtually all below or about $50 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1}$ both for the 1:1 and for the 2:1 adducts (at $c_{\text{III}} = 0.01\text{-}0.02 \text{ mole/l. approx.}$),

indicating weak electrolyte behaviour in acetonitrile. For Ph_2PCl systems, the 2:1 adducts were generally strong electrolytes, the 1:1 adducts being weak electrolytes.

The adducts isolated were virtually all solids (as opposed to the oils obtained in later systems); it would appear that the species PhPCl_4 and Ph_2PCl_3 are relatively stable, and form - both in solution and as solid phases - whenever possible. The species indicated in solution and isolated as solid adducts from the $\text{PhPCl}_2\text{-Hal}_2$; $\text{Ph}_2\text{PCl-Hal}_2$ and $\text{PCl}_3\text{-Hal}_2$ systems are listed overleaf in Summary Chart 1.

SUMMARY CHART 1: Conductometric Analyses of Hal₂ with PhPCL₂, Ph₂PCL and PCL₃ in Acetonitrile

System	Ratio of conductance break	Solution colour before break	Composition of species indicated	Δm at break	Δm at break	U.V. indicates	Species isolated
PhPCL ₂ -Cl ₂	1:1	colourless	PhPCL ₄	16.88	0.02884	-	PhPCL ₄
PhPCL ₂ -Br ₂	2:1	pale yellow	PhPCL ₂ ·Br ₄	37.60	0.00974	Br ₃ ⁻	PhPCL ₂ Br ₂ PhPCL ₂ Br ₄
PhPCL ₂ -I ₂	2:1	red	PhPCL ₂ ·I ₄	45.70	0.0116	I ₃ ⁻	-
PhPCL ₂ -ICl	1:1	red-brown	PhPCL ₂ ·ICl	11.24	0.0146	I ₃ ⁻	PhPCL ₅ I
	1.5:1	deep red	PhPCL ₂ ·(ICl) _{1.5}	6.49	0.0129	I ₃ ⁻ ; I ₂ Cl ⁻	-
PhPCL ₂ -IBr	≈ 2.1	red-brown	PhPCL ₂ ·I ₂ Br ₂	38.70	0.0203	IBr ₂ ⁻ ; I ₂	PhPCL ₂ ·IBr at 1:1
PhPCL ₂ -ICl ₃	0.67:1 1:1	yellow-brown pale yellow	PhPCL ₂ ·(ICl ₃) _{0.67} PhPCL ₂ ·ICl ₃	52.52 51.50	0.0211 0.0198	I ₃ ⁻ ; I ₂ Cl ⁻ ICl ₂ ⁻	PhPCL ₅ I
PhPCL ₂ ·Cl ₂ -ICl	0.5:1	pale yellow	PhPCL ₄ ·(ICl) _{0.5}	110.00	0.0106	ICl ₂ ⁻	PhPCL ₇ I
PhPCL ₂ ·Cl ₂ -IBr	0.25:1 0.5:1	pale yellow orange	PhPCL ₄ (IBr) _{0.25} PhPCL ₄ (IBr) _{0.5}	? 31.80	? 0.0034	ICl ₂ ⁻ ; IBr ₂ ⁻	orange solid (mixture?)
Ph ₂ PCL-Cl ₂	no break	-	-	(at 1:1) 2.54	0.0231	-	Ph ₂ PCL ₃
Ph ₂ PCL-Br ₂	no break	pale yellow orange	for 1:1 for 2:1	55.41 93.20	0.0156 0.0124	- Br ₃ ⁻	Ph ₂ PCLBr ₂ Ph ₂ PCLBr ₄
Ph ₂ PCL-I ₂	1:1	red	Ph ₂ PCL·I ₂	61.10	0.0142	I ₃ ⁻	Ph ₂ PI ₃
Ph ₂ PCL-ICl	0.67:1	yellow-brown	Ph ₂ PCL(ICl) _{0.67} for 1:1	46.61 81.81	0.0127 0.0060	I ₃ ⁻	Ph ₂ PCL ₃
Ph ₂ PCL-IBr	no break	yellow-brown red	for 1:1 for 2:1	46.02 76.30	0.0241 0.0207	I ₃ ⁻ ; Br ₃ ⁻ IBr ₂ ⁻ ; I ₂	Ph ₂ PCL·IBr
Ph ₂ PCL-ICl ₃	≈ 0.67:1	pale yellow	Ph ₂ PCL·(ICl ₃) _{0.67}	27.03	0.0015	I ₃ ⁻ ; ICl ₂ ⁻	Ph ₂ PCL ₄ I (at 1:1)
Ph ₂ PCL·Cl ₂ -ICl	0.5:1	pale yellow	Ph ₂ PCL ₃ (ICl) _{0.5}	103.90	0.0121	not performed	Ph ₂ PCL ₄ I (at 1:1)
PCL ₃ -ICl	3:1	brown	PCL ₃ ·(ICl) ₃	31.68	0.0129	ICl ₂ ⁻ ; I ₂	no attempt
PCL ₃ -ICl ₃	1:1	pale yellow	PCL ₃ ·(ICl ₃)	90.60	0.0164	ICl ₂ ⁻	no attempt

PART II

PART II:

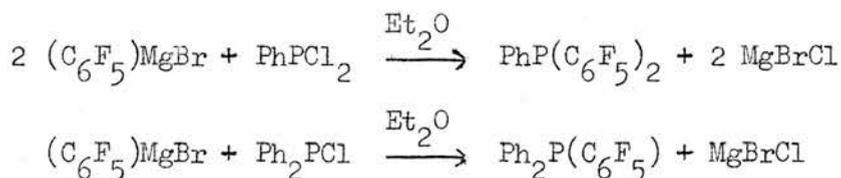
SOME REACTIONS OF PHENYLBIS(PENTAFLUOROPHENYL)PHOSPHINE
AND BIS(PHENYL)PENTAFLUOROPHENYLPHOSPHINE WITH HALOGENS

	Page
1. <u>Introduction</u>	91
2. <u>Results and Discussion</u>	94
(a) Reactions of $\text{PhP}(\text{C}_6\text{F}_5)_2$ with Halogens	94
(i) Reaction of $\text{PhP}(\text{C}_6\text{F}_5)_2$ with chlorine	94
(ii) Reaction of $\text{PhP}(\text{C}_6\text{F}_5)_2$ with bromine	96
(iii) Reaction of $\text{PhP}(\text{C}_6\text{F}_5)_2$ with iodine	97
(iv) Reaction of $\text{PhP}(\text{C}_6\text{F}_5)_2$ with iodine bromide .	100
(b) Reactions of $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ with Halogens	102
(i) Reaction of $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ with chlorine	102
(ii) Reaction of $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ with bromine	104
(iii) Reaction of $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ with iodine	106
(iv) Reaction of $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ with iodine bromide .	108
(v) Reaction of $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5) \cdot \text{Br}_2$ with iodine bromide	110
(vi) Reaction of $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5) \cdot \text{I}_2$ with iodine bromide	112
3. <u>Summary</u>	114

1. Introduction

Although the fluoroalkyl derivatives of Group V(b) elements have been extensively studied by several workers, it is only relatively recently that interest in the chemistry of the corresponding fluoroaryl derivatives has become apparent.

To a certain extent, lack of convenient synthetic methods inhibited initial interest in these compounds, and the major breakthrough in this respect was the synthesis of the Grignard reagent, pentafluorophenylmagnesium bromide (C_6F_5MgBr), by Tatlow¹³⁵ and co-workers. The preparation of tris(pentafluorophenyl)phosphine¹³⁶ by the reaction of $(C_6F_5)MgBr$ with phosphorus trichloride was reported in 1960; the substituted derivatives $(C_6F_5)_n-PHal_{(3-n)}$ (where Hal = Cl or Br) have since been obtained by the reaction of $(C_6F_5)MgBr$ and the corresponding phosphorus (III) halide in the appropriate mole ratio.^{137,138} Hence the $PhP(C_6F_5)_2$ and $Ph_2P(C_6F_5)$ used in the following work were prepared by:-



The replacement of the phenyl group by the pentafluorophenyl group might be expected to bring about some significant changes in the reactions of phosphines with halogens. The more electronegative (C_6F_5) group (with electronegativity lying between that of Br (2.95) and I (2.56)) would be expected to give a stronger interaction between the unshared pair of electrons on the P atom and the pi-electron system of the aromatic nucleus: in other words, tris(pentafluorophenyl)phosphine is more acidic (in the Lewis sense) than triphenylphosphine.

The reactions of $(C_6F_5)_3P$ with various halogens and inter-

halogens have been studied conductometrically by Ali: the dichloride $(C_6F_5)_3PCl_2$ (shown to be a non-electrolyte in acetonitrile solution) was isolated as a solid, in contrast to the corresponding dibromide whose formation in solution was indicated, however. Many tetrahalides with the exception of a Cl-containing species were indicated as being formed in solution (being strong electrolytes and producing $[(C_6F_5)_3PHal^+]$ and $[Hal_3^-]$ ions); however, attempted isolation of these adducts consistently yielded oily products. The following work investigates the corresponding reactions of $PhP(C_6F_5)_2$ and $Ph_2P(C_6F_5)$.

2. Results and Discussion

(a) The Reactions of Phenylbis(pentafluorophenyl)phosphine with Halogens

(i) The $PhP(C_6F_5)_2$ -chlorine system

The results of the conductometric analysis of the $PhP(C_6F_5)_2-Cl_2$ system are contained in Table XXIV and depicted graphically in Figure 18. Once again, precipitation occurs in the titration vessel (ca. 0.5:1 mole ratio), causing a break in the conductance-composition graph (cf. behaviour of conductance in $PhPCl_2-Br_2$ system, titration (b)). There is a genuine break, however, at the 1:1 ratio, accompanied by the appearance of a

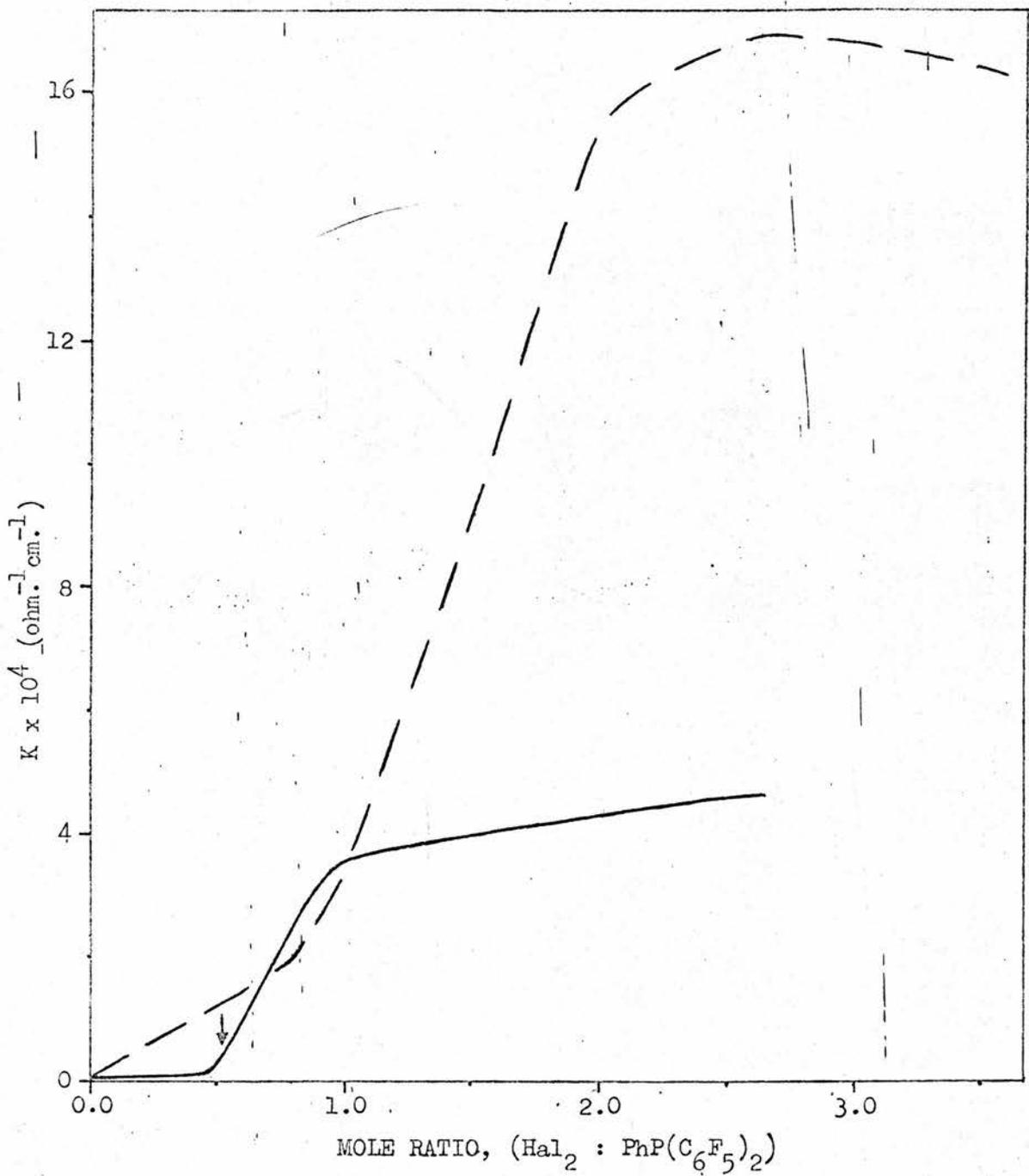


FIGURE 18: Conductometric Analysis of the Systems:

PhP(C₆F₅)₂-Cl₂ —————
(arrow denotes appearance of precipitate)

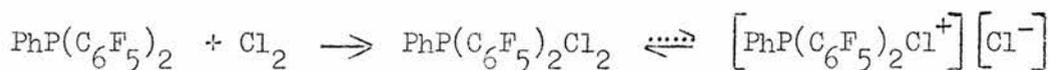
PhP(C₆F₅)₂-Br₂ - - - - -

TABLE XXIV: Conductometric Analysis of the System
 $\text{PhP}(\text{C}_6\text{F}_5)_2\text{-Cl}_2$

Mole ratio $\frac{(\text{Cl}_2)}{(\text{C}_6\text{F}_5)_2\text{PPh}}$	$\frac{\text{K} \times 10^4}{(\text{ohm} \cdot \text{cm}.)}$	Mole ratio $\frac{(\text{Cl}_2)}{(\text{C}_6\text{F}_5)_2\text{PPh}}$	$\frac{\text{K} \times 10^4}{(\text{ohm} \cdot \text{cm}.)}$	Mole ratio $\frac{(\text{Cl}_2)}{(\text{C}_6\text{F}_5)_2\text{PPh}}$	$\frac{\text{K} \times 10^4}{(\text{ohm} \cdot \text{cm}.)}$
0.000	0.0215	0.978	3.542	1.956	4.247
0.163	0.0288	1.141	3.662	2.119	4.372
0.326	0.0346	1.304	3.791	2.282	4.372
0.489*	0.0416	1.467	3.932	2.445	4.372
0.652	1.319	1.630	4.043		
0.815	2.243	1.793	4.158		

(Asterisk denotes appearance of precipitate, which remains throughout.)

yellow-green colouration in the solution which previously had been colourless. Beyond the 1:1 ratio, the conductance rises only slowly, the pale greenish colouration and whitish precipitate persisting throughout: there is thus little evidence of reaction beyond the 1:1 ratio. The molar conductance at the 1:1 mole ratio is $\Lambda_m = 12.64 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ($c_m = 0.0282 \text{ mole/l.}$), typical of weak electrolyte behaviour. On attempted isolation of the adduct which precipitates so readily, it is found that the solid is quite unstable out of solution, degenerating into a viscous oil immediately on removal of last traces of solvent. This oil does, however, give an analysis near that required for $\text{PhP}(\text{C}_6\text{F}_5)_2\text{Cl}_2$. It appears, therefore, that the given reaction proceeds:-



(ii) The PhP(C₆F₅)₂-bromine system

Table XXV and Figure 18 contain the results of the conductometric analysis of the PhP(C₆F₅)₂-Br₂ system:-

TABLE XXV: Conductometric Analysis of the System
PhP(C₆F₅)₂-Br₂

Mole ratio $\frac{(\text{Br}_2:\text{C}_6\text{F}_5)_2}{\text{PPh}}$	$\frac{K \times 10^4}{(\text{ohm} \cdot \text{cm} \cdot \text{l}^{-1})}$	Mole ratio $\frac{(\text{Br}_2:\text{C}_6\text{F}_5)_2}{\text{PPh}}$	$\frac{K \times 10^4}{(\text{ohm} \cdot \text{cm} \cdot \text{l}^{-1})}$	Mole ratio $\frac{(\text{Br}_2:\text{C}_6\text{F}_5)_2}{\text{PPh}}$	$\frac{K \times 10^4}{(\text{ohm} \cdot \text{cm} \cdot \text{l}^{-1})}$
0.000	0.021	1.253	7.633	2.662	16.824
0.104	0.580	1.357	8.156	2.871	16.850
0.208	0.915	1.462	8.994	3.080	16.957
0.313	1.172	1.566	10.313	3.289	16.564
0.418	1.430	1.683	12.051	3.497	16.374
0.522	1.682	1.801	13.794	3.706	16.189
0.626	1.915	1.905	14.844	3.915	16.007
0.731	2.134	2.010	15.772	4.124	15.830
0.835	3.405	2.114	16.067	4.333	15.657
0.940	4.751	2.219	16.437	4.541	15.487
1.044	6.085	2.349	16.693		
1.148	6.919	2.506	16.758		

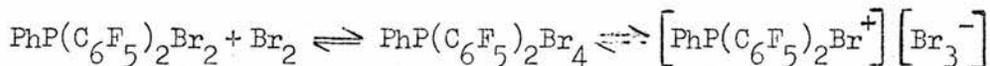
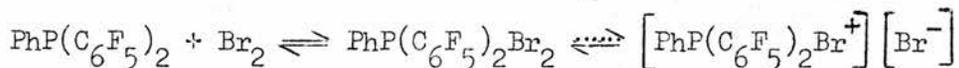
There are two inflections in the graph, the first at the 1:1 ratio, and the second near Br₂:PhP(C₆F₅)₂ :: 2:1. However, neither of these is a sharp break, the curve having the "rounded" appearance suggestive of an equilibrium system. This is further supported by the U.V. spectra, which show tribromide ions present from the start of the titration; a system of simultaneous equilibria is thus indicated. The molar conductance values calculated at the 1:1 and 2:1 Halogen:Phosphine ratios are:-

$$1:1; \quad \Lambda_m = 24.78 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0223 \text{ mole/l.})$$

$$2:1; \quad \Lambda_m = 75.20 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0197 \text{ mole/l.})$$

indicative of weak and strong electrolyte behaviour, respectively. Attempted isolation of adduct at the 1:1 mole ratio yields a yellow viscous oil, whose analysis approximates that required for $\text{PhP}(\text{C}_6\text{F}_5)_2\text{Br}_2$: thus Ali's pattern of oils for 1:1 adducts in the $(\text{C}_6\text{F}_5)_3\text{P-Hal}_2$ system seems to be re-emerging here.

The reaction therefore appears to proceed by:-



both these equilibria existing from the beginning, but as more bromine is added to the system the equilibrium shifts towards formation of $\text{PhP}(\text{C}_6\text{F}_5)_2\text{Br}_4$.

(iii) The $\text{PhP}(\text{C}_6\text{F}_5)_2$ -iodine system

Once again, a "smooth" conductance-composition profile is observed for the $\text{PhP}(\text{C}_6\text{F}_5)_2\text{-I}_2$ case (see Figure 19, p. 98), the relevant statistics being listed in Table XXVI below. In addition, the ultraviolet absorption of triiodide ion from the outset of the titration ($\lambda_{\text{max.}} = 291, 360 \text{ m}\mu$), together with the isolation of an unstable viscous oil with analysis approximating that required for $\text{PhP}(\text{C}_6\text{F}_5)_2\text{I}_2$ from the reagents in 1:1 ratio, strongly suggests a reaction scheme entirely analogous to that written

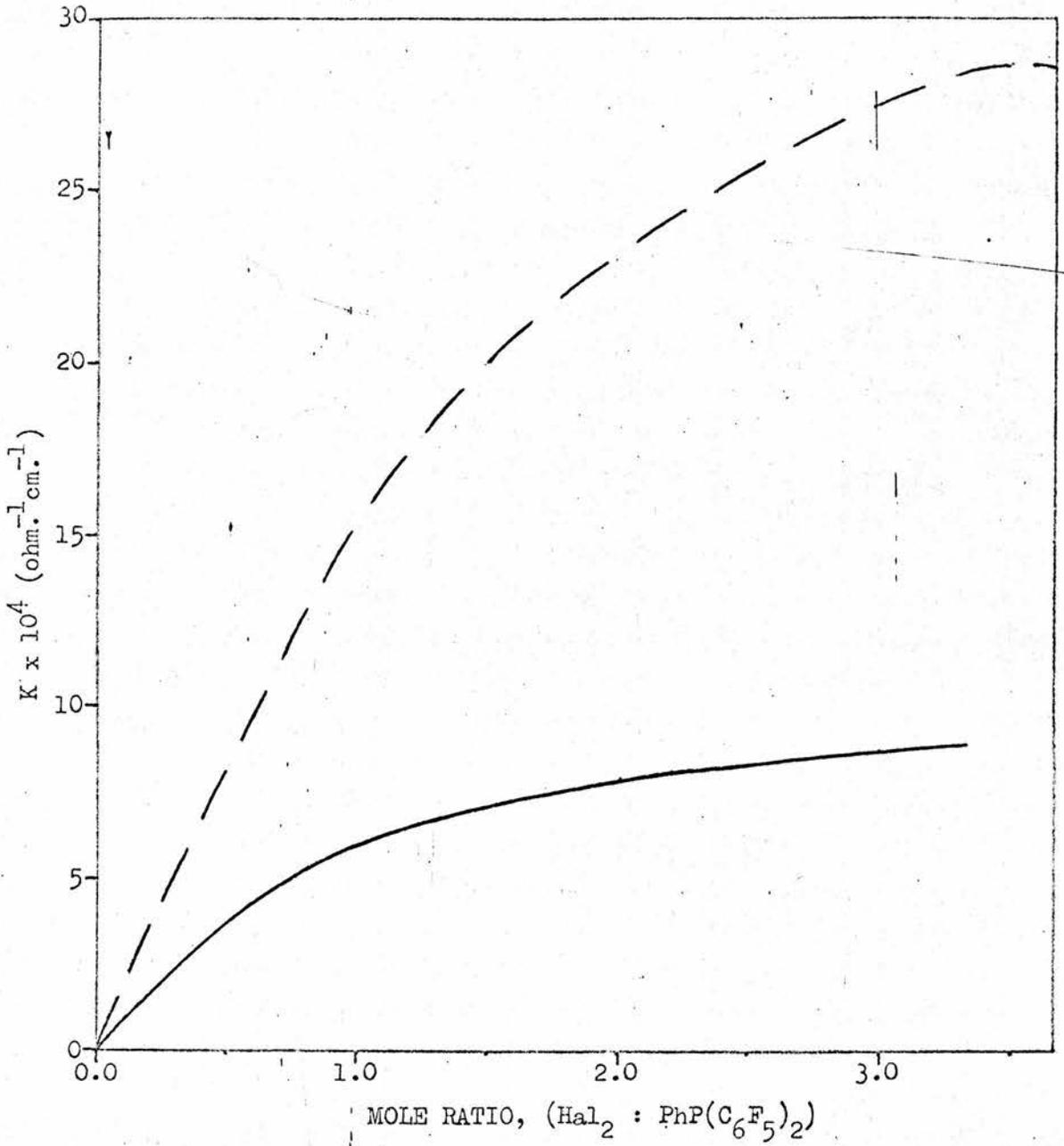
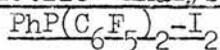


FIGURE 19: Conductometric Analysis of the Systems:

PhP(C₆F₅)₂-I₂: —————

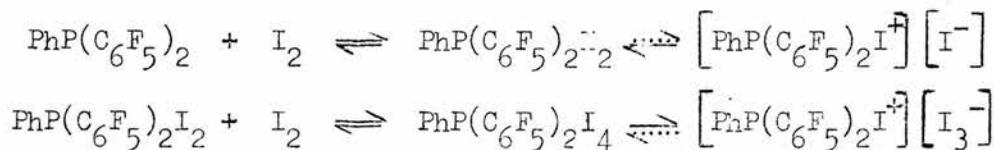
PhP(C₆F₅)₂-Br₂: - - - - -

TABLE XXVI: Conductometric Analysis of the System



Mole ratio $(\text{I}_2 : (\text{C}_6\text{F}_5)_2\text{PPh})$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio $(\text{I}_2 : (\text{C}_6\text{F}_5)_2\text{PPh})$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio $(\text{I}_2 : (\text{C}_6\text{F}_5)_2\text{PPh})$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$
0.000	0.0193	1.214	6.677	2.538	8.340
0.110	1.128	1.325	6.839	2.703	8.431
0.221	2.155	1.435	7.049	2.871	8.540
0.331	3.108	1.546	7.265	3.035	8.639
0.441	3.861	1.656	7.409	3.200	8.746
0.552	4.290	1.767	7.550	3.366	8.835
0.662	4.814	1.877	7.700	3.533	8.900
0.772	5.358	1.988	7.907	3.755	8.950
0.883	5.660	2.098	8.104	4.031	9.008
0.993	6.037	2.209	8.169	4.301	9.067
1.104	6.318	2.375	8.241	4.660	9.119

for the $\text{PhP}(\text{C}_6\text{F}_5)_2\text{-Br}_2$ system directly above:-



The relevant molar conductance values, are:-

$$1:1; \quad \Lambda_m = 57.56 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0106 \text{ mole/l.})$$

$$2:1; \quad \Lambda_m = 83.91 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0095 \text{ mole/l.})$$

again indicating weak and strong electrolyte behaviour at the 1:1 and 2:1 Halogen:Phosphine mole ratios, respectively.

(iv) The PhP(C₆F₅)₂-iodine bromide system

Yet again, a conductance-composition graph in Figure 19 (p. 98) (from the data in Table XXVII) without any definite break suggests a system of several equilibria. Again, weak and strong

TABLE XXVII: Conductance Analysis of the System
PhP(C₆F₅)₂-IBr

Mole ratio (IBr:(C ₆ F ₅) ₂ PPh)	$\frac{\kappa \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio (IBr:(C ₆ F ₅) ₂ PPh)	$\frac{\kappa \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio (IBr:(C ₆ F ₅) ₂ PPh)	$\frac{\kappa \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$
0.000	0.028	1.335	18.255	2.698	26.813
0.142	2.750	1.448	19.412	2.868	27.500
0.256	4.206	1.562	20.332	3.039	27.857
0.398	5.500	1.676	21.238	3.209	28.224
0.511	7.526	1.789	22.113	3.380	28.411
0.625	10.239	1.903	22.941	3.607	28.411
0.738	12.363	2.016	23.571	3.834	28.224
0.880	14.300	2.130	24.101	4.061	28.039
0.994	15.714	2.244	24.655	4.288	27.677
1.108	16.500	2.357	25.235	4.516	27.325
1.221	17.298	2.528	26.000		

electrolyte behaviour of the 1:1 and 2:1 Halogen:Phosphine ratios respectively is indicated by:-

$$1:1; \quad \Lambda_m = 39.29 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0395 \text{ mole/l.})$$

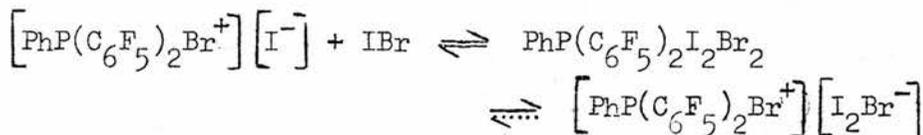
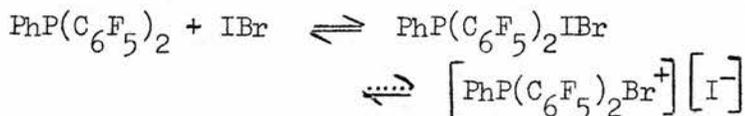
$$2:1; \quad \Lambda_m = 66.07 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0355 \text{ mole/l.})$$

Yet again, a dark viscous oil is obtained on trying to isolate a 1:1 adduct; it is extremely difficult to remove the last traces

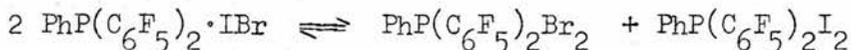
of solvent from the oil (as shown by ca.0.6% N in the microanalysis); however, the analysis does approach that required by $\text{PhP}(\text{C}_6\text{F}_5)_2\text{IBr}$.

Below the 2:1 Halogen:Phosphine mole ratio, $[\text{I}_2\text{Br}^-]$ absorption is evident in the ultraviolet spectrum, giving way to a mixture of I_3^- , IBr_2^- and possibly Br_3^- , and finally IBr_2^- is the only trihalide absorption present (beyond the 2:1 ratio).

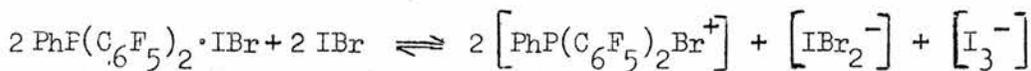
Thus we expect the simultaneous equilibria to be set up -



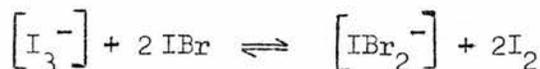
and we would expect $2 [\text{I}_2\text{Br}^-] \rightleftharpoons [\text{I}_3^-] + [\text{IBr}_2^-]$. However, it is not at all unlikely that some rearrangement will take place involving the mixed halogen phosphorus (V) compound; and this would occur in the sense:-



and these "simple" halides would react with IBr to give, at the 2:1 ratio:-



and eventually more iodine bromide would react with triiodide ion thus:-



so that the trihalide ion content is - to an overwhelming degree - iododibromide, one of the symmetric and relatively stable trihalide ions.

(b) The Reactions of Bis(phenyl)pentafluorophenylphosphine with Halogens

(i) The $Ph_2P(C_6F_5)$ - chlorine system

The conductance-composition graph for the $Ph_2P(C_6F_5)-Cl_2$ system (shown in Figure 20 from the data of Table XXVIII) is relatively simple, exhibiting a marked inflection at the 1:1 mole

TABLE XXVIII: Conductometric Analysis of the System $Ph_2P(C_6F_5)-Cl_2$

Mole ratio $(Cl_2 : (C_6F_5)PPh_2)$	$K \times 10^4$ (ohm ⁻¹ cm. ⁻¹)	Mole ratio $(Cl_2 : (C_6F_5)PPh_2)$	$K \times 10^4$ (ohm ⁻¹ cm. ⁻¹)	Mole ratio $(Cl_2 : (C_6F_5)PPh_2)$	$K \times 10^4$ (ohm ⁻¹ cm. ⁻¹)
0.000	0.179	0.867	13.033	1.706	16.595
0.205	0.184	1.023	14.944	1.910	16.734
0.341	2.853	1.159	15.699	2.113	16.865
0.478	6.349	1.296	15.994	2.317	16.943
0.614	9.079	1.432	16.288	2.523	17.000
0.750	11.283	1.569	16.489		

ratio. In contrast to the $PhP(C_6F_5)_2-Cl_2$ system, however, the molar conductance at the 1:1 ratio is high:-

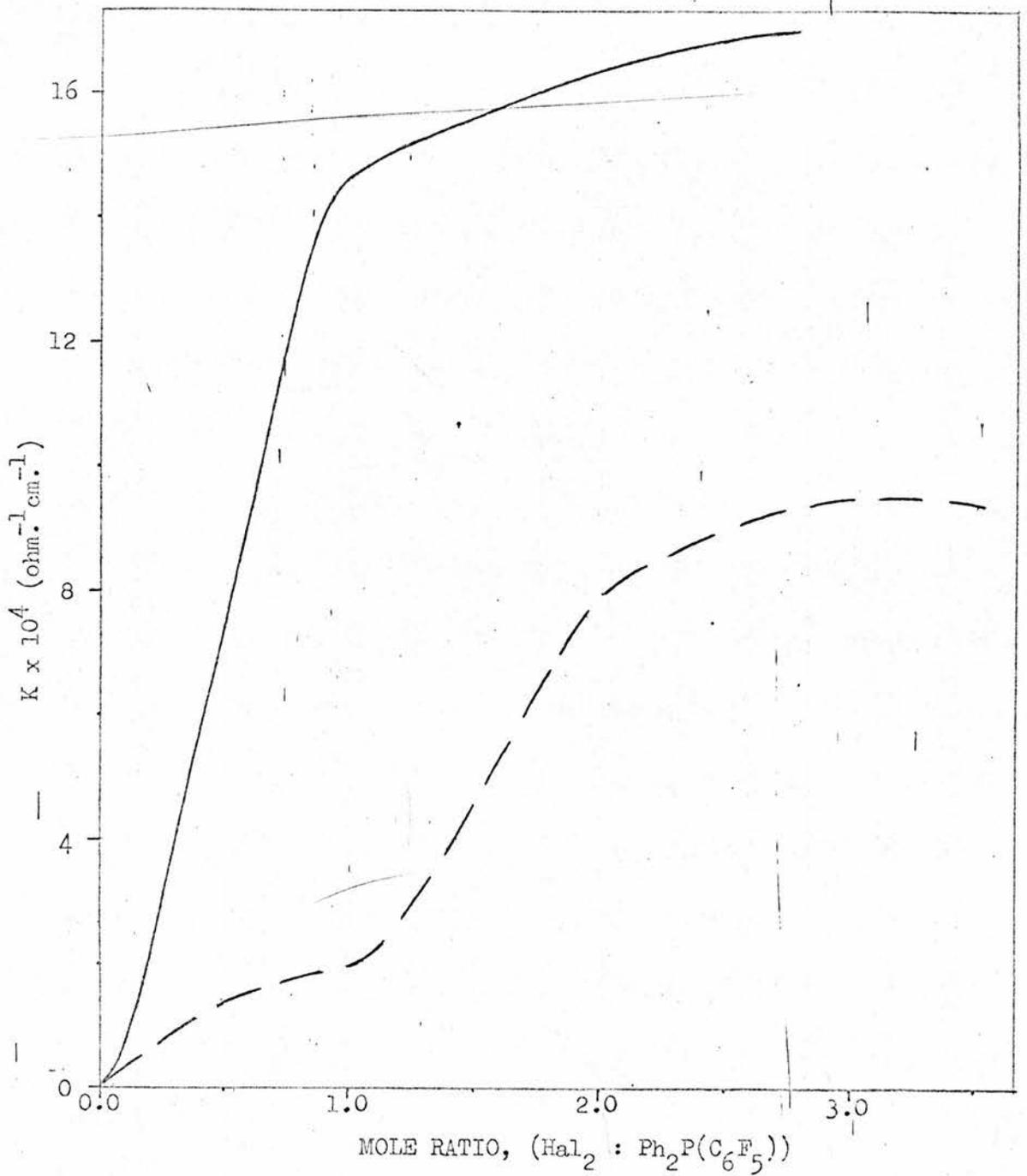
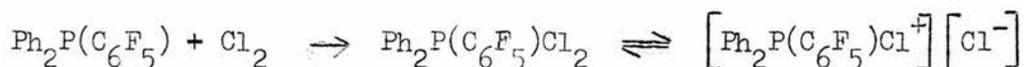


FIGURE 20: Conductometric Analysis of the Systems:

Ph₂P(C₆F₅)-Cl₂: —————
Ph₂P(C₆F₅)-Br₂: - - - - -

$$\Lambda_m = 69.35 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0212 \text{ mole/l.})$$

and a solid adduct (with good analysis for $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{Cl}_2$) can be isolated from the reagents in acetonitrile. There is no evidence for the formation of trichloride ion (a rare species in acetonitrile solution) after the 1:1 ratio, although this is not an impossibility as the 1:1 adduct is a fairly strong electrolyte. The reaction may best be represented:-



(ii) The $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ -bromine system

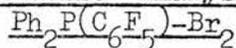
Table XXIX and Figure 20 show the results of the conductometric analysis of the $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ - Br_2 system. The graph contains two inflections, near the 1:1 and 2:1 Halogen:Phosphine ratios respectively. This system, in fact, is remarkably similar in character to the Ph_3P - Br_2 and Ph_3As - Br_2 systems studied by Beveridge: all these systems contain 1:1 and 2:1 inflections indicating the existence in solution of the dihalide and tetrahalide adducts ($\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{Br}_2$ and $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{Br}_4$ in this case), the former showing weak electrolyte and the latter showing strong electrolyte character. For the present system we have:-

$$1:1; \quad \Lambda_m = 25.62 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0084 \text{ mole/l.})$$

$$2:1; \quad \Lambda_m = 110.01 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0073 \text{ mole/l.})$$

In addition all three systems mentioned show the presence of

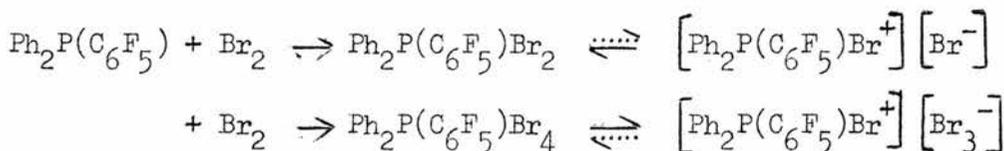
TABLE XXIX: Conductometric Analysis of the System



Mole ratio $\frac{(\text{Br}_2 : (\text{C}_6\text{F}_5)\text{PPh}_2)}$	$\frac{K \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio $\frac{(\text{Br}_2 : (\text{C}_6\text{F}_5)\text{PPh}_2)}$	$\frac{K \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio $\frac{(\text{Br}_2 : (\text{C}_6\text{F}_5)\text{PPh}_2)}$	$\frac{K \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$
0.000	0.068	1.439	4.564	2.919	9.491
0.121	0.593	1.547	5.465	3.053	9.533
0.229	0.894	1.654	6.208	3.188	9.576
0.336	1.205	1.762	6.897	3.322	9.597
0.444	1.449	1.870	7.435	3.457	9.597
0.551	1.644	1.977	7.944	3.591	9.597
0.659	1.758	2.085	8.266	3.726	9.576
0.767	1.810	2.192	8.580	3.860	9.555
0.874	1.849	2.300	8.773	3.995	9.533
1.009	2.234	2.408	8.956	4.129	9.512
1.116	2.732	2.515	9.147	4.264	9.470
1.224	3.300	2.650	9.286	4.398	9.429
1.332	3.936	2.784	9.387	4.533	9.387

tribromide ion ($\lambda_{\text{max.}} = 269 \text{ m}\mu$) after the 1:1 ratio only, the originally colourless solution having assumed a yellow colouration at that point.

The course of this reaction therefore would appear fairly straightforward:-



Unfortunately, the species $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{Br}_2$ and $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{Br}_4$ indicated as being stable in solution are not easily isolated as solid

adducts: only viscous oils of low halogen content can be isolated from the reagents - both in 1:1 and in 2:1 mole ratio - in acetonitrile solution.

(iii) The $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ -iodine system

Conductometric analysis of the $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-I}_2$ system gives the results listed in Table XXX and depicted graphically in Figure 21. The smooth curve, attaining a maximum just beyond the 2:1 Halogen-Phosphine ratio, together with the ultraviolet spectra

TABLE XXX: Conductometric Analysis of the System
 $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-I}_2$

Mole ratio $(\text{I}_2:(\text{C}_6\text{F}_5)\text{PPh}_2)$	$\text{K} \times 10^4$ (ohm. ⁻¹ cm. ⁻¹)	Mole ratio $(\text{I}_2:(\text{C}_6\text{F}_5)\text{PPh}_2)$	$\text{K} \times 10^4$ (ohm. ⁻¹ cm. ⁻¹)	Mole ratio $(\text{I}_2:(\text{C}_6\text{F}_5)\text{PPh}_2)$	$\text{K} \times 10^4$ (ohm. ⁻¹ cm. ⁻¹)
0.000	0.073	1.233	9.908	2.535	14.252
0.125	1.986	1.343	10.619	2.673	14.348
0.222	2.879	1.454	11.289	2.812	14.252
0.332	3.698	1.565	11.753	2.950	14.205
0.457	4.668	1.704	12.222	3.116	14.158
0.568	5.465	1.814	12.768	3.282	14.066
0.679	6.337	1.953	13.323	3.449	13.883
0.789	7.126	2.064	13.619	3.629	13.750
0.900	7.930	2.174	13.883	3.809	13.533
1.011	8.597	2.285	14.020	4.003	13.323
1.122	9.306	2.396	14.158	4.169	13.119

which show the presence of triiodide ion from the outset of the titration suggest immediate formation of the tetrahalide $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{I}_4$,

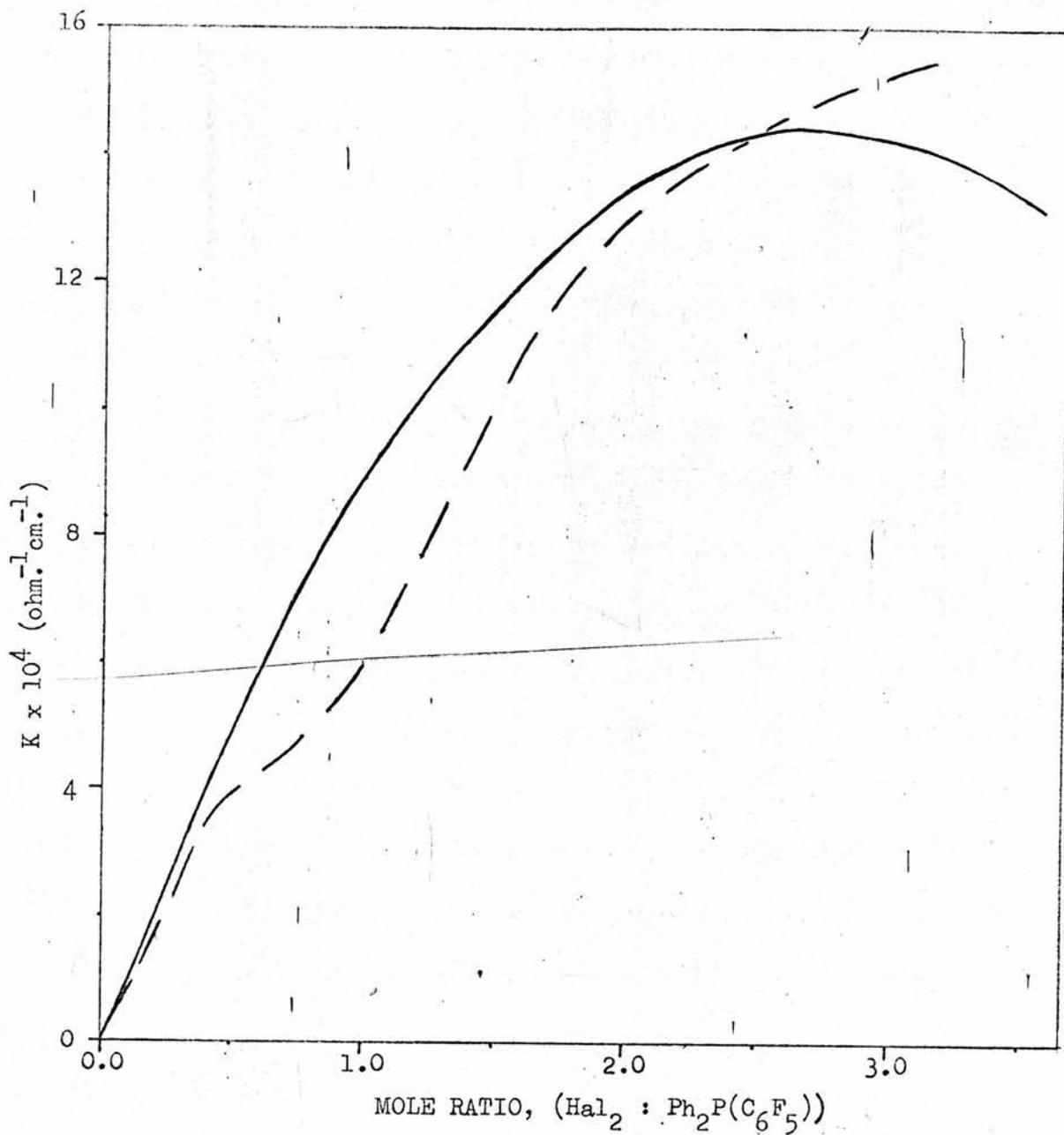


FIGURE 21: Conductometric Analysis of the Systems:

$\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-I}_2$: ————

$\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-IBr}$: - - - - -

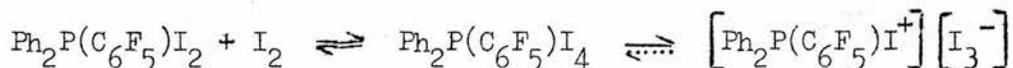
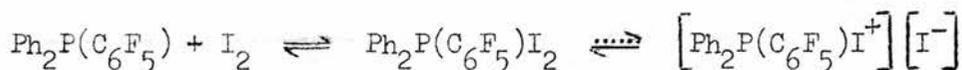
probably in equilibrium with the dihalide, the equilibrium shifting towards the tetrahalide as more iodine is added to the system.

The molar conductance values at the 1:1 and 2:1 ratios are:-

$$1:1; \quad \Lambda_m = 65.14 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0132 \text{ mole/l.})$$

$$2:1; \quad \Lambda_m = 117.68 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0114 \text{ mole/l.})$$

indicating the reaction scheme to be written:-



Yet again, no solid adduct can be isolated: a dark, viscous oil formed by the reagents in 2:1 Halogen:Phosphine ratio gives an analysis suggesting it to be the tetrahalide, $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{I}_4$.

(iv) The $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ -iodine bromide system

Table XXXI and Figure 21 contain the conductometric data for the $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ -IBr system, the graph showing no sharp breaks but having shallow inflections at the 1:1 and 2:1 Halogen:Phosphine ratios. It would thus appear that the system is one involving equilibria, and the presence of trihalide ion absorption in the ultraviolet region (a mixture of $[\text{I}_3^-]$ and $[\text{IBr}_2^-]$, possibly arising from disproportionation of $[\text{I}_2\text{Br}^-]$) from the start of the titration suggests that these equilibria overlap. The molar conductance values at the 1:1 and 2:1 Halogen:Phosphine ratios are:-

$$1:1; \quad \Lambda_m = 38.18 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0156 \text{ mole/l.})$$

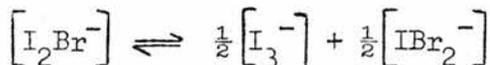
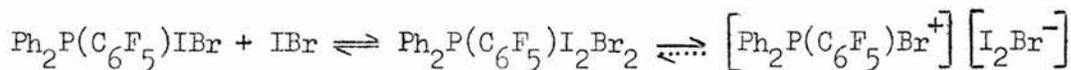
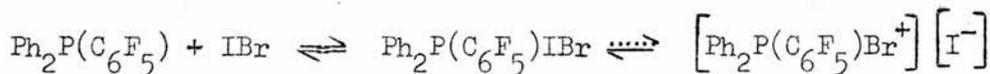
$$2:1; \quad \Lambda_m = 94.80 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0137 \text{ mole/l.})$$

suggesting weak and strong electrolyte behaviour respectively.

TABLE XXXI; Conductometric Analysis of the System
Ph₂P(C₆F₅)₂-IBr

Mole ratio (IBr : (C ₆ F ₅) ₂ Ph ₂)	$\frac{\kappa \times 10^4}{(\text{ohm}^{-1} \text{ cm}^{-1})}$	Mole ratio (IBr : (C ₆ F ₅) ₂ Ph ₂)	$\frac{\kappa \times 10^4}{(\text{ohm}^{-1} \text{ cm}^{-1})}$	Mole ratio (IBr : (C ₆ F ₅) ₂ Ph ₂)	$\frac{\kappa \times 10^4}{(\text{ohm}^{-1} \text{ cm}^{-1})}$
0.000	0.096	1.258	7.296	2.574	14.844
0.114	1.788	1.373	7.930	2.717	15.000
0.229	2.681	1.487	8.597	2.860	15.159
0.343	3.300	1.602	9.449	3.003	15.267
0.458	3.730	1.716	10.362	3.146	15.321
0.572	4.165	1.830	11.440	3.289	15.376
0.686	4.564	1.945	12.363	3.461	15.432
0.801	4.988	2.059	13.282	3.804	15.543
0.915	5.564	2.174	13.839	4.147	15.487
1.030	6.129	2.288	14.348	4.490	15.376
1.144	6.724	2.431	14.642	4.662	15.321

Beyond the 2:1 mole ratio the only trihalide ion absorption is that of IBr₂⁻ (λ_{max.} = 256, 370 mμ). The proposed reaction is therefore:-



This system matches the Ph₂P(C₆F₅)₂-Br₂ and Ph₂P(C₆F₅)₂-I₂ cases

in not yielding solid adducts. From IBr and $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ in the 2:1 ratio a dark viscous oil was obtained whose analysis tends to suggest it to be $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{I}_2\text{Br}_2$.

(v) The $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{Br}_2$ -iodine bromide system

The conductometric titration of $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\cdot\text{Br}_2$ with IBr was performed as a "double halogen" titration: i.e. bromine in acetonitrile was run into the acetonitrile solution of $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ until the (pre-calculated) 1:1 mole ratio was reached - being monitored also by the appearance of yellow colouration in the titration mixture. The bromine/acetonitrile burette was then swiftly replaced by a burette containing a standard solution of iodine bromide in acetonitrile. The titration then proceeded in the normal fashion, and the results of the titration starting from the first addition of iodine bromide can be found listed in Table XXXII and depicted graphically in Figure 22.

The conductance-composition graph is, in fact, entirely featureless, with no distinct inflections evident, suggesting an equilibrium system. The ultraviolet examination shows simply $[\text{IBr}_2^-]$ absorption throughout the duration of the iodine bromide addition, suggesting the reaction follows the expected course. The value of the molar conductance of the 1:1 mole ratio is:-

$$\Lambda_m = 97.78 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0091 \text{ mole/l.})$$

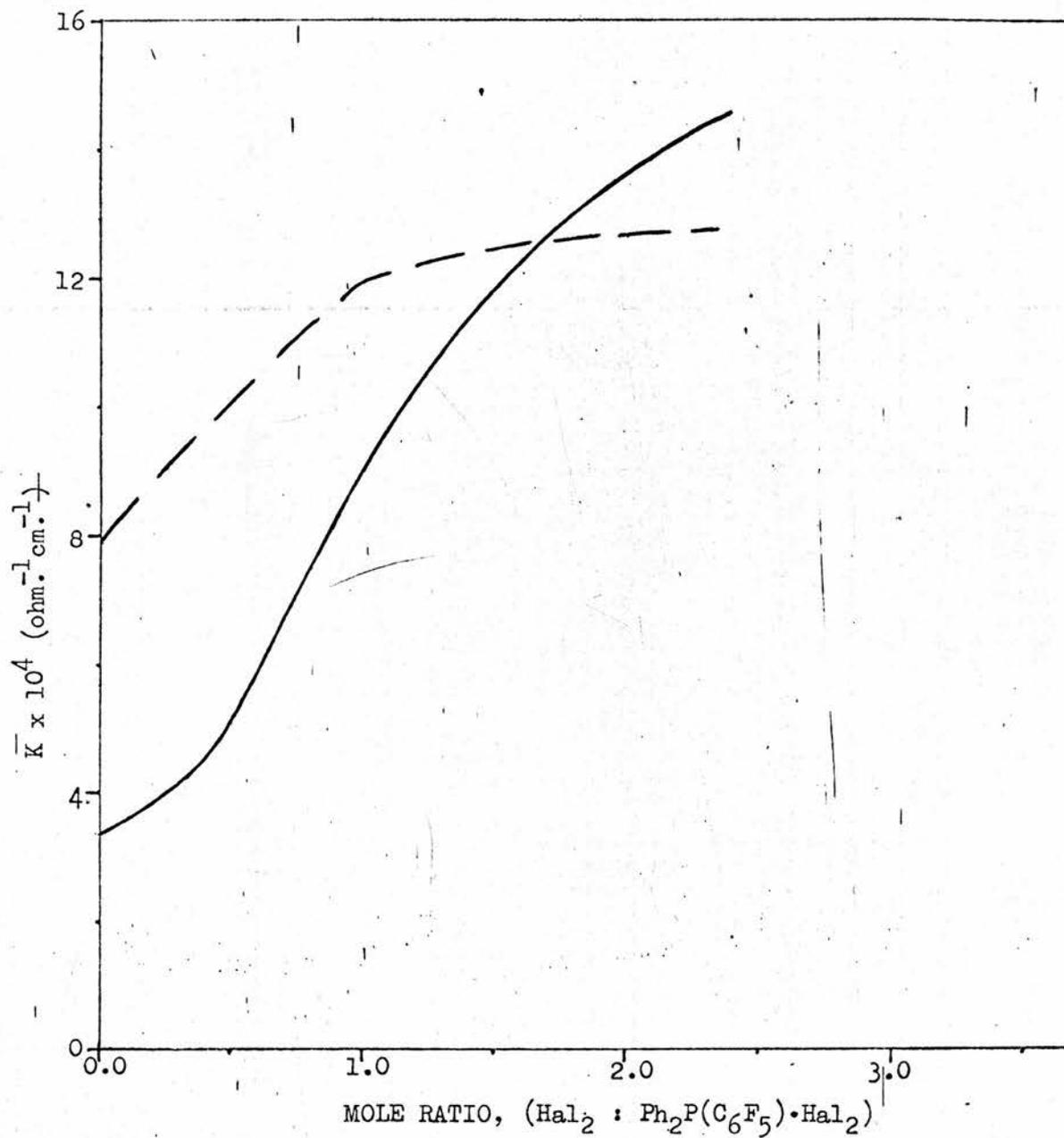


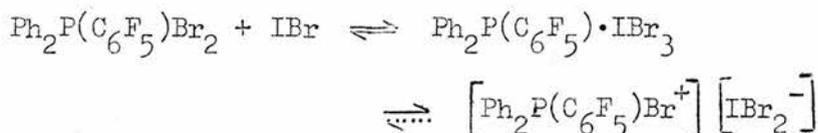
FIGURE 22: Conductometric Analysis of the Systems:

$\text{Ph}_2\text{P}(\text{C}_6\text{F}_5) \cdot \text{Br}_2\text{-IBr}$: —————
 $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5) \cdot \text{I}_2\text{-IBr}$: - - - - -

TABLE XXXII: Conductometric Analysis of the System
 $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)_2\cdot\text{Br}_2\text{-IBr}$

Mole ratio $(\text{IBr}:\text{C}_6\text{F}_5\text{PPh}_2\text{Br}_2)$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio $(\text{IBr}:\text{C}_6\text{F}_5\text{PPh}_2\text{Br}_2)$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio $(\text{IBr}:\text{C}_6\text{F}_5\text{PPh}_2\text{Br}_2)$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$
0.001	3.372	1.020	8.932	1.832	13.358
0.119	3.572	1.092	9.661	1.920	13.567
0.236	3.896	1.180	10.273	1.991	13.726
0.353	4.330	1.269	10.818	2.069	13.881
0.472	4.929	1.358	11.282	2.140	14.009
0.591	5.781	1.446	11.839	2.215	14.137
0.710	6.634	1.537	12.286	2.288	14.288
0.828	7.690	1.624	12.638		
0.914	8.260	1.725	13.017		

suggesting strong electrolyte behaviour and thus the equation:-



Having now examined routes to the "symmetric" and "asymmetric" tetrahalides $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)_2\text{I}_2\text{Br}_2$ and $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)_2\text{IBr}_3$, it only remains to examine the obvious route to $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)_2\text{I}_3\text{Br}$.

(vi) The $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)_2\cdot\text{I}_2$ -iodine bromide system

The $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)_2\text{I}_2\text{-IBr}$ conductometric titration was also performed in the manner used in reaction (v) immediately above, i.e. IBr/MeCN was titrated into an equimolar mixture of $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)_2$ and

I_2 in acetonitrile. The results of this titration from the beginning of iodine bromide addition can be found in Table XXXIII and Figure 22:-

TABLE XXXIII: Conductometric Analysis of the System
 $Ph_2P(C_6F_5)_2 \cdot I_2 - IBr$

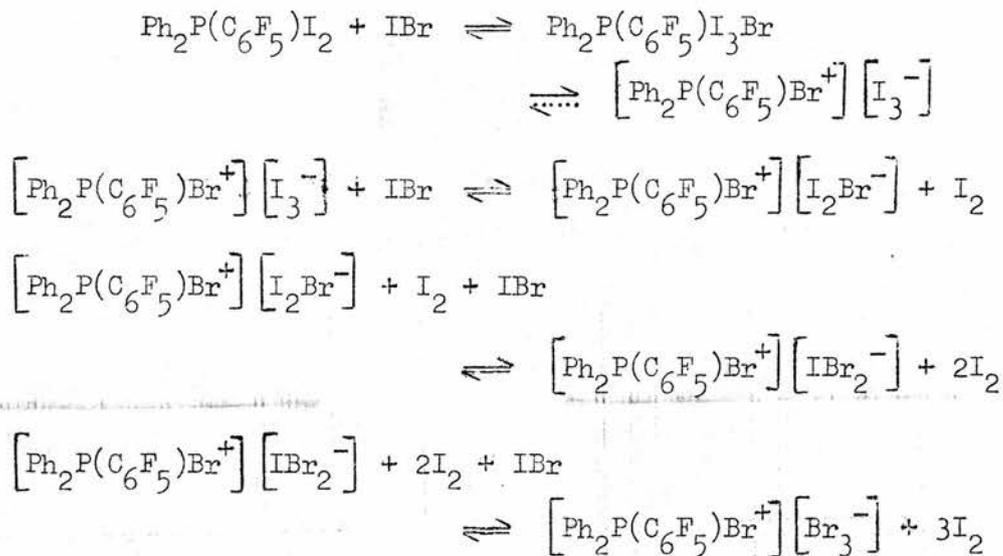
Mole ratio $\frac{(C_6F_5)_2PPh_2}{(IBr)} I_2$	$K \times 10^4$ $\frac{\Omega^{-1} \text{ cm.}^{-1}}{(\text{ohm.}^{-1} \text{ cm.}^{-1})}$	Mole ratio $\frac{(C_6F_5)_2PPh_2}{(IBr)} I_2$	$K \times 10^4$ $\frac{\Omega^{-1} \text{ cm.}^{-1}}{(\text{ohm.}^{-1} \text{ cm.}^{-1})}$	Mole ratio $\frac{(C_6F_5)_2PPh_2}{(IBr)} I_2$	$K \times 10^4$ $\frac{\Omega^{-1} \text{ cm.}^{-1}}{(\text{ohm.}^{-1} \text{ cm.}^{-1})}$
0.001	7.841	0.769	11.159	1.617	12.569
0.110	8.569	0.878	11.611	1.752	12.600
0.220	9.047	0.987	11.898	1.893	12.600
0.330	9.379	1.097	12.065	2.027	12.642
0.440	9.771	1.206	12.204	2.167	12.677
0.550	10.194	1.345	12.382	2.305	12.709
0.660	10.663	1.483	12.569		

In this case, the titration graph is relatively simple, showing an inflection at the 1:1 mole ratio, where the molar conductance is:-

$$\Delta m = 123.76 \text{ ohm.}^{-1} \text{ cm.}^2 \text{ mole}^{-1} \quad (c_m = 0.0096 \text{ mole/l.})$$

suggesting a strong 1:1 electrolyte in solution. Ultraviolet examination shows the triiodide ion present from the start of the IBr addition to have been replaced by $[I_2Br^-]$ after the 1:1 ratio, and beyond the 2:1 Halogen:Phosphine ratio virtually all the $[I_2Br^-]$ has been replaced by a mixture of $[IBr_2^-]$ and $[Br_3^-]$ ions.

All the evidence therefore suggests the scheme:-



It would appear, therefore, that $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{I}_n\text{Br}_{(4-n)}$ ($n = 0, 1, 2, 3, 4$) are all formed in acetonitrile solution.

3. Summary

Although by no means simple, the $\text{PhP}(\text{C}_6\text{F}_5)_2\text{-Hal}_2$ and $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-Hal}_2$ systems do lend themselves somewhat more to generalisation than those systems investigated in Part I of this thesis, although, of course, the omission of ICl and ICl_3 possibly aids this.

In virtually all cases (both for $\text{PhP}(\text{C}_6\text{F}_5)_2$ and $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$) the 1:1 halogen adducts are weak electrolytes and the 2:1 adducts strong electrolytes in acetonitrile, although the species $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{Cl}_2$ does give an unexpectedly high molar conductance,

viz., $\Lambda_m = 69.35 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ($c_m = 0.0212 \text{ mole/l.}$). All the tetrahalides isolated are viscous oils - a result in agreement with the findings of Ali on the $(\text{C}_6\text{F}_5)_3\text{P-Hal}_2$ systems; indeed, the only dihalide which can be isolated as a solid is $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{Cl}_2$.

The findings of Part II are listed in tabular form overleaf in Summary Chart 2.

SUMMARY CHART 2: Conductometric Analyses of Hal₂ with PhP(C₆F₅)₂ and Ph₂P(C₆F₅)₂ in Acetonitrile

System	Ratio of conductance break	Solution colour before break	Composition of species indicated	λ_m at break	Cm at break	U.V. indicates	Species isolated
PhP(C ₆ F ₅) ₂ -Cl ₂	1 : 1	colourless	PhP(C ₆ F ₅) ₂ ·Cl ₂	12.64	0.0282	—	PhP(C ₆ F ₅) ₂ ·Cl ₂ (oil)
PhP(C ₆ F ₅) ₂ -Br ₂	1 : 1	colourless	PhP(C ₆ F ₅) ₂ ·Br ₂	24.78	0.0223	Br ₃ ⁻	PhP(C ₆ F ₅) ₂ ·Br ₂ (oil)
	2 : 1	yellow	PhP(C ₆ F ₅) ₂ ·Br ₄	79.20	0.0197	Br ₃ ⁻	—
PhP(C ₆ F ₅) ₂ -I ₂	no break	red from early stage	for 1:1 for 2:1	(57.56 (83.91	0.0106 0.0095	I ₃ ⁻ I ₃ ⁻	PhP(C ₆ F ₅) ₂ ·I ₂ (oil) —
	no break	red from early stage	for 1:1 for 2:1	(39.29 (66.07	0.0395 0.0355	I ₃ ⁻ ; Br ₃ ⁻ ; IBr ₂ ⁻ IBr ₂ ⁻	PhP(C ₆ F ₅) ₂ ·IBr (oil) —
Ph ₂ P(C ₆ F ₅) ₂ -Cl ₂	1 : 1	colourless	Ph ₂ P(C ₆ F ₅) ₂ ·Cl ₂	69.35	0.0212	—	Ph ₂ P(C ₆ F ₅) ₂ ·Cl ₂
Ph ₂ P(C ₆ F ₅) ₂ -Br ₂	1 : 1	colourless	Ph ₂ P(C ₆ F ₅) ₂ ·Br ₂	25.62	0.0084	—	oils of dubious analysis
	2 : 1	yellow	Ph ₂ P(C ₆ F ₅) ₂ ·Br ₄	110.01	0.0073	Br ₃ ⁻	
Ph ₂ P(C ₆ F ₅) ₂ -I ₂	2 : 1	red	Ph ₂ P(C ₆ F ₅) ₂ ·I ₂	117.68	0.0114	I ₃ ⁻	Ph ₂ P(C ₆ F ₅) ₂ ·I ₂ (oil)
	1:1(?) 2:1(?)	red-brown red	Ph ₂ P(C ₆ F ₅) ₂ ·IBr Ph ₂ P(C ₆ F ₅) ₂ ·I ₂ ·Br ₂	38.18 94.80	0.0156 0.0137	I ₃ ⁻ ; IBr ₂ ⁻ IBr ₂ ⁻	— Ph ₂ P(C ₆ F ₅) ₂ ·IBr ₂ (oil)
Ph ₂ P(C ₆ F ₅) ₂ -IBr	no break	yellow, becoming orange	for 1:1 for 2:1	97.78 182.39	0.0091 0.0075	IBr ₂ ⁻ IBr ₂ ⁻	no attempt
	1 : 1	red	Ph ₂ P(C ₆ F ₅) ₂ ·IBr	123.76	0.0096	I ₃ ⁻	no attempt

P A R T I I I

PART III:

SOME REACTIONS OF TRI(p-TOLYL)PHOSPHINE WITH HALOGENS

	Page
1. <u>Introduction</u>	117
2. <u>Results and Discussion</u>	119
(i) Reaction of $(\underline{p}\text{Me}-\text{C}_6\text{H}_4)_3\text{P}$ with chlorine ..	119
(ii) Reaction of $(\underline{p}\text{Me}-\text{C}_6\text{H}_4)_3\text{P}$ with bromine ..	121
(iii) Reaction of $(\underline{p}\text{Me}-\text{C}_6\text{H}_4)_3\text{P}$ with iodine ..	127
(iv) Reaction of $(\underline{p}\text{Me}-\text{C}_6\text{H}_4)_3\text{P}$ with iodine bromide ..	131
(v) Reaction of $(\underline{p}\text{Me}-\text{C}_6\text{H}_4)_3\text{P}\cdot\text{Br}_2$ with iodine ..	133
(vi) Reaction of $(\underline{p}\text{Me}-\text{C}_6\text{H}_4)_3\text{P}\cdot\text{Br}_2$ with iodine bromide	136
(vii) Reaction of $(\underline{p}\text{Me}-\text{C}_6\text{H}_4)_3\text{P}\cdot\text{IBr}$ with iodine ..	137
3. <u>Summary</u>	139



1. Introduction

Although the reactions of halogens with the compound tri-p-tolyl arsine have been studied conductometrically by Inglis, no phosphine containing the p-tolyl group has yet been investigated in this sphere.

In contrast to the pentafluorophenyl group used in the previous section, the p-tolyl group is a less electronegative group than the phenyl group. The electron-donating character of the methyl group is transferred through the π -bonding of the benzene

ring on to the central P atom, making this atom less electronegative here than in the "standard" triarylphosphine case, viz., Ph_3P .

The work of Harris and Inglis on triarylsarsines has shown that the molar conductance of the dihalide adducts increases with decrease in the electronegativity of the substituent aryl group; an interesting correlation therefore exists with the observations of Downs and Schmutzler (referred to in the General Introduction)⁶⁹ on the introduction of methyl groups into the PF_5 molecule with respect to the strength of the axial (P-F) bonds, if it is assumed that ionisation of an Ar_3PHal_2 molecule involves ionisation of one of the apical (P-Hal) bonds, as has been suggested.¹³⁹

Another factor expected to affect the degree of ionisation of the dihalides, and also the stability of the tetrahalides, is the stability of the resultant halotriarylphosphonium ion $[\text{Ar}_3\text{PHal}^+]$. The tendency of the p-tolyl group to increase electron density on the P atom will stabilise $[(\text{pMe-C}_6\text{H}_4)_3\text{PHal}^+]$ and promote ionisation of the dihalides, relative to the triphenyl analogue. Thus both these factors would lead us to expect higher molar conductance values for the dihalides, and higher stability of the tetrahalide adducts relative to the corresponding Ph_3P systems.

2. Results and Discussion

(i) The [pMe-(C₆H₄)]₃P-chlorine system

The simple conductometric profile obtained for the (p-tol.)₃P-Cl₂ system can be seen in Figure 23, the relevant data being listed in Table XXXIV:-

TABLE XXXIV: Conductometric Analysis of the System

<u>[pMe(C₆H₄)]₃P-Cl₂</u>					
Mole ratio $\frac{(\text{Cl}_2 : [\text{Me}(\text{C}_6\text{H}_4)]_3\text{P})}{([\text{Me}(\text{C}_6\text{H}_4)]_3\text{P})}$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio $\frac{(\text{Cl}_2 : [\text{Me}(\text{C}_6\text{H}_4)]_3\text{P})}{([\text{Me}(\text{C}_6\text{H}_4)]_3\text{P})}$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio $\frac{(\text{Cl}_2 : [\text{Me}(\text{C}_6\text{H}_4)]_3\text{P})}{([\text{Me}(\text{C}_6\text{H}_4)]_3\text{P})}$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$
0.000	0.383	0.974	26.787	1.947	28.388
0.162	4.948	1.136	27.830	2.111	28.388
0.325	9.693	1.298	28.007	2.272	28.388
0.487	14.528	1.460	28.194	2.434	28.553
0.649	19.216	1.623	28.194	2.595	28.553
0.811	23.934	1.786	28.194		

The graph shows a most pronounced break at the 1:1 mole ratio, at which point also the originally colourless solution takes on a yellow-green colouration (showing unreacted chlorine to be present in solution). The molar conductance value at the 1:1 Halogen: Phosphine ratio, viz.:

$$\Lambda_m = 89.34 \text{ ohm}^{-1} \text{cm}^2 \text{mole}^{-1} \quad (c_m = 0.0303 \text{ mole/l.})$$

is indicative of strong electrolyte behaviour for the formal

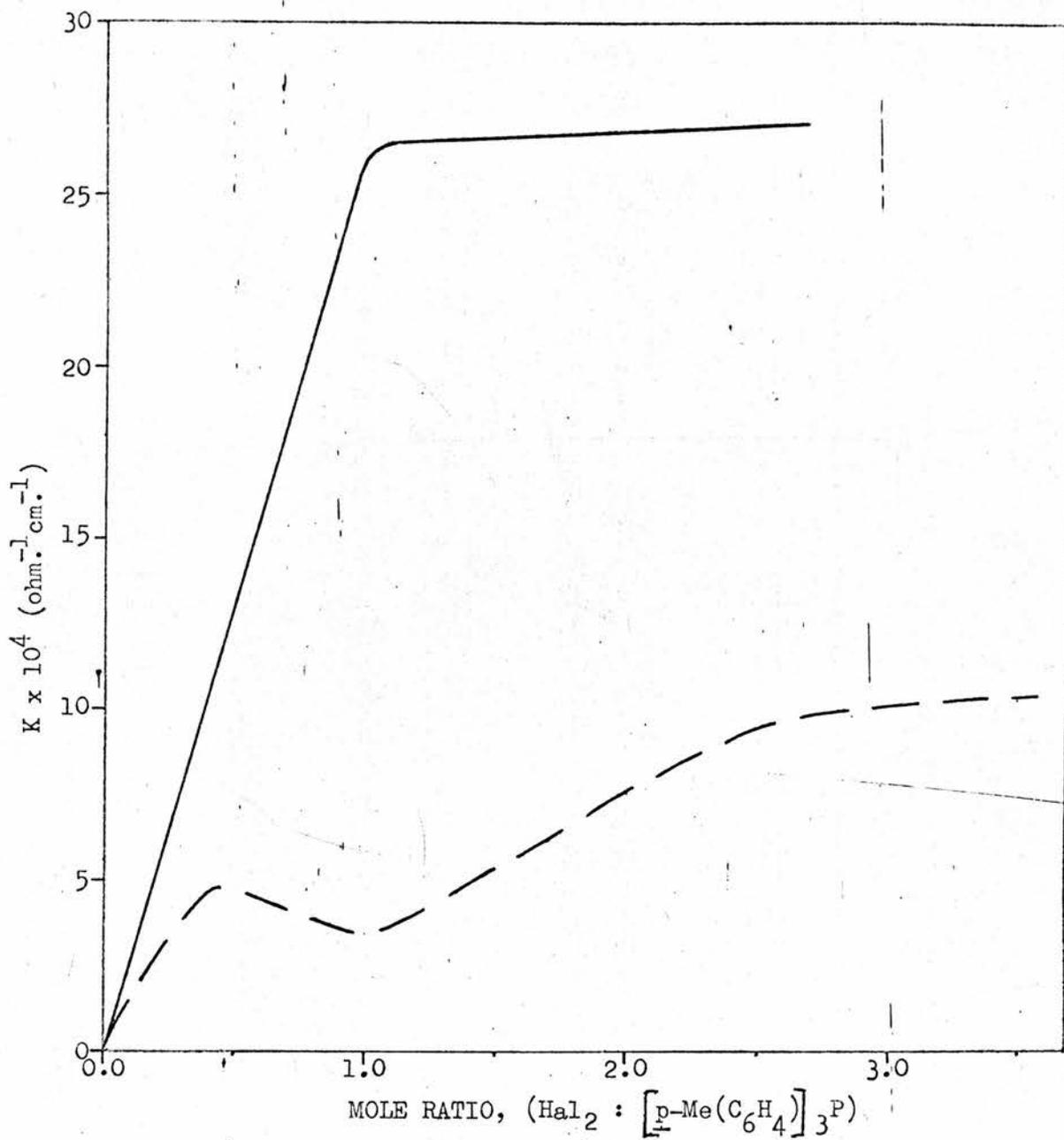
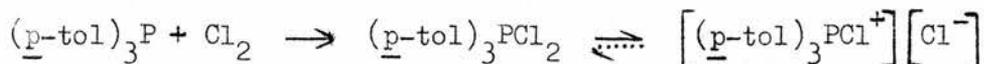


FIGURE 23: Conductometric Analysis of the Systems:

$[\underline{p}\text{Me}(\text{C}_6\text{H}_4)]_3\text{P}-\text{Cl}_2$: —————

$[\underline{p}\text{Me}(\text{C}_6\text{H}_4)]_3\text{P}-\text{Br}_2$: - - - - -

(p-tol.)₃PCl₂ species indicated as being formed in acetonitrile solution. Thus we may write:-



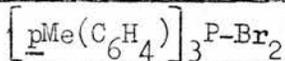
no further reaction occurring being suggested both by the flattening-off in the conductance-composition graph and by the greenish colour of the solution beyond the 1:1 ratio.

On applying the usual method for attempted preparation of chloro-adducts, viz., slow passage of Cl_{2(g)}/N_{2(g)} through an acetonitrile solution of the phosphine, no solid adduct could be isolated - even on trying the ether-precipitation technique (which might have been expected to eventually precipitate the strong-electrolyte 1:1 adduct indicated above). On performing the same reaction in the non-polar solvents CCl₄ and petroleum ether, however, solids were obtained, although from the former only with difficulty. Although neither analysis is as good as might ideally be wished, it certainly appears that the solid obtained in both cases is (p-tol)₃PCl₂: certainly infra-red spectra of these solids showed (by the absence of (P=O) absorption) no signs of hydrolysis having taken place.

(ii) The (p-tol)₃P-bromine system

Table XXXV and Figure 23 contain the results of the conductometric analysis of the (p-tol)₃P-Br₂ system. The graph shows two fairly sharp breaks at the Halogen:Phosphine ratios of 0.5:1

TABLE XXXV: Conductometric Analysis of the System



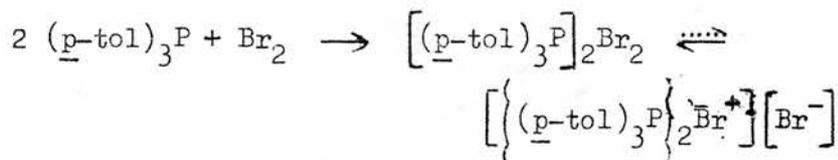
Mole ratio $(\text{Br}_2 : \left[\text{Me}(\text{C}_6\text{H}_4)_3\text{P} \right])$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio $(\text{Br}_2 : \left[\text{Me}(\text{C}_6\text{H}_4)_3\text{P} \right])$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$	Mole ratio $(\text{Br}_2 : \left[\text{Me}(\text{C}_6\text{H}_4)_3\text{P} \right])$	$\frac{\text{K} \times 10^4}{(\text{ohm}^{-1} \text{cm}^{-1})}$
0.000	0.075	1.058	3.605	2.705	9.728
0.088	1.676	1.176	3.865	2.881	9.862
0.176	3.000	1.294	4.248	3.058	9.977
0.265	4.086	1.411	4.714	3.234	10.070
0.353	4.588	1.529	5.232	3.410	10.142
0.441	4.638	1.646	5.869	3.587	10.214
0.529	4.165	1.793	6.631	3.763	10.239
0.617	3.900	1.940	7.321	3.940	10.239
0.706	3.698	2.087	8.110	4.116	10.263
0.794	3.605	2.234	8.720	4.292	10.263
0.882	3.516	2.381	9.167	4.469	10.263
0.970	3.432	2.528	9.512	4.645	10.263

and 1:1 respectively, and also an inflection at the 2:1 ratio. It appears therefore that species of the stoichiometries $\left[(\text{p-tol})_3\text{P} \right]_2^- \text{Br}_2$ and $\left[(\text{p-tol})_3\text{P} \right] \text{Br}_2$ both exist in acetonitrile solution. The solution is found to assume a yellow colouration only after the 1:1 ratio, the appearance of this colouration being accompanied by the incidence of tribromide ion absorption ($\lambda_{\text{max.}} = 269 \text{ m}\mu$) in the ultraviolet spectrum. The values of the molar conductance at the 0.5:1 and 1:1 mole ratios are:-

$$0.5:1; \quad \Lambda_m = 58.00 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0089 \text{ mole/l.})$$

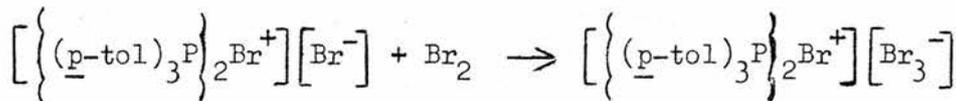
$$1:1; \quad \Lambda_m = 45.83 \text{ ohm}^{-1} \text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0075 \text{ mole/l.})$$

The cation formed by the weak 0.5:1 ratio electrolyte is very probably of the type found by Ali in his work with Ph_3P , ¹³³ viz., $[(\text{Ar}_3\text{P})_2\text{Hal}^+]$:-

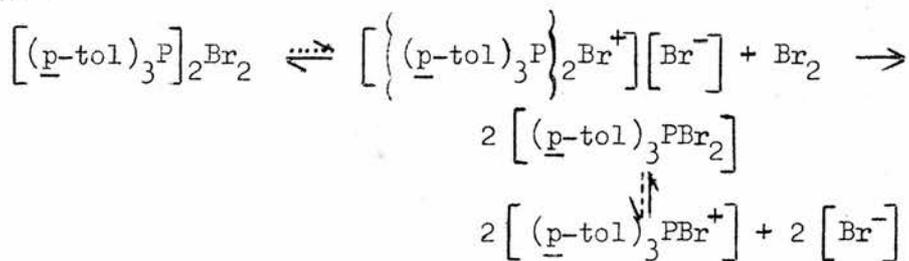


and obviously the absence of $[\text{Br}_3^-]$ absorption (colourless solution) below the 1:1 mole ratio rules out the possibility for the 0.5:1

→ 1:1 stage of:-



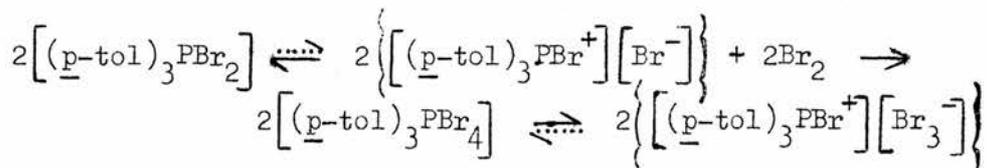
and points to the addition of the further mole of Br_2 to proceed thus:-



The extra moles of Br_2 required to form the indicated 2:1 adduct in acetonitrile of molar conductance

$$2:1; \quad \Lambda_m = 116.08 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0067 \text{ mole/l.})$$

would be expected then to add:-



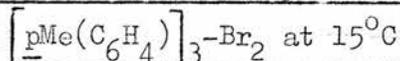
Although yellow crystalline material appears to be formed in cold acetonitrile solution containing the reagents in 1:1 ratio, this redissolves swiftly on removal from the refrigerator. However, a yellow "crust" of solid may be obtained with difficulty from this solution by removing all last traces of solvent by direct pumping: analysis suggests the formula $(\underline{p}\text{-tol})_3\text{PBr}_2$. With bromine and tri- \underline{p} -tolylphosphine in the 2:1 ratio, no solid can be isolated from acetonitrile solution, even on ether addition. However, this 2:1 reaction, performed in CCl_4 solution, is found to yield an orange solid whose analysis (though poor) suggests it to be $(\underline{p}\text{-tol})_3\text{PBr}_4$.

Vapour Pressure Study: In view of the extreme difficulty encountered in attempting to isolate solids of good analysis from the systems $\text{PhP}(\text{C}_6\text{F}_5)_2\text{-Br}_2$, $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-Br}_2$; and $(\underline{p}\text{-tol})_3\text{P-Br}_2$, it was decided that useful information on the stoichiometry of the solid phases formed in these systems might be obtained from the respective vapour pressure titrations. (See "Experimental" section below for description of technique and apparatus used.) These experiments were performed near room temperature, in fact 15°C .

None of these systems gave a typical "stepwise" phase diagram, suggesting that the (solid \rightleftharpoons gas) equilibrium is not readily established in these systems. Indeed, in the $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{-Br}_2$ system, on two separate occasions, an anomalously high vapour

pressure was found at mole ratio $\text{Br}_2:\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ lying between 4:1 and 5:1. Evolution of hydrogen bromide gas might be a possible reason. The diagrams obtained for the systems involving $\text{PhP}(\text{C}_6\text{F}_5)_2$ and $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ were rather featureless, with no regular pattern. That obtained for the $(\text{p-tol})_3\text{P}-\text{Br}_2$ system is depicted in Figure 24, the relevant data being listed in Table XXXVI.

TABLE XXXVI: Vapour Pressure Study of the System



Mole ratio $\text{Br}_2:(\text{p-tol})_3\text{P}$	Manometer limbs (mm. Hg.)		Vapour pressure (mm. Hg.)
	Fixed	Variable	
8.73	628.93	536.26	92.67
8.28	629.19	541.74	87.45
7.17	629.24	547.74	81.50
6.75	629.30	551.65	77.65
6.31	630.14	568.42	61.72
5.84	630.05	607.67	22.38
5.64	630.29	620.70	9.59
5.45	630.48	620.24	10.24
5.25	630.69	626.49	4.20
5.03	631.12	625.19	5.93
4.86	631.03	626.78	4.25
4.65	631.21	626.85	4.36
4.36	631.29	627.15	4.14
4.06	631.36	626.71	4.65
3.69	630.97	626.27	4.70
3.42	631.00	627.52	3.48
3.20	631.32	627.92	3.40

Although not the ideal "step" curve one might have expected, there is a distinct break at the 6:1 ratio. This would suggest formation of $(\text{p-tol})_3\text{PBr}_{12}$, or $[(\text{p-tol})_3\text{PBr}^+][\text{Br}_{11}^-]$, but since the $[\text{Br}_{11}^-]$ entity is as yet unestablished, this result might be

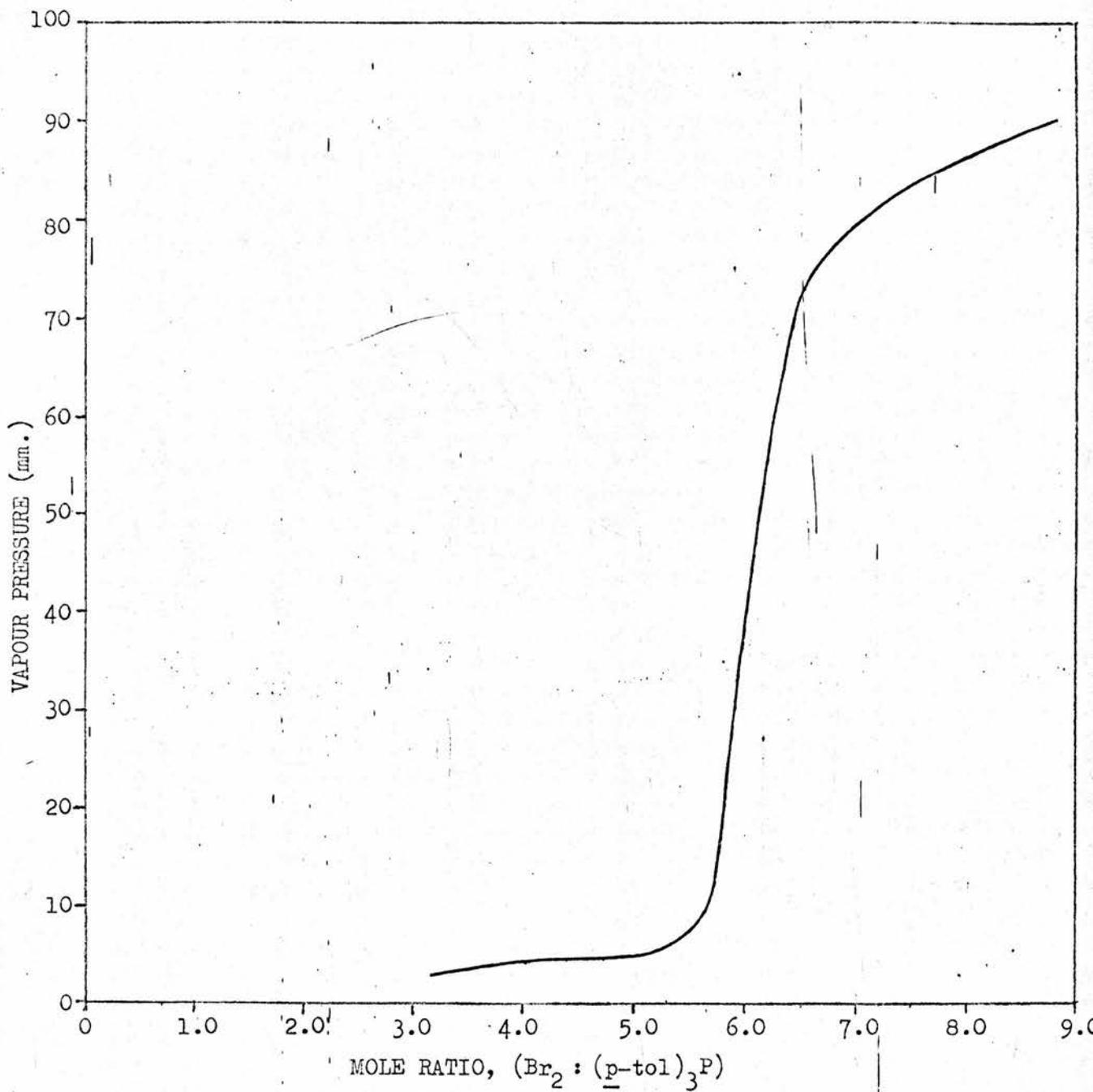


FIGURE 24: Vapour-pressure Study of the System
(p-tol)₃P-Br₂ at 15°C

regarded somewhat dubiously, although $[\text{Me}_4\text{N}^+][\text{I}_{11}^-]$ is known. In any case, at low ratios, i.e. below 3:1, the vapour pressure is very low (ca. 3 mm.) and the material in the sample bulb is a thick gel. This behaviour at low ratio was found in all three systems studied, and gives some justification for the difficulty in isolating solid adducts (as opposed to viscous oils) in these cases. (Although no conclusive evidence for $[\text{Br}_{11}^-]$ has yet been presented, it is interesting to note that Ali indicated the formation at 0°C of the solid adduct $(\text{C}_6\text{F}_5)_3\text{PBr}_{10}$, or $[(\text{C}_6\text{F}_5)_3\text{PBr}^+][\text{Br}_9^-]$ by vapour pressure titration.)

(iii) The (p-tol)₃P-iodine system

The general form of the conductometric titration graph for the (p-tol)₃P-I₂ system (shown in Figure 25, from data in Table XXXVII) is remarkably similar to that obtained for the (p-tol)₃P-Br₂ system directly above. The only minor differences are that the maximum (at the Halogen:Phosphine :: 0.5:1 ratio) and the minimum (at the 1:1 ratio) are "smoothed" out to give the intervening portion of the curve a flat aspect, and that beyond the 2:1 ratio (where again there is an inflection) the conductance actually tails off and the line therefore assumes a negative gradient. This latter effect is simply due, of course, to the poor conductance of molecular iodine in acetonitrile solution, the volume of which is constantly increasing. Since the excess bromine in the previous system causes the conductance almost to remain constant (in fact

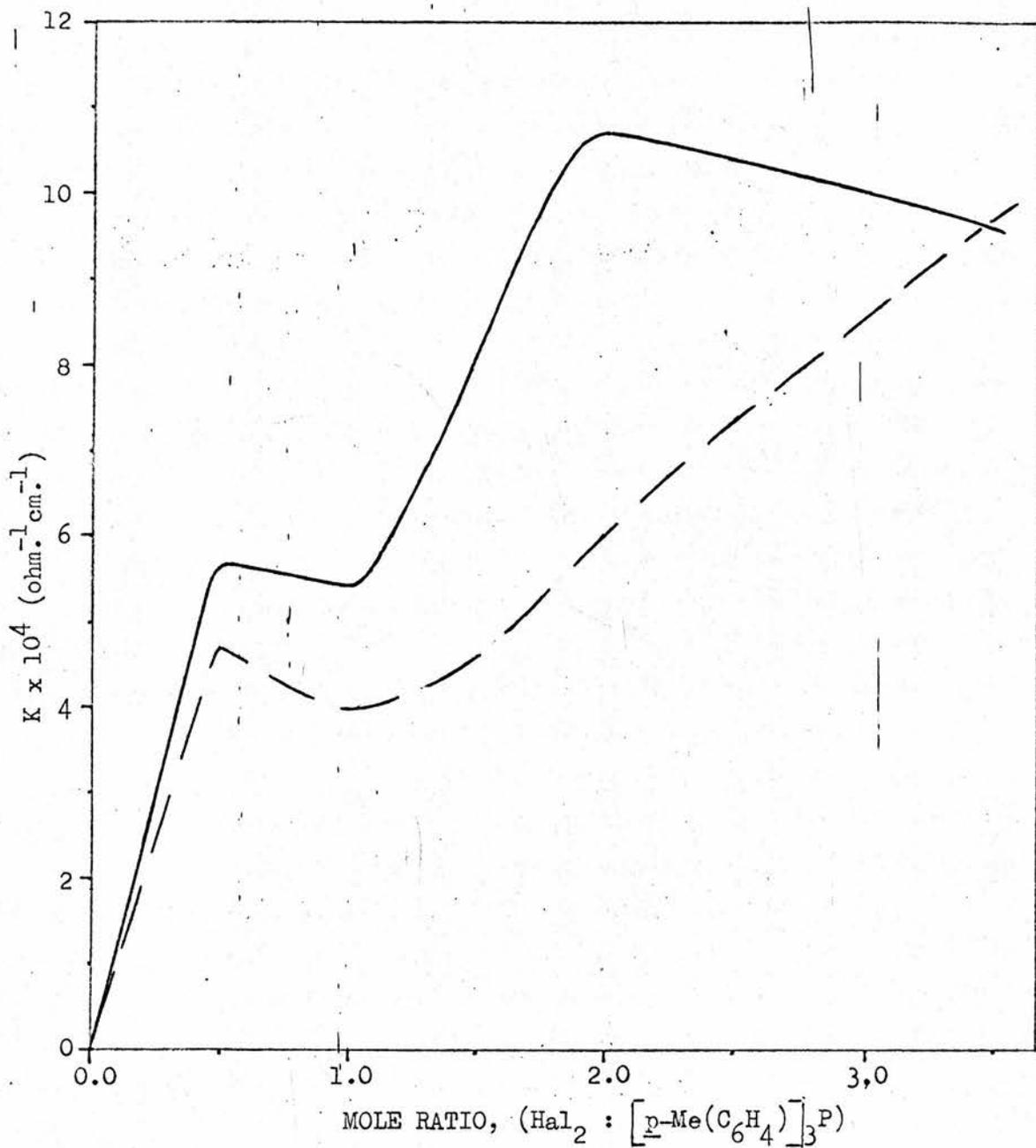
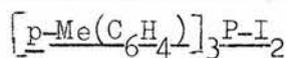


FIGURE 25: Conductometric Analysis of the Systems:

$[p\text{-Me}(\text{C}_6\text{H}_4)]_3\text{P-I}_2$: —————

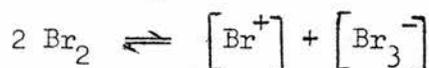
$[p\text{-Me}(\text{C}_6\text{H}_4)]_3\text{P-I-Br}$: - - - - -

TABLE XXXVII: Conductometric Analysis of the System

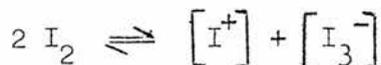


Mole ratio $\frac{\text{I}_2}{\left[\text{Me(C}_6\text{H}_4\text{)} \right]_3 \text{P}}$	$\frac{\text{K} \times 10^4}{(\text{ohm. cm.}^{-1})}$	Mole ratio $\frac{\text{I}_2}{\left[\text{Me(C}_6\text{H}_4\text{)} \right]_3 \text{P}}$	$\frac{\text{K} \times 10^4}{(\text{ohm. cm.}^{-1})}$	Mole ratio $\frac{\text{I}_2}{\left[\text{Me(C}_6\text{H}_4\text{)} \right]_3 \text{P}}$	$\frac{\text{K} \times 10^4}{(\text{ohm. cm.}^{-1})}$
0.000	0.0665	1.307	7.248	2.747	10.240
0.133	1.966	1.414	7.765	2.880	10.080
0.240	5.293	1.520	8.388	3.014	10.000
0.347	5.650	1.627	8.973	3.146	9.855
0.454	5.838	1.733	9.491	3.280	9.693
0.560	5.856	1.840	9.942	3.413	9.578
0.667	5.862	1.947	10.400	3.546	9.497
0.774	5.876	2.080	10.710	3.680	9.400
0.880	5.900	2.212	10.710	3.946	9.220
0.987	6.123	2.346	10.670	4.212	9.025
1.094	6.398	2.481	10.550	4.350	8.900
1.200	6.887	2.612	10.400	4.611	8.702

to continue to rise very slowly), it must be assumed that the self-ionisation of Br_2 in acetonitrile:-



occurs to a greater extent than the corresponding reaction of I_2 in the same solvent:-



Such an assumption is, in fact, borne out by ultraviolet examination which shows (in contrast to the I_2 case) marked tribromide ion absorption ($\lambda_{\text{max.}} = 269 \text{ m}\mu$) for a solution of molecular bromine in acetonitrile.

Moreover, the molar conductance values are of the same order as the corresponding values for the (p-tol)₃P-Br₂ system:-

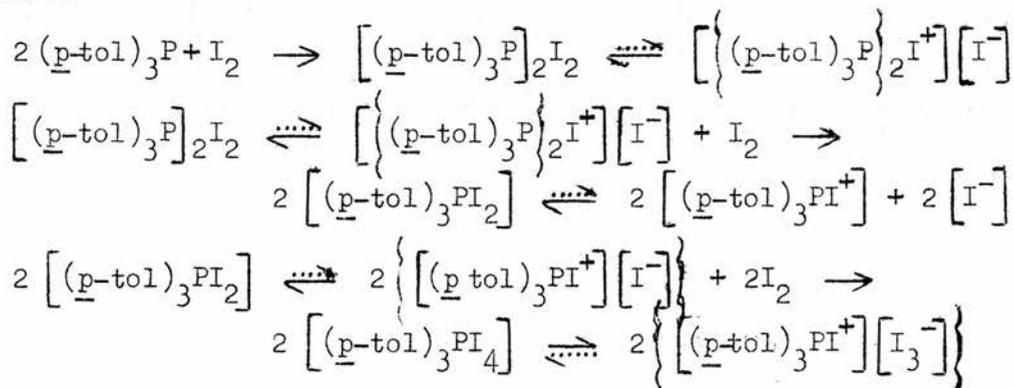
$$0.5:1; \quad \Lambda_m = 55.97 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0105 \text{ mole/l.})$$

$$1:1; \quad \Lambda_m = 63.31 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0098 \text{ mole/l.})$$

$$2:1; \quad \Lambda_m = 121.39 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0087 \text{ mole/l.})$$

and also (as before) the relevant trihalide ion absorption - here I₃⁻, λ_{max.} = 291, 360 mμ - becomes evident after the 1:1 mole ratio.

We may thus write a scheme analogous to that used directly above:-



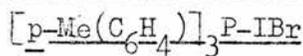
Solid adducts can be isolated fairly easily from concentrated acetonitrile solutions of the reagents in both the 0.5:1 and 1:1 Halogen:Phosphine ratios, the former being yellow, the latter orange in colour. The analysis of the former did not approach that of any feasible product, but was near that demanded by an equimolar mixture of $[(\text{p-tol})_3\text{P}]_2\text{I}_2$ and $(\text{p-tol})_3\text{P} \cdot \text{I}_2$: the analysis of the latter shows it to be $(\text{p-tol})_3\text{P} \cdot \text{I}_2$. The analysis of the

2:1 adduct - obtained by ether precipitation from acetonitrile solution - shows nitrogen to be present but, even so, strongly suggests it to be $(p\text{-tol})_3\text{PI}_4$.

(iv) The $(p\text{-tol})_3\text{P}$ -iodine bromide system

Once again, a similar type of profile is obtained for the conductometric analysis of the $(p\text{-tol})_3\text{P}$ -IBr system: the data are listed in Table XXXVIII and the graph contained in Figure 25 (p. 128). Here, however, the minimum at the 1:1 ratio is

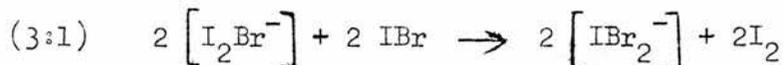
TABLE XXXVIII: Conductometric Analysis of the System



Mole ratio IBr: $[p\text{-Me}(\text{C}_6\text{H}_4)]_3\text{P}$	$\frac{K \times 10^4}{(\text{ohm}^{-1} \text{ cm.}^{-1})}$	Mole ratio IBr: $[p\text{-Me}(\text{C}_6\text{H}_4)]_3\text{P}$	$\frac{K \times 10^4}{(\text{ohm}^{-1} \text{ cm.}^{-1})}$	Mole ratio IBr: $[p\text{-Me}(\text{C}_6\text{H}_4)]_3\text{P}$	$\frac{K \times 10^4}{(\text{ohm}^{-1} \text{ cm.}^{-1})}$
0.000	0.034	1.115	4.083	2.818	8.160
0.0984	1.581	1.246	4.200	2.982	8.351
0.197	3.016	1.377	4.332	3.147	8.447
0.295	4.003	1.508	4.461	3.342	8.543
0.393	4.559	1.671	4.758	3.538	8.781
0.492	4.709	1.836	5.291	3.735	8.993
0.590	4.420	1.997	5.943	3.933	9.065
0.688	4.159	2.163	6.682	4.132	9.141
0.786	4.083	2.327	7.260	4.331	9.218
0.885	4.003	2.491	7.683	4.529	9.292
0.984	3.968	2.655	7.954	4.727	9.358

extremely shallow, and the inflection at the 2:1 Halogen:Phosphine ratio is weak. The molar conductance values are:-

Beyond the 2:1 ratio, we can expect the familiar reaction:-



Only an oil adduct can be isolated from concentrated solutions of the reagents in the 2:1 ratio in acetonitrile, even an attempted ether precipitation. Despite showing a fraction of one per cent N present, the analysis of the oil shows good agreement with that required for $(\underline{p}\text{-tol})_3\text{PI}_2\text{Br}_2$.

(v) The $(\underline{p}\text{-tol})_3\text{PBr}_2$ -iodine system

Table XXXIX and Figure 26 contain the relevant data and conductance-composition graph for the $(\underline{p}\text{-tol})_3\text{PBr}_2\text{-I}_2$ system, the graph being of the smooth, rounded variety, and rather featureless save for an extremely shallow maximum near the 2.8:1 Halogen:Phosphine ratio. A system of equilibria is thus indicated. The value of the molar conductance at the 2:1 mole ratio is:-

$$\Lambda_m = 137.78 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0057 \text{ mole/l.})$$

indicating, as expected, strong electrolyte behaviour. The ultra-violet spectra are complicated showing a mixture of trihalide ions generally present. Below the 2:1 ratio, it appears that $\left[\text{I}_3^- \right]$, $\left[\text{I}_2\text{Br}^- \right]$ and $\left[\text{IBr}_2^- \right]$ are all present: beyond 2:1, $\left[\text{I}_3^- \right]$ and $\left[\text{IBr}_2^- \right]$ are probably present, and are accompanied by molecular iodine. Although there is no 1:1 inflection to indicate the existence in solution of $(\underline{p}\text{-tol})_3\text{PBr}_2\text{I}_2$ - indicated and proposed in the

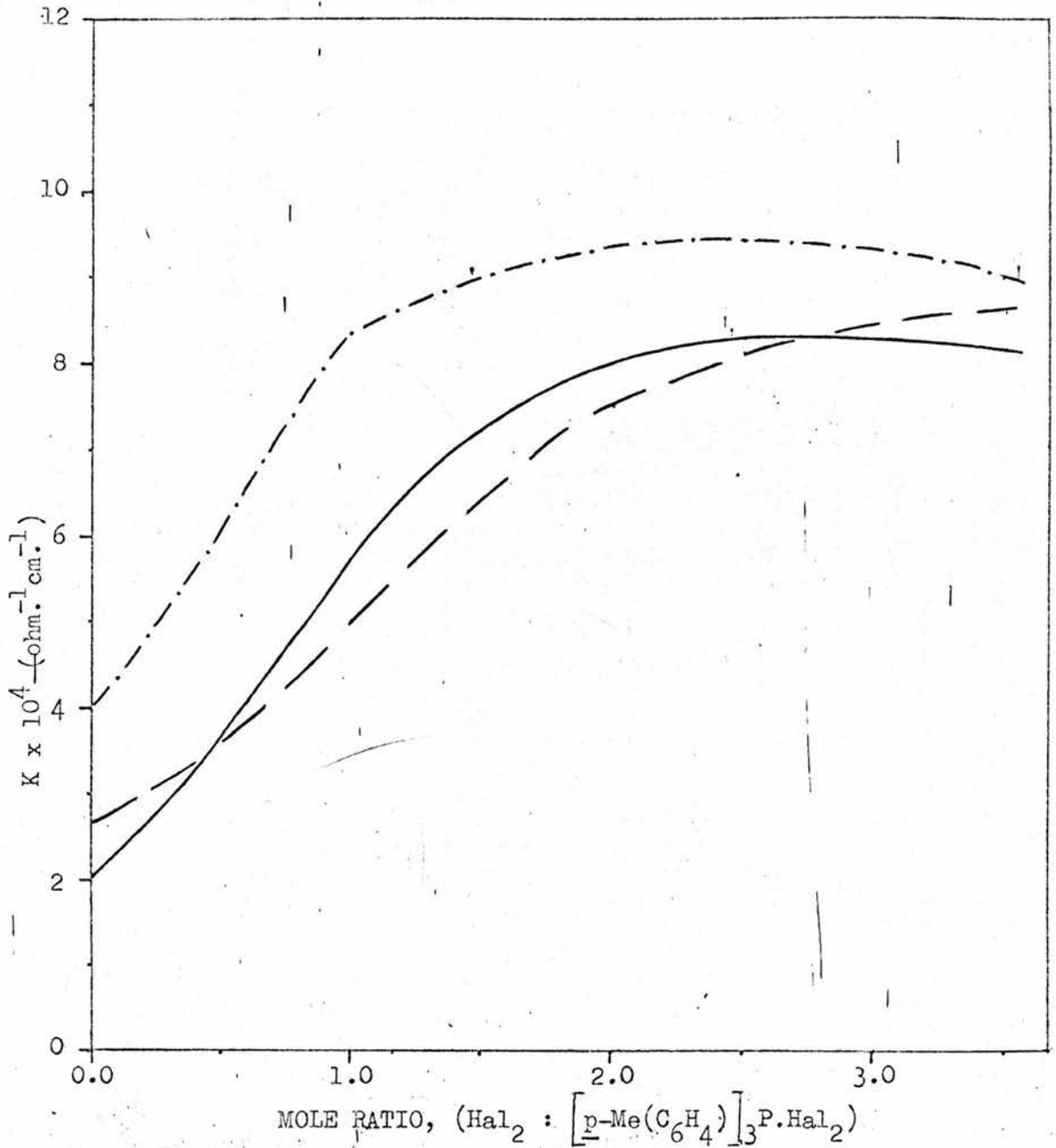
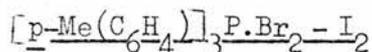


FIGURE 26: Conductometric Analysis of the Systems:

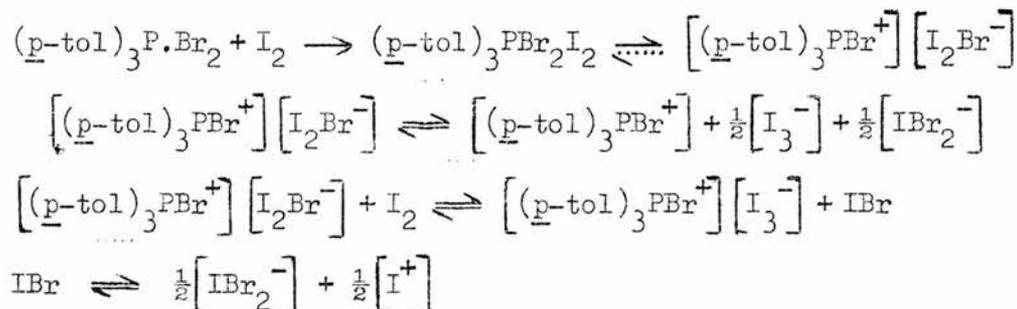
- $[p\text{-Me}(\text{C}_6\text{H}_4)]_3\text{P.Br}_2\text{-I}_2$:
- $[p\text{-Me}(\text{C}_6\text{H}_4)]_3\text{P.Br}_2\text{-IBr}$:
- $[p\text{-Me}(\text{C}_6\text{H}_4)]_3\text{P.IBr-I}_2$:

TABLE XXXIX: Conductometric Analysis of the System



Mole ratio $\frac{[\text{I}_2]}{[\text{Me}(\text{C}_6\text{H}_4)]_3\text{P.Br}_2}$	$\frac{\text{K} \times 10^4}{(\text{ohm. cm.}^{-1})}$	Mole ratio $\frac{[\text{I}_2]}{[\text{Me}(\text{C}_6\text{H}_4)]_3\text{P.Br}_2}$	$\frac{\text{K} \times 10^4}{(\text{ohm. cm.}^{-1})}$	Mole ratio $\frac{[\text{I}_2]}{[\text{Me}(\text{C}_6\text{H}_4)]_3\text{P.Br}_2}$	$\frac{\text{K} \times 10^4}{(\text{ohm. cm.}^{-1})}$
0.000	2.040	1.447	7.281	3.345	8.243
0.119	2.278	1.608	7.586	3.535	8.243
0.257	2.677	1.770	7.844	3.762	8.218
0.386	3.126	1.931	7.939	3.994	8.210
0.515	3.570	2.090	8.037	4.210	8.180
0.643	4.158	2.252	8.108	4.440	8.143
0.771	4.684	2.413	8.200	4.660	8.115
0.900	5.244	2.574	8.243	4.890	8.083
1.029	5.883	2.766	8.259	5.110	8.056
1.158	6.406	2.958	8.259	5.340	8.031
1.286	6.834	3.153	8.243	5.560	7.992

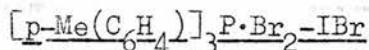
immediately preceding reaction - it seems likely that this reaction will, in fact, proceed via that species. This could certainly help explain the mixture of trihalide absorptions observed. It is likely that the course followed by the reaction is:-



(vi) The (p-tol)₃P.Br₂-iodine bromide system

A possible route to the investigation of the existence of the species (p-tol)₃PIBr₃ in solution or in the solid state is the conductometric analysis of the system (p-tol)₃PBr₂-IBr. The results obtained are tabulated in Table XL and depicted graphically in Figure 26. Again the graph is fairly featureless, with

TABLE XL: Conductometric Analysis of the System



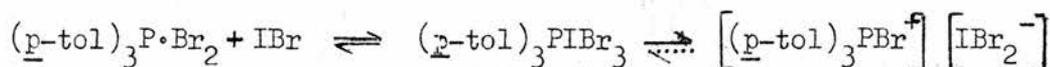
Mole ratio IBr: [Me(C ₆ H ₄) ₃ PBr ₂]	$K \times 10^4$ (ohm. ⁻¹ cm. ⁻¹)	Mole ratio IBr: [Me(C ₆ H ₄) ₃ PBr ₂]	$K \times 10^4$ (ohm. ⁻¹ cm. ⁻¹)	Mole ratio IBr: [Me(C ₆ H ₄) ₃ PBr ₂]	$K \times 10^4$ (ohm. ⁻¹ cm. ⁻¹)
0.000	2.695	1.995	7.841	4.418	8.641
0.133	2.695	2.213	8.033	4.642	8.682
0.310	2.914	2.413	8.146	4.859	8.710
0.486	3.375	2.650	8.241	5.092	8.746
0.665	3.932	2.874	8.379	5.303	8.798
0.841	4.462	3.096	8.440	5.527	8.839
1.017	5.102	3.317	8.475	5.748	8.881
1.195	5.850	3.541	8.508	5.967	8.910
1.371	6.507	3.756	8.543	6.190	8.967
1.549	7.141	3.983	8.574	6.323	9.008
1.769	7.600	4.203	8.609	6.496	9.067

simply a "blunt" inflection near the 2:1 Halogen:Phosphine ratio; there is thus no evidence from the graph for the existence of (p-tol)₃PIBr₃ in acetonitrile solution. However, a possible inflection may be masked either by the slight conductivity of the IBr titrant itself in acetonitrile (see final equilibrium quoted

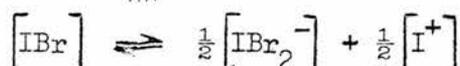
in (v) above), or by the overall reaction being one involving equilibria. This possibility is strengthened both by the fact that U.V. examination shows the expected $[\text{IBr}_2^-]$ absorption ($\lambda_{\text{max.}} = 256, 370 \text{ m}\mu$) from the start of the IBr addition, and by the fact that an orange-brown solid adduct was obtained - of good analysis for $(\underline{p}\text{-tol})_3\text{PIBr}_3$ from the reagents in 1:1 mole ratio in carbon tetrachloride solution. At this ratio, the molar conductance of the acetonitrile solution is:-

$$1:1; \quad \Lambda_m = 110.62 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0046 \text{ mole/l.})$$

indicative of the strong electrolyte behaviour which is expected of $(\underline{p}\text{-tol})_3\text{PIBr}_3$. The proposed reaction is therefore:-



with excess IBr simply contributing:-



(vii) The $(\underline{p}\text{-tol})_3\text{PIBr}$ -iodine system

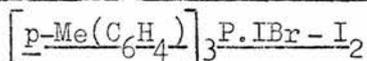
An inflection at the 1:1 mole ratio is observed in the conductance-composition graph for the $(\underline{p}\text{-tol})_3\text{PIBr}-\text{I}_2$ system; the relevant data for the curve in Figure 26 are listed in Table XLI. The existence of $(\underline{p}\text{-tol})_3\text{PI}_3\text{Br}$ in acetonitrile solution is therefore indicated; indeed, isolation of a brown solid whose analysis gave good agreement with that required for $(\underline{p}\text{-tol})_3\text{PI}_3\text{Br}$ can be achieved from concentrated CCl_4 solutions of the reagents in the

1:1 mole ratio. The molar conductance at the 1:1 mole ratio is:-

$$\Lambda_m = 139.43 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (c_m = 0.0060 \text{ mole/l.})$$

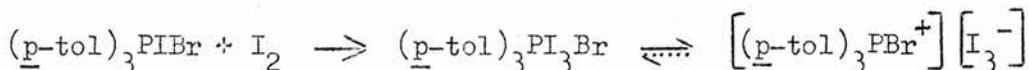
the very high value being in agreement with the strongly-conducting nature expected of the species ' $(\underline{p}\text{-tol})_3\text{PI}_3\text{Br}'$.

TABLE XI: Conductometric Analysis of the System



$\text{I}_2 : \left[\underline{p}\text{-Me}(\text{C}_6\text{H}_4) \right]_3\text{PIBr}$	$\text{K} \times 10^4$ ($\text{ohm}^{-1} \text{ cm}^{-1}$)	$\text{I}_2 : \left[\underline{p}\text{-Me}(\text{C}_6\text{H}_4) \right]_3\text{PIBr}$	$\text{K} \times 10^4$ ($\text{ohm}^{-1} \text{ cm}^{-1}$)
0.000	3.967	2.538	9.194
0.155	4.470	2.726	9.194
0.310	5.027	2.943	9.148
0.464	5.724	3.156	9.069
0.619	6.596	3.373	9.006
0.774	7.484	3.590	8.958
0.929	8.209	3.839	8.892
1.084	8.610	4.090	8.818
1.238	8.839	4.334	8.773
1.394	9.069	4.583	8.711
1.547	9.148	4.802	8.641
1.703	9.182	5.080	8.580
1.858	9.194	5.328	8.509
2.012	9.194	5.573	8.441
2.167	9.194	5.759	8.390
2.354	9.194	5.942	8.340

The reaction therefore appears to follow the expected course:-



and this is further supported by the presence of triiodide ion absorption in the U.V. spectra from the start of iodine addition. At high Halogen:Phosphine ratios the conductance might be expected to

tail off somewhat (as has been previously observed) due to the poor conducting properties of molecular iodine in acetonitrile solution.

3. Summary

Most conductance-composition graphs obtained for the $(\underline{p}\text{-tol})_3\text{P-Hal}_2$ series contain well-defined inflections or breaks, and discontinuity at the Halogen:Phosphine :: 0.5:1 ratio is common to $(\underline{p}\text{-tol})_3\text{P-Hal}_2$ for $\text{Hal}_2 = \text{Br}_2; \text{I}_2; \text{IBr}$. As in Part II, again the 1:1 adducts are weak electrolytes, while the 2:1 adducts are strong electrolytes in acetonitrile, the anomaly again being a dichloride, viz., $(\underline{p}\text{-tol})_3\text{PCl}_2$ which has $\Lambda_m = 89.34 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ($c_m = 0.0303 \text{ mole/l.}$).

Indeed, it is found that the dihalides do exhibit higher molar conductance values in acetonitrile than their analogues formed from Ph_3P by Beveridge, as expected from the nature of the $(\underline{p}\text{-tolyl})$ substituent group on the central phosphorus atom. Moreover, many relatively stable tetrahalide adducts can be isolated as solids: the series of adducts $(\underline{p}\text{-tol})_3\text{PBr}_n\text{I}_{4-n}$ for $n = 0, 1, 2, 3, 4$ is obtained, all being solids except the case where $n = 2$, when a viscous oil is obtained. Summary Chart 3 on page 141 tabulates the complete findings of Part III of this thesis.

Thus, looking at Parts I, II and III overall, no general overall pattern can be claimed to have emerged, partly due to the fact that most of the work deals with asymmetrically substituted phosphines (as opposed to Ph_3P , $(\text{C}_6\text{F}_5)_3\text{P}$ of earlier investigations) and partly due to the extreme moisture sensitivity of most of the compounds involved. In spite of rigorous precautions taken to obtain reproducibility, experimental results were not always consistent, and absence of any consistent picture of reactions allied to analytical difficulties made interpretations difficult. In some cases, therefore, only a likely reaction path can be proposed, as opposed to the definite affirmation which would ideally have been wished.

SUMMARY CHART 3: Conductometric Analyses of Hal₂ with (p-tol)₃P in Acetonitrile

System	Ratio of conductance break	Solution colour before break	Composition of species indicated	Δm at break	c_m at break	U.V. indicates	Species isolated
(p-tol) ₃ P-Cl ₂	1 : 1	colourless	(p-tol) ₃ P·Cl ₂	89.34	0.0303	—	(p-tol) ₃ P·Cl ₂
(p-tol) ₃ P-Br ₂	0.5 : 1	colourless	(p-tol) ₃ P·(Br) ₂ 0.5	58.00	0.0089	—	—
	1 : 1	pale yellow	(p-tol) ₃ P·Br ₂	45.83	0.0075	Br ₃ ⁻	(p-tol) ₃ P·Br ₂
(p-tol) ₃ P-I ₂	2 : 1	yellow	(p-tol) ₃ P·Br ₄	116.08	0.0067	Br ₃ ⁻	(p-tol) ₃ P·Br ₄
	0.5 : 1	yellow	(p-tol) ₃ P·(I ₂) _{0.5}	55.97	0.0105	—	yellow solid (?)
(p-tol) ₃ P-I ₂	1 : 1	orange	(p-tol) ₃ P·I ₂	63.31	0.0098	I ₃ ⁻	(p-tol) ₃ P·I ₂
	2 : 1	red	(p-tol) ₃ P·I ₄	121.39	0.0087	I ₃ ⁻	(p-tol) ₃ P·I ₄
(p-tol) ₃ P-IBr	0.5 : 1	colourless	(p-tol) ₃ P·(IBr) _{0.5}	70.08	0.0067	—	—
	1 : 1	yellow	(p-tol) ₃ P·IBr	61.61	0.0064	I ₃ ⁻ ; I ₂ Br ⁻	—
(p-tol) ₃ P·Br ₂ -I ₂	2 : 1	orange	(p-tol) ₃ P·I ₂ Br ₂	103.14	0.0058	IBr ₂ ⁻ ; I ₂	(p-tol) ₃ P·I ₂ Br ₂ (oil)
	no break	yellow, becoming red	for 2 : 1 —	137.78	0.0057	I ₃ ⁻ ; I ₂ Br ⁻ ; IBr ₂ ⁻	no attempt
(p-tol) ₃ P·Br ₂ -IBr	2 : 1	yellow	(p-tol) ₃ PBr ₂ ·(IBr) ₂	189.83	0.0041	IBr ₂ ⁻	(p-tol) ₃ P·Br ₃ I (at 1:1)
	1 : 1	orange	(p-tol) ₃ P·I ₃ Br	139.43	0.0060	I ₃ ⁻	(p-tol) ₃ P·I ₃ Br

A P P E N D I X :

SOME HALOGEN ADDUCTS
OF PHENYLDIBROMOPHOSPHINE

APPENDIX :

SOME HALOGEN ADDUCTS OF PHENYLDIBROMOPHOSPHINE

After studying the PhPCl_2 -Halogen and Ph_2PCl -Halogen systems, some preliminary work was done on the reactions of phenyldibromophosphine (PhPBr_2) with halogens, in order to see whether the behaviour of the bromophosphine differed in any way from that of the chlorophosphines.

The transition from chlorine to bromine atom (essentially a decrease in haloatom electronegativity) might be expected to affect significantly the formation of halogen adducts, both in solution and in the solid state. In particular, a comparison of the PhPBr_2 reactions (in the light of previous PhPCl_2 studies) could be made with the reactions of the analogous pair of phosphorus (III) halides, viz., PBr_3 and PCl_3 , with halogens.

Lack of time prevented study of PhPBr_2 -Halogen systems other than Halogen = Br_2 ; however it was — and still is — hoped that an extensive study of such systems will be the subject of more thorough research in the near future.

1. Results and Discussion

Conductometric Titration

A conductometric titration study of the PhPBr_2 - Br_2 system in methyl cyanide gave the results listed in Table XLIII and illustrated in Figure 27.

It is evident that there are two fairly sharp changes in gradient in the conductometric titration graph, the first occurring

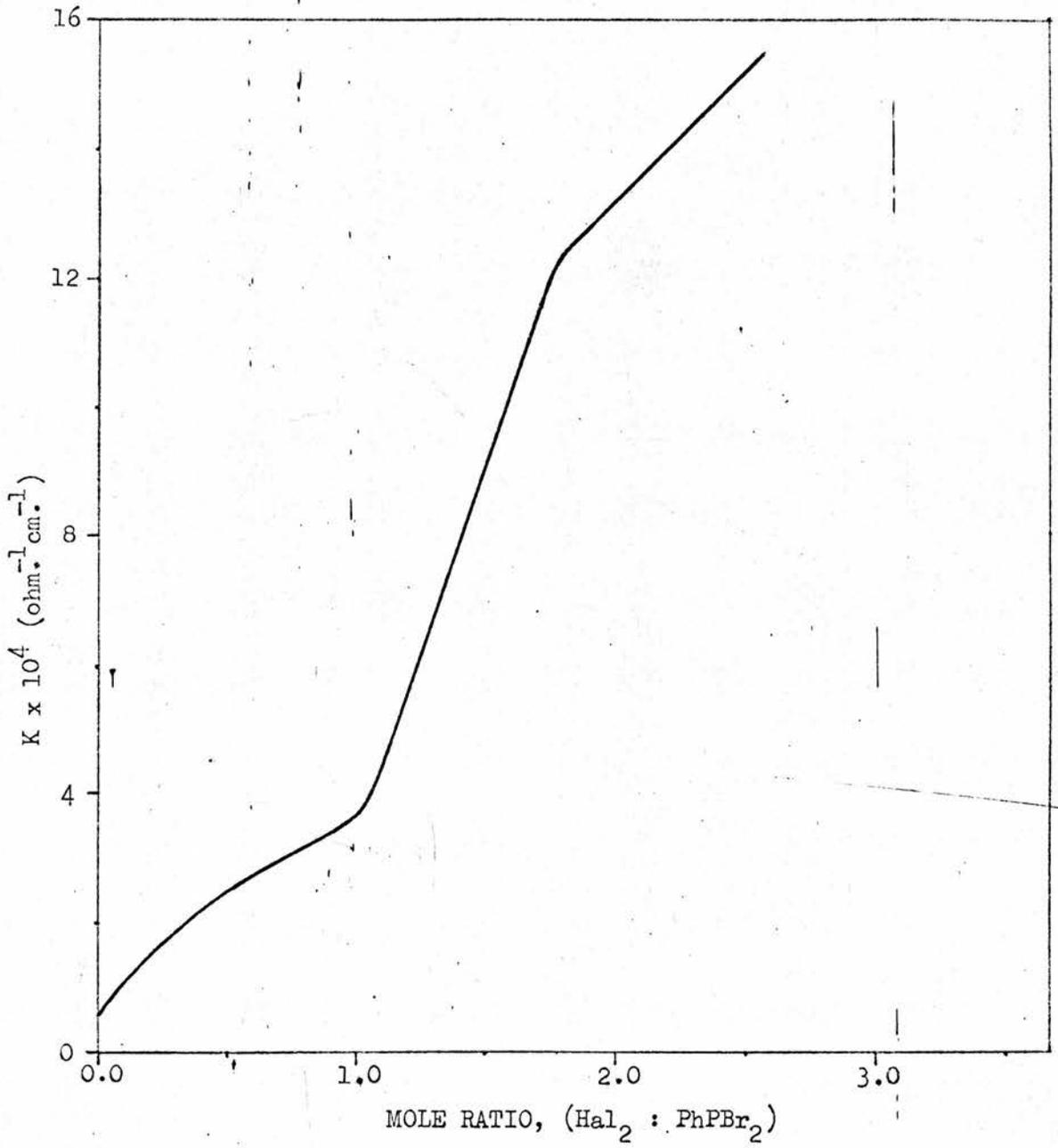


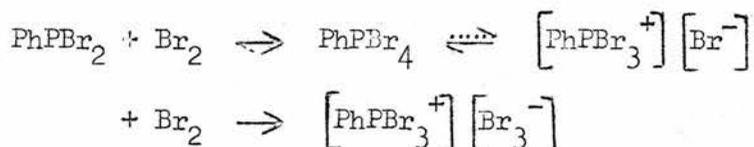
FIGURE 27: Conductometric Analysis of the System PhPBr₂-Br₂

TABLE XLII: Conductometric Analysis of the System $\text{PhPBr}_2\text{-Br}_2$

Mole ratio ($\text{Br}_2 : \text{PhPBr}_2$)	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)	Mole ratio ($\text{Br}_2 : \text{PhPBr}_2$)	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)
0.000	0.83	1.204	5.14
0.093	1.15	1.297	5.88
0.185	1.28	1.389	6.95
0.278	1.54	1.481	8.27
0.370	2.60	1.574	9.35
0.463	2.61	1.667	10.34
0.556	2.63	1.759	11.29
0.649	2.65	1.851	11.88
0.741	3.09	1.944	12.36
0.834	3.25	2.037	13.10
0.926	3.40	2.132	13.41
1.019	3.90	2.223	13.99
1.110	4.33	2.315	14.18

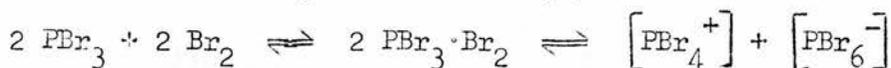
at the 1:1 mole ratio and the second very near the 2:1 mole ratio, the steepest portion of the graph lying between the two mole ratios quoted above. The conductance graph shows a gently rising slope up to the 1:1 ratio, the solution being colourless at low mole ratios and only assuming a pale yellow colouration on approaching the 1:1 ratio. Beyond 1:1, when the conductance rose sharply, the solution was a deep yellow colour. The inflections at 1:1 and 2:1 mole ratios clearly indicate the formation in solution of the compounds PhPBr_4 and PhPBr_6 . The molar conductance value at the 1:1 ratio was $\Lambda_m = 21.11 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1}$, ($c_m = 0.018 \text{ mole/l.}$), and at the 2:1 ratio was $\Lambda_m = 94.58 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1}$, ($c_m = 0.014 \text{ mole/l.}$), suggesting that the above compounds were weak and strong electrolytes respectively. Ultraviolet

examination of the solution indicated formation of tribromide ion beyond the 1:1 ratio. The reactions taking place in solution may thus be represented by:-



Relatively stable yellow solids were easily isolated from the reagents in both 1:1 and 2:1 mole ratio in acetonitrile, the 2:1 adduct being a deep yellow in colour while the 1:1 adduct was pale yellow. Analysis results showed, however, that the former (PhPBr_6) did slowly lose bromine.

From the above, it can be seen that, while analogous in some respects, the $\text{PhPBr}_2\text{-Br}_2$ system was a more stable system than $\text{PhPCl}_2\text{-Br}_2$ and consequently slightly easier to handle. The difference in character due to the $\text{Cl} \rightarrow \text{Br}$ transition was not nearly so significant in the PhPHal_2 case as in the PHal_3 case, however, for in the latter case it was found¹⁴⁰ that acetonitrile was totally unsuitable as a solvent for the $\text{PCl}_3\text{-Br}_2$ conductometric titration, and, furthermore, attempted preparation of adducts gave a gelatinous solid containing N (indicating solvent interaction). It is interesting to note, however, that in the $\text{PBr}_3\text{-Br}_2$ case no inflection was evident in the conductometric graph beyond the 1:1 mole ratio, suggesting no $[\text{Br}_3^-]$ formation: hence the reaction scheme proposed for acetonitrile solution was:-

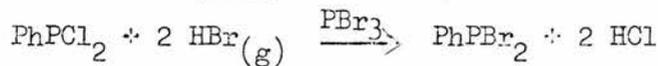


in strict analogy with the ionisation of PCl_5 in acetonitrile.

2. Experimental

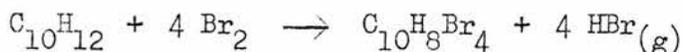
- (a) Conductometric titration apparatus was exactly as described in the main "Experimental" portion of this thesis.
- (b) See the main "Experimental" part also for purification of acetonitrile and bromine.
- (c) Preparations

(1) Phenyldibromophosphine (PhPBr_2): PhPBr_2 was prepared twice, both preparations utilising the reaction of Nannelli, Feistel and Moeller,¹⁴¹ viz.:-



The preparations differed, however, with regard to source of hydrogen bromide gas.

(i) The method initially employed for production of $\text{HBr}_{(g)}$ followed that of D.R. Duncan,¹⁴² i.e. bromine was dropped on to tetralin under an atmosphere of nitrogen, and the gas produced was bubbled through a wash-bottle containing tetralin before passing into the mixture of phenyldichlorophosphine and phosphorus tribromide:-



The reaction mixture was refluxed for 12 hours, and on completion PBr_3 was removed by vacuum distillation (b.p. 29°C ; ca. 2mm.). The higher-boiling fraction was heated directly by a naked flame, and the fraction of boiling-point range $259\text{--}261^\circ\text{C}$ was collected. (Yield: 65%.)

(ii) In the second preparation, hydrogen bromide gas from a cylinder (Air Products Ltd.) was passed through silica gel before being bubbled into phenyldichlorophosphine in phosphorus tribromide under nitrogen at reflux temperature (oil bath). The mixture was refluxed for 8-9 hours, and then allowed to cool under nitrogen. The yellow-orange solution was transferred to a Vigreux Flask in the dry-box. Distillation at the oil-pump gave a continuous flow of distillate (ca. $20\text{--}80^\circ\text{C}$), and hence a mixed product. Open-flame heating at atmospheric pressure was thus employed. PBr_3 was collected at ca. 173°C , and the yellow fraction of boiling-point range $259\text{--}261^\circ\text{C}$ was collected as phenyldibromophosphine product (Yield: 63.6%, cf. lit. 80%; however literature method used reflux for 20 hours). Analysis of PhPBr_2 collected gave C, 26.42; H, 1.84 (PhPBr_2 requires C, 26.88; H, 1.88%).

(2) Bromine adducts of phenyldibromophosphine:

(i) $\text{PhPBr}_2\text{--Br}_2$ in 1:1 mole ratio. On adding acetonitrile solutions of PhPBr_2 and Br_2 directly in the 1:1 mole ratio, a

yellow precipitate immediately came down. The solid was washed with acetonitrile, then attached to the line for pumping to remove last traces of solvent. (Found: C, 16.91; H, 1.16; Br, 73.9. PhPBr₄ requires C, 16.82; H, 1.17; Br, 74.8%.)

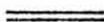
(ii) PhPBr₂-Br₂ adduct from mole ratio Br₂:PhPBr₂ :: 2:1.

A yellow solid was again easily isolated from the reagents in the 2:1 mole ratio. It was washed and dried as for the 1:1 adduct, directly above. (Found: C, 14.13; H, 1.02; Br, 80.2. PhPBr₆ requires C, 12.24; H, 0.85; Br, 81.63%.)

EXPERIMENTAL

EXPERIMENTAL

	Page
1. <u>General Techniques</u> 149
(a) Handling of Materials 149
(b) Vacuum System 150
(c) Conductance Measurements 155
(d) Conductometric Titrations 156
(e) Infra-red Spectra 157
(f) Ultra-violet Spectra 157
(g) Analyses 157
2. <u>Purification of Materials</u> 160
(a) Solvents 160
(b) Reagents 161
3. <u>Preparations</u> 163
(a) Starting Materials 163
(b) Part I 167
(c) Part II 174
(d) Part III 177



1. General Techniques

(a) Handling of Materials

As the large majority of the compounds studied in this work were extremely moisture-sensitive, strict precautions were required to ensure 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 compounds to both atmospheric moisture and elevated temperatures. Compounds so handled were stored in sample tubes sealed by a greased or teflon-sleeved ground-glass joint and kept either in the dry box or in a desiccator over phosphorus pentoxide.

(b) Vacuum System

The vacuum system consisted of a rotary oil pump (without the backing of a Hg pump) connected via two protective sludge traps to a main line from which branched various sub-sections designed for special operations, e.g. conductometric titrations involving chlorine, vapour pressure measurement, and freeze-drying.

(i) Vapour pressure measurement

For vapour pressure studies, an all-glass system was used (Figure 28). 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 accelerate a small delicately-balanced mirror which reflected a parallel beam of light on to a scale situated at a distance of 1 metre. The zero point of the instrument on the scale was adjusted.

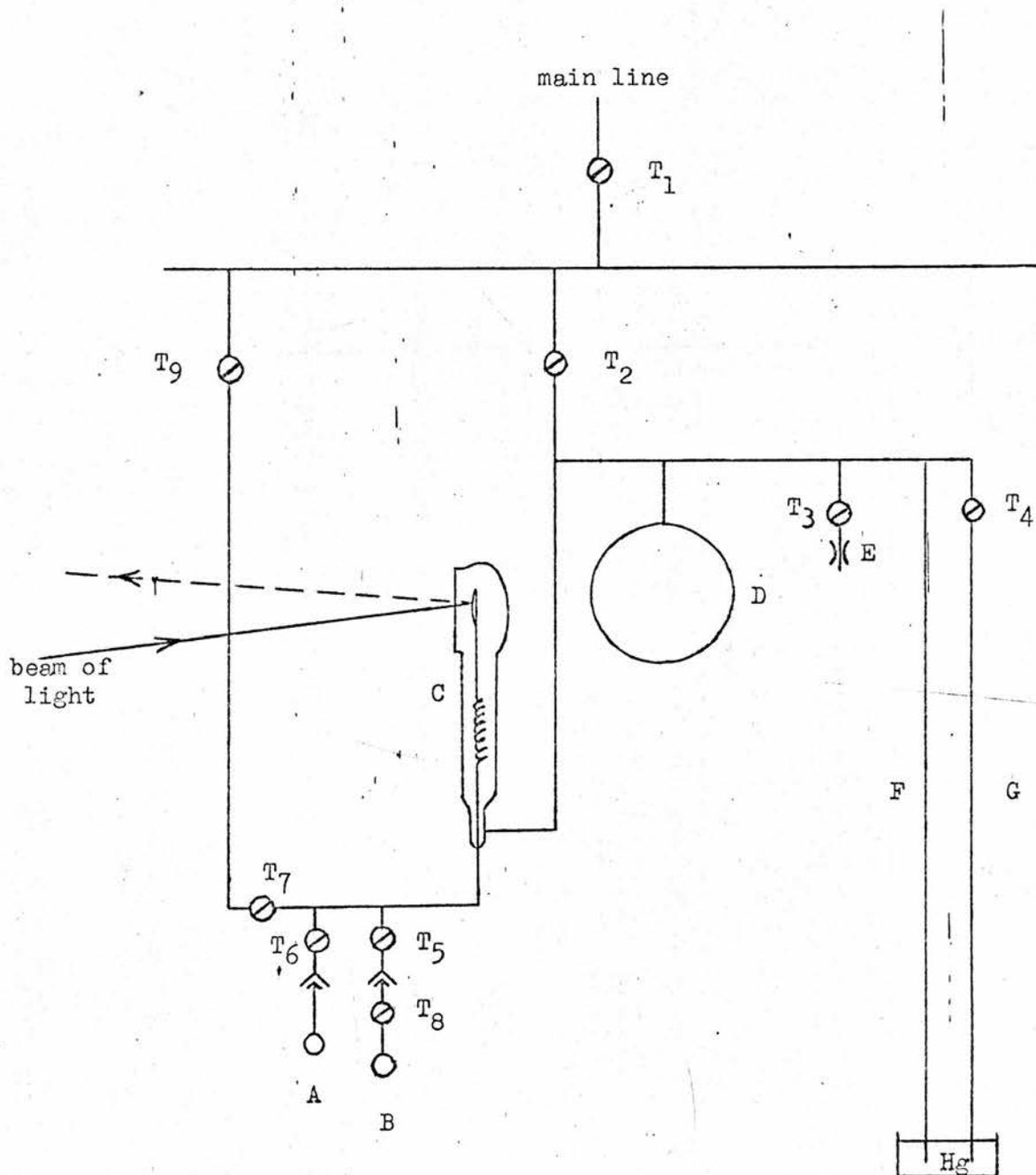


FIGURE 28: Vacuum System for Vapour Pressure Study

The phosphine under investigation was kept in tube A, and initially this bulb also contained a known excess of bromine - this having been achieved by vacuum distillation of bromine from the weighed bulb (B). Before the vapour pressure titration began, bulb B was carefully re-evacuated and weighed, in preparation for receiving aliquots of the excess bromine over the phosphine. For vapour pressure readings during the titration, tube A was kept immersed in a large water-bath at constant temperature (15°C). The vapour pressure of the contents of tube 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 tube A, some of the excess bromine was then distilled off into tube B by temperature difference, liquid nitrogen being used to surround B during this process. Tube B was allowed to assume room temperature, then removed (closing taps T_5 and T_8) and re-weighed.

Thus the new mole ratio of bromine to phosphine in tube 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 - giving access to the main line - were used.

(ii) Conductometric titrations using chlorine

These titrations were carried out in a specially-designed vacuum system. The dry chlorine (having been treated with conc. sulphuric acid and phosphorus pentoxide) was condensed into the trap A of the fractionation line of the system (Figure 29), cooled to -80°C by means of an acetone-Drikold bath. Having first been pumped off to remove the more volatile impurities, it was then fractionally distilled into trap B by closing tap T_4 and cooling B to -183°C by means of a liquid air bath. When the distillation was complete, tap T_3 was closed and the chlorine again fractionally distilled into trap C by warming trap B and now cooling trap C to -80°C . The pure, dry chlorine was stored in trap C for the duration of the conductometric titration. Taps T_6 and T_7 enclose D, a bulbous tube of known (and fixed) volume, immediately adjacent to trap C. Tube D was calibrated by opening tap T_6 , keeping tap T_7 closed and thus allowing chlorine vapour from trap C at -80°C to fill the tube. Tap T_6 was then closed, and the chlorine in D distilled into a light bulb E for weighing. The process was repeated several times for consistent results. The average weight

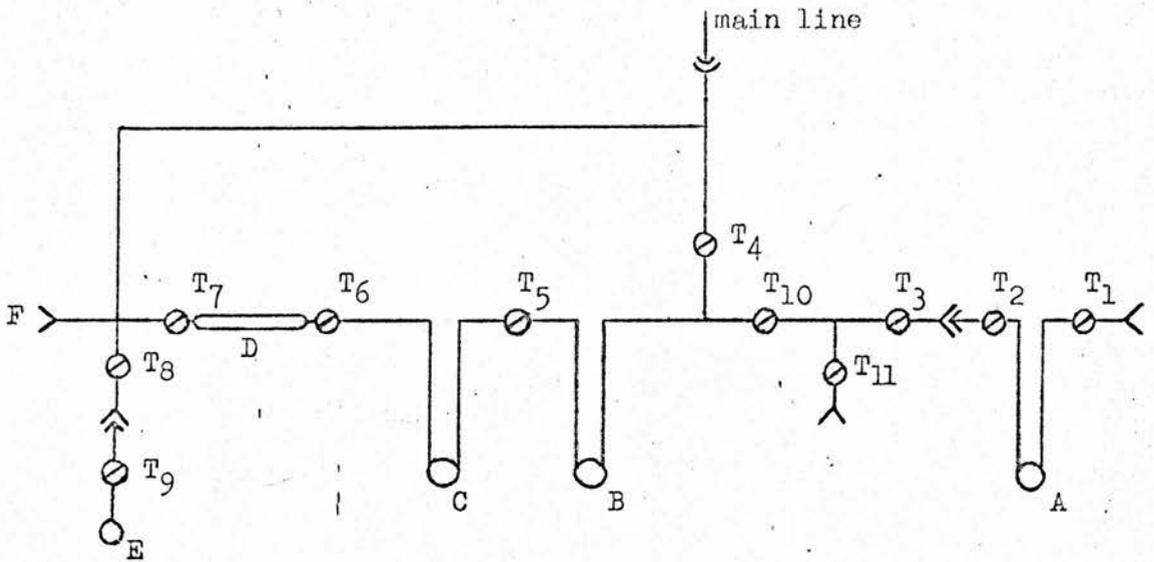


FIGURE 29: Vacuum System for Conductometric Titrations Using Chlorine

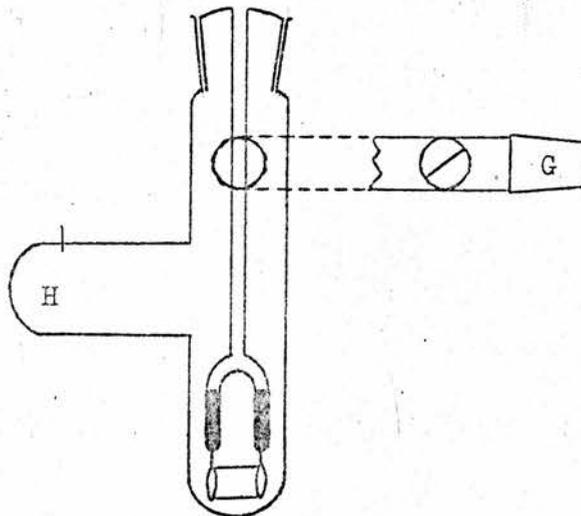


FIGURE 30: Conductance Cell for Chlorine Titrations

(and hence volume) of chlorine in D was thus calculated. (This value was checked by performing a titration of chlorine against Ph_3P - a system known to give a break at the 1:1 ratio.) The specially modified conductance cell (Figure 30) was attached to the vacuum system at F (Figure 29).

The methyl cyanide solution of the compound under investigation was frozen (liquid air) in the cold finger H, and known weights of chlorine from D were distilled into H: on melting and forming a solution, rotation of the cell about the joint G brought the solution into contact with the platinum electrodes. When solution was complete, the resistance was measured repeatedly to constant value. Appropriate mole ratios could be obtained by successive distillations of chlorine.

(c) Conductance Measurements

A standard pair of smooth platinum dipping electrodes (whose cell constant was checked regularly against standard potassium chloride solutions) was used in a sealed cell. 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. Resistance was measured on a Phillips PR 9500 Resistance Bridge operating on 1000 c/s current, readings being repeated until

constant (thus also giving a monitor for complete solution). Molar conductances were 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:^{143,144} information may be obtained not only on the stoichiometry of the reaction products but also on their electrolytic nature.

Methyl cyanide is a convenient 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 electrolytes exhibit Λ_m ca. 100 $\text{ohm}^{-1}\text{cm}^2 \text{mole}^{-1}$, and weak electrolytes have Λ_m ca. 10-20 $\text{ohm}^{-1}\text{cm}^2 \text{mole}^{-1}$ in acetonitrile.

The apparatus used was designed in order that the titration could be performed on a relatively small scale and without the solutions' coming into contact with atmospheric moisture or tap grease; a description of the apparatus and its operation has been published.¹⁴⁵ The electrodes and resistance bridge used were as described above. The conductance was measured when equilibrium had been attained (as shown by constant resistance readings) after each addition of halogen solution.

(e) Infra-red Spectra

Infra-red spectra were recorded on a Perkin-Elmer model 257 Grating Infrared Spectrophotometer over the range 4000-625 cm^{-1} . A Perkin-Elmer model 137 Infracord was also occasionally used. The samples were prepared in the dry-box as mulls in nujol, and placed between plates of sodium chloride.

(f) Ultra-violet Spectra

Ultra-violet spectra were recorded on a Unicam SP 800B UV/visible recording spectrophotometer. Stoppered quartz cells of 1 cm. or 0.5 cm. path length were used, measurements being made at room temperature (ca.18°C).

(g) 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.

Halogen analyses were carried out by two different methods: (i) Volhard's Method, and (ii) Potentiometric Titration.¹⁴⁶ The former was used much in the early part of the research, but was latterly superseded by the potentiometric method which was found to give satisfactory results for mixed halide solutions and was a most convenient method.

Before analysis, the solids (ca.0.1-0.15 g.) were hydrolysed

with excess (ca.20 ml.) 2 M solution hydroxide, the hydrolysis being performed in a closed system to prevent possible escape of hydrogen halide. The solution was allowed to stand for some 1-2 hours, then boiled to ensure complete hydrolysis. It was then cooled, made just acidic (by conc. H_2SO_4) and then treated with sulphur dioxide to reduce any hypohalite ion present. Further boiling served both to drive off any excess sulphur dioxide and to reduce the bulk of the solution. After cooling, the solution was neutralised with concentrated ammonia. The solution was then made up to 100 ml. by distilled water. Aliquots of 20 ml. were used for the Volhard titrations, each aliquot portion being first acidified with 4 ml. 6 M boiled-out nitric acid. To these aliquot portions 5 ml. 0.1 M silver nitrate solution was added, and the resultant silver halide precipitate allowed to coagulate in the dark. The hydrolysate was filtered off and titrated against standard 0.1 M ammonium thiocyanate solution, using ferric alum indicator.

The above procedure, while giving total halogen content, could not give individual percentages in the cases where more than one halogen was present. Hence the potentiometric titration was used in such cases. It was found that for optimum results the 20 ml. aliquot portions (as described above) should be treated as follows:- The aliquot is diluted with its own volume of distilled water, ca.2.4 g. AR barium nitrate is added, followed by ca.10 ml.

AR acetone (to aid precipitation) and finally 5-6 drops boiled-out 6M nitric acid. To this halide solution is added standard (0.1 M or 0.05 M) silver nitrate solution from a burette, the solution being 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. When the potential changed somewhat more rapidly as the end-point was approached, 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 were 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. Purification of Materials

(a) Solvents

(i) Methyl cyanide: Two methods were used to purify methyl cyanide. Originally, the method of Forcier and Olver¹⁴⁷ was used. The commercial solvent (Hopkins and Williams) was first

refluxed over sodium hydride (1 g./l.) to remove acrylonitrile, acid impurities and water, then distilled, refluxed over phosphorus pentoxide (2 g./l.) to remove basic impurities, and distilled again. A final reflux over calcium hydride followed by distillation removed any last traces of water. A final distillation on the vacuum line was performed to try to ensure removal of all last traces of hydride. Unfortunately, it appeared from some early conductometric titration results that the solvent still had reducing power even after vacuum distillation: hence an alternative method was adopted.

In a modified version of Smith and Witten's method,¹⁴⁸ the crude solvent was slowly trickled through a long column of potassium hydroxide pellets to remove acidic impurities, and then slowly trickled through a column of finely-ground calcium chloride to remove ammonia and water. It was then 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. The chief disadvantage of this method was the loss of a portion of the solvent by polymerisation, possibly because all acrylonitrile had not been removed. The specific conductance of methyl cyanide purified by this method was always $\text{ca. } 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$; the boiling range was 81-82°C.

(ii) Carbon tetrachloride: A variation of the method of Popov and Schmorrr¹⁴⁹ was used to obtain pure carbon tetrachloride.

The crude solvent (500 ml.) was refluxed for 10 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 on to phosphorus pentoxide, and then distilled several times on to fresh phosphorus pentoxide, b.p. = 75.5-76.0°C.

(iii) Diethyl Ether: Diethyl ether was dried by refluxing it over sodium wire after preliminary drying over calcium chloride. It was then stored over fresh sodium wire; directly before use, it was refluxed over lithium aluminium hydride (2 g./l.) and redistilled.

(iv) Chloroform: The commercial grade solvent was freed from ethanol by washing with a large volume of water. It was then dried by passage through a column of alumina, and stored over silica gel.

(b) Reagents

(i) Chlorine: Commercial chlorine (I.C.I. cylinder) was dried by passage through concentrated sulphuric acid and a drying tower packed with phosphorus pentoxide. When used for conductometric titrations it was further purified on the vacuum line. For synthetic use it was diluted with dry oxygen-free nitrogen.

(ii) Bromine: AnalaR 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°C (ice/salt bath) and distilled in vacuo into small ampoules cooled to -183°C (liquid air). Thus known weights of bromine were stored in sealed ampoules. Solutions were made by breaking a given ampoule under a known weight of solvent.

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

(iv) Iodine bromide: Commercial iodine bromide (B.D.H.) was resublimed and stored in a teflon-sleeved, ground-glass-joint sample tube in a desiccator. For conductometric titrations, iodine bromide solution was made by breaking a bromine ampoule alongside its molar equivalent of finely-powdered iodine under a known weight of solvent.

(v) Iodine chloride: Iodine monochloride was prepared by a modification of the method of Cornog and Karges.¹⁵⁰ Finely-powdered iodine was carefully added to twice its molar equivalent of liquid chlorine at -78°C (acetone-Drikold bath). The contents of the flask immediately congealed to a solid; however, on allowing the flask to assume room temperature, the uncombined chlorine evaporated. The weight of iodine still to be added to bring the

composition of the impure product to correspond to that implied by the formula 'ICl' was computed and added. The contents of the flask were allowed to stand in a liquid condition for fully 24 hours before two "recrystallisations" were performed. (the word "crystallisation" here implying the gradual cooling of the liquid phase until approximately 80% of it had solidified, then decanting off the supernatant liquid). The ICl so prepared was analysed by potentiometric titration, as described above.

(vi) Iodine trichloride: Iodine trichloride was prepared by the method of Booth and Morris.¹⁵¹ Finely-powdered iodine was carefully added to liquid chlorine at -78°C (acetone-Drikold bath), whereupon an orange flocculent mass of iodine trichloride immediately formed. When the liquid space was filled, the excess chlorine was evaporated into a second container for repetition of the process. The product was analysed by potentiometric titration.

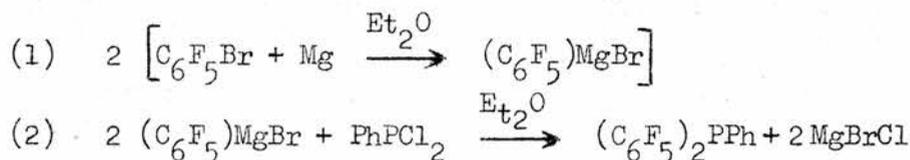
3. Preparations

(a) Starting Materials

(i) Phenyldichlorophosphine: The commercial grade material (from the Aldrich Chemical Co., Inc., Milwaukee, Wis.) was redistilled once at the oil pump. The fraction collected had b.p. range $50-52^{\circ}\text{C}/0.1\text{ mm}$.

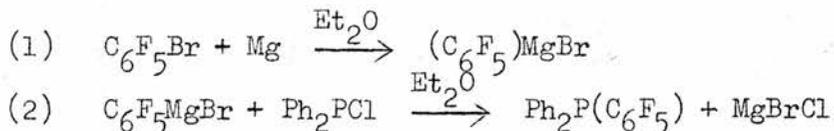
(ii) Diphenylchlorophosphine: The commercial grade material (also from the Aldrich Chemical Co., Inc.) was redistilled once at the oil pump. The fraction collected had b.p. range 105-110°C/0.1 mm.

(iii) Phenylbis(pentafluorophenyl)phosphine: Phenylbis(pentafluorophenyl)phosphine was prepared by a method analogous to that of Wall, Donadio and Pummer¹³⁶ for tris(pentafluorophenyl)phosphine: 14.12 g. (57.12 m.moles) bromopentafluorobenzene (from the Imperial Smelting Corporation, Ltd.) in 25-ml. diethyl ether were added to 1.39 g. (57.12 m.moles) pure magnesium raspings in a 250-ml. 3-necked flask under nitrogen over a period of twenty minutes. The mixture was allowed to stir for forty-five minutes, no cooling being found necessary. The mixture was then refluxed for fifteen minutes after which it was cooled to ca. -30°C (acetone-Drikold bath). 5.117 g. (28.56 m.moles) PhPCl₂ in 20 ml. diethyl ether were then added dropwise to the cool solution, this process taking twenty-five minutes. The mixture was stirred continuously while being allowed to warm to room temperature over ninety minutes, and was stirred for a further eighty minutes at room temperature. Finally the mixture was refluxed for twenty-five minutes, the overall reaction being:-



The mixture was then cooled to 0°C over one hour, ca.40 ml. ice-water was added, and finally 3M HCl was carefully added until the solution was acidic. The mixture was then transferred to a separating funnel, and the ether layers collected and dried over anhydrous magnesium sulphate; after treatment on the rotary-film evaporator, a brown oil remained. The brown oil was azeotrope-dried with benzene, then chromatographed on an alumina column, first with benzene and secondly with 40/60 petroleum ether. On evaporation of solvent, a colourless oil remained, which transformed into a white waxy solid on cooling in the refrigerator. This solid slowly gave up petrol on being treated over a day or so at the oil pump. Finally the solid was sublimed from a heating block at oil-pump pressure, yielding white crystals: the temperature of sublimation was 80-90°C/ca.0.6 mm., m.p. 59-60°C (Found: C, 48.79%; H, 1.13%. $\text{PhP}(\text{C}_6\text{F}_5)_2$ requires C, 48.89%; H, 1.14%). As a further check on purity, an infra-red spectrum of the solid (as a nujol mull) was recorded: the (C_6F_5) group absorptions were all found to be present.

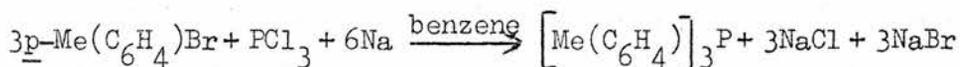
(iv) Bis(phenyl)pentafluorophenylphosphine: The method used in the preparation of bis(phenyl)pentafluorophenylphosphine was exactly analogous to that described immediately above. The overall reaction may be represented:-



and was performed on the 45.00 m.mole scale.

A brownish oil was again obtained, which, after azeotropic-drying and chromatographing with benzene, was sublimed from a heating block at oil-pump pressure, yielding white crystals; the temperature of sublimation was 125-140°C/ca.0.6 mm. m.p. 60-62°C (Found: C, 61.96%; H, 3.28%. $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$ requires C, 61.38%; H, 2.86%). An infra-red spectrum of the solid (as a nujol mull) was again recorded, all (C_6F_5) group absorptions being found present.

(v) Tri-p-tolylphosphine: Tri-p-tolylphosphine was prepared by Mr. J. Bews by the reaction of p-bromotoluene, phosphorus trichloride and sodium,¹⁵² using benzene as solvent:-



50 g. (2175.0 m.moles) finely-sliced sodium were covered with 500 ml. benzene in a 2-litre, 3-necked flask fitted with a reflux condenser, a mercury-seal stirrer and a dropping funnel containing 80 g. (468.0 m.moles) p-bromotoluene and 28 g. (204.0 m.moles) phosphorus trichloride in a few ml. benzene. Approximately 5 ml. reaction mixture was added to the flask, which was then heated in a heating-mantle with vigorous stirring until the mixture started to boil. The mantle was then removed and mixture steadily added at such a rate that gentle boiling was maintained. The contents of the flask were stirred and refluxed for sixteen hours, and then

left to settle for three days. The flask was then re-heated, the solids filtered off and the filtrate collected. The solid was boiled with benzene and refiltered, the extraction process being repeated twice. The combined filtrates were treated in the rotary film evaporator, and the resulting solid recrystallised from ethanol, m.p. 143-146°C (Found: C, 83.05%; H, 7.13%. Tri-p-tolyl-phosphine requires C, 82.87%; H, 6.95%).

(b) Part I: A. Phenyl-dichlorophosphine adducts

(i) PhPCl₂-Cl₂

A mixture of dry chlorine gas and dry oxygen-free nitrogen was passed into an acetonitrile solution of phenyl-dichlorophosphine at 0°C (ice-bath). After the white precipitate had all come down, the chlorine flow was stopped, but the nitrogen was allowed to continue to flow until the system slowly acquired room temperature (ca. 20°C). The reaction tube was then swiftly transferred to the vacuum system for degassing, then the solvent was removed by vacuum distillation. The white solid residue was carefully washed with acetonitrile, then attached to the line once more for removal of last traces of solvent by pumping. M.p. 68-71°C (Found: Cl, 57.68; PhPCl₄ requires Cl, 56.84%).

(ii) PhPCl₂-Br₂

Mole ratio Br₂:PhPCl₂ :: 0.5:1. Acetonitrile solutions of

the two reagents in the above mole ratio were slowly mixed by direct addition in the dry-box. A pale yellow precipitate began to come down from the first drop of Br_2 solution added. After complete addition, the precipitate was allowed to settle for 2-3 minutes, then the excess solvent was carefully sucked off. The yellow solid was washed twice with acetonitrile, and then transferred to the vacuum system where the last traces of solvent were removed by pumping. M.p. $199-201^\circ\text{C}$ (Found: Cl, 20.2; Br, 48.4. $\text{PhPBr}_2\text{Cl}_2$ requires Cl, 20.9; Br, 47.2%).

Mole ratio $\text{Br}_2:\text{PhPCL}_2 :: 2:1$. The procedure directly above was repeated, with the mole ratio $\text{Br}_2:\text{PhPCL}_2 :: 2:1$. Again, precipitate appeared immediately, but redissolved. Ether addition effected re-precipitation, and after washing with ether and removal of solvent, a yellow solid remained. M.p. $202-204^\circ\text{C}$ (Found: C, 14.30; H, 1.02; Br, 62.85; Cl, 11.46. $\text{PhPBr}_4\text{Cl}_2$ requires C, 14.46; H, 1.01; Br, 64.10; Cl, 14.25%).

(iii) $\text{PhPCL}_2-\text{I}_2$

Acetonitrile solutions of the reagents were mixed by direct addition in the dry-box in the mole ratios $\text{I}_2:\text{PhPCL}_2 ::$ (a) 0.5:1; (b) 1:1; (c) 2:1. In case (a) no precipitate came down, and removal of the solvent by pumping left a dark, viscous oil. Addition of excess diethyl ether to the acetonitrile solution simply increased its mobility. In cases (b) and (c), a dark brown solid appeared to have been formed, but on solvent removal again

degenerated into a dark, sludgy oil. Owing to the obvious state of decomposition of the product, analysis was considered superfluous.

(iv) PhPCl₂ - ICl

In the case of PhPCl₂ and ICl in 1:1 mole ratio, direct addition of acetonitrile solutions gave an orange precipitate: this solid was again washed (MeCN) and solvent traces removed by pumping. M.p. 128-131°C (Found: C, 17.48; H, 1.24; I, 31.0; Cl, 48.5. PhPICl₅ requires C, 17.46; H, 1.21; I, 30.8; Cl, 48.0%).

(v) PhPCl₂ - IBr

On mixing acetonitrile solutions of the reagents in the 1:1 mole ratio in the dry-box, no precipitate came down, nor could addition of diethyl ether induce precipitation. The original acetonitrile solution was therefore attached to the vacuum system, where - after degassing - the solvent was removed by vacuum distillation. Eventually a red-brown solid appeared when only ca. 1 ml. solvent remained. The solid was pumped directly for several hours to try to ensure the removal of all last traces of solvent. (Found: C, 17.14; H, 1.30; Hal, 75.47. PhPIBrCl₂ requires C, 18.68; H, 1.31; Hal, 71.96%.)

(vi) PhPCl₂ - ICl₃

The acetonitrile solutions of the reagents in 1:1 mole

ratio behaved exactly as those in the $\text{PhPCl}_2\text{-IBr}$ case directly above. The solid eventually produced on solvent removal was orange, but tended to decompose to a dark oily liquid if kept at reduced pressure. Analysis, however, showed relative number of atoms, $\text{Cl:I} :: 4.9:1$. (Found: C, 17.20; H, 1.22; I, 29.3; Cl, 40.0. PhPICl_5 requires C, 17.46; H, 1.21; I, 30.8; Cl, 43.0%.)

(vii) $\text{(PhPCl}_2 + \text{Br}_2) - \text{Br}_2$

Addition of Br_2 in acetonitrile to an acetonitrile suspension of $\text{PhPBr}_2\text{Cl}_2$ produced a yellow-orange solution. On addition of diethyl ether, however, a fine yellow precipitate came down. The precipitate was washed twice with ether, and attached very briefly to the vacuum system for removal of all last traces of solvent. M.p. $203\text{-}205^\circ\text{C}$ (Found: Hal, 78.40; $\text{PhPBr}_4\text{Cl}_2$ requires Hal, 78.35%.)

(viii) $\text{(PhPCl}_2 + \text{Cl}_2) - \text{ICl}$

Addition of an acetonitrile solution of iodine chloride to a suspension of PhPCl_4 in acetonitrile, such that $\text{ICl:PhPCl}_4 :: 0.5:1$, produced a yellow solution. Addition of diethyl ether, however, brought down a yellow-orange solid, which was washed twice with ether before being briefly attached to the vacuum system for drying. M.p. $104\text{-}108^\circ\text{C}$ (Found: C, 16.20; H, 1.30; I, 24.7; Cl, 49.5 ($\therefore \text{Cl:I} :: 7.18:1$); PhPICl_7 requires C, 14.94; H, 1.04; I, 26.25; Cl, 51.40%).

(ix) (PhPCl₂ + Cl₂) - IBr

The addition procedure was exactly parallel to that described for PhPCl₄-ICl above, the mole ratio employed again being 0.5:1. Ether addition to the yellow-orange solution produced an orange solid, m.p. 120-124°C. Analysis results were dubious, probably due to the presence of I, Br and Cl together. (Found: Hal, 75.08; PhPIBrCl₆ requires Hal, 79.51; PhPIBrCl₄ requires Hal, 76.35%; but individual I, Br, Cl %'s do not fit any formula.)

- Part I: B. Diphenylchlorophosphine Adducts

(i) Ph₂PCl-Cl₂

A procedure entirely analogous to the PhPCl₂-Cl₂ case was followed. The white solid obtained was washed with acetonitrile and dried on the vacuum system. M.p. 192-197°C (Found: C, 49.43; H, 3.47; Cl, 35.62. Ph₂PCl₃ requires C, 49.44; H, 3.46; Cl, 36.46%).

(ii) Ph₂PCl-Br₂

Mole ratio Br₂:Ph₂PCl :: 1:1. On mixing acetonitrile solutions of the two reagents (in the 1:1 mole ratio), white precipitate began to come down from the first drop added. The solid was washed with acetonitrile, and attached to the vacuum system for drying. M.p. 223-227°C (Found: C, 38.08; H, 2.60; Br, 43.9; Cl, 8.71; Ph₂PBr₂Cl requires C, 37.86; H, 2.63; Br, 42.0; Cl, 9.32%).

Mole ratio Br₂:Ph₂PCl :: 2:1. Direct mixing of acetonitrile solutions of the reagents in the above mole ratio gave a warm, cloudy solution, from which orange-red crystals came down on addition of diethyl ether. Reddish crystals remained after washing with ether and drying on the vacuum line. (Found: Hal, 63.0; Ph₂PBr₄Cl requires Hal, 65.7%.)

(iii) Ph₂PCl - I₂

On direct mixing of acetonitrile solutions of the reagents in the 1:1 mole ratio, an orange-brown precipitate soon appeared. After decanting excess solvent, the precipitate was washed with acetonitrile then pumped on the vacuum system to remove last traces of solvent. M.p. 142-145°C (Found: C, 25.94; H, 1.73; Hal, 65.61. Ph₂PI₃ requires C, 25.43; H, 1.79; Hal, 67.21%. The qualitative test for chloride - using potassium dichromate and concentrated sulphuric acid - gave a negative result).

(iv) Ph₂PCl - ICl

On mixing directly acetonitrile solutions of the two reagents in the 1:1 mole ratio, no precipitate appeared. After preliminary degassing, the solvent was removed by vacuum distillation: when only a small amount of solvent remained, a yellow solid crust appeared in the reaction tube. After washing with the minimum volume of acetonitrile and pumping dry on the vacuum system, the solid was white in colour. M.p. 184-188°C (Found: C, 48.21;

H, 3.44; Hal, 30.53. Ph_2PCl_3 requires C, 49.44; H, 3.46; Hal, 36.46 %).

(v) $\text{Ph}_2\text{PCl} - \text{IBr}$

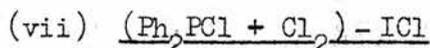
Mole ratio IBr: $\text{Ph}_2\text{PCl} :: 1:1$. No precipitate could be induced to come down, even on adding ether to the acetonitrile solution of the above reagents in 1:1 ratio. The original acetonitrile solution was therefore attached to the vacuum system for degassing and solvent removal. Eventually, a red-brown crust remained on the walls of the tube: this solid was pumped directly for several hours to try to ensure complete solvent removal. (Found: C, 33.56; H, 2.32; I, 30.10; Br, 20.38; Cl, 7.29. Ph_2PIBrCl requires C, 33.70; H, 2.36; I, 29.70; Br, 18.70; Cl, 8.30%.)

Mole ratio IBr: $\text{Ph}_2\text{PCl} :: 2:1$. Behaviour exactly analogous to the 1:1 mole-ratio case was observed. (Found: C, 33.67; H, 2.37, Ph_2PIBrCl requires C, 33.70; H, 2.36%.)

(vi) $\text{Ph}_2\text{PCl} - \text{ICl}_3$

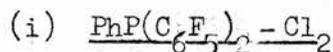
No solid could be obtained from the acetonitrile solutions of these reagents in 1:1 mole ratio, even on direct pumping. A dark viscous oil remained. (Found: C, 31.56; H, 2.31; I, 26.9; Cl, 28.0. Ph_2PICl_4 requires C, 31.80; H, 2.22; I, 28.0; Cl, 31.25%.)

(vii) / ...

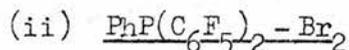


In view of the inability to isolate a solid from the $\text{Ph}_2\text{PCl}-\text{ICl}_3$ system, an acetonitrile solution of iodine chloride was added to Ph_2PCl_3 suspended in acetonitrile, the reagents being in 1:1 mole ratio. Yet again, only a dark viscous oil could be isolated. (Found: C, 33.80; H, 2.30. Ph_2PICl_4 requires C, 31.80; H, 2.22%.)

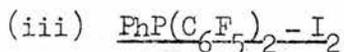
(c) Part II: A. Phenylbis(pentafluorophenyl)phosphine Adducts



The standard procedure for the preparation of chlorine adducts, viz., the passage of $\text{Cl}_2(\text{g})/\text{N}_2(\text{g})$ into an acetonitrile solution of the phosphine at 0°C , was employed. However, no solid, but only a pale green oil, could be isolated. In spite of direct pumping, the analytical data indicate some tightly-held solvent still present. (Found: C, 44.83; H, 1.20; Hal, 9.33. $\text{PhP}(\text{C}_6\text{F}_5)_2\text{Cl}_2$ requires C, 42.15; H, 0.98; Hal, 13.82%.)

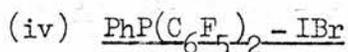


The reagents in the 1:1 mole ratio gave - exactly as in the ' Cl_2 ' case above - a viscous yellow oil. (Found: C, 38.05; H, 1.00; Hal, 25.78. $\text{PhP}(\text{C}_6\text{F}_5)_2\text{Br}_2$ requires C, 35.91; H, 0.84; Hal, 26.56%.)



Exactly the same pattern for $\text{PhP}(\text{C}_6\text{F}_5)_2$ - halogen 1:1 adducts was observed in the 'I₂' case: addition of diethyl ether to the dark acetonitrile solution simply increased its mobility.

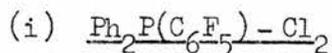
Analysis of the viscous, dark oil finally obtained showed ca.1% nitrogen present, hence denoting traces of solvent still present, in spite of direct pumping for several hours. (Found: C, 33.08; H, 1.20; Hal, 30.23. $\underline{\text{PhP}(\text{C}_6\text{F}_5)_2\text{I}_2}$ requires C, 31.06; H, 0.72; Hal, 36.44%.)



Only a dark, viscous oil could be obtained from the reagents at 1:1 mole ratio, in spite of prolonged pumping. Thus all adducts of $\text{PhP}(\text{C}_6\text{F}_5)_2$ investigated have been found to be viscous oils. Again, a trace of nitrogen (ca.0.6%) was present in the analytical data. (Found: C, 36.85; H, 1.04; Hal, 31.14.

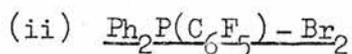
$\underline{\text{PhP}(\text{C}_6\text{F}_5)_2\text{IBr}}$ requires C, 33.31; H, 0.78; Hal, 31.87%.)

- Part II: B. Bis(phenyl)pentafluorophenylphosphine Adducts



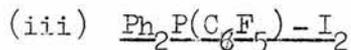
The standard 'Cl₂ adduct' procedure gave a pale green oil. However, on removing excess solvent by vacuum distillation, a white precipitate came down. The solid was washed twice with a

small volume of ether, then attached to the vacuum system for drying. M.p. 113-115°C (Found: C, 51.77; H, 2.38; Hal (analysed a few days later than C,H analyses), 13.24. $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{Cl}_2$ requires C, 51.09; H, 2.38; Hal, 16.77%.)



Mole ratio $\text{Br}_2:\text{Ph}_2\text{P}(\text{C}_6\text{F}_5) :: 1:1$. In spite of treatment with diethyl ether, and direct pumping at the oil pump, no solid could be isolated from the 1:1 mole ratio acetonitrile solution: a pale yellow viscous oil was obtained. Analysis figures showed a much lower percentage halogen present than could match any feasible adduct's molecular formula. (Found: Hal, 16.78; $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{Br}_2$ requires Hal, 31.21%.)

Mole ratio $\text{Br}_2:\text{Ph}_2\text{P}(\text{C}_6\text{F}_5) :: 2:1$. Behaviour identical to the 1:1 mole ratio case was observed. Even percentage halogen found almost matches that given above for the 1:1 case, and is thus too low to fit any reasonable formula (Found: Hal, 19.81%).



No solid could be obtained from the acetonitrile solutions of the above reagents in the mole ratio $\text{I}_2:\text{Ph}_2\text{P}(\text{C}_6\text{F}_5) :: 2:1$, in spite of ether addition, and direct pumping. A dark red, viscous oil remained. (Found: Hal, 53.30. $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{I}_4$ requires Hal, 59.00; and $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{I}_2$ requires Hal, 41.91%.)

(iv) $\underline{\text{Ph}_2\text{P}(\text{C}_6\text{F}_5) - \text{IBr}}$

The mole ratio $\text{IBr}:\text{Ph}_2\text{P}(\text{C}_6\text{F}_5) :: 2:1$ was employed, and the behaviour observed paralleled that for the $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)/\text{I}_2$ system exactly. A dark red viscous oil remained. (Found: Hal, 47.50; $\underline{\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)\text{I}_2\text{Br}_2}$ requires Hal, 53.97%.)

(d) Part III: Tri-p-tolylphosphine Adducts

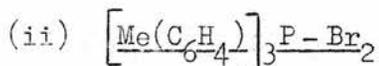
(i) $\left[\text{Me}(\text{C}_6\text{H}_4)\right]_3\text{P}-\text{Cl}_2$

In MeCN. The standard 'Cl₂ adduct' procedure gave no solid, only a pale green viscous oil, even on treatment with diethyl ether. It was therefore decided to change solvents.

In CCl₄. Although an oil again formed, and did not yield solid on treatment with ether, it was found that on prolonged direct pumping the oil produced a whitish crust of solid. (Found: C, 70.93; H, 6.13; Cl, 14.54. $\left[\text{Me}(\text{C}_6\text{H}_4)\right]_3\text{PCl}_2$ requires C, 67.28; H, 5.64; Cl, 18.92%.)

In 40/60 petroleum ether. A white sludge appeared in the reaction tube on passing the Cl₂(g)/N₂(g) mixture. After decanting excess solvent, the sludge was washed with CCl₄, then diethyl ether. Trituration with ether gave a whitish solid, which was transferred to a clean tube and attached to the vacuum system for pumping. M.p. 75-77°C (Found: C, 63.38; H, 5.64; Cl, 23.34.)

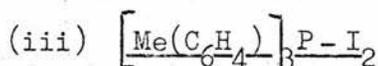
$[\text{Me}(\text{C}_6\text{H}_4)]_3\text{PCl}_2$ requires C, 67.28; H, 5.64; Cl, 18.92%.)



Mole ratio $\text{Br}_2 : [\text{Me}(\text{C}_6\text{H}_4)]_3\text{P} :: 1:1$. Although the acetonitrile solutions of the above reagents in 1:1 mole ratio initially produced an oil, on direct pumping a yellow solid crust formed. M.p. 174-177°C (Found: C, 56.30; H, 5.09; Br, 32.23; a trace of N was also detected. $[\text{Me}(\text{C}_6\text{H}_4)]_3\text{PBr}_2$ requires C, 54.3%; H, 4.56; Br, 34.46%.)

Mole ratio $\text{Br}_2 : [\text{Me}(\text{C}_6\text{H}_4)]_3\text{P} :: 2:1$. No solid could be obtained from the acetonitrile solutions of the above reagents in the 2:1 mole ratio, even on ether addition. An orange-red oil was obtained, whereupon it was decided to change solvent.

Mole ratio $\text{Br}_2 : [\text{Me}(\text{C}_6\text{H}_4)]_3\text{P} :: 2:1$ in CCl_4 . On direct mixing of CCl_4 solutions, a yellow emulsion immediately formed, which gave way to an orange solution containing an orange solid. The excess solvent was carefully decanted, and the solid attached to the vacuum system for pumping in order to remove the last traces of solvent. M.p. 118-122°C (Found: C, 41.68; H, 3.58; Br, 49.37. $[\text{Me}(\text{C}_6\text{H}_4)]_3\text{PBr}_4$ requires C, 34.65; H, 3.39; Br, 51.31%.)

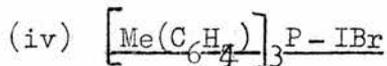


Mole ratio $\text{I}_2 : [\text{Me}(\text{C}_6\text{H}_4)]_3\text{P} :: 0.5:1$. On mixing the acetonitrile solutions, a fine, pale yellow precipitate immediately came

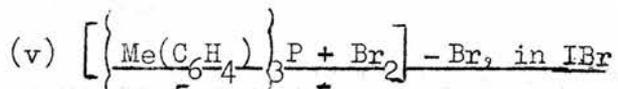
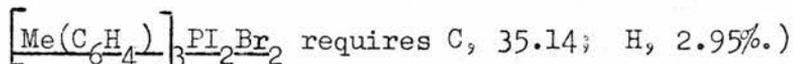
down. After decanting excess solvent, the solid was washed briefly with acetonitrile, and then attached to the vacuum system for the removal of last traces of solvent. M.p. 203-206°C (Found: C, 54.96; H, 4.70; I, 37.18. $\left[\text{Me}(\text{C}_6\text{H}_4) \right]_3\text{P} \cdot \text{I}_2$ requires C, 58.54; H, 4.91; I, 29.47; an equimolar mixture of $\left[\text{Me}(\text{C}_6\text{H}_4) \right]_3\text{P} \cdot \text{I}_2$ and $\left[\text{Me}(\text{C}_6\text{H}_4) \right]_3\text{P} \cdot \text{I}_2$ requires C, 53.30; H, 4.47; I, 35.72%).

Mole ratio $\text{I}_2 : \left[\text{Me}(\text{C}_6\text{H}_4) \right]_3\text{P} :: 1:1$. On mixing the acetonitrile solutions directly, a dark red solution formed: an orange precipitate came down within 5 minutes, however. (Freeze-drying of the mother liquor yielded a second crop of crystals.) The excess solvent was decanted, and the solid pumped dry on the vacuum line. M.p. 198-201°C (Found: C, 45.44; H, 3.97; I, 45.24. $\left[\text{Me}(\text{C}_6\text{H}_4) \right]_3\text{P} \cdot \text{I}_2$ requires C 45.28; H, 3.80; I, 45.50%).

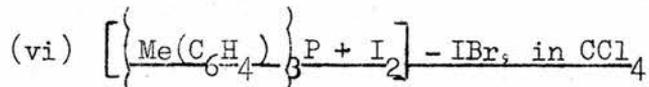
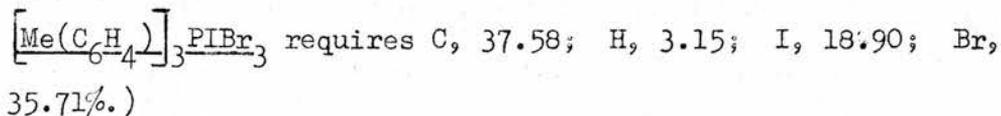
Mole ratio $\text{I}_2 : \left[\text{Me}(\text{C}_6\text{H}_4) \right]_3\text{P} :: 2:1$. Mixture of the acetonitrile solutions of the reagents in the 2:1 mole ratio yielded a dark red solution, but no precipitate, even on ether addition. However, a brown precipitate could be induced either by cooling the acetonitrile/ether solution overnight in the refrigerator, or by removal of acetonitrile/ether solvent by freeze-drying on the vacuum line. M.p. 88-92°C (Found: C, 30.90; H, 2.66; I, 61.08; also a trace of nitrogen present. $\left[\text{Me}(\text{C}_6\text{H}_4) \right]_3\text{PI}_4$ requires C, 26.63; H, 2.61; I, 62.54%).



On mixing the reagents in the 2:1 mole ratio, using acetonitrile as solvent, no precipitate came down, even on ether addition. After solvent removal by freeze-drying, a dark, viscous oil remained. (Found: C, 34.47; H, 3.21; also N, ca.0.6.



On mixing $\left[\text{Me}(\text{C}_6\text{H}_4) \right]_3 \text{PBr}_2$ and IBr in the 1:1 mole ratio in CCl_4 , a red-brown solid came down. Pumping on the vacuum line after decanting excess solvent left an orange-brown solid, m.p. 130-132°C. (Found: C, 37.30; H, 3.20; I, 18.25; Br, 32.22.



The reagents in 1:1 mole ratio in CCl_4 gave exactly analogous behaviour to the $\left[\text{Me}(\text{C}_6\text{H}_4) \right]_3 \text{PBr}/\text{IBr}$ system above. A brown solid was isolated, m.p. 126-130°C. (Found: C, 32.48; H, 2.63; I, 47.64; Br, 10.69. $\left[\text{Me}(\text{C}_6\text{H}_4) \right]_3 \text{PI}_3\text{Br}$ requires C, 32.98; H, 2.77; I, 49.78; Br, 10.44%.)

REFERENCES

REFERENCES

1. BOYLE: Experiments and Consideration Concerning Colour (London, 1664)
2. H.S. BOOTH and A.R. BOZARTH: J.Amer.Chem.Soc. 55 (1933), 3890
3. H.S. BOOTH and S.G. FRARY: J.Amer.Chem.Soc. 61 (1939), 2934
4. R.E.D. CLARK: J.Chem.Soc. (1930), 2737
5. M.G. RAEDER: Z.anorg.Chem. 210 (1933), 145.
6. M.L. DELWAULLE and F. FRANÇOIS: J.Chim.phys. 46 (1949), 80
7. M.L. DELWAULLE: Compt.rend. 224 (1947), 389
8. E. FLUCK, J.R. VAN WAZER and L.C.D. GROENWEGHE: J.Amer.Chem.Soc. 81 (1959), 6363
9. M.L. DELWAULLE and G. SCHILLING: Compt.rend. 244 (1957), 70
10. M.L. DELWAULLE and F. FRANÇOIS: Compt.rend. 223 (1946), 796
11. C.J. WILKINS: J.Chem.Soc. (1951), 2726
12. W. PREETZ and E. BLASIUS: Z.anorg.Chem. 332 (1964), 140
13. J. FISCHER and E. RUDZITIS: J.Amer.Chem.Soc. 81 (1959), 6375
14. T. KENNEDY and D.S. PAYNE: J.Chem.Soc. (1959), 1228
15. E.L. MUEPPTERTIES, T.A. BITHER, M.W. FARLOW and D.D. COFFMAN: J.Inorg.Nuclear Chem. 16 (1960), 52
16. H.S. BOOTH and A.R. BOZARTH: J.Amer.Chem.Soc. 61 (1939), 2927
17. M.H. MOISSAN: Compt.rend. 100 (1885), 1348
18. L. KOLDITZ and K. BAUER: Z.anorg.Chem. 302 (1959), 241
19. A.L. HENNE and P. TROTT: J.Amer.Chem.Soc. 69 (1947), 1820
20. L. KOLDITZ: Z.anorg.Chem. 289 (1957), 128
21. R.P. CARTER and R.R. HOLMES: Inorg.Chem. 4 (1965), 738
22. A.L. ALLRED and A.L. HENSLEY: J.Inorg.Nuclear Chem. 17 (1961), 53.
23. R.R. HOLMES: J.Inorg.Nuclear Chem. 19 (1961), 363

24. F.J. BRINKMANN, H. GERDING and K. OLIE: Rec.Trav.chim. 88 (1969), 1358
25. J.E. GRIFFITHS, R.P. CARTER and R.R. HOLMES: J.Chem.Phys. 41 (1964), 863.
26. J.E. GRIFFITHS: J.Chem.Phys. 42 (1965), 2632
27. H.M. DESS, R.W. PARRY and G.L. VIDALE: J.Amer.Chem.Soc. 78 (1956), 5730
28. L. KOLDITZ: Z.anorg.Chem. 280 (1955), 313
29. H.M. DESS and R.W. PARRY: J.Amer.Chem.Soc. 78 (1956) 5735
30. O. RUFF, J. ZEDNER, M. KNOCH and H. GRAF: Ber. 42 (1909) 4021
31. N.E. AUBREY and J.R. VAN WAZER: J.Inorg.Nuclear Chem. 27 (1965), 1761
32. L. KOLDITZ and W. REHAK: Z.anorg.Chem. 341 (1965), 100
33. N.V. SIDGWICK and H.M. POWELL: Proc.Roy.Soc. A 176 (1940), 153
34. R.J. GILLESPIE and R.S. NYHOLM: Quart.Rev. 11 (1957), 339
35. R.J. GILLESPIE: Canad.J.Chem. 38 (1960), 818
36. R.J. GILLESPIE: J.Amer.Chem.Soc. 82 (1960), 5978
37. R.J. GILLESPIE: Canad.J.Chem. 39 (1961), 318
38. R.J. GILLESPIE: J.Chem.Educ. 40 (1963), 295
39. R.J. GILLESPIE: Angew.Chem., Internat.Edn. 6 (1967), 819
40. R.J. GILLESPIE: J.Chem.Educ. 47 (1970), 18
41. E.L. MUETTERTIES and R.A. SCHUNN: Quart.Rev. 20 (1966), 245
42. I.J. WORRALL: Molecular Symmetry, R.I.C. Lecture Series (1967), No. 2
43. R.S. DRAGO: Physical Methods in Inorganic Chemistry, Reinhold Publishing Corp. (New York, 1965), Ch. 4
44. S. BERRY: J.Chem.Phys. 32 (1960), 933
45. E.L. MUETTERTIES, W. MAHLER, K.J. PACKER and R. SCHMUTZLER: Inorg.Chem. 3 (1964), 1298
46. R.J. GILLESPIE: J.Chem.Soc. (1963), 4672
47. G.E. KIMBALL: J.Chem.Phys. 8 (1940), 188
48. F.A. COTTON: J.Chem.Phys. 35 (1961), 228
49. R.E. RUNDLE: Survey Progr.Chem. 1 (1963), 81
50. G.C. PIMENTEL: J.Chem.Phys. 19 (1951), 446

51. E.E. HAVINGA and E.H. WIEBENGA: Rec.Trav.chim. 78 (1959), 724
52. E.H. WIEBENGA, E.E. HAVINGA and K.H. BOSWIJK: Adv.Inorg.Chem. Radiochem. 3 (1961), 133
53. K.W. HANSEN and L.S. BARTELL: Inorg.Chem. 4 (1965), 1775
54. L.S. BARTELL and K.W. HANSEN: Inorg.Chem. 4 (1965), 1777
55. R.F. HUDSON: Angew.Chem., Internat.Edn. 6 (1967), 749
56. R.J. HACH and R.E. RUNDLE: J.Amer.Chem.Soc. 73 (1951), 4321
57. G.B. CARPENTER: J.Chem.Educ. 40 (1963), 385
58. R.E. RUNDLE: J.Amer.Chem.Soc. 85 (1963), 112
59. R.J. GILLESPIE: Inorg.Chem. 5 (1966), 1634
60. L.S. BARTELL: Inorg.Chem. 5 (1966), 1635
61. L.S. BARTELL: Inorg.Chem. 9 (1970), 1594
62. R.R. HOLMES and J.A. GOLEN: Inorg.Chem. 9 (1970), 1596
63. R.R. HOLMES and W.P. GALLAGHER: Inorg.Chem. 2 (1963), 433
64. R.R. HOLMES, R.P. CARTER and G.E. PETERSON: Inorg.Chem. 3 (1964), 1748
65. R.R. HOLMES: J.Chem.Phys. 46 (1967), 3718
66. R. ROGOWSKI and K. COHN: Inorg.Chem. 7 (1968), 2193
67. E.L. MUETTERTIES, W. MAHLER and R. SCHMUTZLER: Inorg.Chem. 2 (1963), 613
68. A.J. DOWNS and R. SCHMUTZLER: Spectrochim. Acta 21 (1965) 1927
69. A.J. DOWNS and R. SCHMUTZLER: Spectrochim. Acta 23 A (1967) 681
70. R. SCHMUTZLER: Chapter 2 in Halogen Chemistry, ed. V. Gutmann, Academic Press (London, 1967), Vol. 2
71. Y. MORINO, K. KUCHITZU and T. MORITANI: Inorg.Chem. 8 (1969), 867
72. E.A. COHEN and C.D. CORNWELL: Inorg.Chem. 7 (1968), 398
73. L.O. BROCKWAY and J.Y. BEACH: J.Amer.Chem.Soc. 60 (1938), 1836
74. H.A. BENT: Canad.J.Chem. 38 (1960), 1235
75. D. CLARK, H.M. POWELL and (independently) A.F. WELLS: J.Chem. Soc. (1942), 642
76. H.M. POWELL and D. CLARK: Nature 145 (1940), 971
77. G. WITTIG and M. RIEBER: Annalen 562 (1949), 187

78. P.J. WHEATLEY: J.Chem.Soc. (1964), 2206
79. P.J. WHEATLEY and G. WITTIG: Proc.Chem.Soc. (1962), 251
80. P.J. WHEATLEY: J.Chem.Soc. (1964), 3718
81. E.G. ROCHOW, D.T. HURD and R.N. LEWIS: The Chemistry of Organometallic Compounds, John Wiley & Sons, Inc. (New York, 1957), p. 215
82. J.R. VAN WAZER, Phosphorus and its Compounds, Interscience Publishers, Inc. (New York, 1956), Vol. 1, p. 263
83. A. SCHMIDPETER and H. BERECHT: Angew.Chem., Internat.Edn. 6 (1967), 564
84. J. GOUBEAU and R. BAUMGARTNER: Z.Elektrochem. 64 (1960), 598
85. A.F. WELLS: Z.Krist. 99 (1938), 367
86. K. ISSLEIB and W. SIEDEL: Z.anorg.Chem. 288 (1956), 201
87. G.S. HARRIS: Proc.Chem.Soc. (1961), 65
88. A.D. BEVERIDGE and G.S. HARRIS: J.Chem.Soc. (1964), 6076
89. A.D. BEVERIDGE, G.S. HARRIS and F. INGLIS: J.Chem.Soc. (A) (1966), 520
90. G.A. WILEY and W.R. STINE: Tetrahedron Letters (1967), 2321
91. G.S. HARRIS and M.F. ALI: Tetrahedron Letters (1968), 37
92. D.S. PAYNE: J.Chem.Soc. (1953), 1052
93. G.S. HARRIS and D.S. PAYNE: J.Chem.Soc. (1956), 4617
94. J.N. WILSON: J.Amer.Chem.Soc. 80 (1958), 1338
95. L. KOLDITZ: Z.anorg.Chem. 284 (1956), 144
96. L. KOLDITZ: Z.anorg.Chem. 286 (1956), 307
97. W.L. GROENEVELD: Rec.Trav.chim. 71 (1952), 1152
98. Y.B. BUR'YANOV: Chem.Abs. 51 (1957), 6417
99. Y.A. FIALKOV and Y.B. BUR'YANOV: Chem.Abs. 54 (1960), 16249
100. W.L. GROENEVELD: Rec.Trav.chim. 75 (1956), 594
101. A.A. KUZ'MENKO and Y.A. FIALKOV: Zhur. obshchei Khim. 21 (1951), 473
102. A.I. POPOV and E.H. SCHMORR: J.Amer.Chem.Soc. 74 (1952), 4672
103. W.F. ZEILEZNY and N.C. BAENZIGER: J.Amer.Chem.Soc. 74 (1952) 6151
104. I.D. MUZYKA and Y.A. FIALKOV: Chem.Abs. 46 (1952), 6983

105. S.G.W. GINN and J.L. WOOD: Chem.Comm. (1965), 262
106. J.C. SLATER: Acta cryst. 12 (1959), 197
107. R.C.L. MOONEY: Z.Krist. 98 (1938), 377
108. R.J. ELEMA, J.L. DE BOER and A. VOS: Acta cryst. 16 (1963),
243
109. W.G. SLY and R.E. MARSH: Acta cryst. 10 (1957), 378
110. E.E. HAVINGA and E.H. WIEBENGA: Acta cryst. 11 (1958), 733
111. W.J. JAMES, R.J. HACH, D. FRENCH and R.E. RUNDLE: Acta
cryst. 8 (1955), 814
112. S.S. HUBARD: J.Phys.Chem. 46 (1942), 227
113. E.E. HAVINGA, K.H. BOSWIJK and E.H. WIEBENGA: Acta cryst. 7
(1954), 487
114. A.E. VAN ARKEL and J.H. DE BOER: Rec.Trav.chim. 47 (1928),
593
115. E.H. WIEBENGA and D. KRACHT: Inorg.Chem. 8 (1969), 738
116. C.D. CORNWELL and R.S. YAMASAKI: J.Chem.Phys. 27 (1957),
1060
117. F. EPHRAIM: Ber. 50 (1917), 1069
118. H.W. CREMER and D.R. DUNCAN: J.Chem.Soc. (1931), 2243
119. J.W. MELLOR: Comprehensive Treatise on Chemistry, Suppl. II,
Longmans, Green & Co., Ltd. (New York, 1956),
Part I, pp. 369, 482, 488, 709, 744, 837
120. H.W. CREMER and D.R. DUNCAN: J.Chem.Soc. (1933), 181
121. Y. YAGI and A.I. POPOV: J.Inorg.Nuclear Chem. 29 (1917), 2223
122. A. WURTZ: Compt.rend. 24 (1847), 288
123. H. WICHELHAUS: Ber. 1 (1868), 77
124. A. MICHAELIS: Ber. 5 (1872), 411
125. M. TARIBLÉ: Compt.rend. 116 (1893), 1521
126. T. MILOBEDZKI and S. KRAKOWIECKI: Chem.Abs. 23 (1929), 1833
127. L. KOLDITZ and A. FELTZ: Z.anorg.Chem. 293 (1957), 286
128. G.S. HARRIS and D.S. PAYNE: J.Chem.Soc. (1956), 4613
129. Y.A. FIALKOV and A.A. KUZ'MENKO: Zhur. obshchei Khim. 21
(1951), 433
130. A.A. KUZ'MENKO: Ukrain.Khim.Zhur. 18 (1952), 589
131. A.I. POPOV, D.H. GESKE and N.C. BAENZIGER: J.Amer.Chem.
Soc. 78 (1956), 1793

132. R.S. NYHOLM: Proc.Chem.Soc. (1961), 276
133. M.F. ALI: Ph.D. Thesis (University of St. Andrews, 1968)
134. R.E. BUCKLES and J.F. MILLS: J.Amer.Chem.Soc. 76 (1954),
3716
135. E. NIELD, R. STEPIENS and J.C. TATLOW: J.Chem.Soc. (1959),
166
136. L.A. WALL, R.E. DONADIO and W.J. PUMMER: J.Amer.Chem.Soc.
82 (1960), 4846
137. D.D. MAGNELLI, G. TESI, J.U. LOWE and W.E. McQUISTION:
Inorg.Chem. 5 (1966), 457
138. (a) M. GREEN and D. KIRKPATRICK: Chem. Comm. (1967), 57
(b) M. GREEN and D. KIRKPATRICK: J.Chem.Soc.(A) (1968), 483
139. H.J. EMELEUS and G.S. HARRIS: J.Chem.Soc. (1959), 1494
140. G.S. HARRIS: Ph.D. Thesis (University of Glasgow, 1956)
141. P. NANNELLI, G.R. FEISTEL and T. MOELLER: Inorg.Synth. 9
(1967), 73
142. D.R. DUNCAN: Inorg.Synth. 1 (1939), 151
143. A.D. BEVERIDGE and G.S. HARRIS: J.Chem.Soc. (1964), 6076
144. A.D. BEVERIDGE, G.S. HARRIS and F. INGLIS: J.Chem.Soc. (A)
(1966), 520
145. G.S. HARRIS and D.S. PAYNE: J.Chem.Soc. (1956), 3038
146. D. JAQUES: J.Chem.Educ. 42 (1965), 429
147. G.A. FORCIER and J.W. OLVER: Analyt.Chem. 37 (1965), 1447
148. J.W. SMITH and L.B. WITTEN: Trans.Faraday Soc. 47 (1951),
1304
149. A.I. POPOV and E.H. SCHMORR: J.Amer.Chem.Soc. 74 (1952),
4672
150. J. CORNOG and R.A. KARGES: Inorg.Synth. 1 (1939), 165
151. H.S. BOOTH and W.C. MORRIS: Inorg.Synth. 1 (1939), 167
152. A.E. GODDARD: A Textbook of Inorganic Chemistry, ed.
J. Newton Friend, Griffin & Co., Ltd. (London,
1936), Vol. XI, Part III, p. 53.