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A STUDY BY ^{31}P N.M.R. OF PHOSPHORUS COMPOUNDS AND COMPLEXES IN LIQUID HYDROGEN CHLORIDE

by

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Declaration

The work described in this thesis was carried out in the University of Durham between September 1970 and August 1972. This work has not been submitted, either wholly or in part, for a degree in this or any other University and is the original work of the author except where acknowledged by reference.

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ABSTRACT

The oxidation and exchange reactions of simple phosphorus compounds and the behaviour of a range of low valent triphenylphosphine complexes of the transition metals in liquid hydrogen chloride at room temperature were studied by ^{31}P nuclear magnetic resonance spectroscopy.

When oxidation did occur, the phosphorus was oxidised from the +3 to the +5 oxidation state. In general, five co-ordinate fluorine containing phosphorus(V) species were produced from the oxidation of phosphorus(III) fluoride and four co-ordinate species of type $PBr_xCl_{4-x}^+$ $(0 \leq x \leq 4)$ from the oxidation of phosphorus(III) bromide or chloride. The ^{31}P n.m.r. chemical shifts of the complete series $PBr_xCl_{4-x}^+$ $(0 \leq x \leq 4)$ were recorded in solution for the first time, stabilised by tetrachloroborate anions in liquid hydrogen chloride.

The protonation of a series of oxygen containing phosphorus(V) compounds in the solvent at room temperature was investigated using ^{31}P n.m.r. spectroscopy. A measure of the "acidity" of liquid hydrogen chloride was obtained from comparison of chemical shift values with values for the protonated species in other acidic room temperature solvents.

The behaviour of the boron trihalides and tetrahaloborate ions in the solvent at room temperature was studied by ^{11}B n.m.r. spectroscopy.

The behaviour of low valent triphenylphosphine complexes of iron, cobalt, nickel, copper, ruthenium, rhodium, palladium, iridium, platinum and gold in the solvent was investigated using ^{31}P n.m.r., and where appropriate ^{11}B n.m.r., spectroscopy. Protonation of the iron(0) complexes $Fe(CO)_{5-x}(Ph_3P)_x$ (x = 1,2) in the presence of the Lewis acid BCl_3 was observed. Oxidative addition reactions took place between the iridium(I) and rhodium(I) complexes $(Ph_3P)_2M(CO)Cl$ (M = Ir,Rh) and the solvent. Finally, the oxidation of platinum(0) to platinum(II) in reactions between tris- and tetrakis(triphenylphosphine)platinum(0) and liquid hydrogen chloride was observed.

Products were characterised by elemental analysis, Raman and infrared, and ^{31}P and ^{11}B nuclear magnetic resonance spectroscopy.

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CHAPTER 1

1.1 Introduction

The study of non-aqueous solvents is a well established branch of Inorganic Chemistry. Many possible types of system have now been investigated, the most recent addition being fused salts. The general field of solvent systems has been the subject of many reviews including those by Addison,[1] Audrieth and Kleinberg,[2] Emeleus and Anderson,[3] Gutmann,[4] Drago and Purcell,[5] and most recently Waddington.[6] The main aim of these researches has been to compare similarities and differences in the chemical behaviour of the solvents and that of water, and results tend to suggest that although water possesses "very good" solvent properties, it is by no means unique and similar reactions can occur in other liquid inorganic substances. The emphasis in recent work has largely been directed towards useful preparations, though in many cases the modes of ionisation of the solvents are still open to doubt.

The solvent properties of liquid hydrogen chloride were first studied a little over a century ago by Gore,[7] who rather hazardously prepared his hydrogen chloride in a totally enclosed system from ammonium chloride and concentrated sulphuric acid, the reagents used until a few years ago. His experiments were necessarily of a qualitative nature, being confined to visually observing any reaction between the solvent and mostly simple inorganic materials. Of the sixty six compounds studied only ten were found to be soluble and Gore concluded that "liquid hydrogen chloride has but a feeble solvent power for solid bodies in general". This statement is still true today for inorganic salts with high lattice energy. Leaving his work on liquid hydrogen chloride, he later investigated the solvent properties of liquid hydrogen fluoride which was found to be a rather better solvent. It is interesting to note that of the two solvent systems investigated the problem of cooling required for liquid hydrogen chloride work was much more serious than the extreme reactivity of liquid hydrogen fluoride.

After a break of almost fifty years the work in liquid hydrogen chloride was resumed for about a decade at McGill University by Archibald, McIntosh and Steele.[8] Again cooling was a major problem, there being no supply of liquid air, and the low temperatures required (-100°C) were obtained by evaporating ether previously cooled with solid carbon dioxide. The results obtained at McGill are collected together and published in a long paper,[8] divided into four sections. Each of these is complete in itself and describes elegant experimental work carried out under difficult conditions.

In the first section physical and thermodynamic properties of the hydrogen halides are described. The variation of vapour pressure and density as a function of temperature, surface energy and viscosity were studied. Surface energies were measured using the method of Ramsay and Shields, the apparatus being cleverly redesigned for use at low temperatures. Viscosities were measured, again using apparatus specially designed for use at low temperatures. The second section deals with solubility, conductivity and ebullioscopic measurements. Some of the results were anomalous, probably due to the presence of triple ions and ion pairs as well as single ions. The measurement of transport numbers in liquid hydrogen bromide is described in the third section, this being experimentally the most difficult part of the work. Again temperature was the critical factor in the choice of solvent. A slurry of solid carbon dioxide in ether gives a temperature of -81°C, at which point hydrogen bromide is a liquid with a vapour pressure of less than one atmosphere. Faraday's Laws of Electrolysis were found to obtain in the solvent and Hittorf's method was used for the determination of transport numbers. The results of the work are set out in the last section but little correlation could be established between dissolving power, dielectric constant, conductivity and abnormalities in molecular weight determinations.

There was then a slight change in the emphasis of the work and the basic properties of oxygen in organic compounds were investigated. The compounds formed by the hydrogen halides with methanol, acetaldehyde, acetic acid and ethyl acetate were studied.[9] Phase diagrams were derived for hydrogen chloride with methanol,[10] dimethyl[10] and diethyl ether,[11] hydrogen sulphide,[12] benzene,[12] propionic acid[12] and methyl chloride.[13] Compounds were detected in the first three cases only. The addition compounds of acetone and hydrogen chloride were also investigated.[14] In the water-hydrogen chloride system the compounds $HCl.3H_2O$, m.p. -24.4, $HCl.2H_2O$, m.p. -17.7[15] and $HCl.H_2O$ m.p. -15.4°C have been detected,[16] more recent work showing that $HCl.H_2O$ has the structure $H_3O^+Cl^-$ with every hydrogen joined by a hydrogen bond to the nearest chloride ion.[17] The phase diagram study of hydrogen chloride with π orbital donor molecules has been carried out. Nitriles were the first to be studied,[18] and then the work was extended to olefines, acetylenes and aryl compounds.[19]

Direct work on the solvent properties of liquid hydrogen chloride was restarted in the late 1950's by Dr. T.C. Waddington with the assistance of Dr. F. Klanberg. At this stage many refinements of method were introduced. Vacuum line techniques were used and there was a plentiful supply of liquid nitrogen available for cooling purposes. Many acid-base type reactions were studied and the work was published in six papers.[20] The first[20a] discusses the existence of hexachlorogermanates and the failure of germanium tetrachloride to act as a solvo-acid. The second paper[20b] is a note on the preparation of new co-ordination compounds of boron with the halogens as ligands. The next paper[20c] deals with compounds derived from nitrosyl chloride which are formed in liquid hydrogen chloride. The conductivities of a selection of possible solvo-acids and solvobases are reported.[20d] These were utilised in the preparation of the new compounds Me_4NSO_3Cl, PCl_4BF_3Cl, PH_4BF_3Cl, PH_4BCl_4, and $PCl_3O.BF_3$,[20e] whose infrared spectra are reported.[20f]

The higher hydrogen halides, hydrogen bromide and hydrogen iodide were also studied during this period[21,22,23] and comparisons were made between them and hydrogen fluoride and chloride. The work described is mainly an extension of the liquid hydrogen chloride system, tetrabromoborates and tetraiodoborates having been prepared. Liquid hydrogen iodide is extremely difficult to handle being readily photolysed to hydrogen and iodine, the latter substance being virtually impossible to remove.

Further acid-base reactions in liquid hydrogen chloride were investigated by Professor T.C. Waddington and Dr. M.E. Peach.[24] Conductiometric titrations were extensively used in this study, in which it was observed that strong aquo-acids did not function as acids in the solvent. Only chloride ion acceptors showed acidic properties. Strong bases were also investigated. They could function as either chloride ion donors or proton acceptors and illustrated the role of liquid hydrogen chloride as a chloridotropic or a protonic solvent. The acidic behaviour of boron compounds,[25] non-metallic fluorides,[26] strong aquo-acids and aquo-acid anhydrides were investigated.[24] The basic properties of some simple derivatives of groups IV, V and VI[27] and of compounds containing multiple bonds,[28] particularly double bonded oxygen[29] were studied. Many of the group IV, V and VI compounds were observed to act as bases by acquiring a proton forming "onium" species.[27] This behaviour is paralleled in liquid hydrogen fluoride by many organic compounds containing oxygen or nitrogen.[30-33] Infra-red spectroscopy (in the range 4000 to 400 cm^{-1}) proved to be a useful technique in this work; not only in rapid characterisation of compounds with known infra-red absorptions, but also enabling useful structural information of unknown compounds to be deduced.

Several new compounds were prepared. Using diboron tetrachloride as a solvoacid, the tetrachlorodiborate anion $B_2Cl_6^{2-}$ was isolated as its tetramethylammonium and tetrachlorophosphonium salts.[34] Acetyl heptachlorodialuminate was isolated, and end-points corresponding to the formation of tetrachloroaluminate and heptachlorodialuminate were observed in a conductiometric titration.[35] N,N-diphenylhydrazinium,[27] azobenzinium and m-azotoluenium[28] tetrachloroborates were prepared and isolated.

Phosphorus pentafluoride was found to act as a source of hexafluorophosphate ion in liquid hydrogen chloride and some protonated bases were stabilised at room temperature using this anion.[26] Phosphorus trifluoride dichloride was always produced in these reactions.

The study of group VI compounds was extended by Peach.[36] Dimethylchlorosulphonium and methyldichlorosulphonium ions were prepared and characterised as their tetrachloroborates and hexafluorophosphates, and the ethyl analogues as tetrachloroborates. Dimethyl selenium and dimethyl tellurium were found to be strong solvobases and could be oxidised to their dichlorides. Sulphur, selenium and tellurium tetrachlorides showed neither acidic nor basic properties in the solvent, while sulphur monochloride and dichloride, selenium monochloride and tellurium dichloride were non-basic. New compounds prepared include $Me_2S_2.BCl_3$ and $Me_2Te.BCl_3$..

Archibald, McIntosh and Steele[8] had investigated the variation of equivalent conductivity with concentration in the liquid hydrogen halides but were unable to arrive at any firm conclusion other than the fact that some association was taking place. This phenomenon was reinvestigated[22,37] and on replotting their results it was found that the equivalent conductivity was proportioned to the square root of the concentration for values greater than about 0.2 molar. The variation of the conductivities of salts with concentration in solvents of low dielectric constant has been studied by Fuoss and Kraus,[38,39] who found that plots of log Λ against log c showed a minimum which moved to higher concentrations as the dielectric constant of the solvent increased. With aqueous solutions the point was at too high a concentration to be observed. To explain their observations Fuoss and Kraus postulated that a simple salt AB can dissolve to form ion pairs A^+B^- which dissociate into single ions, A^+ and B^-, at low concentrations and triple ions at high concentrations. The measurements in liquid hydrogen chloride[37] were not sufficiently accurate to deduce the nature of the species in solution at low concentrations, but they did indicate triple ion formation in more concentrated solutions. Fuoss and Kraus predict that for a solvent with dielectric constant about 9 the minimum should occur at a concentration near 2.5×10^{-2}M. Liquid hydrogen chloride has a dielectric constant of

9.3 at -95°C[40] and it was found that the minimum occurred at a concentration in the region of 10^{-2}M. The minimum in liquid hydrogen sulphide, dielectric constant 10.2,[40] also occurs at a concentration of about 10^{-2}M.[41]

While this work was being carried out Professor T.C. Waddington and Dr. J.A. Salthouse reported the preparation in liquid hydrogen chloride of the compounds $Bu^n_4N^+HBrCl^-$ and $Bu^n_4N^+HClI^-$, containing the previously unknown mixed hydrogen dihalide anions.[42] The hydrogen dihalide anions HF_2^-,[43] HCl_2^-,[44] HBr_2^-,[45] and HI_2^- [46] are all known as their salts, the former for many years, though its structure has only fairly recently been elucidated.[47] The new compounds $Me_4N^+HClNO_3^-$ and $Me_4N^+DClNO_3^-$ were prepared[48] along with the deuterated species of all the known hydrogen dihalide anions and their infrared spectra recorded. Some controversy has surrounded the interpretation of the infra-red vibrational spectra of the HCl_2^- ion, and it has been suggested that the ion exists in two forms depending on the nature of the associated cation;[44,49] in compounds of the first type the HCl_2^- ion is unsymmetric, (e.g. $CsHCl_2$, Me_4NHCl_2) whereas in compounds of the second type the ion is symmetric [e.g. $(C_2H_5)_4NHCl_2$, $(C_3H_7)_4NHCl_2$]. A recent inelastic neutron scattering and Raman study of $CsHCl_2$[50] has confirmed the noncentrosymmetricity of the HCl_2^- ion in this compound postulated by Evans and Lo[49] and a nuclear quadrupole resonance investigation of the ion in a number of compounds has indicated that there are in fact two different structures dependent upon counterion.[51]

The reactions of the tetra-alkylammonium halides in liquid hydrogen chloride with the halogens, interhalogens and related compounds were investigated.[52] Some of the reactions were acid-base type whilst others were oxidations. Because oxidation-reduction reactions had been little studied in non-aqueous systems, the experiments in liquid hydrogen chloride were confined in the first instance to systems where the oxidation products might be reasonably well known. Only in one case was there evidence for the formation of an AB_4^- ion, the most common ion was of the AB_2^- (A and B are similar or dissimilar halogens). When, instead of a halogen, nitrosyl chloride or dinitrogen tetroxide was used to oxidise iodide ion in the solvent, nitric oxide and iodine were liberated.

The reactions of the halogens and related compounds with phosphorus (III) compounds in liquid hydrogen chloride were then investigated.[53] Where oxidation occurred the phosphorus was oxidised from the +3 to the +5 oxidation state. The new ions bromotrichlorophosphonium and triphenylchlorophosphonium were stabilised as their tetrachloroborate salts.

Of the higher group V trihalides investigated only arsenic trifluoride gave any reaction in liquid hydrogen chloride, being solvolysed to arsenic trichloride.[54] The remaining compounds were neither protonated nor oxidised by halogens. The new adduct $Me_2AsCl.BCl_3$ was isolated. Oxidation of the arsenic from the +3 to the +5 oxidation state did occur when triphenylarsine was treated with the halogens and interhalogens in the solvent, and the triphenylchloroarsonium cation was stabilised in the tetrachloroborate salt. In these oxidation studies the techniques of weight analysis[55] and conductiometric titration were extensively used to follow reactions.

Following these fruitful studies, the reactions of pentacarbonyliron in liquid hydrogen chloride with the halogens, nitrosyl chloride, boron trichloride and phosphorus pentafluoride were reported.[56] Conductiometric titrations with the solvoacids BCl_3 and PF_5 indicated that pentacarbonyliron was protonated in the solvent and the new cationic species $Fe(CO)_5H^+$ was isolated as the hexafluorophosphate salt. Pentacarbonyliron was oxidised in the solvent by chlorine and bromine to $Fe(CO)_5Cl^+$ and $Fe(CO)_5Br^+$ respectively. Again stable tetrachloroborates were isolated and characterised. The pentacarbonyl also reacted with nitrosyl chloride in liquid hydrogen chloride, to give the compound $Fe(CO)_5NO^+Cl^-$. The structure of the cations produced was discussed in terms of their infra-red and ultraviolet absorption spectra and magnetic properties.

The reactions of tetracarbonylnickel and tricarbonylnitrosylcobalt in the solvent did not parallel those of pentacarbonyliron.[57] Titrations of these compounds against phosphorus pentafluoride showed a break at ca. 1.0:1.0, which indicated adduct formation rather than protonation. Solid products were not isolated from these reactions, nor from the reaction between tetracarbonylnickel and boron trichloride. Two new compounds tetrachlorotricarbonyldinickel and dichlorodinitrosylnickel were prepared and isolated and their structures discussed in terms of their infra-red spectra and magnetic properties. The reactions of tricarbonylnitrosylcobalt in the solvent with chlorine and nitrosyl chloride yielded only cobalt(III) chloride.

Interesting studies of π-cyclopentadienyl iron carbonyls in liquid hydrogen chloride have recently been reported from these laboratories.[58] π-Cyclopentadienyldicarbonyliron dimer is monobasic in liquid hydrogen chloride giving the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2H^+$ ion which has been stabilised in its tetrachloroborate and hexafluorophosphate salts. Mössbauer, proton magnetic resonance and infra-red spectroscopic evidence indicate that this cation consists of two $(\pi\text{-}C_5H_5)Fe(CO)_2$ units linked by a symmetric Fe-H-Fe bridge. Reaction of a solution of the dimer with nitrosyl chloride or chlorine gave mixtures containing π-cyclopentadienyldicarbonyliron chloride. This latter compound and π-cyclopentadienyltricarbonyliron chloride act as bases in the solvent forming $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Cl^+BCl_4^-$ and $(\pi\text{-}C_5H_5)Fe(CO)_3{}^+BCl_4^-$ respectively on treatment with boron trichloride.

1.2 Theory of the Solvent.

The conductivity of pure liquid hydrogen chloride is 0.35×10^{-8} mho cm^{-1} at -85^o [59] whilst that of pure water is 5×10^{-8} mho cm^{-1} at 18^oC.[60] These values are of the same order of magnitude and to account for them self-ionisation is assumed. In the case of water the simplest possible equilibrium involved would be

$$H_2O \rightleftarrows H^+ + OH^-$$

It is, however, generally accepted that the proton is solvated and the equilibrium is more often written:

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$

In these postulated equilibria the anion is shown unsolvated which is probably untrue, but the degree of solvation is not known. Following the location of the species $H_9O_4{}^+$ in solution,[61] the series of cations H_3O^+,[17] $H_5O_2{}^+$,[62] $H_7O_3{}^+$ and $H_9O_4{}^+$ [63] have been characterised by X-ray crystallography, indicating that the degree of solvation of the proton is indeed far higher than shown.

For the hydrogen halides the basic process involved is

$$HX \rightleftarrows H^+ + X^-$$

and to account for association effects the equilibrium is usually written

$$3HX \rightleftarrows H_2X^+ + HX_2^-$$

The exact degree of solvation in solution is unknown.

In the liquid hydrogen fluoride system there is some evidence for the existence of the hydrofluoronium ion H_2F^+. The ion has been detected by conductivity measurements, Raman and infrared spectra as a hexafluoroantimonate in the HF/SbF_5 system,[64] and there is some suggestion of its existence in the mixtures HF/BrF_5[65,66] and HF/IF_5.[66] Hantzsch[67] claimed to have prepared $H_2F^+ClO_4^-$ which was explosive. H_2FBF_4 was both unstable and explosive, while H_2FHSO_4 could not be isolated.[67] There is ample evidence for the existence of the hydrogen difluoride ion HF_2^- [2,6,68,69] and the isolation of crystalline $Cs^+H_6F_7^-$ is indicative of even higher solvation of the anion.[69]

The ion H_2Cl^+ may exist in the compounds $HCl.HClO_4$ which is explosive, $HCl.H_2SO_4$ which could not be isolated as a solid[67] and $HCl.HBr$.[70] This latter compound was detected in the phase diagram HCl/HBr and has been claimed to have the structure $H_2Cl^+Br^-$.[71] del Fresno compared the H_2Cl^+ and H_2Br^+ ions with the isoelectronic K^+ and Rb^+ ions and then examined the lattice energies of the alkali metal chlorides and bromides. By this somewhat unconvincing process the structure $H_2Br^+Cl^-$ was eliminated. Observations consistent with the presence of H_2Cl^+ [72,73] and H_2Br^+ [74] have been made in gas phase spectroscopic studies.

The existence of the hydrogen dichloride ion is firmly established. For many years it was known that organonitrogen bases formed halide salts containing an extra formula unit or more of the hydrogen halide,[75,76] but it was only recently realised[77] that this probably pointed to the existence of acid halide ions such as hydrogen dichloride, HCl_2^-. The ion was finally isolated and characterised more completely as its tetramethylammonium salt.[44] The alkali metals do not form stable hydrogen dichloride salts at room temperature owing to the high dissociation pressure of the hydrogen chloride, 4.4 atm. for $Cs^+HCl_2^-$.[78] West's reported preparation of this salt[79] was shown to be incorrect, the compound isolated being $CsCl.\frac{3}{4}HCl.\frac{3}{4}H_2O$ [78] and having the structure $4Cs^+Cl^-.3H_3O^+Cl^-$.[80] Reports concerning the structure of the HCl_2^- ion have been given earlier in this thesis. There is evidence for the low temperature existence of $Cl(HCl)_2^-$, but this anion could not be stabilised at room temperature,[81] unlike the stable series $F(HF)_x^-$ $(2 \leq x \leq 5)$ from the liquid hydrogen fluoride system.[68,69]

The hydrogen dihalide ions have been characterised in the liquid hydrogen bromide[22,45,46,82] and hydrogen iodide[21,46,83] systems, and the low temperature existence of the species $X(HX)_2^-$ has been postulated.[81]

Thus for the liquid hydrogen halides the equilibrium

$$3HX \rightleftarrows H_2X^+ + HX_2^-$$

may be assumed to represent the minimum degree of solvation of the species H^+ and X^- in solution. The self-ionisation of liquid hydrogen chloride

$$3HCl \rightleftarrows H_2Cl^+ + HCl_2^-$$

leads to two definitions of acids and bases in the solvent, depending on whether the primary step in the equilibrium is considered as proton or chloride ion transfer. Acids can then be defined as proton donors or chloride ion acceptors and bases as proton acceptors or chloride ion donors. This is of course a difference of emphasis rather than principle. Liquid hydrogen chloride can thus be considered as either a protonic or as a chloridotropic solvent. This double identity can be seen in its reactions, some of which are typical of protonic solvents and others characteristic of chloridotropic solvents. Useful protonic solvents for comparison are HF, HCN, H_2SO_4 and CH_3COOH.[2] The reactions of organic[84] and inorganic compounds[85] in sulphuric acid have been the subject of two extensive reviews. Hydrogen chloride is a simpler system for the study of organic compounds than H_2SO_4 in which sulphonation occurs as a side effect. Chloridotropic solvents for comparison include $AsCl_3$,[4] $SbCl_3$,[86] ICl,[4,87] and CNCl.[88]

The physical constants of the hydrogen halides and those of water are shown in Table1.21.Hydrogen fluoride and water are very similar in that they have long liquid ranges, high boiling points, and high dielectric constants. The anomalously high boiling points are indicative of extensive association in the liquids. By reason of the high dielectric constants many substances are soluble, including many ionic inorganic substances i.e. "simple salts".[2,30,94-97] In these cases the solvation energy is greater than the lattice energy. The three higher hydrogen halides would be expected to show similar solvent properties as they have short liquid ranges, similar values of Trouton's constant and low dielectric constants. The lower values of Trouton's constant and absence of anomalously high boiling points indicate that the degree of association in these liquids is lower than that found in water and hydrogen fluoride. As a consequence of the low dielectric constants ordinary simple salts are insoluble in the higher hydrogen halides as the lattice energy will be much greater than the solvation energy. Only ionic salts of low lattice energy will be soluble, and as lattice energy is proportional to $\frac{1}{r_+ + r_-}$ (where r_+, r_- are cationic and anionic radii respectively) a

TABLE 1.2.1

Physical Properties of Water and the Hydrogen Halides

	H_2O	HF	HCl	HBr	HI
Molecular weight	18.0	20.0	36.5	80.9	127.9
M.p. ($^{\circ}$C)	0.0	-83	-114.6	-88.5	-50.9
B.p. ($^{\circ}$C)	100.0	19.5	-84.1	-67.0	-35.0
Liquid range (C$^{\circ}$)	100.0	102.5	30.5	21.5	15.9
Critical temp. ($^{\circ}$C)		230	51.5	89.8	150.9
Density of liquid (g.cm^{-3} near m.p.)	1.0 (0°)	1.2 (-80°)	1.2 (-114°)	2.6 (-84°)	2.9 (-47°)
Molecular volume (cm^3)	18.0	16.7	30.4	31.1	44.1
Latent heat: (cal.mole^{-1})					
Fusion	1440	1094	476	600	686
Vaporisation	9720	7230	3860	4210	4724
Trouton's Constant	26.0	24.7	20.4	20.4	19.8
Dielectric constant of liquid	84.2 (0°)	175 (-73°)	9.3 (-95°)	7.0 (-85°)	3.4 (-50°)
Viscosity (centipoises)	1.00 (22°)	0.24 (0°)	0.51 (-95°)	0.83 (-67°)	1.35 (-35.4°)
Specific conductivity (μmho.cm^{-1})	0.05 (18°) (60)	0.1 (-80°) (89)	0.0035 (-85°) (59)	0.00014 (-84°) (22)	0.00085 (-45°) (90)
H-X stretching frequency (cm^{-1})	3658* (91)	3961 (92)	2886 (92)	2558 (92)	2230 (92)
Dipole moment (D)	1.87	1.92	1.08	0.78	0.38
Vibration-Rotation Constant ω_e (cm^{-1}) (6a)		4138.33	2996.94 2998.48	2649.65	2309.53

* value for OH radical

Values quoted in this table are taken either from Mellor (40) or from the Handbook of Chemistry and Physics (90) unless a specific reference is shown.

cation of large radius is required. This condition is satisfied by the tetraalkylammonium cations whose halides are found to be soluble in the higher hydrogen halides. It is not expected that the tetraalkylammonium ions will be solvated to any extent as they are large and symmetrical, but the halide ions will be solvated as is usual.[98] A further direct consequence of the low dielectric constant is the complex variation of equivalent conductivity with concentration observed in the higher liquid hydrogen halides.[22,37]

The mechanism of conduction in liquid hydrogen chloride is unknown, but it has been postulated that chloride ion transfer could occur.[99] Salthouse suggested that in basic solutions in the solvent the process

Cl ----- H ----- Cl^- H ----- Cl

Cl -----H   Cl ----- H ----- Cl^-

could occur. This means that all univalent bases should have virtually the same molar conductivity at infinite dilutions.

Recent work[37] has neither confirmed nor disproved this postulate, but this is in all probability due to the practical difficulties encountered in attempting to accurately measure equivalent conductivities at very low concentrations. Such a mechanism would be analogous to the process of "proton jumping" encountered in aqueous acidic solutions.

1.3 Outline of Present Work

The work described in this thesis is initially a direct continuation of the oxidation studies begun by Dr. J.A. Salthouse and later an extension of the studies of transition metal complexes in the solvent. The early oxidation studies of phosphorus(III) compounds were carried out at low temperatures and reactions followed by conductiometric titrations. In this study ^{31}P nuclear magnetic resonance was used to follow oxidation and exchange reactions in the solvent at room temperature. ^{31}P n.m.r. spectra of liquid hydrogen chloride solutions and of solid products enabled reactions in the solvent to be more closely followed and more fully understood. Where oxidation did take place, the phosphorus was oxidised from the +3 to the +5 oxidation state. Phosphorus trichloride and phosphorus tribromide were oxidised by bromine and chlorine respectively in the solvent. The ^{31}P chemical shifts of species $PBr_xCl_{4-x}^+$ $(0 \le x \le 4)$, stabilised as tetrachloroborates, were measured in liquid hydrogen chloride. ^{11}B nuclear magnetic resonance was used to investigate the boron containing anions produced.

Covalent 5-co-ordinate species were obtained on oxidation of phosphorus trifluoride, and the slow exchange of these compounds with the solvent was followed. Attempts to produce iodine containing oxidised species were unsuccessful, only phosphorus(III) interhalogen exchange products being observed.

With the exception of phosphorus tribromide the phosphorus(III) halides did not exchange with the solvent. In this case PBr_3, PBr_2Cl and $PBrCl_2$ were the species in solution. An identical composition was produced by the total solvolysis of phosphorus trichloride in liquid hydrogen bromide.

A range of low valent triphenylphosphine complexes of the transition metals were studied in the solvent at room temperature. Complexes examined include those of iron, cobalt, nickel, copper, ruthenium, rhodium, palladium, iridium, platinum and gold.

The techniques of conductiometric titration and weight analysis were of little use owing to the low solubilities of many of the compounds studied. ^{31}P n.m.r, and ^{11}B n.m.r. where appropriate, were used to follow reactions in the solvent at room temperature. Many reactions could not be followed by nuclear magnetic resonance due to low solubilities of the starting materials even at room temperature, formation of insoluble products, or unfavourable magnetic properties of certain transition metal nuclei. In some cases reactions went to completion even though the starting material appeared to be largely insoluble.

The triphenylphosphine substituted iron carbonyls $Fe(CO)_4Ph_3P$ and $Fe(CO)_3(Ph_3P)_2$ were shown to be protonated in liquid hydrogen chloride by the Lewis acid boron trichloride and the new compound $Fe(CO)_3(Ph_3P)_2H^+BCl_4^-$ was isolated. Oxidative addition took place when trans-chlorocarbonybis(triphenylphosphine)iridium(I) was placed in the solvent and the stable product $Ir(Ph_3P)_2(CO)Cl.HCl$ was characterised. Evidence is also presented for the formation of the unstable rhodium analogue $Rh(Ph_3P)_2(CO)Cl.HCl$ from $Rh(Ph_3P)_2(CO)Cl$ in the solvent.

Tetrakis(triphenylphosphine)platinum(0) and tris(triphenylphosphine)-platinum(0)) were oxidised by the solvent to cis-dichlorobis(triphenylphosphine)platinum(II). The reactions of tetrakis(triphenylphosphine)-palladium(0) and cis-dichlorobis(triphenylphosphine)palladium(II) were more complex.

Tetrakis(trifluorophosphine)nickel(0) dissolved in liquid hydrogen chloride without protonation or dissociation. A low temperature conductiometric titration against boron trichloride indicated adduct formation, but no new compound could be isolated. The corresponding trichlorophine compound, $Ni(PCl_3)_4$, was insoluble in the solvent at room temperature though there is evidence for some reaction.

The behaviour of white phosphorus in liquid hydrogen chloride and its oxidation by chlorine to phosphorus trichloride in the solvent were investigated using ^{31}P nuclear magnetic resonance spectroscopy. A similar study of phosphine was carried out.

The protonation of a series of oxygen containing phosphorus(V) compounds in liquid hydrogen chloride at room temperature was investigated using ^{31}P nuclear magnetic resonance spectroscopy. Some idea of the "acidity" of the solvent was derived from comparison of chemical shift values with values for the protonated species in other acidic room temperature solvents. No attempt was made to isolate products in this section of the work.

Reactions in other non-aqueous solvents were performed in cases where a useful comparison could be made with work in liquid hydrogen chloride, or when an interesting reaction could conveniently be followed by nuclear magnetic resonance methods. The oxidation study of boron trichloride in liquid sulphur dioxide is an example of the latter case.

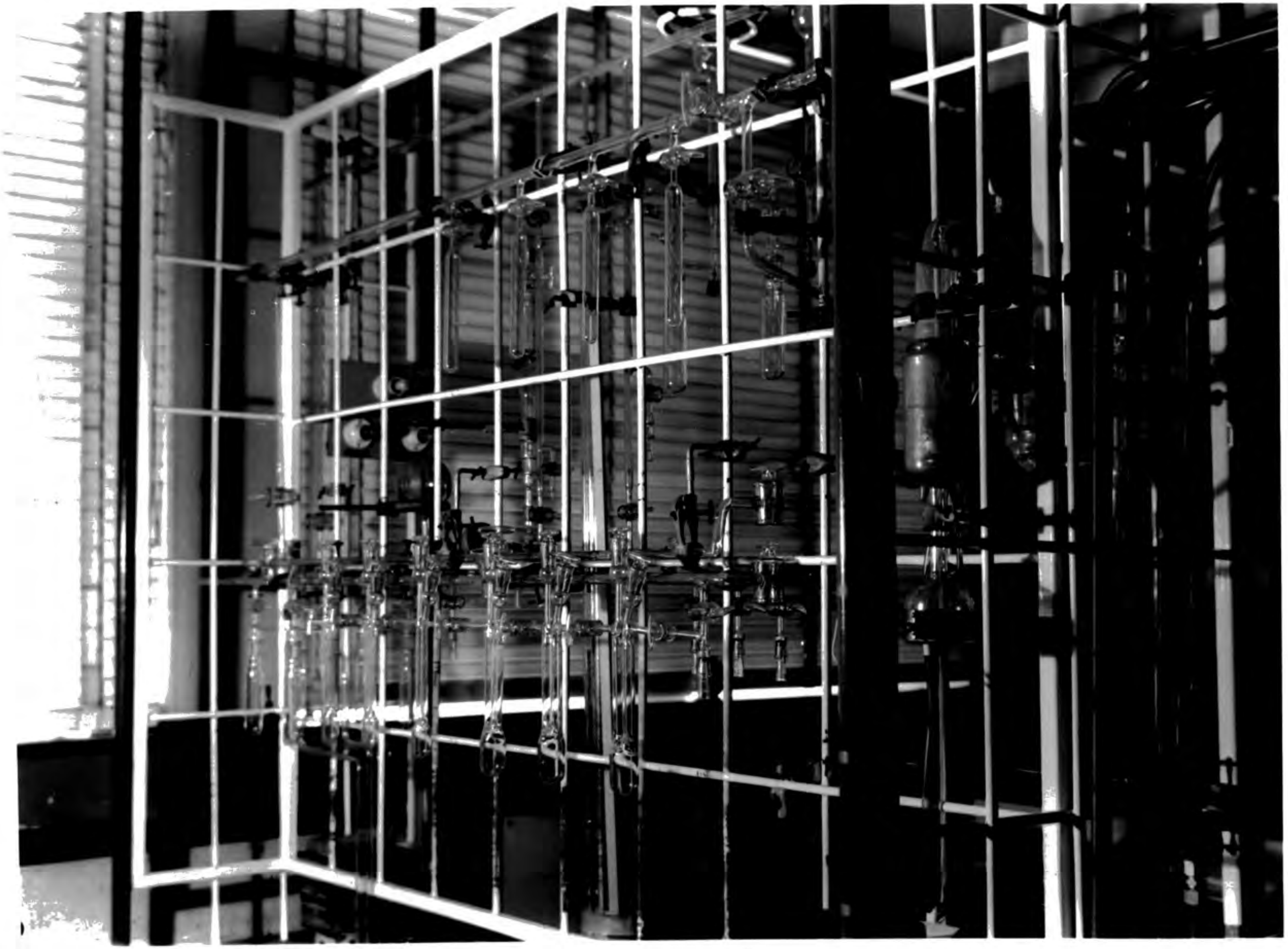
Products were characterised by elemental analysis, Raman and infra-red, and ^{31}P and ^{11}B nuclear magnetic resonance spectroscopy.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

Plates 2.1.1, 2.1.2

The Vacuum System



2.1 The Vacuum System

Throughout the course of the experimental work described in this thesis volatile materials were handled in a conventional pyrex glass vacuum system, shown diagrammatically in Figure 2.1.1 and in Plates 2.1.1 and 2.1.2. Such systems have been in use for many years, and have been described in some detail.[24,81] All recent work in the three higher hydrogen halide solvent systems has been carried out using similar vacuum systems, so only a brief description mentioning new developments will be given here.

The vacuum was produced by a two stage mercury diffusion pump backed by a rotary oil pump. These two pumps were protected by two traps cooled in liquid nitrogen, and if necessary, the diffusion pump could be by-passed and pumping carried out using only the rotary pump. This was occasionally done when for example the 20 litre bulbs were initially evacuated or when chlorine was being pumped out of the system, in order to protect the diffusion pump. Using the diffusion pump pressures of the order of 10^{-4} mm. of mercury could be maintained in the system. All glass taps on the vacuum system were greased with Apiezon-L grease. Previous workers[24,81] have used Kel-F grease which is resistant to attack by many reactive chlorides and fluorides which seriously attack Apiezon-L. However, in this work the vacuum holding properties of Apiezon-L were found to be superior to those of Kel-F, and it was preferable to regrease with Apiezon-L when chemical attack so necessitated. Wherever possible, the vapour pressure of halogens, boron trichloride, etc. was kept to a minimum to reduce attack on the grease.

Pressures were measured using a spiral-gauge as a null-point instrument. This particular spiral was constructed in these laboratories by Mr. R. Hart. A deflection of 90° was produced by a pressure of about 50 cm. of mercury.

The system contained a train of six traps used for fractionation of volatile substances. The first three traps were of conventional dimensions and the other traps were made significantly larger and of thicker glass. This was to enable large quantities (about 1 mole) of hydrogen chloride to be safely frozen and melted in the bulbs. Low temperatures required during fractionation were maintained using slush baths - melting organic solvents contained in Dewar vessels. A list of commonly used slush baths is given in Table 2.1.1.

After purification volatile substances were stored in various ways dictated by either their saturation vapour pressures or thermal stabilities. Six bulbs were provided for storage of gases on the line. These bulbs were fitted with TF6/13 Rotaflo valves in preference to greased taps, as the teflon sleeve forming the front and back seals is immune from chemical attack. A greased tap was always used to back rotaflo valves used for this purpose. Hydrogen chloride was stored in four 20 litre bulbs and chlorine in two 10 litre bulbs. Other highly volatile compounds such as boron trifluoride and phosphorus pentafluoride were stored frozen down at liquid nitrogen temperature. Less volatile substances such as bromine and boron trichloride were stored in pyrex ampoules fitted with TF6/13 rotaflo valves and B14 cones for connection to the vacuum line. Substances liable to decompose if stored at room temperature e.g. phosphorus pentafluoride which reacts with water absorbed in the glass of storage bulbs at room temperature[100] were kept frozen down at -196°C.

Fig.2.1.1

The Vacuum System

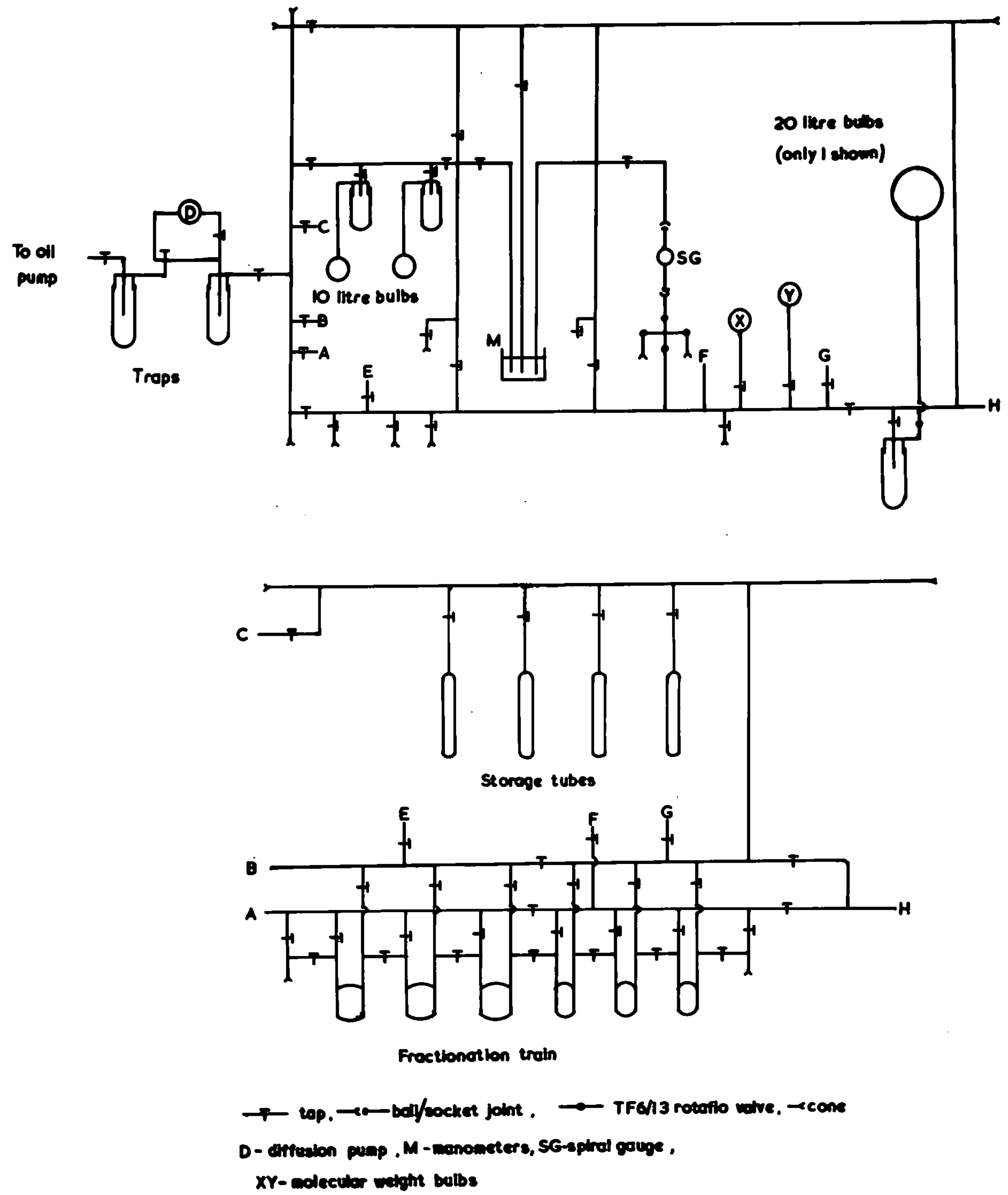

To oil pump
D
Traps
C
B
A
E
10 litre bulbs
M
SG
F
X
Y
G
20 litre bulbs
(only 1 shown)
H
C
Storage tubes
E
F
G
B
A
H
Fractionation train
tap, ball/socket joint, TF6/13 rotaflo valve, cone
D - diffusion pump, M - manometers, SG-spiral gauge,
XY- molecular weight bulbs

TABLE 2.1.1

Temperature °C	Coolant
-23	Carbon tetrachloride slush
-45	Chlorobenzene slush
-64	Chloroform slush
-78	Ethanol/solid carbon dioxide slurry
-84	Acetone/solid carbon dioxide slurry or Ethyl acetate slush
-95	Toluene slush
-112.5	Carbon disulphide slush
-126	Methylcyclohexane slush
-131	n-Pentane slush
-160	Isopentane slush
-196	Liquid nitrogen

TF6/13 rotaflo valves were also used in place of greased taps on the section at the base of the spiral gauge enabling quantities of corrosive gases to be accurately measured without risk of contamination or absorption in the grease.

Highly poisonous chemicals were not stored on the vacuum line, but were kept in ampoules and stored in a refrigerator or in a dewar containing liquid nitrogen.

The spiral gauge was calibrated by observing the deflection produced by known pressures of air measured on the mercury manometers using a cathetometer. Various parts of the line were then calibrated for volume by observing pressure changes produced on expanding air into the system from a molecular weight bulb of known volume. Ideal gas behaviour was assumed to operate.

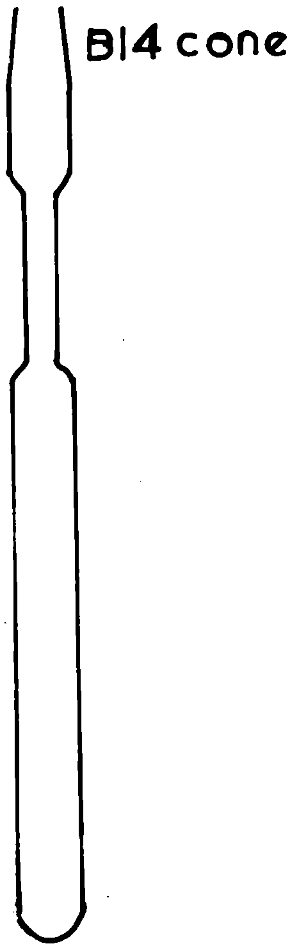
2.2 Reactions in liquid hydrogen chloride

Reactions in liquid hydrogen chloride at $-95^{o}C$ were carried out using the reaction tubes previously described.[24,81] Reactions in the solvent at room temperature were carried out in silica ampoules. Figure 2.2.1 shows typical reaction tubes.

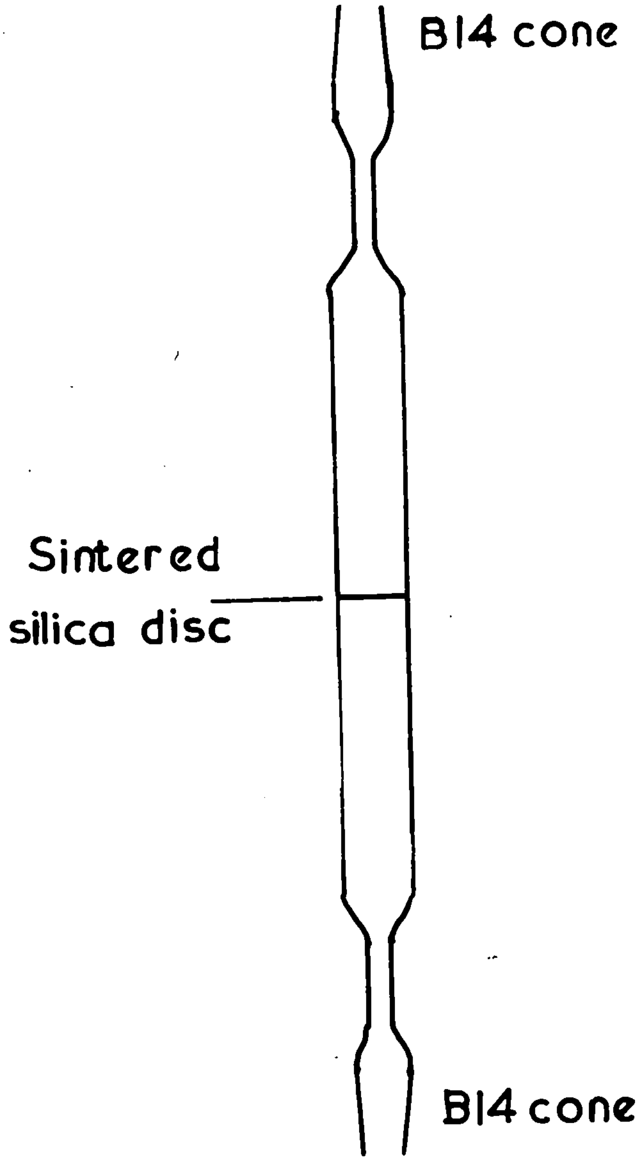
Quartz tubing supplied by Thermal Syndicate Ltd. was used for the construction of these ampoules. The main body of the ampoule shown in Fig.2.2.1(a) was of 13 mm. O.D. and the neck of 6 mm. O.D. tubing fitted with a B14 cone for connection via a cone-tap-socket adaptor to the vacuum line. The neck was usually about 10 cm. in length and was constricted when volatile materials only were to be condensed into the tube, or left unconstricted when solids were to be placed inside. The length of the main body of the tube was varied as required.

Fig.2.2.1

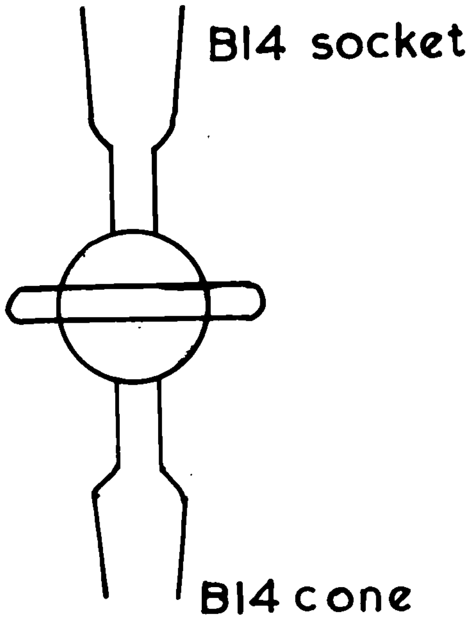
Ampoules

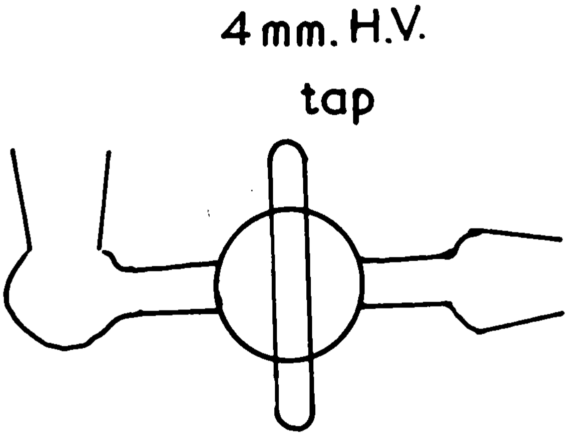

B14 cone

(a)


B14 cone
Sintered silica disc
B14 cone

(b)


B14 socket
B14 cone


4 mm. H.V. tap

Cone-tap-socket adaptors consist of a B14 cone attached to a 4 mm. H.V. tap which is joined to a B14 socket. Two types were used, linear and right angled, and are shown in Figure 2.2.1. The overall length of the linear adaptor was about 15 cm. The right angled type were used when long ampoules of types (a) and (b) were taken into the dry box. The total length of an ampoule was increased by only 2 cm. when fitted with this type of adaptor.

In a typical experiment the solid reactant would be placed inside the reaction tube whilst inside the dry box and a cone-tap-socket adaptor fitted. The tube would then be evacuated on the vacuum system taking care not to pump fine particles of solid out of the tube with the nitrogen. Hydrogen chloride gas and any other volatile reactant would be condensed into the tube at -196^{o} and the neck sealed leaving as long a neck as possible to facilitate opening later.

Tubes of type (b) were constructed of similar materials incorporating sintered silica discs at the mid-point. These tubes were designed to permit filtration of liquid hydrogen chloride solutions. Porosity 1 sinters were found to be sufficient to effect separation in experiments. Discs of finer porosities tended to seal during construction of the tubes. As this type of tube has not been used before in liquid hydrogen chloride work, a short description of its use will be given. The solid reactant is loaded into the tube whilst inside a dry box, so that it is resting on top of the sinter. Cone-tap-socket adaptors are fitted and the tube evacuated on the vacuum line. The neck of the tube is then sealed as closely as possible to the main body of the tube so that a rounded end is produced. When cool the tube is inverted so that the solid falls away from the sinter and on to the newly sealed end.

Hydrogen chloride and any other volatile compounds are then condensed at -196° into the tube, ensuring that all the condensate is below the sinter, via the remaining inlet. The tube is then sealed at the second neck.

Sealed tubes containing hydrogen chloride were placed in -84° baths to allow the hydrogen chloride to melt. This was always an anxious moment as the forces of expansion produced on the melting of hydrogen chloride are sufficient to crack even stout tubes. Having survived the first stage tubes were then placed in chlorobenzene slush baths and allowed to warm to room temperature overnight. 13 mm. O.D. quartz tubes were quite able to stand the 40 atm. pressure due to the saturated vapour pressure of hydrogen chloride at room temperature, but in cases where hydrogen and/or carbon monoxide were evolved during reaction explosions occasionally occurred. All tubes containing liquid hydrogen chloride were stored in brick emplacements inside fume cupboards.

There were two methods available for opening sealed tubes. Type (a) were cooled to a temperature at which hydrogen chloride had a low vapour pressure and then opened to the vacuum line using an ampoule breaker. Filtration was effected by inverting tubes of type (b) and warming the upper part of the tube with the hand. When filtration was complete the hydrogen chloride filtrate was frozen solid in liquid nitrogen and the tube cracked open below the sinter. This latter operation was performed in a dry nitrogen filled glove bag. The section of tube containing the solid product was placed inside a larger tube, evacuated and transferred to the dry box for further handling. The section of tube containing the frozen filtrate was placed in a -95° bath to allow the hydrogen chloride to melt and evaporate.

2.3 Conductiometric titrations

The cells used and the technique of conductiometric titration have been described previously.[24,81] Conductances were measured on a Wayne-Kerr Universal Bridge B224. Both capacitance and conductance could be balanced and read, and the balance point was found using a null-point indicator.

2.4 The Dry Box

As many of the involatile compounds studied were sensitive to oxygen and to moisture they were handled inside a dry nitrogen filled glove box. During use and for several hours afterwards the box atmosphere was recycled through liquid nitrogen cooled traps. At all other times the box was continually purged with dry nitrogen. Phosphoric oxide was exposed inside the box to remove any traces of moisture which may be carried in.

2.5 ^{31}P nuclear magnetic resonance spectra

^{31}P nuclear magnetic resonance spectra were obtained using a Perkin Elmer R10 high resolution nuclear magnetic resonance spectrometer operating at 24.29 MHz, fitted with a Digiac computer of average transients. The instrument's permanent magnets maintain a field of 14,000 Gauss, 1.4 Tesla. Samples were contained in 8.5 mm. O.D. non-spinning tubes; either glass closed with neoprene rubber bungs or sealed silica ampoules.

The maximum field-sweep width available on the R10 was 200 ppm. and this was in certain cases found to be inadequate for recording solid state spectra.[101]

The magnitude of field sweep covered by one chart length is determined by the scale factor control which switches different values of resistance in series with the magnet sweep coils. By adjustment of potentiometers the ratios of the resistances in the complete sweep circuit are made equal to the ratios on the scale factor calibration. To extend the field sweep width beyond 200 ppm a further circuit containing a smaller fixed resistance and a variable resistance was inserted. The variable resistance was altered until a field sweep width of 367 ppm was obtained.

Signal enhancement was achieved by the use of a computer of average transients - 'CAT'. Accumulation was triggered by the revolving recorder drum at the beginning of each sweep. The signal from the output amplifier was fed into an analogue/digital converter and was accumulated in the computer. After processing the accumulated spectrum was fed back to the R10 and could be plotted on the chart recorder. The program also incorporated a facility for making a paper tape of the spectrum which could be stored and used to produce further copies of the spectrum as required.

Samples were prepared either in the dry box or on the vacuum line. Solids were ground to a fine powder and run in 8.5 mm. O.D. glass tubes closed with neoprene rubber bungs. The end of the tube was finally wrapped in Parafilm as an extra seal. Solution samples in solvents of low volatility were made up in a like manner. Silica tubes were used for samples when liquid hydrogen chloride was the solvent. These tubes were sealed in the vacuum line and warmed to room temperature in the manner already described for reaction tubes. The operating temperature of the R10 is $34.2^{o}C$, at which temperature the vapour pressure, of hydrogen chloride is 56 atm. To ensure that the tubes would stand this pressure they were all tested in a water bath to 40°C, when a pressure of almost 70 atm. would be reached. During this process the water bath was surrounded by bricks and placed behind a blast screen inside a fume cupboard. Higher pressures than 70 atm. could of course be reached if hydrogen or carbon monoxide were evolved in sufficient quantities from reactions inside the n.m.r. tube. Throughout this work chemical shifts were measured relative to P_4O_6 as external reference[102] but have been expressed relative to 85% phosphoric acid to facilitate comparison with literature data.

The use of ^{31}P n.m.r. spectroscopy as an analytical probe in this work embodies several advantages over other analytical techniques such as infra-red spectroscopy e.g. the infra-red spectrum of a triphenylphosphine-metal complex is a complex affair owing to the presence of the many absorptions due to the triphenylphosphine ligand. Absorptions of real interest, metal-phosphorus or metal-halogen stretches, are likely to be weak and/or outside the range of the instrument used.

First and foremost ^{31}P n.m.r. spectroscopy provides information concerning the phosphorus nucleus itself. No other, confusing, bands are present. Generally changes in ^{31}P chemical shifts on change of co-ordination are large and a rapid assignment can be made on this basis. Table 2.5.1 shows the change in the ^{31}P chemical shift as the co-ordination number of the phosphorus atom changes from 3 to 6 in the series PCl_3 through to PCl_6^-. There is a change in the oxidation state of the phosphorus from +3 in PCl_3 to +5 in PCl_4^+ in addition to the change in co-ordination. However, the large changes in chemical shift values along the series PCl_4^+ to PCl_6^- are entirely due to changes in co-ordination. There is no change in oxidation state.

TABLE 2.5.1

Variation in ^{31}P Chemical Shift on Change of Co-ordination Number

PCl_3	PCl_4^+	PCl_5	PCl_6^-
-219.5	-80	+80	+300

Values are expressed in ppm referenced to 85% H_3PO_4.[103]

The phenomenon of spin-spin splitting i.e. the appearance of fine structure on the chemically shifted peaks in a ^{31}P n.m.r. spectrum due to the ^{31}P nucleus associated with a given resonance interacting through the electronic structure with other magnetically active nuclei in the same molecule, provides additional information through the multiplicity of the splitting and the magnitude of the coupling constant J.

It is worth noting that spin-spin splitting is not observed in every possible case. Any process which affects the lifetime of a spin state may cause the splitting to vanish. The tetrachlorophosphonium ion PCl_4^+ shows a single peak for ^{31}P resonance even though the isotopes ^{35}Cl and ^{37}Cl each have a spin of $\frac{3}{2}$. The lifetime of the spin states of the chlorine nuclei are reduced to a very small value because of rapid spin-lattice relaxation arising from the nuclear quadrupole moment of the ^{35}Cl and ^{37}Cl nuclei. A rapid exchange process causes the broadening of components of spin multiplets and in conditions of high rates of exchange a single line will result, e.g. a single line due to the NH_4^+ cation in neutral solution is observed in ^{14}N n.m.r., but a pentet is observed in acid solution.[104]

Simple first-order splitting was encountered during this work. This type of splitting occurs when a ^{31}P nucleus is coupled by a chemical bond or a sequence of bonded atoms to n magnetic nuclei which are different from the ^{31}P nucleus being observed but equivalent to each other. In the case where the n nuclei are phosphorus atoms situated in differing environments in the molecule, complications can arise if the coupling constant between the different ^{31}P atoms is large compared to the relative chemical shifts between these atoms. This is pseudo-first-order splitting.

The multiplicity of a ^{31}P peak due to first-order splitting is predicted by simple rules. The number of peaks is given by $(2nI + 1)$ where n is the number of different but equivalent magnetic nuclei and I is the nuclear spin of the coupled nuclei. When $I > \frac{1}{2}$, the ^{31}P signal is split into $(2nI + 1)$ peaks of equal intensities. For nuclei with $I = \frac{1}{2}$ e.g. hydrogen or fluorine, the relative intensities of the $(n + 1)$ peaks are in the ratio of the binomial coefficients. Table 2.5.2 illustrates the number of peaks observed and their relative intensities for a phosphorus atom directly bonded to hydrogen atoms.[105]

TABLE 2.5.2

Multiplicity and relative intensities of multiplets in phosphorus-hydrogen compounds

	Number of lines	Relative intensities
PH	1	1:1
PH_2	3	1:2:1
PH_3	4	1:3:3:1
PH_4	5	1:4:6:4:1

Polyisotopic elements directly bonded to phosphorus can produce quite complicated ^{31}P n.m.r. spectra. There will be one signal, a singlet,from the phosphorus bonded to any non-magnetic nuclei, and a multiplet for each magnetic isotope present. The chemical shifts of the singlet and the multiplets will of course be the same, and the ratio of intensities of each system will be that of the ratio of the isotopic abundances of the element. Relevant nuclear properties of elements encountered in this work are given in Table 2.5.3.

While the overall intensity of a ^{31}P n.m.r. signal remains constant when spin-spin splitting occurs, the actual intensity of each of the component parts is reduced and the signal may be more difficult to observe. Catting can often oversome this difficulty, but in instances where coupling is with a nucleus of low abundance and high spin number I, and the material is but poorly soluble, the signal may still escape detection. The palladium-triphenylphosphine complexes examined in this work fall into this category. The complexes were not very soluble, the magnetic isotope ^{105}Pd is only 22.23% abundant and $I = \frac{5}{2}$. A 32 fold improvement in signal to noise ratio did not reveal the expected six-line pattern.

A variable temperature probe was not available during the course of this work; so n.m.r. measurements could only be taken at 34.2°C, the operating temperature of the instrument. Thus, species which are thermally stable at low temperatures but not at room temperatures, and the splitting of exchange-averaged signals into two contributing signals on cooling could not be observed. Salthouse[53] has reported the oxidation of phosphorus(III) chloride with bromine in liquid hydrogen chloride at low temperatures to give the PCl_3Br^+ cation, detecting its formation by

TABLE 2.5.3

Nuclear Properties

(Values taken from ref.106)

Isotope	Natural abundance %	Spin I in multiplets of h/2π
^{1}H	99.9844	1/2
^{2}H	1.56×10^{-2}	1
^{10}B	18.83	3
^{11}B	81.17	3/2
^{19}F	100	1/2
^{31}P	100	1/2
^{35}Cl	75.4	3/2
^{37}Cl	24.6	3/2
^{57}Fe	2.245	
^{59}Co	100	7/2
^{61}Ni	1.25	
^{63}Cu	69.09	3/2
^{65}Cu	30.91	3/2
^{79}Br	50.57	3/2
^{81}Br	49.43	3/2
^{99}Ru	12.81	3
^{101}Ru	16.98	5/2
^{103}Rh	100	1/2
^{105}Pd	22.23	5/2
^{127}I	100	5/2
^{191}Ir	38.5	3/2
^{193}Ir	61.5	3/2
^{195}Pt	33.7	1/2
^{197}Au	100	3/2

conductiometric titration and isolating it as the compound $PCl_3Br^+BCl_4^-$. A 1:1 mixture of PCl_3 and Br_2 in liquid hydrogen chloride at room temperature exhibited only one ^{31}P n.m.r. signal, that of PCl_3. Evidently the HCl_2^- ion is large enough to stabilise the PCl_3Br^+ cation at -95°, but fails to do so at room temperature. The addition of the solvoacid boron trichloride gave BCl_4^- anions which were large enough counterions to stabilise PCl_3Br^+ and other mixed phosphorus(V) cations at room temperature. It would have been interesting to determine the temperature at which PCl_3Br^+ disproportionates in the presence of HCl_2^- ions using a variable temperature probe.

2.6 ^{11}B nuclear magnetic resonance spectra

^{11}B n.m.r. spectra were similarly obtained on the R10 spectrometer tuned to 19.27 MHz. These spectra were generally easier to obtain than ^{31}P spectra, even resonances from solids could often be detected in a single sweep. The range of ^{11}B chemical shifts is much narrower than the range of ^{31}P shifts, but again changes in co-ordination number of the boron produce relatively large changes in ^{11}B chemical shift values. See Table 2.6.1.

TABLE 2.6.1

Variation in ^{11}B chemical shift on change in co-ordination number

(^{11}B chemical shifts relative to $B(OMe)_3$)

BCl_3 -29 (125)	BCl_4^- +11.6 (147)
BF_3 +8.9 (107)	BF_4^- +19.9 (147)

Throughout the work presented here trimethylborate was used as external reference, and results have been expressed relative to this standard. Both trimethylborate and borontrifluoride diethyletherate are quoted as standards in the literature. The ^{11}B chemical shift of $BF_3.Et_2O$ relative to $B(OMe)_3$ has been reported as +18.1 p.p.m.[107] and +18.3 p.p.m.[147] In this work a value of +18.75 p.p.m. was observed. First-order spin-spin splitting was occasionally encountered where coupling constants were large enough to be observed on the R10. As with phosphorus a variable temperature probe would have been of value. Only one ^{11}B resonance was observed in solution containing equimolar quantities of BCl_3 and BCl_4^- ion, an exchange-averaged signal between the values for these species.

2.7 Other Physical Measurements

Infrared Spectra

Infrared spectra in the range 4000 to 250 cm^{-1} were obtained using a Perkin Elmer 457 Grating Infrared Spectrophotometer.

Raman Spectra

Raman spectra were recorded by Drs. P. Gates and F.K. Ryan at Royal Holloway College using a Cary 81 Raman Spectrophotometer.

Molecular Weights

Molecular weights in benzene were determined using a Mechrolab Vapour Pressure Osmometer Model 301A. The instrument could be flushed with nitrogen.

Melting Points

Melting points were determined in a Gallenkamp melting point apparatus.

Elemental Analyses

Carbon, hydrogen and nitrogen were determined by microcombustion using a Perkin Elmer 240 Elemental Analyser. Throughout the course of this work the reliability of this instrument was variable. In all cases unknown substances were accompanied by standard substances when submitted for analysis so that a reliable calibration could be made. Greater reliance was placed upon metal, phosphorus and halogen analyses.

Metals were determined by atomic absorptiometry using a Perkin Elmer 403 Atomic Absorption Spectrophotometer.

Phosphorus was determined colorimetrically as the phosphomolybdivanado complex. Compounds were decomposed by heating with sodium peroxide in a nickel Parr bomb. The residue was washed out, acidified with concentrated nitric acid and made up to 100 ml. with distilled water. A suitable aliquot was taken, treated with Ammonium Molybdate Ammonium Vanadate reagent and the colour measured at 420µ using a Unicam SP500 spectrophotometer.

Chlorine was determined by potentiometric titration. Compounds were decomposed in a nickel Parr bomb by heating with sodium peroxide. The residue was washed out, acidifed with concentrated nitric acid and made up to 100 ml. with distilled water. A suitable aliquot was then titrated against N/100 silver nitrate solution using Ag, AgCl electrodes in an acetone medium.

Bromine and Iodine were determined iodometrically following a Schoniger Oxygen Flask combustion of the compound as described by Ingram.[108]

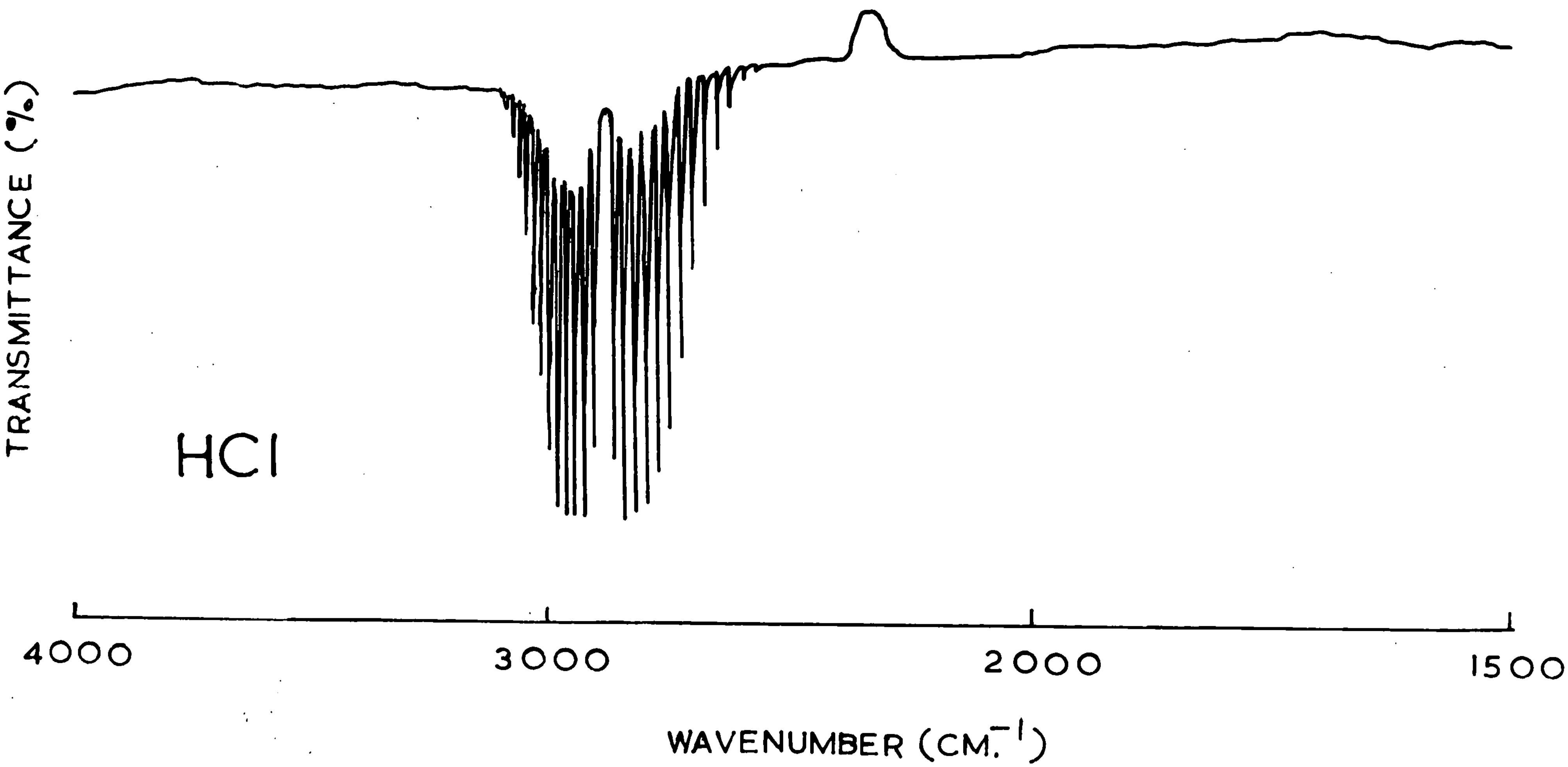
2.8 Preparation and Purification of Starting Materials

Hydrogen Chloride

Hydrogen chloride Electronic Grade was purchased from British Oxygen Chemicals Ltd. The gas was admitted to the vacuum line direct from the cylinder into the fractionation train at a pressure of 1-2 cm. of mercury measured on a manometer which also acted as a safety valve. The hydrogen chloride passed through two traps cooled to -84° and one at -95° before being condensed in the larger traps at -196°. The level of liquid nitrogen surrounding these traps was slowly raised until the traps were about two thirds full of solid hydrogen chloride. At this point no more hydrogen chloride was admitted to the line. Pumping was maintained throughout this process so that any air which might have leaked into the system would be pumped away. The solid hydrogen chloride was pumped for an hour to remove any traces of permanent gases and then melted in a toluene bath. At this temperature, -95°, liquid hydrogen chloride has a vapour pressure of 400 mm.[93] and is 11 Centigrade degrees below its boiling point. Pure liquid hydrogen chloride is a clear, colourless, "water-white" liquid. Any water present is seen as white particles as $H_3O^+Cl^-$ is insoluble in liquid hydrogen chloride. If no foreign bodies were observed in the liquid the infrared spectrum of the gas would be obtained using a 10 cm. path length gas cell fitted with KBr windows, and if this were satisfactory the hydrogen chloride would then be transferred to a 20 litre bulb for storage as a gas. If at this stage the hydrogen chloride was found to be impure, then it would be slowly refractionated through the train from -95°, through n-pentane slush bath, -131°, and condensed at -196°. Hydrogen chloride for conductiometric titration was always purified by this method and was stored in a 20 litre bulb reserved for "conductance HCl". The infrared spectrum of gaseous

Fig.2.8.1

Infrared spectrum of gaseous hydrogen chloride


TRANSMITTANCE (%)
HCl
4000
3000
2000
1500
WAVENUMBER (CM.$^{-1}$)

hydrogen chloride is shown in Figure 2.8.1.

Boron Trichloride

Boron trichloride was purchased from British Oxygen Chemicals Ltd. and purified by treatment with mercury. The gas was transferred via the line into a rotaflo ampoule containing mercury cooled to -196°. At all times the vapour pressure of the BCl_3 was kept as low as possible to minimise attack on the grease. The BCl_3 was allowed to reach room temperature and was left with the mercury, to remove traces of chlorine, overnight. The rotaflo was cooled to -84° and evacuated to remove any hydrogen chloride. The boron trichloride was then transferred to a clean rotaflo ampoule for storage. The vapour pressure of BCl_3 is 2 atm. at 33.2° [93] and it is thus perfectly safe to store in a rotaflo ampoule. Rotaflo values are guaranteed to stand 6 atm. pressure and in this department have been known to stand 10 atm.

Chlorine

Chlorine was purchased from I.C.I. Mond Division and was purified by low pressure fractional distillation in the trap train. The chlorine was distilled from -45° through a -84° trap and was condensed at -131°. Pumping was maintained throughout the fractionation to remove any hydrogen chloride or non-condensable gases. The chlorine was stored on the line in 10 litre bulbs.

Bromine

B.D.H. Analar bromine was dried over phosphoric oxide for 24 hours and then distilled into the vacuum line. The first fraction was pumped away as it might have contained hydrogen bromide, and the middle fraction was condensed in a rotaflo ampoule maintained at -84°. The ampoule was evacuated to remove traces of hydrogen bromide and non-condensable gases and the bromine was then stored in the ampoule at room temperature.

Phosphoruspentafluoride

Phosphoruspentafluoride was prepared by the thermal decomposition of p-chlorobenzenediazonium hexafluorophosphate, "Phosfluorogen A", at 180°.[100]

$$ClC_6H_4N_2{}^+PF_6{}^- \rightarrow ClC_6H_4F + N_2 + PF_5$$

Phosfluorogen A (7 g., 25 mmole) and an equal bulk of white sand were placed in a large external trap. The trap was evacuated and heated at 100° for 1 hour to remove traces of water. The reaction vessel was connected via a second external trap to the fractionation train. The reactant was slowly heated and evolution of gas began at 155°. Virtually all the p-chlorofluorobenzene produced was retained in the off-line trap and the remainder in the first train trap, both at -84°. PF_5 was condensed in the second train trap at -196°. The nitrogen liberated was monitored on a manometer and pumped away at intervals. Evolution of gas virtually ceased within 15 minutes. The purity of the product was determined by infra-red spectroscopy. Absorptions due to traces of SiF_4 and OPF_3 were observed in addition to those of PF_5. No further purification was carried out as SiF_4 is relatively inert and the ^{31}P n.m.r. data of OPF_3 are known, and neither compound was expected to interfere in the reactions in which the PF_5 was to be used. The PF_5 was stored on the vacuum line frozen down at -196° to prevent reaction with water absorbed in the glass.

Transition metal complexes

Tetrakis(triphenylphosphine)platinum(0)

The method of preparation was that described by Ugo et al.[109]

$$K_2PtCl_4 + 2KOH + 4Ph_3P + C_2H_5OH \rightarrow Pt(Ph_3P)_4 + 4KCl + CH_3CHO + 2H_2O$$

Ph_3P (15.4 g., 0.0588 mmole) was dissolved in 200 ml. absolute ethanol at 65°. When the solution was clear, a solution of 1.4 g. KOH in a mixture of 32 ml. of ethanol and 8 ml. of water was added. Then K_2PtCl_4 (5.24 g., 0.0126 mmole) dissolved in 50 ml. of water was slowly added to the alkaline Ph_3P solution while stirring at 65°. The addition should be completed in about 20 minutes. A pale yellow compound began to separate within a few minutes of the first addition. After cooling, the compound was separated by filtration, washed with 150 ml. of warm ethanol, then with 60 ml. of cold water, and again with 50 ml. of cold ethanol. The resulting pale ivory yellow powder was dried in vacuo overnight (2 hours recommended in lit.). Yield 12.4 g., 79%. The compound was always stored and handled under pure nitrogen.

Analyses: Found C,70.28; H,4.54; P,10.26; Pt,15.69; $(Ph_3P)_4Pt$ requires C,69.5; H,4.86; P,9.96; Pt,15.59.

Tris(triphenylphosphine)platinum(0)

Again the method of Ugo et al[109] was used, but more practical detail will be given here than is given in the original work.

$(Ph_3P)_4Pt$ 6.5 g. suspended in 270 ml. absolute ethanol in a 1 litre flask was refluxed with vigorous stirring for 2 hours. The colour of the suspension changed from pale ivory yellow to a deep cadmium sulphide yellow. The hot suspension, still at reflux temperature, was rapidly filtered through a 12 cm. Buchner funnel, washed with 30 ml. of cold ethanol and dried in vacuo overnight. The resulting deep yellow powder was quite different in appearance from the starting material. It is important to filter off the product while the suspension is hot otherwise association of Ph_3P and $(Ph_3P)_3Pt$ occurs and the product is contaminated with $(Ph_3P)_4Pt$. Yield 3.0 g., 66%. The compound was stored and handled under pure nitrogen.

Analyses: Found C,65.77; H,5.97; P,9.76; Pt,20.36. $(Ph_3P)_3Pt$ requires C,66.0; H,4.59; P,9.48; Pt,19.88.

The infrared spectra of $(Ph_3P)_nPt$ (n = 3,4) are almost identical, corresponding absorptions being within 2-3 cm^{-1} in the spectra of the two compounds.[109] ν_{Pt-P} in $(Ph_3P)_3Pt$ occurs at 422 cm^{-1} [110] and ν_{Pt-P} in $(Ph_3P)_4Pt$ at 424 cm^{-1}.[111] Ziolo et al[112] have reported the photoluminescence of phosphine complexes of d^{10} metals; $(Ph_3P)_3Pt$ appearing bright red and $(Ph_3P)_4Pt$ appearing bright orange under an ordinary "black light" source. The only satisfactory discriminant however is platinum analysis.

Triphenylphosphinetetracarbonyliron(0) and bis(triphenylphosphine)-tricarbonyliron(0)

These compounds were prepared by a modification of the method of Davison et al.[113]

A solution of Ph_3P (9 g., 34.4 mmole) in dry distilled tetrahydrofuran (30 ml.) was added to a hot solution of $Fe_3(CO)_{12}$ (3 g., 5.95 mmole) in tetrahydrofuran (30 ml.), and the mixture heated under reflux. After 7 minutes the hot solution, which had become yellow brown was quickly filtered through a sintered glass plate. Any yellow solid which crystallised out due to cooling during filtration was rinsed through the sinter with tetrahydrofuran (2 x 10 ml.). The clear yellow filtrate was concentrated on a steam bath in a rapid stream of nitrogen until crystals appeared. Cooling gave the tricarbonyl. The yellow filtrate was concentrated to 10-20 ml. and on cooling a pale yellow solid which was a mixture of the tri- and tetracarbonyls was obtained. The mixture was soxhlet extracted overnight with 40-60 pet. ether. The tetracarbonyl was obtained as yellow plates from the extract on cooling. The insoluble residue was more of the tricarbonyl. Both compounds were characterised by comparing their infra-red spectra with published spectra[113] and by elemental analysis.

Analysis: first crop of crystals;

Found C,70.32; H,4.21; P,9.39; Fe,8.49. $(Ph_3P)_2(CO)_3Fe$ requires C,70.85; H,4.6; P,9.34; Fe,8.43.

Yellow plates; Found C,61.8; H,3.14; P,7.26; Fe,13.18. $(Ph_3P)(CO)_4Fe$ requires C,61.5; H,3.5; P,7.21; Fe,13.15;

Tetrakis(phosphorus(III)fluoride)nickel(0)

This compound, $(PF_3)_4Ni$, was prepared by a method reported by Nixon.[114]

Nickelocene (1.42 g., 7.53 mmole) was placed inside a 350 ml. capacity pyrex ampoule whilst inside the dry box. The ampoule was attached to the vacuum line, cooled to -196° and evacuated. Sufficient PF_3 to give a pressure of 6 atm. at 60° was condensed into the ampoule. The ampoule was sealed and warmed slowly to room temperature. After a short time it was placed inside a cold oven which was slowly heated to 60°. After 11 days the ampoule was removed, cooled to -196° and opened to the vacuum line using an ampoule breaker. The temperature was allowed to rise to room temperature and the volatile contents of the ampoule were condensed into the first trap of the fractionation train. The passage of $(PF_3)_4Ni$ vapour could be detected by the orange discharge produced when a Tessler coil was held near the line. The volatiles were slowly fractionated to separate the $(PF_3)_4Ni$ from unused PF_3. The first trap was held at -140° (40-60 pet.ether slush bath), the second at -84° and the final trap at -196°. PF_3 passed the -84° trap but the $(PF_3)_4Ni$ was retained. The -140° bath was replaced when the majority of the PF_3 had distilled over by -45° and -22° baths to enable quantitative transfer of the $(PF_3)_4Ni$ into the middle trap. An infrared spectrum of the clear colourless liquid obtained at room temperature showed absorptions at 900, 863, 526 and 510 cm^{-1} and no other absorptions. These values were in excellent agreement with literature values for $(PF_3)_4Ni$.[115] Yield 1.60 g., 51.5%. The compound was stored in sealed ampoules at -30°. A "long tube" breathing apparatus was always worn when transferring this highly toxic material.

Tetrakis(phosphorus(III)chloride)nickel(0)

$(PCl_3)_4Ni$ was obtained using Smith's preparation.[116]

In a well ventilated fume cupboard, nickel carbonyl (5.15 ml., 40 mmole) was transferred under nitrogen from the cylinder into a 250 ml. 3-neck flask fitted with a gas inlet, dropping funnel and reflux condenser. Phosphorus(III) chloride (30 ml., 340 mmole) nearly 100% excess, was carefully added to the vigorously stirred $Ni(CO)_4$ over a period of 1 hour. The initial vigorous evolution of carbon monoxide has totally ceased by this time. The mixture was stirred for 24 hours, refluxed for 2 hours and then left to cool. Well formed pale greenish yellow crystals were filtered off and dried under a strong current of nitrogen, then in vacuo for 2 hours.

The infra-red spectrum of this material in the region 4000-250 cm^{-1} contained only 3 absorptions at 523, 491 and 327 cm^{-1}.

Analyses. Found: Ni,9.80; P,20.5; Cl,69.4; $(PCl_3)_4Ni$ requires: Ni,9.84; P,20.3; Cl,69.8.

Dichlorobis(triphenylphosphine)nickel(II)

$(Ph_3P)_2NiCl_2$ was prepared by the method of Venanzi.[117]

Nickel(II) chloride hexahydrate (4.76 g., 20 mmole) in water (4 ml.) was diluted with glacial acetic acid (100 ml.) and triphenylphosphine (10.5 g., 40 mmole) in glacial acetic acid (50 ml.) added. The olive-green microcrystalline ppt. when kept in contact with its mother liquor for 24 hours, gave dark blue crystals which were filtered off, washed with glacial acetic acid and dried in a vacuum desiccator (H_2SO_4; KOH). Further washing with dry ether and drying in vacuo were necessary to remove the last traces of acetic acid. Yield 10.5 g., 80%. Found: C,65.58; H,3.12; $(Ph_3P)_2NiCl_2$ requires C,66.1; H,4.6.

trans-Chlorocarbonylbis(triphenylphosphine)rhodium(I)

The procedure described by Evans et al[118] was followed.

Rhodium(III) chloride trihydrate (2 g., 7.6 mmole) in absolute ethanol (70 ml.) was slowly added to 300 ml. boiling absolute ethanol containing a two-fold excess of triphenylphosphine (7.2 g., 27.5 mmole). The red solution became turbid but cleared in 5 minutes (2 minutes lit.). Then sufficient 37% formaldehyde solution (10-20 ml.) was added to cause the red solution to become pale yellow in about 1 minute, and yellow microcrystals to precipitate. After slow cooling the crystals were separated on a 12 cm. Buchner funnel, washed with ethanol and ether and dried in vacuo. Recrystallisation from benzene was not necessary.

Yield 4.4 g., 84%.

Found: C,63.58; H,3.81; Cl,5.19; Rh,15.1; $(Ph_3P)_2Rh(CO)Cl$ requires: C,64.0; H,4.33; Cl,5.12; Rh,15.3.

Other starting materials

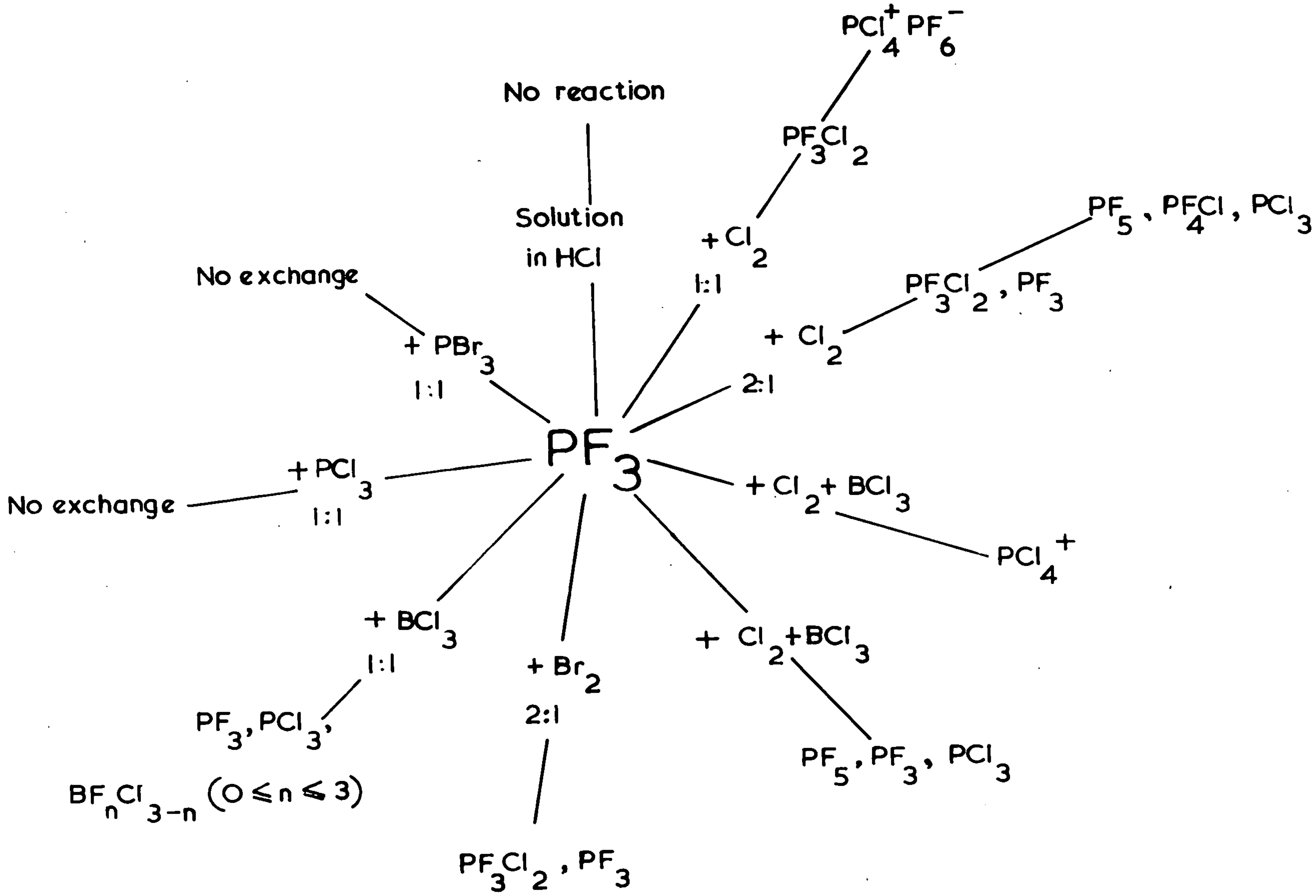
Other starting materials were either purchased in their highest available purity grade, or were donated, and were used without further purification.

CHAPTER 3

OXIDATION AND EXCHANGE REACTIONS OF SIMPLE PHOSPHORUS COMPOUNDS

Fig.3.1.1

Reactions of phosphorus(III) fluoride



PF_3
No reaction
Solution in HCl
$PCl_4^+ PF_6^-$
PF_3Cl_2
$+ Cl_2$ 1:1
PF_5, $PFCl_4$, PCl_3
PF_3Cl_2, PF_3
$+ Cl_2$ 2:1
No exchange
$+ PBr_3$ 1:1
$+ PCl_3$ 1:1
No exchange
$+ Cl_2 + BCl_3$
PCl_4^+
$+ BCl_3$ 1:1
PF_3, PCl_3, BF_nCl_{3-n} $(0 \leq n \leq 3)$
$+ Br_2$ 2:1
PF_3Cl_2, PF_3
$+ Cl_2 + BCl_3$
PF_5, PF_3, PCl_3

3.1 Phosphorus(III) fluoride

Results and Discussion

Phosphorus(III) fluoride was reacted with the oxidising agents chlorine and bromine in liquid hydrogen chloride. The reaction with chlorine was repeated in the presence of the Lewis acids boron trichloride and boron trifluoride. In all cases the phosphorus was oxidised from the +3 to the +5 oxidation state usually producing pentaco-ordinated covalent fluorine containing phosphorus(V) compounds. Tetraco-ordinate fluorine containing phosphorus(V) cations were not produced, the only tetraco-ordinate species observed being the tetrachlorophosphonium ion. All reactions were followed by ^{31}P nuclear magnetic resonance spectroscopy at 34.2°C. The results of the experiments are shown in Fig.3.1.1.

The ^{31}P n.m.r. spectrum of phosphorus(III) fluoride in liquid hydrogen chloride indicated that the phosphorus(III) fluoride had dissolved without protonation or exchange taking place. The observed chemical shift -104.5 p.p.m. is in reasonable agreement with the literature values of -97 p.p.m.[119,120] for the compound, presumably in the gas phase and at -70°.[120] The magnitude of the P-F coupling constant, 1433 Hz, is also in good agreement with the reported values of 1405 Hz,[119] and 1400 Hz from ^{19}F n.m.r.[121]

In the reaction between phosphorus(III) fluoride and chlorine in a 1:1 molar ratio, the colour of the chlorine was completely discharged and the resonance due to phosphorus(III) fluoride in the ^{31}P n.m.r. spectrum was absent. A new signal, split into a 1:3:3:1 quartet, attributable to dichlorotrifluorophosphorus(V) appeared at +31.5 p.p.m. The chemical shift and P-F coupling constant of magnitude 1070 Hz were identical with a sample of PF_3Cl_2 prepared in the inert solvent freon 11 (CCl_3F). Latscha has reported a ^{31}P n.m.r. chemical shift of +27.8 p.p.m. with $^1J_{^{31}P-^{19}F}$ 1050 ± 2 Hz for the neat liquid[232] and Schmutzler obtained the same value for the phosphorus-fluorine coupling constant from a solution of PF_3Cl_2 in pet. ether at 25°.[122] After 1 hour at 34.2° a white solid precipitated and no further ^{31}P resonance could be detected in the solution. It may be assumed that the rapid disproportionation of PF_3Cl_2 to the ionic $PCl_4^+PF_6^-$ had occurred. Thus the reaction in liquid hydrogen chloride can be summarised as

$$PF_3 + Cl_2 \rightarrow PF_3Cl_2$$

and

$$2PF_3Cl_2 \rightarrow PCl_4^+PF_6^-$$

Salthouse[81] followed the reactions colorimetrically at low temperature, observing the appearance of the colour of chlorine only after the molar ratio $Cl_2:PF_3$ has exceeded 1:1. The change PF_3Cl_2 to $PCl_4^+PF_6^-$ in liquid hydrogen chloride occurred to only a very limited extent at low temperature, and other workers have shown that this change slowly takes place in the gas phase over the course of a few days.[123] However, the corresponding reaction in liquid hydrogen chloride at room temperature has now been shown to be both rapid and complete.

To prevent complete oxidation of all the phosphorus present, the experiment was repeated using a molar ratio $PF_3:Cl_2$ of 2:1. At first the ^{31}P n.m.r. spectrum showed the presence of PF_3 and PF_3Cl_2 in roughly equal amounts, but after 3 days the spectrum was much more complex. The ^{31}P n.m.r. data, shown in Table 3.1.1, were consistent with the presence of PCl_3, PF_4Cl and PF_5 in addition to PF_3. Signals due to PF_3Cl_2 were completely absent. The formation of the higher phosphorus(V)

TABLE 3.1.1

^{31}P n.m.r. data and literature values for assignment purposes of species detected in the reaction between PF_3 and Cl_2 in a 2:1 molar ratio in liquid hydrogen chloride

Compound	Solvent	Multiplicity and relative intensities of splitting	δ ^{31}P (p.p.m. rel. to 85% H_3PO_4)	$^1J_{P-F}$ (Hz)
PF_3	HCl neat liquid (119) neat liquid (120)	1:3:3:1	-104.5 -97 -97 (-70°)	1433 1405 (119) 1400 (121)
PF_3Cl_2	HCl CCl_3F neat liquid (121) pet. ether (122)	1:3:3:1	+29.5 ± 2.5 +31.9 +27.8 ± 0.5 (232)	1070 1069 1048 (121) 1050 (122)
PF_4Cl	HCl Isopentane (127)	1:4:6:4:1	+50.7	1000 1000
PF_5	HCl CCl_3F Gas (30 atm.)	1:5:10:10:5:1	+81 +80 ± 1 +79.5	953 ± 1 958 ± 10 952
PCl_3	HCl neat liquid	singlet	-218.5 -219	

fluoro compounds can be explained in terms of the following exchange mechanism

$$PF_3Cl_2 + PF_3 \rightarrow PF_4Cl + PF_2Cl$$

$$PF_3Cl_2 + PF_2Cl \rightarrow PF_4Cl + PFCl_2$$

$$PF_3Cl_2 + PFCl_2 \rightarrow PF_4Cl + PCl_3$$

$$PF_4Cl + PF_2Cl \rightarrow PF_5 + PFCl_2$$

$$PF_4Cl + PFCl_2 \rightarrow PF_5 + PCl_3$$

The ^{31}P chemical shifts of the postulated intermediates PF_2Cl and $PFCl_2$ are not listed in the literature, but their P-F coupling constants have been determined by ^{19}F n.m.r. spectroscopy.[121] Moreover, it would be reasonable to expect the ^{31}P shifts of these two species to lie between the values for PCl_3, -218 p.p.m., and PF_3, -104.5 p.p.m. No signals, other than the components of the PF_3 quartet, were detected in this region; so it may be assumed that any PF_2Cl or $PFCl_2$ produced has reacted further to give PCl_3. At no time was any white solid observed in the ampoule. Thus, the rapid disproportionation of PF_3Cl_2 to $PCl_4^+PF_6^-$ is prevented by the presence of PF_3, other pentaco-ordinated fluorophosphorus species being produced.

In the reaction between phosphorus(III) fluoride and bromine in a 2:1 molar ratio, the colour of the bromine was completely discharged, and the ^{31}P n.m.r. spectrum showed not the expected product PF_3Br_2, but the presence of PF_3Cl_2 in addition to PF_3. The higher field signal, a 1:3:3:1 quartet centred at +30.5 p.p.m. having J_{P-F} 1065 ± 4 Hz, was quite distinct from that of PF_3Br_2, a 1:3:3:1 quartet centred at +50.7 p.p.m.

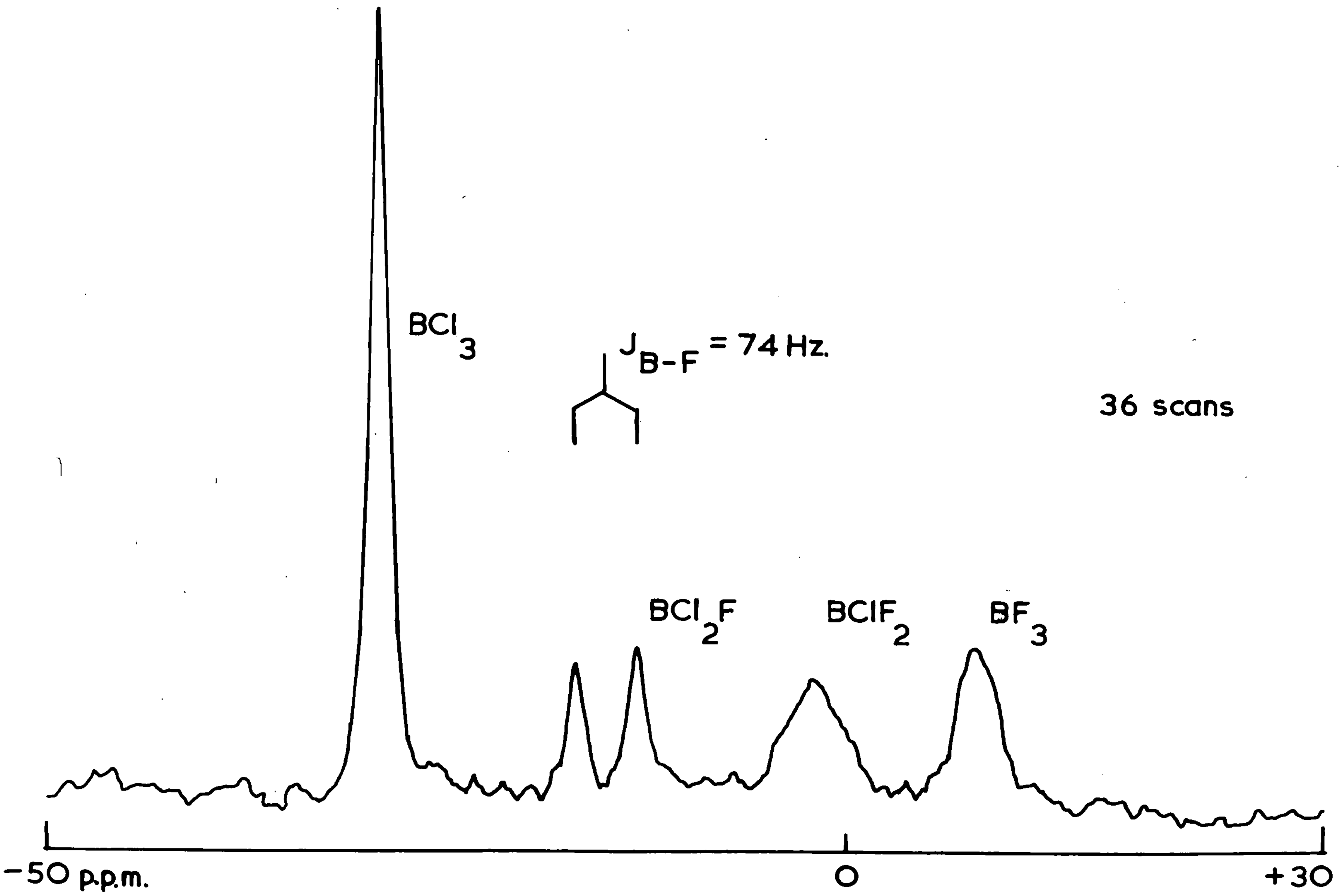
with J_{P-F} 1142 Hz. Mutterties et al report J_{P-F} to be 1140 Hz for PF_3Br_2.[124] Thus, the oxidation of PF_3 to PF_3Br_2, which is then solvolysed to PF_3Cl_2, has taken place. This confirms the earlier low temperature study carried out by Salthouse.[81]

Before investigating the oxidation of phosphorus(III) fluoride by chlorine in the presence of boron trichloride an independent experiment was carried out to investigate the reaction between PF_3 and BCl_3 in a 1:1 molar ratio in liquid hydrogen chloride. The ^{31}P n.m.r. spectrum indicated the presence of both PCl_3 and PF_3 in a molar ratio of 1:1. The ^{11}B n.m.r. spectrum, Fig.3.1.2, recorded immediately afterwards contained four signals at -28.5, -14.5, -1.5 and +8.5 p.p.m. which may be immediately assigned to BCl_3, BCl_2F, $BClF_2$ and BF_3 respectively.[125,126] The spin-spin coupling constant $^1J_{^{11}B-^{19}F}$ of 74 Hz for BCl_2F is in excellent agreement with the literature value determined from ^{19}F work.[128] The same authors report $^1J_{^{11}B-^{19}F}$ values of 34 and 15 ± = Hz for $BClF_2$ and BF_3 respectively, but these splittings were not observed in this work. A molar ratio for BCl_3:BCl_2F:$BClF_2$:BF_3 of 15:6:5:4 was indicated by signal intensities. 72 hours later the n.m.r. spectra were again recorded with similar results, excepting that the PCl_3:PF_3 ratio was 2:1 and the BCl_3:BCl_2F:$BClF_2$:BF_3 ratio was 15:6:4:6. It is apparent that the ratio of chlorine:fluorine bonded to phosphorus and boron is no longer 1:1, approximately twice as much chlorine as fluorine now being bonded to these elements. It is shown in this work that PCl_3, PF_3, BCl_3 and BF_3 all exist as such in liquid hydrogen chloride solution. Baumgarten[129] has reported the formation of $PCl_3.BF_3$ from PCl_3 and BF_3 below -12°, stating that the adduct decomposes into its components above -6°. The formation of a

Fig.3.1.2

^{11}B n.m.r. spectrum

PF_3:BCl_3 in 1:1 molar ratio in liquid hydrogen chloride


BCl$_3$
J_{B-F} = 74 Hz.
36 scans
BCl$_2$F
BClF$_2$
BF$_3$
−50 p.p.m.
0
+30

similar adduct in this reaction, followed by exchange and dissociation, would produce the mixed chlorofluoro species observed. Sovolysis of PF_2Cl and $PFCl_2$, and to some extent of $BFCl_2$ and BF_2Cl, would yield the observed products.

The oxidation of phosphorus(III) fluoride by chlorine was repeated in the presence of the Lewis acids boron trichloride and boron trifluoride, in the hope of stabilising fluorine containing tetraco-ordinate phosphorus(V) cations as their tetrahalogenoborates. Addition of excess BCl_3 to a mixture of PF_3:Cl_2 in a 2:1 molar ratio in liquid hydrogen chloride did cause a tetraco-ordinate phosphorus(V) cation to be produced. The ^{31}P n.m.r. spectrum of the solution indicated the sole presence of the tetrachlorophosphonium ion, PCl_4^+. The ^{11}B n.m.r. spectrum of the solution contained one resonance at +8.2 p.p.m., which is very close to the ^{11}B chemical of BF_3 quoted as +8.1 p.p.m.[125,126] and +8.6 p.p.m. (this work); however, in view of the presence of PCl_4^+, a boron containing anion is required. Chemical shifts for BCl_4^-, $BFCl_3^-$, $BF_2Cl_2^-$, and BF_3Cl^- of +11.6, +11.8 and +13.8 and + 16.6 p.p.m. respectively have been reported[147] and it is suggested that the observed ^{11}B signal is an exchange-averaged signal caused by exchange between fluorine containing boron anions and the excess BCl_3. The reaction may thus be interpreted as an oxidation of PF_3 by Cl_2 to PF_3Cl_2, followed by exchange with BCl_3 until PCl_5, which exists as $PCl_4^+ Cl^-$ solvated in liquid hydrogen chloride, and BF_3 are produced. The BF_3 and/or BCl_3 would accept the solvated halide ion forming a 4-co-ordinate boron anion.

A proposed mechanism for the reaction taking place in solution is initial oxidation of half the PF_3

$$PF_3 + Cl_2 \rightarrow PF_3Cl_2$$

followed by exchange

$$PF_3Cl_2 + BCl_3 \rightarrow PF_2Cl_3 + BCl_2F$$

$$PF_3Cl_2 + BCl_2F \rightarrow PFCl_4 + BClF_2$$

$$PFCl_4 + BClF_2 \rightarrow PCl_5 + BF_3$$

$$\downarrow$$

$$PCl_4^+ + Cl^- \text{ solvated}$$

The remaining PF_3 presumably reacts with BCl_3 in a similar manner to that described previously giving PCl_3 and 3-co-ordinate chlorofluoroboron(III) species. It is possible that the observed ^{11}B chemical shift is an exchange-averaged value derived from both 3- and 4-co-ordinate chlorofluoroboron(III) species since the chemical shifts of the series BF_xCl_{3-x} $(0 \leq x \leq 3)$ and $BF_yCl_{4-y}^-$ $(0 \leq y \leq 4)$ all lie close enough together to give one exchange averaged signal (Table 3.1.2)

It is not possible to write an overall balanced equation explaining the complete oxidation of the phosphorus from the +3 to the +5 oxidation state in this reaction.

The ^{31}P n.m.r. spectrum of the reaction mixture PF_3:Cl_2 in molar ratio 2:1 in the presence of an excess of BF_3 showed signals due to PCl_3, PF_3 and PF_5. The ^{11}B n.m.r. spectrum of the same solution showed a singlet at +8.4 p.p.m. indicating BF_3. A comparison of intensities suggests that the ratio of PF_5:PF_3 is approximately 3:1, PCl_3 being

TABLE 3.1.2

^{11}B n.m.r. data for some chlorofluoroboron(III) species

(^{11}B chemical shifts in p.p.m. referenced to $(MeO)_3B$)

Species	Chemical Shift	Ref.
BCl_3	-27.1	126
BCl_2F	-12.7	126
$BClF_2$	-1.5	126
BF_3	+8.1	126
BCl_4^-	+11.6	147
BCl_3F^-	+11.8	147
$BCl_2F_2^-$	+13.8	147
$BClF_3^-$	+16.6	147
BF_4^-	+19.9	147

present in higher concentration. A reaction scheme accounting for the observed $PF_5:PF_3$ ratio can be postulated as:

$$PF_3 + Cl_2 \rightarrow PF_3Cl_2$$

$$3PF_3Cl_2 + 2PF_3 \rightarrow 3PF_5 + 2PCl_3$$

Again, it is difficult to write a balanced equation and the role of the BF_3 in this reaction is not clear.

The failure to observe exchange products between phosphorus(III) fluoride and phosphorus(III) chloride in liquid hydrogen chloride at room

TABLE 3.1.3

^{31}P n.m.r. data for some fluorophosphorus(V) compounds

(^{31}P chemical shifts in p.p.m. relative to 85% H_3PO_4. $^1J_{P-F}$ in Hz)

Compound	Solvent	δ ^{31}P	$^1J_{P-F}$
PF_5	HCl	+81	953 ± 1
	CCl_3F	+80 ± 1	958 ± 10
		+68 (133)	930 (121,133)
PF_4Cl	HCl	+50.7	1000
	neat liquid		996 (-15°)
	isopentane (127)		1000
PF_3Cl_2	HCl	+31.9	1070
	CCl_3F	+31.9	1069
	neat liquid (121)		1048 (-15°)
	pet. ether (122)		1050 (25°)
			1023,1085 (-130°)
PF_4Br	neat liquid	+72.6 (133)	1075 (-70°)
PF_3Br_2	CCl_3F	+87	1142
	CCl_2F_2 (124)		1140

temperature is really not surprising. A recent ^{19}F n.m.r. study of halogen exchange on trivalent phosphorus[130] indicates that exchange in the gas phase between PF_3 and PCl_3 is slow. Detectable amounts of PF_2Cl were found after 24 hours at 200°, and 24 hours at 300° were necessary before both PF_2Cl and $PFCl_2$ could be identified from a 1:1 mixture of PCl_3 and PF_3. Such extremes of temperature could not be achieved in the quartz ampoules used in the present study, and in the short term exchange products will not be observed. Similar kinetic problems attend the observation of the exchange between PF_3 and PBr_3 in liquid hydrogen chloride, with the added complication that PBr_3 itself exchanges with the solvent (p.75).

Experimental

Behaviour of phosphorus(III) fluoride in liquid hydrogen chloride

PF_3 (0.5 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196° followed by HCl (30 mmole) and the ampoule was then sealed. This quantity of HCl was sufficient to give about 1 ml. of liquid HCl at 34.2°, the operating temperature of the R10. The ampoule was warmed to room temperature and tested as already described (p. 27). The ^{31}P n.m.r. spectrum obtained from a single scan showed 2 peaks of equal intensities and a short CAT run, 22 scans affording a signal/noise improvement of 4-5, showed a 1:3:3:1 quartet. The chemical shift was -104.3 ± 0.2 p.p.m. and coupling constant $^{1}J_{P-F}$ 1433 Hz. Gutowsky et al[119] report δ ^{31}P at -97 p.p.m. but do not state the temperature at which the determination was made, and Meriwether et al[120] report the same value at -70°. The magnitude of the coupling constant $^{1}J_{P-F}$ has been reported as 1405 Hz[119] and 1400 Hz.[121]

Thus, it may be assumed that PF_3 is soluble in liquid hydrogen chloride at room temperature without reaction.

Reaction between chlorine and phosphorus(III) fluoride

PF_3 (2 mmole) was condensed into an 8 mm o.d. quartz ampoule at -196^o followed by HCl (30 mmole) and Cl_2 (2.05 mmole). The ampoule was sealed and tested in the usual way. The solution was clear, but very slightly green due to the slight excess of Cl_2. Signals due to PF_3 were absent in the ^{31}P n.m.r. spectrum of this solution but a 1:3:3:1 quartet was easily observed (a CAT run of 41 scans) at higher field. The ^{31}P chemical shift of this quartet was +31.5 p.p.m. and coupling constant $^1J_{P-F}$ 1070 Hz. This was later shown to be characteristic of dichlorotrifluorophosphorus(V) PF_3Cl_2. After approximately 1 hour in the probe, during which the ^{31}P n.m.r. spectrum was recorded, it became impossible to balance the bridge of the R10. This was due to the precipitation of a white solid, presumably $PCl_4^+PF_6^-$. When precipitation was complete it was again possible to balance the bridge and record the ^{31}P n.m.r. spectrum of the solution. No signal could be detected and it was assumed that the rapid conversion

$$2PF_3Cl_2 \rightarrow PCl_4^+PF_6^-$$

had gone to completion.

The reaction was repeated using a molar ratio $PF_3:Cl_2$ of 2:1.

PF_3 (2 mmole) was condensed into an 8 mm o.d. quartz ampoule at -196^o followed by HCl (27 mmole) and Cl_2 (1 mmole). The tube was sealed and tested in the usual way. A clear colourless solution was obtained. After 12 hours at room temperature the ^{31}P n.m.r. spectrum of the solution was recorded. Two 1:3:3:1 quartets of equal intensities were observed after a CAT run of 22 scans. The quartet centred at -106 p.p.m., $^{1}J_{P-F}$ 1434 Hz was assigned to PF_3, and that at +27.1 p.p.m., $^{1}J_{P-F}$ 1069 Hz, to PF_3Cl_2. (Table 3.1.1).

After a further 72 hours the ^{31}P n.m.r. spectrum of the solution was again recorded. The spectrum was complex, consisting of a singlet at -218.5 p.p.m., a 1:3:3:1 quartet at -104 p.p.m., a 1:4:6:4:1 quintet at +50.7 p.p.m. and a 1:5:10:10:5:1 sextet at +78.6 p.p.m. The $^{1}J_{P-F}$ coupling constants of these multiplets were; 1434 Hz for the quartet, 1003 Hz for the quintet and 946 Hz for the sextet.

On the basis of chemical shift, P-F coupling constants and multiplicity of splitting the resonances can be assigned to PCl_3, PF_3, PF_4Cl and PF_5. Signals due to PF_3Cl_2 were absent. ^{31}P n.m.r. data for this reaction are given in Table 3.1.1.

<u>Preparation and ^{31}P n.m.r. spectra of dichlorotrifluorophosphorus(V) and dibromotrifluorophosphorus(V)</u>

The compounds PF_3Cl_2 and PF_3Br_2 were prepared in an inert solvent in order that their ^{31}P n.m.r. spectrum could be recorded.

PF_3 (2 mmole) was condensed into an 8 mm o.d. quartz ampoule at -196°, followed by freon 11 (1 ml.) and Cl_2 (2 mmole). The ampoule was sealed and warmed to room temperature. A clear colourless solution was obtained. The ^{31}P n.m.r. spectrum of this solution consisted of a 1:3:3:1 quartet, chemical shift +31.9 p.p.m. and P-F coupling constant 1069 Hz. Literature values of $^{1}J_{P-F}$ in PF_3Cl_2 from ^{19}F n.m.r. are; 1048 Hz for the neat liquid at -15°,[121] and 1050 Hz for a pet. ether solution at 25°.[122] A ^{31}P n.m.r. chemical shift of +27.8 ± 0.5 p.p.m. for neat PF_3Cl_2 has also been reported.[232]

PF_3 (1.5 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by freon 11 (1 ml.) and Br_2 (1.5 mmole). The tube was sealed and warmed to room temperature. A clear pale orange solution was obtained. The colour was possibly due to a slight excess of bromine. The ^{31}P n.m.r. spectrum of this solution consisted of a 1:3:3:1 quartet, chemical shift +87 p.p.m. with P-F coupling constant of 1142 Hz. A $^{1}J_{P-F}$ value of 1140 Hz from ^{19}F n.m.r. has been reported for PF_3Br_2 in CCl_2F_2.[124]

Reaction between bromine and phosphorus(III) fluoride

PF_3 (2 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by HCl (27 mmole) and Br_2 (0.180 g., 1.125 mmole). The ampoule was sealed, warmed to room temperature and tested in the usual way. The colour of bromine was completely discharged and the solution was both clear and colourless. The ^{31}P n.m.r. spectrum of this solution consisted of two 1:3:3:1 quartets, the central peaks of which could be seen on a single scan. A short CAT run of 36 scans was sufficient to reveal the complete multiplets. The quartet having shift -104.5 p.p.m. and J_{P-F} 1434 Hz was due to PF_3, the other, δ_p + 30.5 p.p.m. and J_{P-F} 1065 ± 4 Hz, was assigned to PF_3Cl_2. Thus PF_3 is oxidised by Br_2 in liquid hydrogen chloride to PF_3Br_2, which is then sovolysed to PF_3Cl_2.

$$PF_3 + Br_2 \rightarrow PF_3Br_2 \xrightarrow{\text{solvolysis}} PF_3Cl_2$$

This confirms the low temperature observations of Salthouse.[81]

The reaction between phosphorus(III) fluoride and boron trichloride

PF_3 (2.5 mmole) followed by HCl (30 mmole) and BCl_3 (2.5 mmole) was condensed at -196° into an 8 mm. o.d. silica ampoule which was then sealed and tested in the usual manner. A clear colourless solution was obtained at room temperature. The ^{31}P and ^{11}B n.m.r. spectra of the solution were recorded within 24 hours of the ampoule being sealed, and again 72 hours later.

The ^{31}P n.m.r. spectrum contained two signals; a singlet at -220.5 p.p.m. and a 1:3:3:1 quartet at -102.5 p.p.m. with coupling constant $^{1}J_{^{31}P-^{19}F}$ of 1437 Hz. These signals may be immediately assigned to PCl_3 and PF_3 respectively. The intensities of the signals indicated a molar ratio of PCl_3:PF_3 of approximately 1:1.. 72 hours later the same spectrum was observed only the intensity ratio PCl_3:PF_3 had altered to 2:1.

The ^{11}B n.m.r. spectrum recorded initially contained four signals; a sharp singlet at -28.5 p.p.m., a 1:1 doublet at -14.5 p.p.m. with $^{1}J_{^{11}B-^{19}F}$ 74 Hz, a broader singlet at -1.5 ± 0.5 p.p.m., and a sharper singlet at +8.5 p.p.m. These signals may be immediately assigned to BCl_3, $BFCl_2$, BF_2Cl and BF_3 respectively.[125,126] $^{1}J_{^{11}B-^{19}F}$ coupling constants for the series $BFCl_2$, BF_2Cl and BF_3 have been reported as 74, 34 and 15 Hz respectively, determined from ^{19}F work.[128] The signal intensities indicated a molar ratio BCl_3:$BFCl_2$:BF_2Cl:BF_3 of 15:6:5:4. After a further 72 hours the spectrum was again recorded and the same signals were observed. The molar ratio BCl_3:$BFCl_2$:BF_2Cl:BF_3 was approximately 15:6:4:6.

Reaction of phosphorus(III) fluoride with chlorine and boron trichloride

PF_3 (0.5 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196° followed by HCl (22 mmole), Cl_2 (0.25 mmole) and excess BCl_3. The ampoule was sealed and tested in the usual manner. The solution was clear and colourless at room temperature. The ^{31}P n.m.r. spectrum showed the complete absence of any fluorine containing phosphorus compound in either the +3 or +5 oxidation states, consisting of a readily observable singlet at -84.5 p.p.m. This resonance is characteristic of the tetrachlorophosphonium ion PCl_4^+. The chemical shift of PCl_4^+ in solution is dependent upon counterion[131] and values of -87 p.p.m. in nitrobenzene and acetonitrile[132] and -80.3 p.p.m. in liquid hydrogen chloride (this work) have been recorded. The ^{11}B n.m.r. spectrum consisted of a singlet at +8.2 p.p.m.

Reaction of phosphorus(III) fluoride with chlorine and boron trifluoride

PF_3 (2 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196^o followed by HCl (28 mmole), Cl_2 (1 mmole) and an excess of BF_3. The ampoule was sealed and brought up to room temperature in the usual manner. White/glassy crystals under a clear colourless solution were present at room temperature, but dissolved at 34.2^o. The ^{31}P n.m.r. spectrum of the clear colourless solution gave signals at -218.5, -102 and +80 p.p.m. The singlet at -218.5 p.p.m., the 1:3:3:1 quartet at -102 p.p.m. having $^1J_{P-F}$ 1410 Hz and the 1:5:10:10:5:1 with $^1J_{P-F}$ 956 Hz can be assigned to PCl_3, PF_3 and PF_5 respectively. The resonance due to PCl_3 could be observed on a single scan and there was relatively more PF_5 than PF_3 present. The ^{11}B n.m.r. spectrum contained one resonance, a singlet at +8.4 p.p.m. which was assigned to BF_3.[125]

Attempted exchange reactions of phosphorus(III) fluoride

(a) With phosphorus(III) chloride

PF_3 (2 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196^o, followed by HCl (22 mmole) and PCl_3 (0.2 ml., 2.2 mmole). The ampoule was brought up to room temperature and tested in the usual manner. The ^{31}P n.m.r. spectrum contained a singlet at -219.2 p.p.m. and a 1:3:3:1 quartet at -103.7 p.p.m. $^{1}J_{P-F}$ 1434 Hz, due to PCl_3[119] and PF_3 respectively. Thus PF_3 and PCl_3 do not exchange in liquid hydrogen chloride at room temperature on the time scale employed in this experiment.

(b) With phosphorus(III) bromide

PBr_3 (0.2 ml., 2.1 mmole) was syringed into an 8 mm. o.d. quartz ampoule. HCl (22 mmole) was then condensed into the ampoule at -196°, followed by PF_3 (2 mmole). The ampoule was brought up to room temperature and tested in the usual manner. The ^{31}P n.m.r. spectrum consisted of a singlet at -227.5 p.p.m. and a 1:3:3:1 quartet at -103.5 p.p.m. $^{1}J_{P-F}$ 1409 Hz, due to PBr_3[119] and PF_3 respectively. Thus PF_3 and PBr_3 do not exchange in liquid hydrogen chloride solution at room temperature on the time scale employed in this experiment.

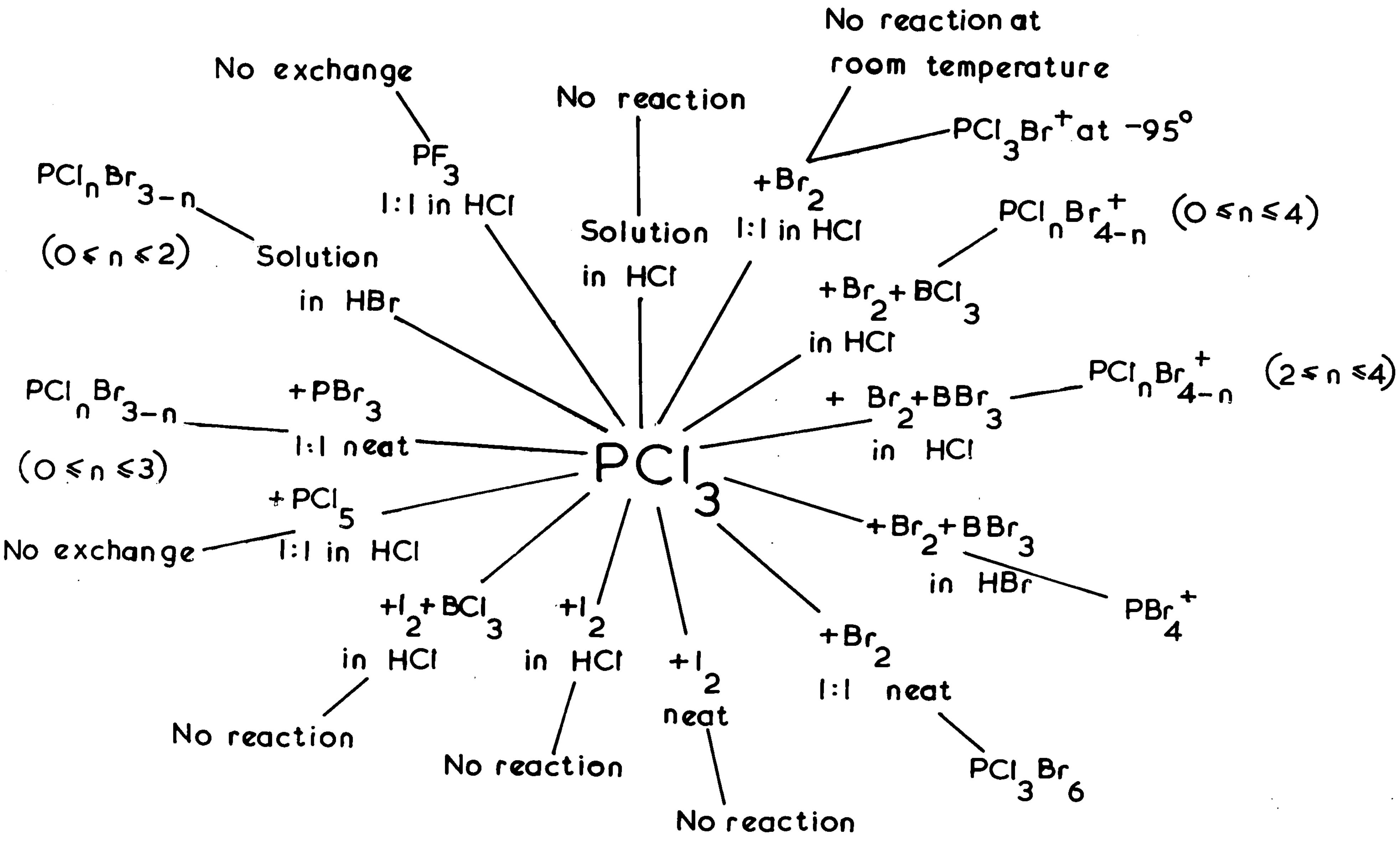
3.2 Phosphorus(III) chloride

Results and Discussion

Phosphorus(III) chloride was reacted with the established oxidising agents bromine and iodine in liquid hydrogen chloride. Oxidation of the phosphorus from the +3 to the +5 oxidation state by bromine producing tetraco-ordinate phosphorus(V) cations of type $PCl_xBr_{4-x}^+$ was only achieved in the presence of the solvoacids boron trichloride and boron tribromide. Phosphorus(III) chloride was not oxidised by iodine even in the presence of boron trichloride. The exchange reaction between phosphorus(III) chloride and the solvent in liquid hydrogen bromide was observed to yield

Fig.3.2.1

Reactions of phosphorus(III) chloride


PCl_3
No reaction
Solution in HCl
+Br_2 1:1 in HCl
No reaction at room temperature
PCl_3Br^+ at −95°
+Br_2+BCl_3 in HCl
$PCl_nBr_{4-n}^+$ (0 ⩽ n ⩽ 4)
+ Br_2+BBr_3 in HCl
$PCl_nBr_{4-n}^+$ (2 ⩽ n ⩽ 4)
+Br_2+BBr_3 in HBr
PBr_4^+
+Br_2 1:1 neat
PCl_3Br_6
+I_2 neat
No reaction
+I_2 in HCl
No reaction
+I_2+BCl_3 in HCl
No reaction
+PCl_5 1:1 in HCl
No exchange
+PBr_3 1:1 neat
PCl_nBr_{3-n} (0 ⩽ n ⩽ 3)
Solution in HBr
PCl_nBr_{3-n} (0 ⩽ n ⩽ 2)
PF_3 1:1 in HCl
No exchange

the species PCl_nBr_{3-n} ($0 \leq n \leq 2$). All reactions were followed by ^{31}P n.m.r. spectroscopy, and where appropriate ^{11}B n.m.r. spectroscopy. The results of the experiments are shown in Fig.3.2.1.

The ^{31}P n.m.r. spectrum of phosphorus(III) chloride in liquid hydrogen chloride indicated that the phosphorus(III) chloride had dissolved without protonation or exchange taking place. The observed chemical shift of -219 p.p.m. is in excellent agreement with literature values of -219.4 p.p.m.,[134] -220 ±1 p.p.m.[135] and -219.5 p.p.m. (this work) for the neat liquid. Phosphorus(III) chloride, however, is solvolysed in liquid hydrogen bromide. The ^{31}P n.m.r. spectrum of its solution in liquid hydrogen bromide contained 3 signals at -227.5, -227.2 and -224.1 p.p.m. No resonance at -219 p.p.m. was observed indicating the absence of phosphorus(III) chloride. The signals at -227.5, -227.2 and -224.1 p.p.m. are assigned to PBr_3, PBr_2Cl and $PBrCl_2$ respectively.[119,136] The solvolysis may be represented by the equation

$$n\,PCl_3 + m\,HBr \rightarrow x\,PBrCl_2 + y\,PBr_2Cl + z\,PBr_3 + m\,HCl$$

There is general agreement in the literature concerning the ^{31}P chemical shift of phosphorus(III) bromide, several workers having reported values in the region -228 ± 1 p.p.m.[119,134,135,136] The assignment of a ^{31}P chemical shift value to PBr_2Cl is not so well established. Fluck et al[136] have reported values for the series PBr_nCl_{3-n} ($0 \leq n \leq 3$), stating that the signals for PBr_3 and PBr_2Cl could not be completely resolved. Two signals were present but were very close together. The ^{31}P chemical shift values for PBr_2Cl and $PBrCl_2$ however, were intermediate between those for PBr_3 and PCl_3. Jones et al[137] have reported shifts of -227 and -228 p.p.m. for PBr_3 and PBr_2Cl respectively. In an attempt to resolve

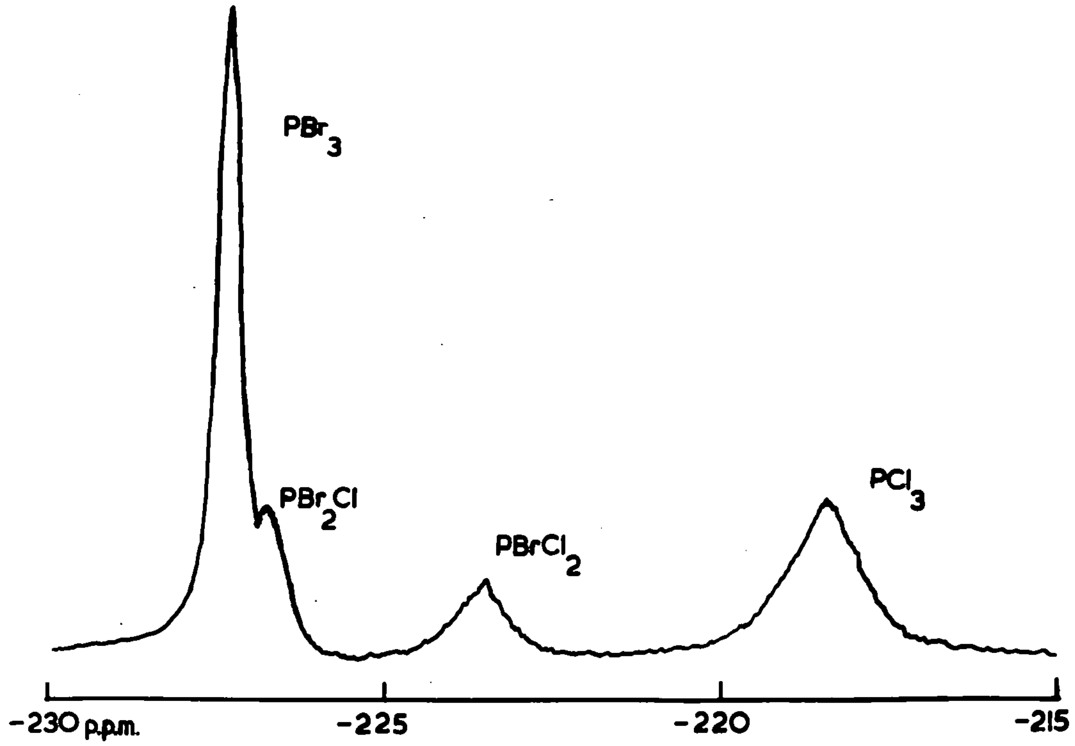


Fig.3.2.2

^{31}P n.m.r. solution spectrum

Phosphorus(III) bromide and phosphorus(III) chloride in a 1:1 molar ratio

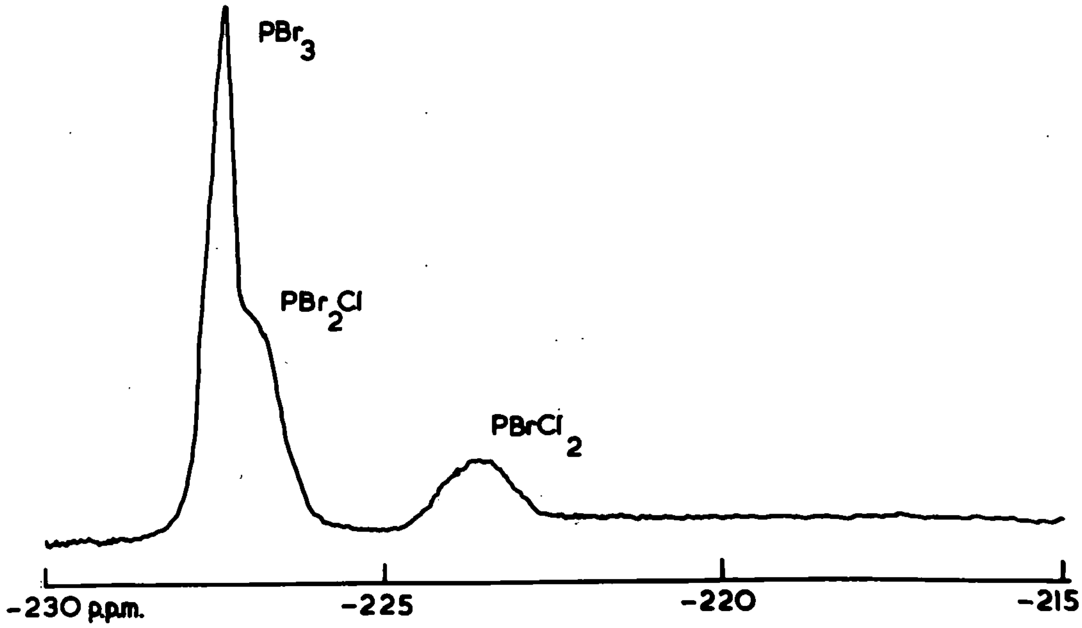


Fig.3.2.3

^{31}P n.m.r. solution spectrum

Phosphorus(III) chloride in liquid hydrogen bromide this inconsistency, the ^{31}P n.m.r. spectrum of a mixture of PBr_3 and PCl_3 in a 1:1 molar ratio was recorded. Three peaks were easily seen, and under conditions of high scale expansion the downfield peak was observed to consist of 2 signals; the major signal at -227.4 p.p.m. and a smaller signal appearing as a shoulder at -226.7 p.p.m. The complete spectrum thus contained 4 signals at -227.4, -226.7, -223.5 and -218.3 p.p.m. which in agreement with Fluck et al were assigned to PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3 respectively. The reported gradual increase in the broadness of the signal on going along the series from PBr_3 to PCl_3 owing to the nuclear quadrupole moment of chlorine being greater than that of bromine was also observed (see Fig.3.2.2.). The actual exchange reactions of phosphorus(III) halides producing mixed halides are of course well established.[136,139-45]

The oxidation of phosphorus(III) chloride by bromine in liquid hydrogen chloride at -95° was observed by Salthouse[81] who followed the reaction conductiometrically and isolated the low temperature oxidation product PCl_3Br^+ as the salt $PCl_3Br^+BCl_4^-$ at room temperature.[53] The colour of bromine in a mixture of PCl_3 and Br_2 in a 1:1 molar ratio in liquid hydrogen chloride was not discharged at room temperature, and the ^{31}P n.m.r. spectrum of the solution contained a single resonance at -218.6 p.p.m. indicating the presence of PCl_3. It is interesting to record, however, that on cooling the ampoule to -84° the colour of the bromine was discharged and a clear colourless solution was formed. The solution remained colourless up to about -35°. This observation is in complete agreement with the earlier work.[81] A probable explanation is that at -95° and up to -35° the PCl_3Br^+ cation is stabilised by solvated halide ion, whereas at higher temperatures and certainly at 34.2° the anions present are not large enough to stabilise this cation. The PCl_3Br^+ would then decompose, the phosphorus reverting to the +3 oxidation state in PCl_3. Unfortunately, because a variable temperature probe was not available it was not possible to follow this process using ^{31}P n.m.r. spectroscopy.

The reaction was repeated taking PCl_3:Br_2 in a 1:2 molar ratio and adding the Lewis acid BCl_3. The colour due to bromine was not discharged at room temperature, but as bromine was present in excess of the stoichiometric ratio for 1:1 reaction initially this was not surprising. Some orange-yellow solid had formed. The ^{31}P n.m.r. spectrum of the solution contained 5 signals and is shown in Fig.3.2.4. The average chemical shifts from several determinations are -87.3, -50.1, -9.7, +34 6 and +81.0 p.p.m., and the signals may be immediately assigned to the ions PCl_4^+, PCl_3Br^+, $PCl_2Br_2^+$, $PClBr_3^+$ and PBr_4^+ respectively. Comparison with the solid state data indicates that the values for PCl_4^+, PCl_3Br^+ and PBr_4^+ are within the previously known ranges.[131] Those for $PCl_2Br_2^+$ and PBr_3Cl^+ differ slightly, the reported ranges being -8.1 to -3.5 p.p.m. and +29 to +30 p.p.m. respectively.[131] These differences are hardly surprising as so few mixtures containing these ions have been examined, and the shift of such ions is dependent upon counterion.[131,146] Also, a small change in chemical shift is to be expected owing to the difference in diamagnetic susceptibility between a solid state and solution sample. The ^{11}B n.m.r. spectrum consisted of a resonance at +3.0 p.p.m. which is shown later in this work to be characteristic of a system containing fast-exchange BCl_3 and BCl_4^-. (p 200) However, a contribution from the species BCl_3Br^-, ^{11}B chemical shift, +15.4 p.p.m.,[147] also rapidly exchanging cannot be entirely ruled out.

Fig.3.2.4

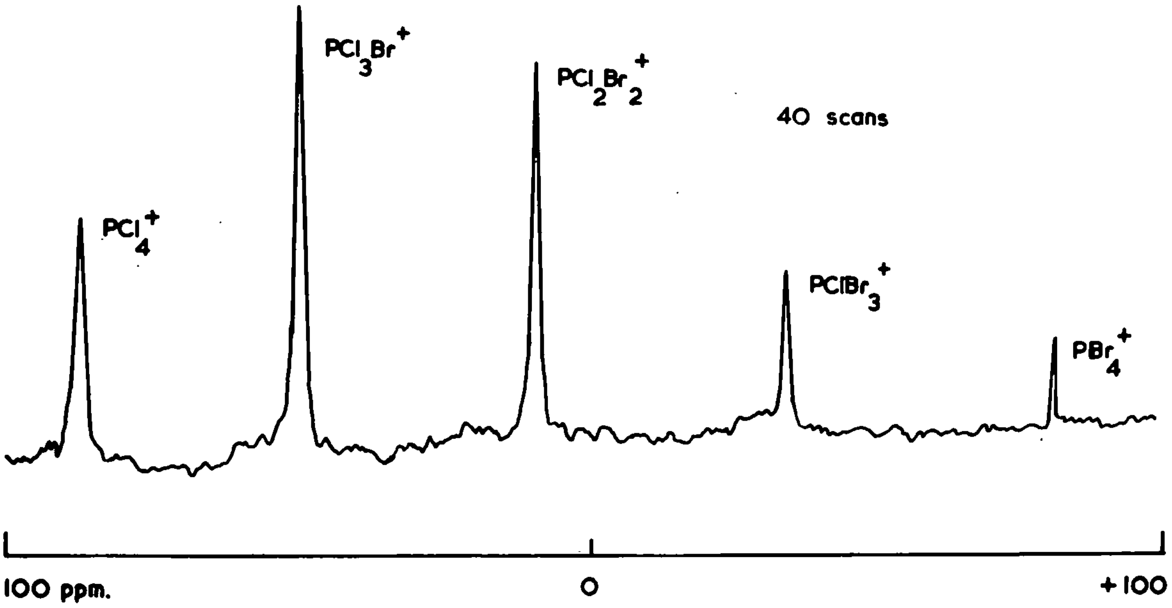
^{31}P n.m.r. solution spectrum

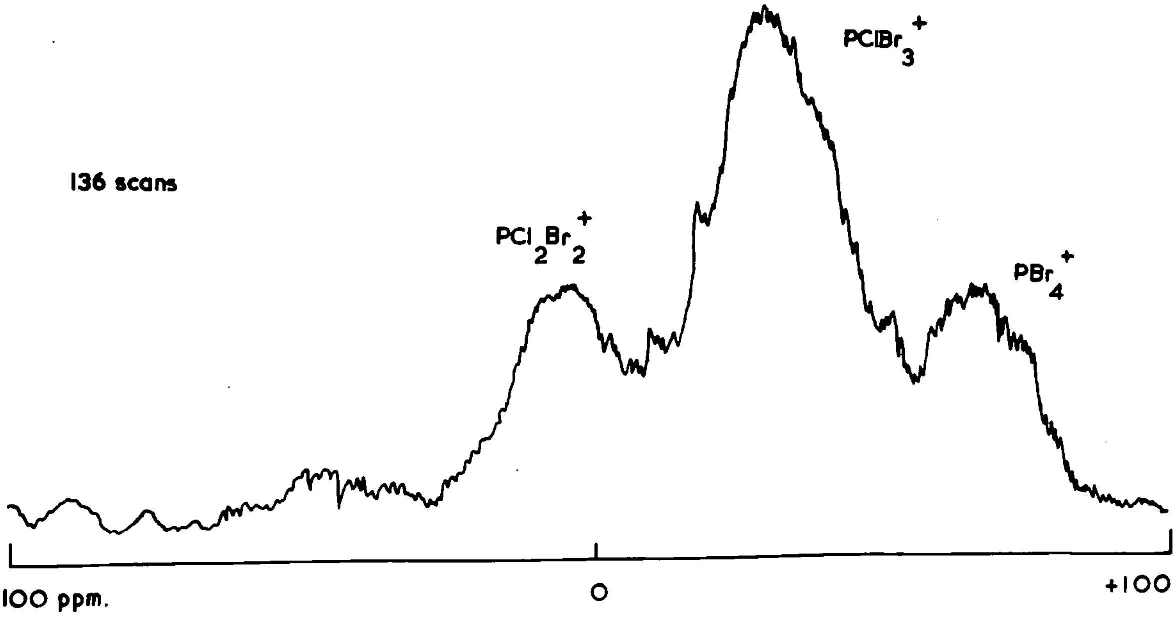
PCl_3 + Br_2 + BCl_3 in liquid hydrogen chloride

Fig.3.2.5

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

PCl_3 + Br_2 + BBr_3 in liquid hydrogen chloride


PCl_4^+
PCl_3Br^+
$PCl_2Br_2^+$
40 scans
$PClBr_3^+$
PBr_4^+
-100 ppm.
0
+100


$PClBr_3^+$
136 scans
$PCl_2Br_2^+$
PBr_4^+
-100 ppm.
0
+100

The reaction may be understood in terms of oxidation of the phosphorus from the +3 oxidation state in PCl_3 to the +5 oxidation state in PCl_3Br^+, followed by exchange to produce the other members of the series. The cations are of course stabilised at room temperature by the BCl_4^- ions present.

$$\begin{tikzcd}
PCl_3 + Br_2 + BCl_3 \arrow[r] & PCl_3Br^+ + BCl_3Br^- \arrow[d, "HCl"', "\text{Solvolysis}"] \\
 & BCl_4^- + HBr
\end{tikzcd}$$

Exchange reactions of type

$$PCl_3Br^+ + Br_2 \rightarrow PCl_2Br_2^+ + BrCl$$

would produce the higher brominated species, and a second type

$$PCl_3Br^+ + BrCl \rightarrow PCl_4^+ + Br_2$$

$$PCl_3Br^+ + HCl \rightarrow PCl_4^+ + HBr$$

could be postulated to explain formation of the PCl_4^+ ion. PCl_3Br^+ was the major cation component of the mixture (see Fig.3.2.4.)

The reaction was repeated using the same ratio of $PCl_3:Br_2$ but using BBr_3 as the solvoacid. No ^{31}P n.m.r. solution signals were obtained from the system, which contained a large amount of yellow solid material under a deep red solution. Three solid state signals were observed, however, at -5, +30 and +64 p.p.m., which may be immediately assigned to the phosphorus(V) cations $PCl_2Br_2^+$, $PClBr_3^+$ and PBr_4^+ respectively. $PClBr_3^+$ formed the major cation component of the mixture. These solid state values were in excellent agreement with published data.[131]

Fig.3.2.6

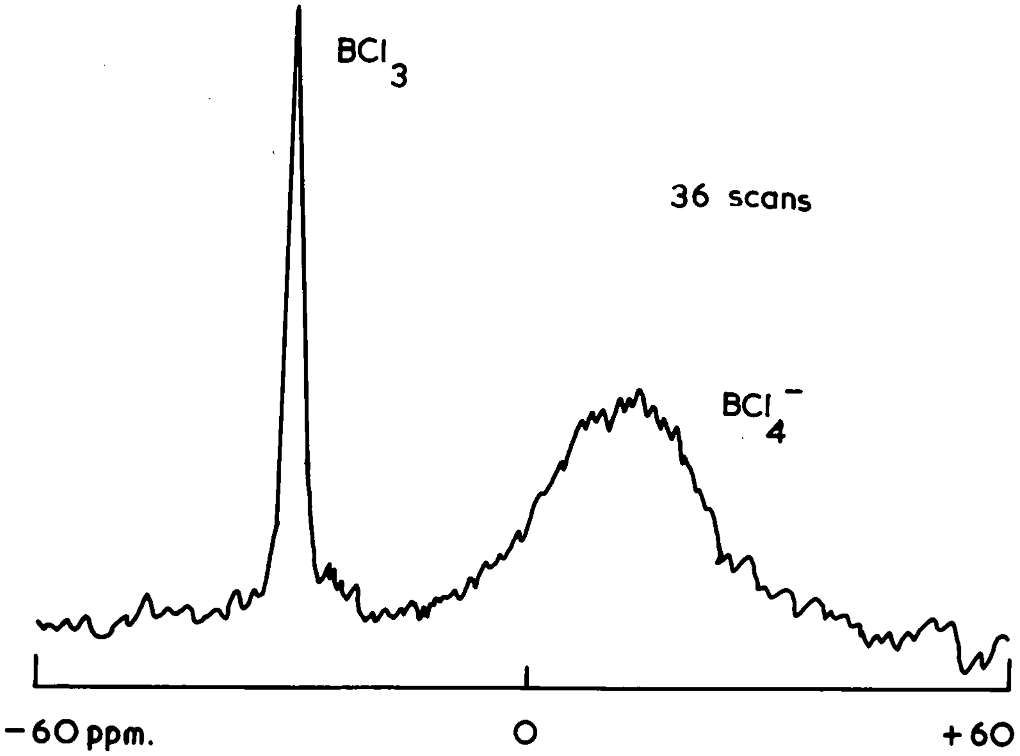
^{11}B n.m.r. solution/solid state spectrum

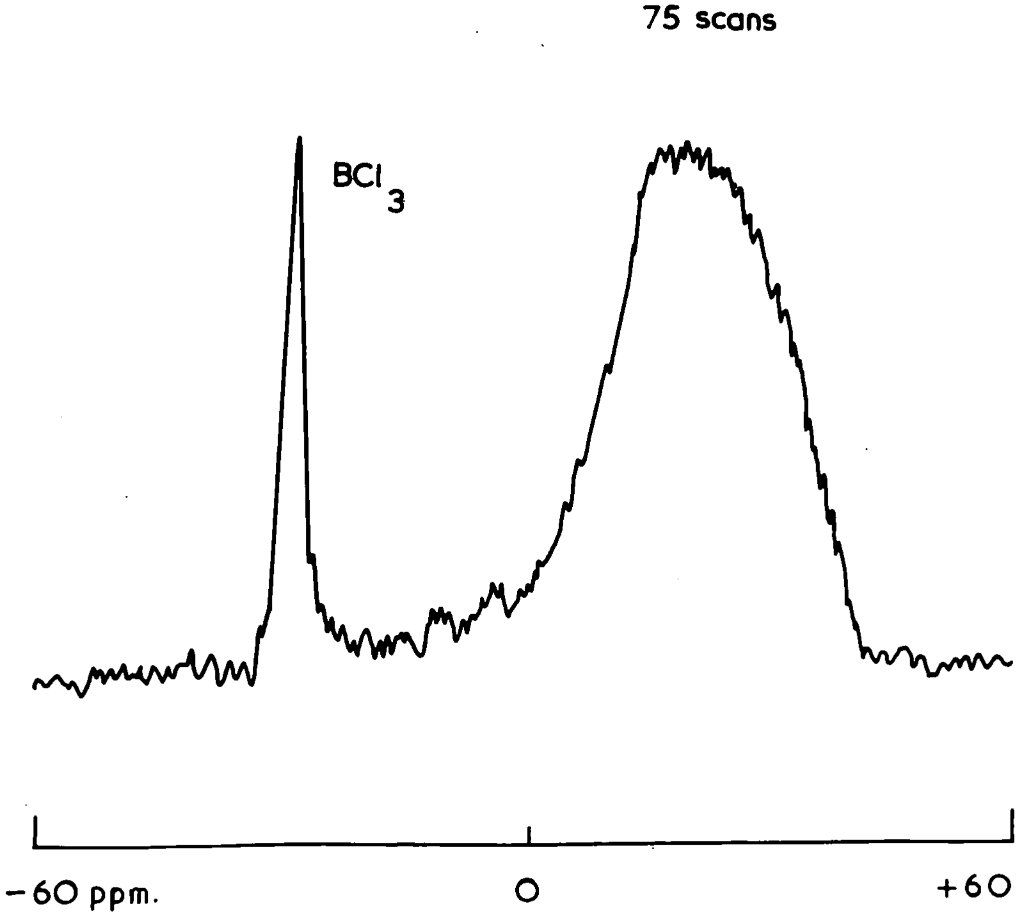
PCl_3 + Br_2 + BBr_3 in liquid hydrogen chloride

Fig.3.2.7

^{11}B n.m.r. solution/solid state spectrum

PCl_3 + Br_2 + BBr_3 in liquid hydrogen bromide


BCl3
36 scans
BCl4−
−60 ppm.
0
+60


75 scans
BCl3
−60 ppm.
0
+60

The ^{11}B n.m.r. spectrum contained two signals, a sharp solution peak at -28.0 p.p.m. and a broad solid state peak at +11.0 p.p.m. which may be assigned to BCl_3 and BCl_4^- respectively.[125,147] The appearance of both BCl_3 and BCl_4^- is readily explained. Later in this work the ^{11}B n.m.r. spectrum of a solution of boron tribromide in liquid hydrogen chloride was recorded, and was observed to consist of a single resonance at -29.0 p.p.m. which is the ^{11}B shift for BCl_3.[125] BBr_3 is thus completely solvolysed in liquid hydrogen chloride, and is indeed a "solvoacid" as it is solvolysed to the established solvoacid BCl_3. The system $PCl_3/2Br_2/BBr_3$ in liquid hydrogen chloride is thus equivalent to the previous system $PCl_3/2Br_2/BCl_3$ in the solvent with the addition of 3 mole equivalents of HBr. The absence of the species PCl_4^+ and PCl_3Br^+ is consistent with this explanation.

$$BBr_3 + 3HCl \rightarrow BCl_3 + 3HBr$$

$$\begin{tikzcd}
PCl_3 + Br_2 + BCl_3 \arrow[r] & PCl_3Br^+ \arrow[dl, "Br_2"'] & BCl_3Br^- \arrow[d, "HCl"] \\
PCl_2Br_2^+ + BrCl & & BCl_4^- + HBr
\end{tikzcd}$$

$$BrCl + HBr \rightarrow HCl + Br_2$$

The postulated mechanism leads to the formation of $PCl_2Br_2^+$, $PClBr_3^+$ and PBr_4^+ and, by removal of BrCl, avoids formation of PCl_4^+. ^{31}P and ^{11}B n.m.r. spectra are shown in Figs. 3.2.5 and 3.2.6 respectively.

To avoid solvolysis of the BBr_3 the reaction was repeated using liquid hydrogen bromide as solvent. The mole ratio PCl_3: Br_2:BBr_3 was

1:2:1. No ^{31}P n.m.r. solution signals were observed, but a broad solid state peak at +66.5 p.p.m., attributable to PBr_4^+, was recorded. The ^{11}B n.m.r. spectrum of this system, shown in Fig.3.2.7., contained 2 signals, one sharp peak at -29.0 p.p.m. which may be immediately assigned to BCl_3 and a broad solid state resonance at +19.0 p.p.m. This signal is almost certainly due to a bromochloroborate anion. Hartman et al[147] have recently reported ^{11}B and ^{19}F n.m.r. data for the mixed haloborate anions in methylenehalide solvents, quoting ^{11}B shifts of +15.4 and +22.1 p.p.m. for the species BCl_3Br^- and $BCl_2Br_2^-$ respectively. Thus, the broad resonance at +19.0 p.p.m. may be assigned to either or both of these anions.

The choice of liquid hydrogen bromide as solvent, to avoid solvolysis of the BBr_3, makes this reaction mixture a very complex one indeed. It has already been shown in this work that PCl_3 is solvolysed in the solvent to PBr_3, PBr_2Cl and $PBrCl_2$, thus the reaction may be thought of as the oxidation of these 3 phosphorus(III) species by Br_2 in the presence of BBr_3, and some HCl from solvolysis of the PCl_3 in liquid hydrogen bromide. BBr_3 is solvolysed to BCl_3 in liquid hydrogen chloride, and mixed bromochloroboron(III) compounds may well be formed from BBr_3 and HCl in liquid hydrogen bromide solution. The formation of PBr_4^+ ions in the reaction mixture $PCl_3 + 2Br_2 + BBr_3$ in liquid hydrogen bromide is hardly surprising, and the formation of mixed bromochloroborate anions may be understood. The presence of both BCl_3 and bromochloroborate anions in the reaction products, together with the absence of any phosphorus(III) species, require the presence of solvated halide ions or polyhalide anions to balance the phosphorus(V) cations.

The reaction between phosphorus(III) chloride and bromine is the subject of somewhat confusing reporting in the literature. According to fairly early work bromine reacts with phosphorus(III) chloride to give PCl_3Br_2.[148,149] The reaction proved, however, to be rather problematical.[150] When phosphorus(III) chloride and bromine react, compounds are readily formed which contain more than 5 halogen atoms per atom of phosphorus; e.g. PCl_2Br_7,[151] PCl_3Br_n ($n = 4$ to 10)[150] and $PCl_3BrBr(Br_2)_n$ ($n = 1$ to 8).[152] Other workers[153] have prepared the compounds PCl_3Br_n ($n = 4$, 8 and 10) and have formulated the compounds as polybromides of structure $[PCl_3Br^+][Br(Br_2)_n]^-$. Compounds with nonstoichiometric compositions have also been reported. Among these is $PCl_3Br_{5.1-5.7}$ which continuously loses Br_2 in vacuum and is converted to $PCl_{4.8}Br_{0.4}$. When the latter is sublimed in vacuo at 50°, $PCl_{4.67}Br_{0.33}$ is produced.[154] This is a substance whose unit cell, it is suggested, should contain $8PCl_4^+$, $4PCl_6^-$ and $4Br^-$ ions.[155] The compound PCl_4Br is also mentioned in the literature.[150,156] Reaction of PCl_3 and Br_2 in $AsCl_3$ solution yields a solid compound containing 5 atoms of halogen per atom of phosphorus, and has been formulated in solution as $PCl_4^+PCl_5Br^-$.[157] Raman and ^{31}P n.m.r spectroscopic and ESCA studies on the solid, however, do not confirm this formulation. The solid P_2Cl_9Br certainly contains PCl_4^+ ions, and also PCl_3Br^+ and PCl_6^- ions, and the presence of two types of Br in the structure is indicated by the ESCA work. In theory, the formula P_2Cl_9Br could be achieved by any combination of the systems $(3PCl_4^+ + 2Br^- + PCl_6^-)_m + (PCl_3Br^+PCl_6^-)_n$.[158]

The reaction between phosphorus(III) chloride and bromine was carried out in this study in the absence of a solvent. A dark red solid was produced in addition to a dark red liquid. The ^{31}P n.m.r. spectrum of the liquid contained signals at -222.9 p.p.m. and -218.1 p.p.m. which may be assigned to $PBrCl_2$[136] and PCl_3[119] respectively. A ruby red crystalline solid sublimed up the ampoule during the period in which it was inside the n.m.r. spectrometer and a preparative scale experiment was carried out in order to obtain a larger sample of this material. The red solid is shown in Plate 3.2.1.

The infrared spectrum of the solid contained absorption at 1309, 640 and 582 cm^{-1} which are characteristic of the PCl_4^+ ion.[20f] Two other absorptions at 496 and 451 cm^{-1} are probably P-Br stretching modes. The Raman spectrum contained frequencies at 661, 450 and 230 cm^{-1} which are characteristic of PCl_4^+,[159] an absorption at 372 cm^{-1} probably assignable to PCl_3Br^+ and a very strong band at 263 cm^{-1} which is almost certainly due to a polybromide anion.[160] The ^{31}P n.m.r. spectrum of the solid contained resonances at -72.5 and -25 p.p.m. which may be assigned to PCl_4^+ and PCl_3Br^+ respectively. These shift values are outside the published ranges for the cations,[131] but it is known that considerable variations can occur depending on counterion.[146] A comparison of peak areas in the ^{31}P n.m.r. spectrum indicates that the cations PCl_4^+ and PCl_3Br^+ are present in roughly 4:1 molar ratio. A formulation of $4PCl_4^+.PCl_3Br^+.5Br_5^-$ would be in agreement with this, and in fair accord with analytical data (see p. 73). However, the Raman spectrum of the material is identical with that of the PCl_3Br_6 of Gates et al,[160] and it is still not clear whether this substance is a stoichiometric compound or a nonstoichiometric mixture. ^{31}P n.m.r. and Raman spectra of the solid are shown in Figs. 3.2.8 and 3.2.9.

The oxidation of phosphorus(III) chloride by bromine under a variety of conditions to produce phosphorus(V) cations was not paralleled by

Plate 3.2.1

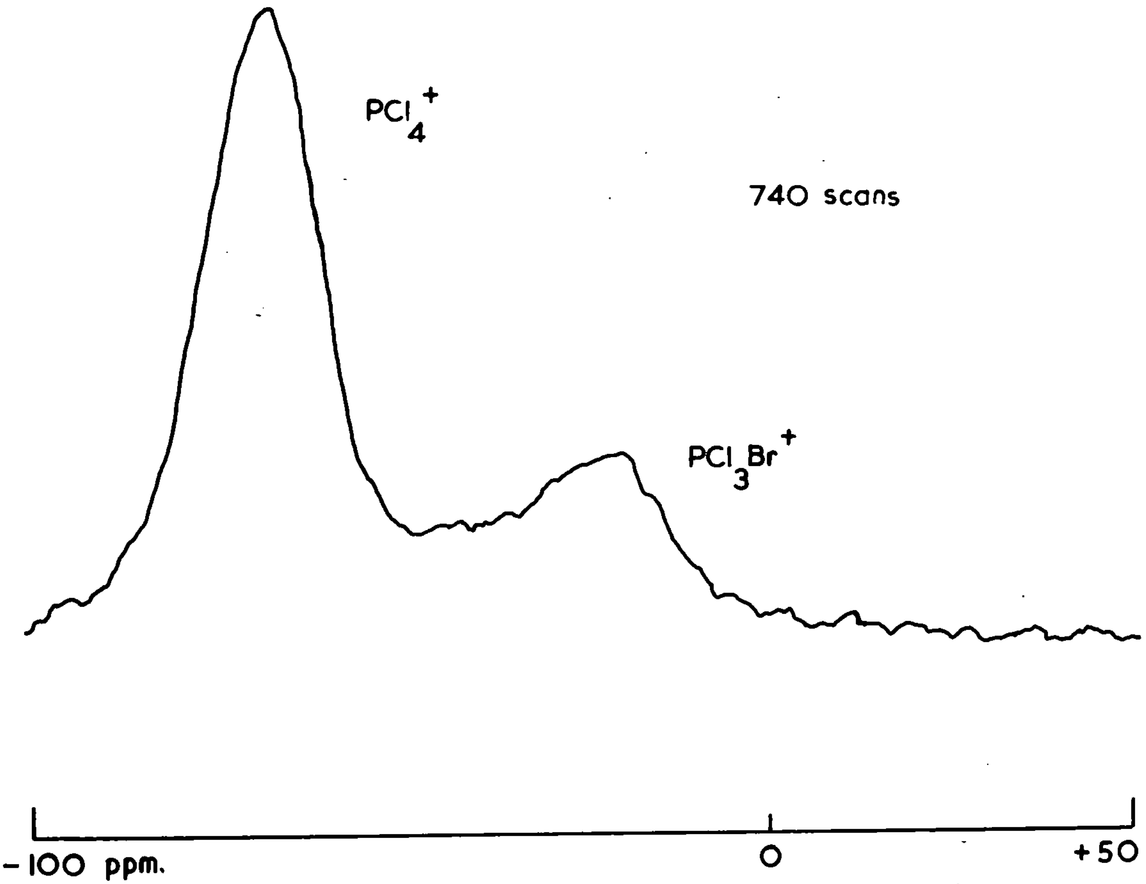
'PCl_3Br_6'

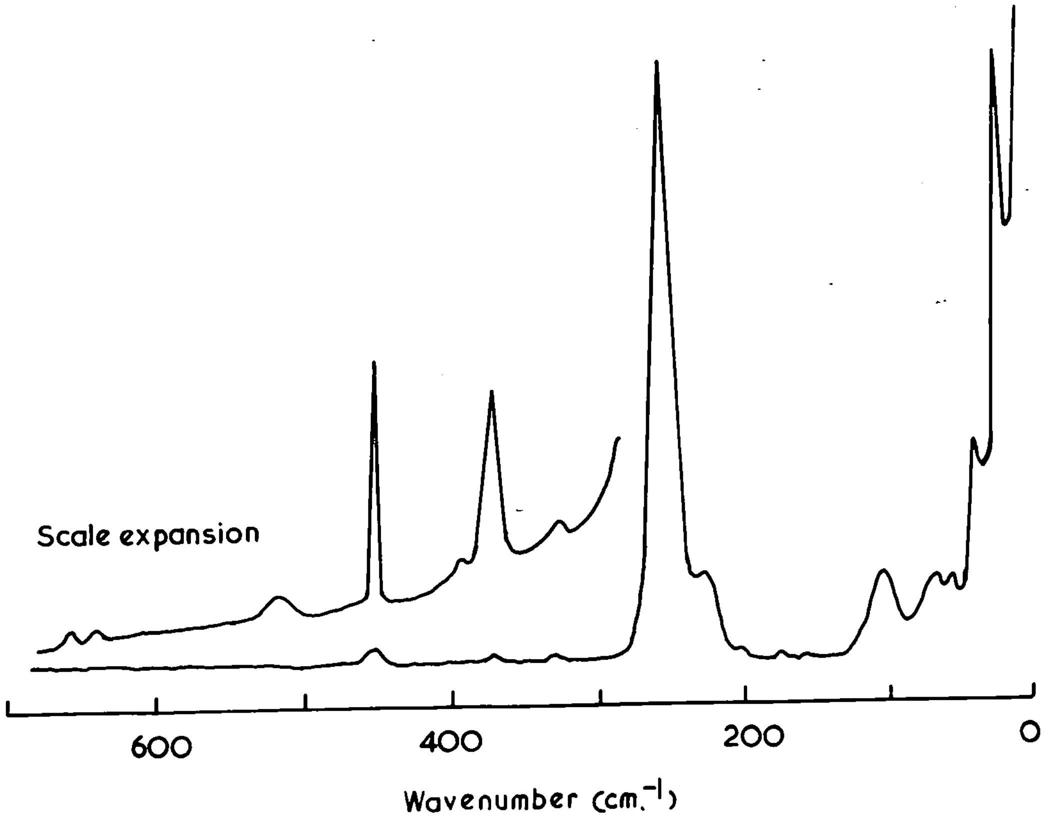
Fig.3.2.8

^{31}P n.m.r. solid state spectrum of PCl_3Br_6

Fig.3.2.9

Raman spectrum of PCl_3Br_6


PCl_4^+
740 scans
PCl_3Br^+
-100 ppm.
0
+50


Scale expansion
600
400
200
0
Wavenumber (cm.$^{-1}$)

iodine. A 1:1 molar ratio of PCl_3:I_2 in liquid hydrogen chloride gave a peak in the ^{31}P n.m.r. spectrum at -219.5 p.p.m. which may be immediately assigned to PCl_3.[119] In this respect, no apparent reaction, the behaviour of the two oxidising agents is similar. Iodine failed to oxidise the phosphorus even in the presence of the solvoacid BCl_3, again the sole resonance in the ^{31}P n.m.r. spectrum was that due to PCl_3. Finally PCl_3 and I_2 were mixed in a 1:1 molar ratio in the absence of a solvent, and although the iodine appeared to be partially dissolved, the sole signal in the ^{31}P n.m.r. spectrum was that due to PCl_3. The failure of iodine to oxidise phosphorus(III) chloride is not too surprising as it is a comparatively weak oxidising agent.

The ^{31}P n.m.r. spectrum of a mixture of PCl_3 and PCl_5 in a 1:1 molar ratio in liquid hydrogen chloride was recorded to determine whether any exchange was taking place between the species PCl_3 and PCl_4^+ in the solvent. Two signals at -220 and -79.5 p.p.m. were observed and may be immediately assigned to PCl_3 and PCl_4^+ respectively. The values of these shifts are within 1 p.p.m. of those observed for each of the species alone in the solvent, and are in excellent agreement with literature values.[119,131] Both signals were sharp and it may be assumed that the two species do not exchange in liquid hydrogen chloride at room temperature.

Experimental

Behaviour of phosphorus(III) chloride in liquid hydrogen chloride

PCl_3 (0.5 ml., 5.5 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by HCl (30 mmole). The ampoule was sealed and tested in the usual manner. A clear, colourless solution was obtained at room temperature. The ^{31}P n.m.r. spectrum of this solution consisted of a single resonance at -219 p.p.m. The reported values for the neat liquid are -219.4 p.p.m.,[134] -220 ± 1 p.p.m.[135] and a value of -219.5 p.p.m. was recorded in this work. It may thus be assumed that PCl_3 is soluble in liquid hydrogen chloride without reaction.

Behaviour of phosphorus(III) chloride in liquid hydrogen bromide

PCl_3 (0.5 ml., 5.5 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196° followed by HBr (30 mmole). The ampoule was sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the clear, colourless solution consisted of 3 resonances at -227.5, -227.2 and -224.1 p.p.m. These may be assigned to PBr_3,[119,134,135,136] PBr_2Cl[136] and $PBrCl_2$[136] respectively. A signal due to PCl_3 was absent. PCl_3 is thus totally solvolysed in liquid hydrogen bromide.

$$PCl_3 \xrightarrow{\text{liq.HBr}} PCl_2Br,\ PClBr_2,\ PBr_3$$

Reaction between phosphorus(III) chloride and bromine

PCl_3 (0.1 ml., 1.1 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196° followed by HCl (30 mmole) and Br_2 (0.215 g., 1.34 mmole). The ampoule was sealed and tested in the usual manner. At room temperature the ampoule contained two Br_2-coloured layers, the lower being more intensely coloured than the upper. The ^{31}P n.m.r. spectrum of this solution showed the sole presence of PCl_3 at -218.6 ± 0.4 p.p.m. On cooling to -84° the colour due to the bromine was discharged. The solution remained clear and colourless up to about -35°.

Reaction between phosphorus(III) chloride, bromine and boron trichloride

PCl_3 (0.1 ml., 1.1 mmole) was condensed into an 8 mm. o.d. quartz ampoule, followed by HCl (30 mmole), Br_2 (0.320 g., 2 mmole) and an excess of BCl_3. The ampoule was sealed and tested in the usual manner. At room temperature the ampoule contained orange-yellow needles under a dark bromine coloured solution. The ^{31}P n.m.r. spectrum of the solution is shown in Fig.3.2.4. Four strong signals are clearly visible, and the weak signal at higher fields was shown to be reproducible in a number of independent scans. Chemical shifts of the five peaks are -87.3, -50.1, -9.7, +34.6 and 81.0 p.p.m. All shifts are subject to an error of ± 2 p.p.m. The peaks may be immediately assigned to the phosphorus(V) cations PCl_4^+, PCl_3Br^+, $PCl_2Br_2^+$, $PClBr_3^+$ and PBr_4^+. Values are in good agreement with solid state data.[131] The ^{11}B n.m.r. spectrum gave a single peak at +3.0 p.p.m. This is shown, later in this work, to be an exchange averaged signal between BCl_3 and BCl_4^-.

The reaction between phosphorus(III) chloride, bromine and boron tribromide

PCl_3 (0.2 ml., 2.2 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by HCl (30 mmole), Br_2 (0.720 g., 4.5 mmole) and BBr_3 (0.666 g., 2.6 mmole). The ampoule was sealed and tested in the usual manner and was observed to contain much yellow solid and a bromine coloured solution at room temperature. The ^{31}P n.m.r. spectrum contained three solid state peaks at -5, +30 and +64 p.p.m. These peaks may be assigned to the phosphorus(V) cations $PCl_2Br_2^+$, $PClBr_3^+$ and PBr_4^+ respectively. These values are in excellent agreement with published solid state data.[131] $PClBr_3^+$ was the major component of the mixture. The ^{11}B n.m.r. spectrum contained 2 signals; a sharp solution peak at -28.0 p.p.m. and a broad solid peak at +11.0 p.p.m. These signals are characteristic of BCl_3[125] and BCl_4^-.[147] The presence of BCl_3 is due to solvolysis of the excess BBr_3 as is shown later in this work (p.198).

The reaction was repeated using the same reactants, but in liquid hydrogen bromide. PCl_3 (0.2 ml., 2.2 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196^o, followed by HCl (30 mmole), Br_2 (0.94 g., 5.8 mmole) and BBr_3 (0.490 g., 1.96 mmole). The ampoule was sealed and tested in the normal manner and contained yellow solid and a bromine-coloured solution at room temperature. The ^{31}P n.m.r. spectrum contained one solid state resonance at +66.5 p.p.m., which may be assigned to PBr_4^+. The ^{11}B n.m.r. spectrum again contained 2 signals; a sharp resonance at -29.0 p.p.m. and a broad resonance at +19.0 p.p.m. The resonance at -29.0 p.p.m. may be assigned to BCl_3. The solid state resonance is certainly due to a mixed bromochloroborate. Hartman[147] reports solution values of +15.4 and +22.1 p.p.m. for BCl_3Br^- and $BCl_2Br_2^-$ respectively. Thus, the broad resonance may be attributed to either or both of these anions.

The reaction between phosphorus(III) chloride and bromine in the absence of a solvent

PCl_3 (1 ml., 11 mmole) was condensed into an 8 mm. o.d. pyrex ampoule at -196^o, followed by an excess of bromine. The ampoule was sealed and allowed to warm to room temperature. A small quantity of dark red solution lay in the base of the ampoule and a dark red crystalline matrix filled about $\frac{1}{3}$ of its volume. The ^{31}P n.m.r. spectrum of the solution contained a weak signal at -222.9 p.p.m. and a strong signal at -218.1 p.p.m. These peaks may be assigned to $PBrCl_2$[136] and PCl_3. Whilst inside the R10, a ruby red crystalline solid sublimed out of the dark red solid in the middle of the ampoule. A large scale preparation was performed to obtain a larger sample of this material. The ruby red crystalline solid is shown in Plate 3.2.1.

PCl_3 (2 ml., 22 mmole) was syringed into an 16 mm. o.d. pyrex ampoule 18 cm. in length. Br_2 (1.20 ml., 22 mole) was condensed into the ampoule at -196°. The ampoule was sealed and allowed to reach room temperature. A mixture of red and yellow solids occupied the lower part of the ampoule, very little liquid remaining. The lower part of the ampoule was placed in an oil bath at 30-34° for 14 days to allow slow sublimation of the ruby red crystalline solid to take place. A very small quantity of yellow crystals also sublimed up the tube, but they were not investigated. The ampoule was taken into the dry box, where it was cracked open and the ruby red crystalline solid removed for investigation. The infrared spectrum of the solid showed absorptions at 1309w, 640s, 582s, 496s and 451s cm^{-1}. The absorptions at 1309w, 640s and 582s cm^{-1} are due to PCl_4^+.(20f) The other 2 absorptions are probably P-Br stretching modes. The Raman spectrum of the solid showed absorptions at 661vw, 644vw, 524vw, 450w, 371w, 332vw, 263vs, 230m, 202vw, 183vw, 160vw, 103m, 70w, 57vw, 43vw and 24w cm^{-1}. The absorptions at 661, 450 and 230 cm^{-1} are characteristic of PCl_4^+,[159] and the absorption at 371 cm^{-1} is probably due to PCl_3Br^+.[160] The very strong band at 263 cm^{-1} is almost certainly due to a polybromide anion.[160] The ^{31}P solid state spectrum contains signals at -72.5 p.p.m. and -25 p.p.m. These shifts are high for PCl_4^+ and PCl_3Br^+ respectively,[131] but do confirm the infrared and Raman findings. A comparison of intensities indicates that PCl_4^+ and PCl_3Br^+ are present in approximately a 4:1 ratio. The compound loses bromine rapidly on exposure to air, but is stable at room temperature if stored in an ampoule. Analyses of mixtures are not always meaningful, but the available data is presented.

Found: P,4.85%; Br,72.12%; Cl,19.95%. $4PCl_4^+.PCl_3Br^+.5Br_5^-$ requires: P,5.3%; Br,71.5%; Cl,23.2%; PCl_3Br_6 requires: P,5.02; Br,77.7; Cl,17.2.

The reaction between phosphorus(III) chloride and iodine

I_2 (0.305 g., 1.2 mmole) was placed inside an 8 mm. o.d. quartz ampoule. HCl (30 mmole) was condensed into the ampoule, on top of the I_2 at -196°, followed by PCl_3 (0.1 ml., 1.1 mmole). The ampoule was sealed and tested in the usual manner. At room temperature a deep purple solution was obtained. The ^{31}P n.m.r. spectrum consisted of a single peak at -218 p.p.m., indicating the sole presence of PCl_3.

The reaction was repeated with the addition of boron trichloride. I_2 (0.280 g., 1.1 mmole) was placed inside an 8 mm. o.d. quartz ampoule. HCl (25 mmole) was condensed into the ampoule at -196°, followed by PCl_3 (0.1 ml., 1.1 mmole) and an excess of BCl_3. The ampoule was sealed and tested in the normal manner, and at room temperature contained a clear violet solution over a little undissolved iodine. The ^{31}P n.m.r. spectrum of the solution contained a single resonance at -219 p.p.m., indicating the sole presence of PCl_3. The ^{11}B n.m.r. spectrum also consisted of a single peak, attributable to BCl_3, at -29.0 p.p.m.

After the failure to observe any oxidised or exchange species in the previous two experiments, the first experiment was repeated in the absence of a solvent.

I_2 (2.75 g., 11 mmole) was placed inside an 8 mm. o.d. pyrex ampoule. PCl_3 (1 ml., 11 mmole) was added by syringe and the ampoule sealed. A clear deep purple solution over much undissolved iodine was obtained. The ^{31}P n.m.r. spectrum of the solution contained one peak at -219.5 p.p.m. which may be assigned immediately to PCl_3.

It appears that iodine will not oxidise phosphorus(III) chloride.

The reaction between phosphorus(III) chloride and phosphorus(III) bromide

The exchange reactions of phosphorus(III) halides are well established.[136,139-145] However, there is some confusion in the literature regarding the ^{31}P chemical shifts of the series PBr_nCl_{3-n} $(0 \leq n \leq 3)$. Jones[137] even quotes a value for PBr_2Cl downfield from PBr_3. Accordingly, the ^{31}P n.m.r. spectrum of a mixture of PCl_3 and PBr_3 in a 1:1 molar ratio was recorded.

PCl_3 (1 ml., 11 mmole) was syringed into an 8 mm. o.d. pyrex ampoule followed by PBr_3 (1 ml., 10.5 mmole). The ampoule was sealed on the vacuum line. The ^{31}P n.m.r. spectrum showed 3 clear peaks on a single scan at -227.4, -223.5 and -218.3 p.p.m. Associated with the peak at -227.4 p.p.m. was a shoulder at -226.7 p.p.m. The resonances at -227.4, -226.7, -223.5 and -218.3 p.p.m. may be safely assigned to PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3 respectively. The peaks broadened along the series PBr_3 to PCl_3 in agreement with the observations of Fluck et al.[136]

The ^{31}P n.m.r. spectrum of a mixture of phosphorus(III) and phosphorus(V) chlorides in liquid hydrogen chloride

PCl_5 (0.979 g., 4.7 mmole) was loaded into an 8 mm. o.d. quartz ampoule. HCl (25 mmole) was condensed into the ampoule at -196^{o}, followed by PCl_3 (0.41 ml., 4.7 mmole). The ampoule was sealed and tested in the usual manner. Not all the PCl_5 was in solution at room temperature, but the greater part had dissolved. The ampoule was inverted and the ^{31}P n.m.r. spectrum of the solution was recorded. Two signals at -220 and -79.5 p.p.m. were observed on a single scan. These resonances may be immediately assigned to PCl_3 and PCl_4^+ respectively.[119,131]

It can thus be assumed that no exchange occurs at room temperature between PCl_3 and PCl_4^+ in liquid hydrogen chloride.

3.3 Phosphorus(III) bromide

Results and Discussion

Phosphorus(III) bromide is shown to be solvolysed by liquid hydrogen chloride and was reacted with the established oxidising agents chlorine and iodine in the solvent. Oxidation of the phosphorus from the +3 to the +5 oxidation state was effected by chlorine, alone and in the presence of boron trichloride.

All reactions were followed by ^{31}P n.m.r., and where appropriate ^{11}B n.m.r. spectroscopy. The results of experiments are shown in Fig.3.3.1.

The ^{31}P n.m.r. spectrum of phosphorus(III) bromide in liquid hydrogen chloride indicated that some solvolysis had occurred (Fig.3.3.2). A large peak at -227.5 p.p.m. with a shoulder at -227.1 p.p.m. and a smaller peak at -224.3 p.p.m. were observed, which may be assigned to PBr_3, PBr_2Cl and $PBrCl_2$ respectively.[119,136] No signal due to PCl_3

$$m\,PBr_3 + n\,HCl \xrightarrow{\text{solvolysis}} x\,PBr_3 + y\,PBr_2Cl + z\,PBrCl_2 + nHBr$$

could be detected. The ^{31}P n.m.r. spectrum of PBr_3 in liquid hydrogen chloride is thus closely comparable with that of PCl_3 in liquid hydrogen bromide. The observed chemical shift of -227.3 p.p.m. for PBr_3 in liquid hydrogen bromide indicates that the compound is soluble in the solvent without reaction.

Fig.3.3.1

Reactions of phosphorus(III) bromide

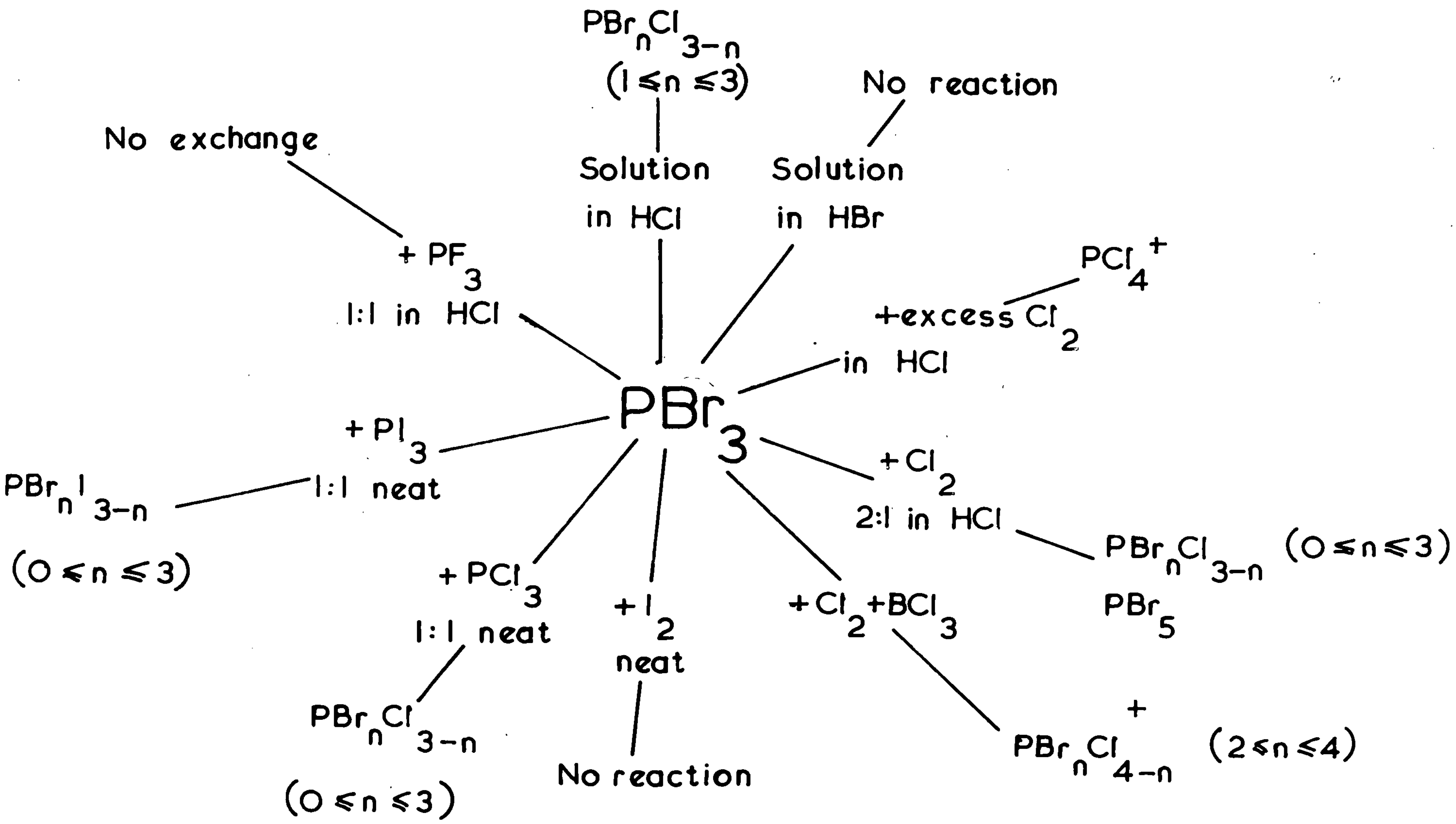
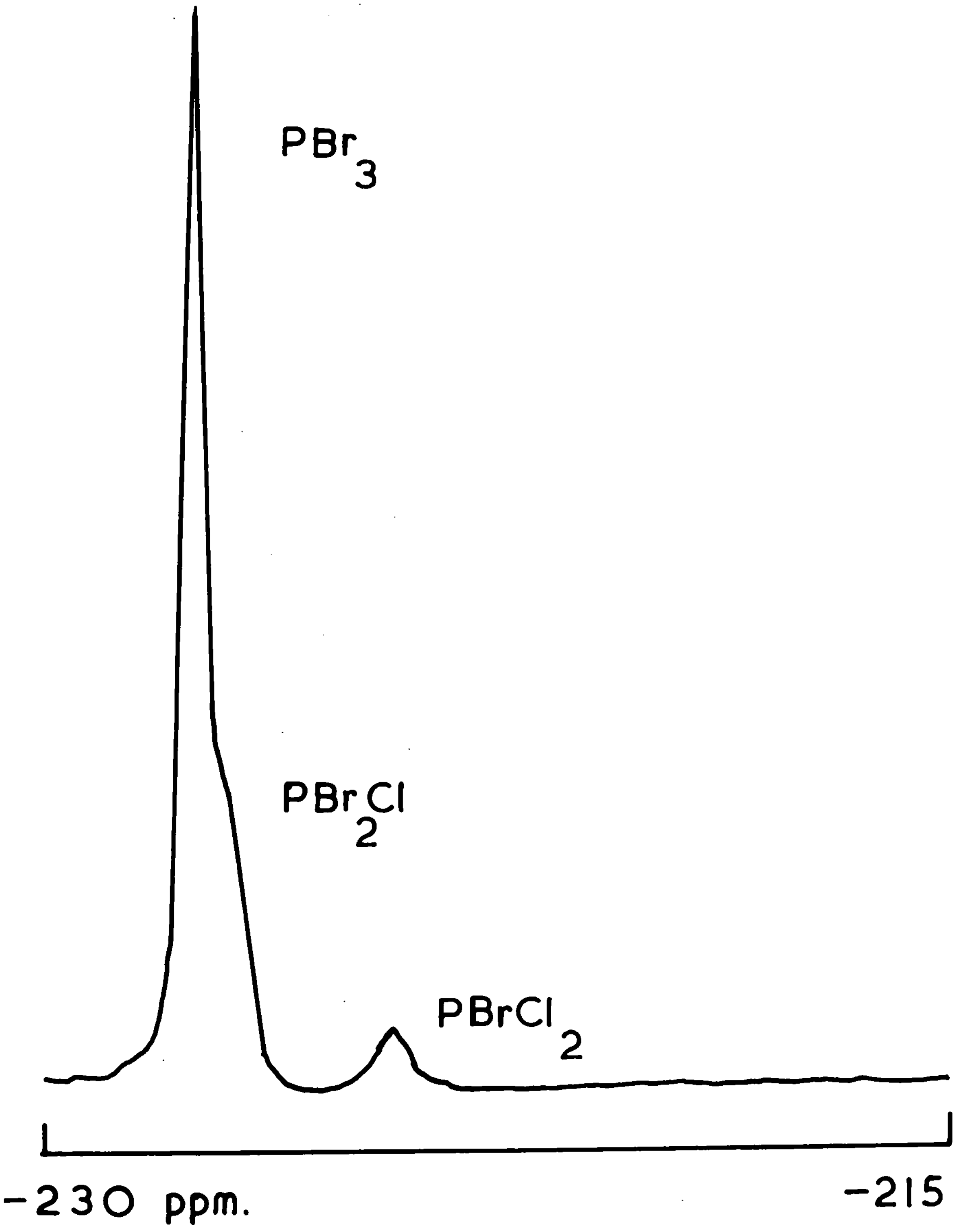

PBr_nCl_{3-n}
$(1 \leqslant n \leqslant 3)$
Solution in HCl
No reaction
Solution in HBr
No exchange
$+ PF_3$
1:1 in HCl
PCl_4^+
$+$excess Cl_2 in HCl
PBr_3
$+ PI_3$
1:1 neat
PBr_nI_{3-n}
$(0 \leqslant n \leqslant 3)$
$+ Cl_2$
2:1 in HCl
PBr_nCl_{3-n} $(0 \leqslant n \leqslant 3)$
PBr_5
$+ PCl_3$
1:1 neat
$+ I_2$
neat
$+ Cl_2 + BCl_3$
PBr_nCl_{3-n}
$(0 \leqslant n \leqslant 3)$
No reaction
$PBr_nCl_{4-n}^+$ $(2 \leqslant n \leqslant 4)$

Fig.3.3.2

^{31}P n.m.r. solution spectrum

Phosphorus(III) bromide in liquid hydrogen chloride


PBr$_3$
PBr$_2$Cl
PBrCl$_2$
-230 ppm.
-215

The reaction between phosphorus(III) bromide and an excess of chlorine in liquid hydrogen chloride at -95° has been reported to yield $PCl_4^+PCl_6^-$, via PBr_3Cl^+ as a postulated intermediate.[53] A mixture of phosphorus(III) bromide and an excess of chlorine in liquid hydrogen chloride at room temperature gave a deep red solution whose ^{31}P n.m.r. spectrum consisted of a broad signal at -97 p.p.m. This signal is assigned to PCl_4^+ even though the value is just outside the published range of chemical shifts of PCl_4^+ in solid state spectra[131] and the ^{31}P shift of PCl_4^+ in liquid hydrogen chloride has been shown to be -80 ± 0.5 p.p.m. The shift is far too high to be assigned to a phosphorus (III) species and is far too low to be assigned to a tetraco-ordinated phosphorus(V) cation containing bromine. The low shift value and the broadness of the peak may be due to an exchange process. In an independent experiment it was shown that PCl_3 and PCl_4^+ do not exchange in the solvent at room temperature, their characteristic shift values of -220 and -79.5 p.p.m. respectively being observed. The deep red colour of the solution suggests the presence of either bromine or a polyhalide anion, and it may be possible to explain the broadness of the peak in terms of exchange with such an anion. The oxidation of chloride ion with bromine in liquid hydrogen chloride at -95° giving $ClBr_2^-$ ions has been reported.[52] The reaction may be understood in terms of initial oxidation of the phosphorus(III) species present by chlorine followed by exchange to produce the observed PCl_4^+ cation.

$$\begin{array}{lcl} PBr_3 & & PBr_3Cl^+ \\ (+\ PBr_2Cl, & +\ 3Cl_2 \ \rightarrow & PBr_2Cl_2^+ + 3Cl^-\ \text{solv.} \\ PBrCl_2) & & PBrCl_3^+ \end{array}$$

$$PBr_3Cl^+ + Cl_2 \rightarrow PBr_2Cl_2^+ + BrCl$$

$$PBr_2Cl_2^+ + BrCl \rightarrow PBrCl_3^+ + Br_2$$

$$PBrCl_3^+ + Cl_2 \text{ (or BrCl)} \rightarrow PCl_4^+ + BrCl \text{ (or } Br_2\text{)}$$

The reaction was repeated using $PBr_3:Cl_2$ in a molar ratio of 2:1 in an attempt to avoid the complete oxidation and exchange of the PBr_3 to PCl_4^+. At room temperature the ampoule contained a clear orange solution over a yellow crystalline solid. The ^{31}P n.m.r. spectrum of the solution contained peaks at -226.3, -223.8 and -219.0 p.p.m., which may be immediately assigned to PBr_2Cl, $PBrCl_2$ and PCl_3 respectively.[136,119] A preparative scale experiment was then carried out to obtain a larger sample of the yellow crystalline solid. The ^{31}P n.m.r. solid state spectrum of this material rather surprisingly yielded no signal in the range associated with phosphorus(V) cations of type $PCl_xBr_{4-x}^+$ $(0 \le x \le 4)$; -96 to +104 p.p.m.[131] Instead a weak signal at -225.5 p.p.m., which may be assigned to either PBr_2Cl or $PBrCl_2$, was recorded. This material was presumably present as a trace impurity. The infrared spectrum of the yellow solid contained absorptions at 471 cm^{-1}, which may be assigned to PBr_4^+,[161] and also at 488 and 390 cm^{-1} which may be assigned to PBr_2Cl.[162] The Raman spectrum contained absorptions at 483, 477, 471, 230, 148, 142 and 72 cm^{-1} which are characteristic of PBr_4^+ in PBr_5[160] in addition to bands at 268 and 172 cm^{-1}. The yellow solid was finally characterised as PBr_5 by elemental analysis. A slightly low value in the phosphorus determination may be due to the presence of a little $PBr_4^+Br_3^-$.[179] It is difficult to explain the failure to observe a signal due to PBr_4^+ in the ^{31}P n.m.r. solid state spectrum, as normally this resonance may be observed in a single sweep.[101]

In this reaction the oxidation of half the phosphorus from the +3 to the +5 oxidation state, followed by exchange with the remaining phosphorus (III) species producing $PBr_4{}^+Br^-$, which is largely insoluble in liquid hydrogen chloride, and the observed phosphorus(III) products may be postulated as a reaction mechanism.

$$PBr_3 + Cl_2 \rightarrow PBr_3Cl^+ + Cl^- \text{ solv.}$$

$$PBr_3Cl^+ + PBr_3 \rightarrow PBr_4{}^+ + PBr_2Cl$$

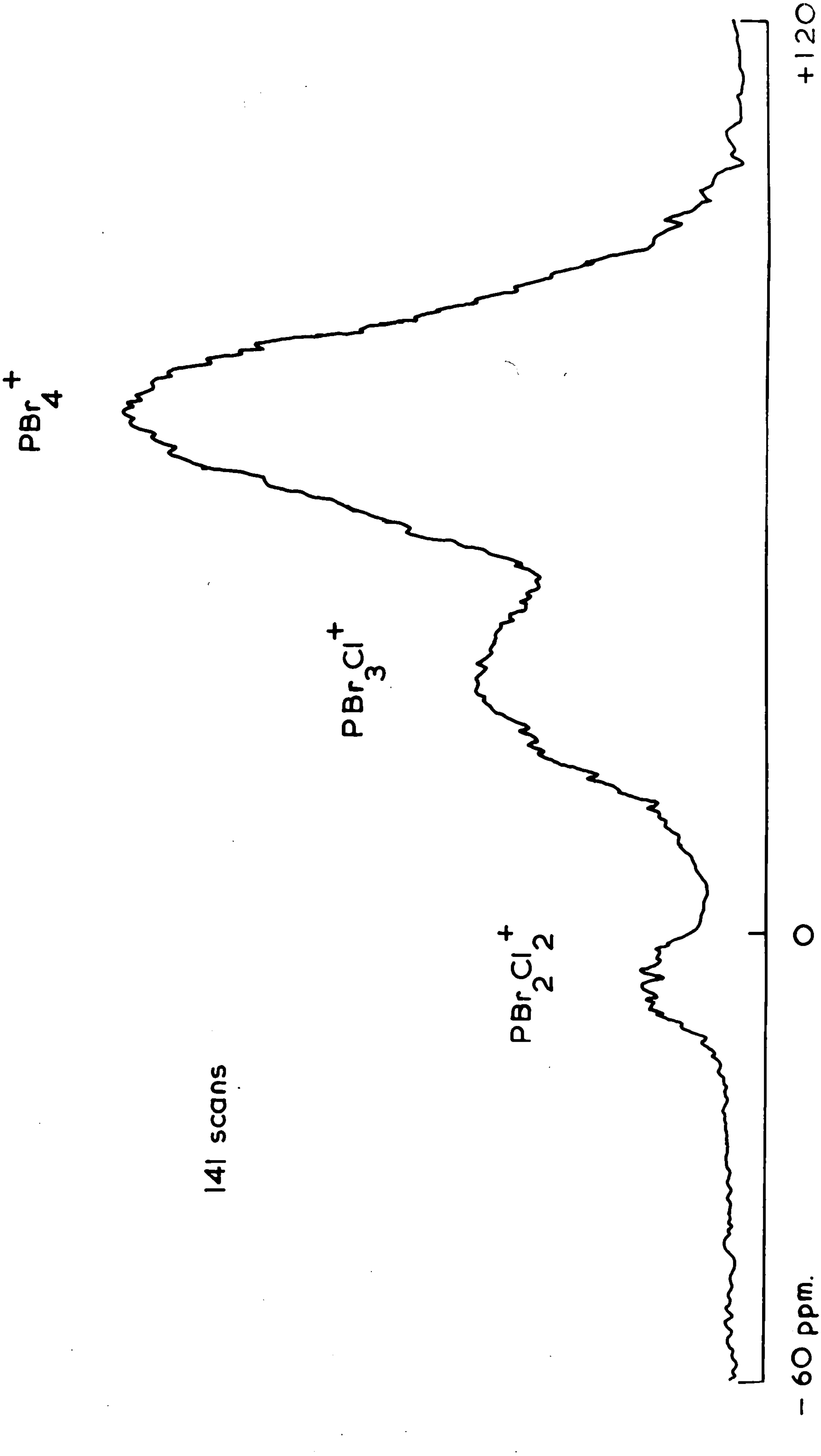
PBr_2Cl and $PBrCl_2$, present as solvolysis products of the PBr_3, may be presumed to act in a similar fashion.

Having obtained $PCl_4{}^+$ and $PBr_4{}^+$ as products of the oxidation of phosphorus(III) bromide with chlorine in liquid hydrogen chloride, the reaction was repeated with the addition of boron trichloride in an attempt to obtain bromochlorophosphonium ions. PBr_3, Cl_2 and BCl_3 were present in a molar ratio of 2:1:2. At room temperature the ampoule contained a clear, very pale green, solution over a white solid. No reproducible signals could be obtained when the ^{31}P and ^{11}B n.m.r. spectra of the solution were recorded and a preparative scale experiment was then carried out in order to obtain a sample of the white solid for investigation. The ^{31}P n.m.r. solid state spectrum indicated the presence of 3 cations; signals at -7.5, +32.5 and +69.5 p.p.m. being assigned to $PBr_2Cl_2{}^+$, PBr_3Cl^+ and $PBr_4{}^+$ respectively. $PBr_4{}^+$ was by far the major cation component of the mixture, and $PBr_2Cl_2{}^+$ was present in only a small quantity. The white colour of the solid is thus somewhat surprising as $PBr_4{}^+$ compounds are usually yellow e.g. $PBr_4{}^+Br^-$, $PBr_4{}^+BBr_4{}^-$. The ^{11}B n.m.r. solid state spectrum contained one broad signal at +14.0 p.p.m. which lies between the reported solution shifts of +11.6 and +15.4 p.p.m. for $BCl_4{}^-$ and BCl_3Br^- respectively.[147] The infrared spectrum contained

Fig.3.3.3

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

$PBr_3 + Cl_2 + BCl_3$ in liquid hydrogen chloride


PBr_4^+
PBr_3Cl^+
$PBr_2Cl_2^+$
141 scans
+120
0
−60 ppm.

strong absorptions at 694 and 673 cm^{-1} which are characteristic of BCl_4^-.[20f,163]

Phosphorus(V) cations of the type $PBr_xCl_{4-x}^+$ (0 ≤ x ≤ 4) possess good scattering properties and are thus ideally suited for study by Raman spectroscopy, whereas tetrahaloborate anions possess relatively ppor scattering properties.[160] The Raman spectrum of the white solid contained lines at 492, 335, 290, 252, 176, 149 and 50 cm^{-1}, of which those at 492, 252 and 149 cm^{-1} are characteristic of PBr_4^+ in the presence of a polyatomic anion.[160] The lines at 290 and 335 cm^{-1} are characteristic of PBr_3Cl^+ and $PBr_2Cl_2^+$ respectively.[160] In the presence of these cations, lines due to BCl_4^- ion were not observed, probably as a result of the large relative difference in their scattering properties. The Raman spectrum of the tetrachloroborate anion has been recorded under more favourable conditions.[164]

Again, oxidation of half the phosphorus(III) species to phosphorus(V) cations may be postulated, followed by exchange with the remaining phosphorus(III) compounds present to produce the observed final composition. It is interesting to note that the mixed bromochlorophosphonium ions, $PBr_2Cl_2^+$ and PBr_3Cl^+, were isolated in this reaction, stabilised as their tetrachloroborate salts, in addition to PBr_4^+. In the previous reaction, the same system but with the absence of boron trichloride, only PBr_5 was isolated, indicating that the mixed bromochlorophosphonium ions are less stable than PBr_4^+, requiring a polyatomic counterion for stabilisation in solution at room temperature.

The possible oxidation of phosphorus(III) bromide with iodine was investigated. The ^{31}P n.m.r. spectrum of a mixture of PBr_3 and I_2 in a 2:1 molar ratio contained only one signal, at -228 p.p.m. which is characteristic of PBr_3.[119] This reaction was not investigated further; as similar attempts to oxidise PCl_3 with this oxidising agent under a variety of conditions were unsuccessful.

Experimental

The behaviour of phosphorus(III) bromide in liquid hydrogen chloride

PBr_3 (1 ml., 10.5 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196° followed by HCl (30 mmole). The ampoule was sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the clear colourless solution contained a large peak at -227.5 p.p.m., with a shoulder at-227.1 p.p.m. and a smaller peak at -224.3 p.p.m. These peaks may be assigned to PBr_3, PBr_2Cl and $PBrCl_2$ respectively. Thus, PBr_3 is partially solvolysed in liquid hydrogen chloride.

The ^{31}P n.m.r. spectrum of PBr_3 in liquid hydrogen bromide was then recorded.

PBr_3 (1 ml., 10.5 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by HBr (30 mmole). The ampoule was sealed and tested in the normal manner. A single resonance at -227.3 p.p.m. was observed in the ^{31}P n.m.r. spectrum of the clear, colourless solution. This peak may be immediately assigned to PBr_3, which, not surprisingly, is soluble in liquid hydrogen bromide without reaction.

The reaction between phosphorus(III) bromide and chlorine

PBr_3 (0.1 ml., 1.05 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by HCl (20 mmole) and a large excess of chlorine. The ampoule was sealed and tested in the usual manner. It was noted at -84° that the ampoule contained a green liquid over a white solid, PBr_3. However, at room temperature a clear deep red solution was present. The ^{31}P n.m.r. spectrum consisted of a broad signal at -97 ± 0.5 p.p.m., which has been assigned to PCl_4^+. This value is just outside the previously reported range for PCl_4^+ in solid state spectra,[131] -96 p.p.m. to -73 p.p.m., but is obviously too high a value for a phosphorus(III) species and too low for a mixed $PCl_nBr_{4-n}^+$ cation.

The reaction was repeated using PBr_3:Cl_2 in a 2:1 molar ratio, in an attempt to prevent complete oxidation and exchange of the PBr_3 to PCl_4^+.

PBr_3 (0.1 ml., 1.05 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by HCl (25 mmole) and Cl_2 (0.5 mmole). The ampoule was sealed and tested in the usual manner. At room temperature the ampoule contained a clear orange solution over a yellow crystalline solid. The tube was inverted, leaving the crystals at the top, and the ^{31}P n.m.r. spectrum of the solution was recorded. Peaks were observed at -226.3, -223.8, and -219.0 p.p.m. which may be assigned at once to PBr_2Cl, $PBrCl_2$ and PCl_3 respectively.

In order to run a ^{31}P n.m.r. solid state spectrum on the yellow crystalline solid, a preparative scale experiment was carried out.

PBr_3 (1.5 ml., 15.75 mmole) was syringed into a 13 mm. o.d. silica ampoule. HCl (120 mmole) was condensed into the ampoule at -196° followed by Cl_2 (7.5 mmole). The ampoule was sealed and warmed to room temperature as previously described. A large quantity of yellow crystals were formed during 12 hours at room temperature. The ampoule was taken into a dry nitrogen filled glove bag and inverted, leaving the crystals at the top. The liquid hydrogen chloride was frozen solid by dipping the lower end of the ampoule into liquid nitrogen. The ampoule was scored at its mid-point and cracked open. The end containing the yellow crystals was placed inside a 24 mm. o.d. reaction tube fitted with a B24 socket and attached to the vacuum line via a cone-tap-cone adaptor for evacuation. This tube was then taken into the dry box prior to removal of the yellow crystals.

A ^{31}P n.m.r. solid state spectrum was recorded. Surprisingly, no signal could be detected in the region associated with tetraco-ordinate phosphorus(V) cations, -96 p.p.m. to +104 p.p.m.,[131] but a very weak signal was present at -225.5 $\pm$ p.p.m. This signal may be assigned to either PBr_2Cl or $PBrCl_2$, presumably present as a trace impurity. The infrared spectrum of the material contained strong absorptions (cm^{-1}) at, 488, 471 and 390. The band at 471 cm^{-1} may be assigned to PBr_4^+ [161] and those at 488 and 390 cm^{-1} to PBr_2Cl.[162] The Raman spectrum of this material showed frequencies at (cm^{-1}), 483m, 477w, 471m, 268m, 230vs, 172w, 148s, 142s and 73s. The triplet at 483, 477 and 471 cm^{-1} and the doublet at 148 and 142 cm^{-1} together with bands at 230 and 72 cm^{-1} are quite characteristic of PBr_5.[160]

Found: P,5.86%; Br,93.2%. PBr_5 requires P,7.19%; Br,92.8%.

The yellow crystals are thus quite definitely PBr_5, and the failure to observe PBr_4^+ in the ^{31}P n.m.r. spectrum is puzzling.

The reaction between phosphorus(III) bromide, chlorine and boron trichloride

PBr_3 (0.1 ml., 1.05 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by HCl (25 mmole), Cl_2 (0.5 mmole) and BCl_3 (1.05 mmole). The ampoule was sealed and tested in the usual manner and at room temperature contained a large quantity of white crystalline solid under a clear solution. The ampoule was inverted and the ^{31}P n.m.r. spectrum of the solution recorded. No reproducible signal could be detected and it was assumed that all the phosphorus must be contained in the white solid. Similarly, no signal could be detected when the ^{11}B n.m.r. spectrum of the solution was recorded.

The experiment was repeated on a larger scale to permit isolation and examination of the white crystalline solid.

PBr_3 (1.5 ml., 15.75 mmole) was syringed into a 13 mm. o.d. quartz ampoule. HCl (110 mmole) was condensed into the ampoule at -196°, followed by Cl_2 (7.5 mmole),and BCl_3 (1.7 ml., 19.6 mmole). The ampoule was sealed and allowed to reach room temperature in the manner previously described. A deep red solution over a dense white precipitate was obtained at this temperature. Over a period of 48 hours the red colour was discharged and the solid became very pale cream in colour. The ampoule was opened using the procedure described earlier (p.81) and the solid was pumped overnight on the vacuum line to remove any traces of excess BCl_3 and other volatile impurity.

The ^{31}P n.m.r. spectrum of the solid contained signals at -7.5, +32.5 and +69.5 p.p.m. which may be assigned to $PCl_2Br_2^+$, $PClBr_3^+$ and PBr_4^+ respectively. $PCl_2Br_2^+$ was present as a very minor component, PBr_4^+ being by far the major component. The ^{11}B n.m.r. spectrum contained a peak at +14.0 p.p.m. which may be assigned to a mixture of BCl_4^- and BCl_3Br^- ions.[147]

The infrared spectrum of the material contained absorptions (cm^{-1}) at 720vs, 694vs, 673vs, 620w, 595s, 500vs and 395w. The absorptions at 694 and 673 cm^{-1} may be assigned to the BCl_4^- ion,[20f,163] and that at 500 cm^{-1} is possibly indicative of ν_{B-Br} in BCl_3Br^-.

The Raman spectrum of the solid contained frequencies (cm^{-1}) at 492s, 335vw, 290m, 252vs, 176w, 149vs and 50vw. The lines at 492, 252 and 149 cm^{-1} are indicative of PBr_4^+ in the presence of a polyatomic anion and those at 290 and 335 cm^{-1} are characteristic of PBr_3Cl^+ and $PBr_2Cl_2^+$.[160] PBr_4^+ was clearly the major component of the mixture. Rather surprisingly lines due to BCl_4^- were not observed.

The solid is thus formulated as largely $PBr_4^+BCl_4^-$, with some $PClBr_3^+BCl_4^-$ and a trace of $PCl_2Br_2^+BCl_4^-$.

The reaction between phosphorus(III) bromide and iodine in the absence of a solvent

PBr_3 (1 ml., 10.5 mmole) was syringed into an 8 mm. o.d. pyrex ampoule containing I_2 (1.27 g., 5 mmole). The ampoule was sealed and was observed to contain a deep purple solution at room temperature. The n.m.r. spectrum of this solution contained one signal at -228 p.p.m. which may be immediately assigned to PBr_3.

3.4 Phosphorus(III) iodide

Results and Discussion

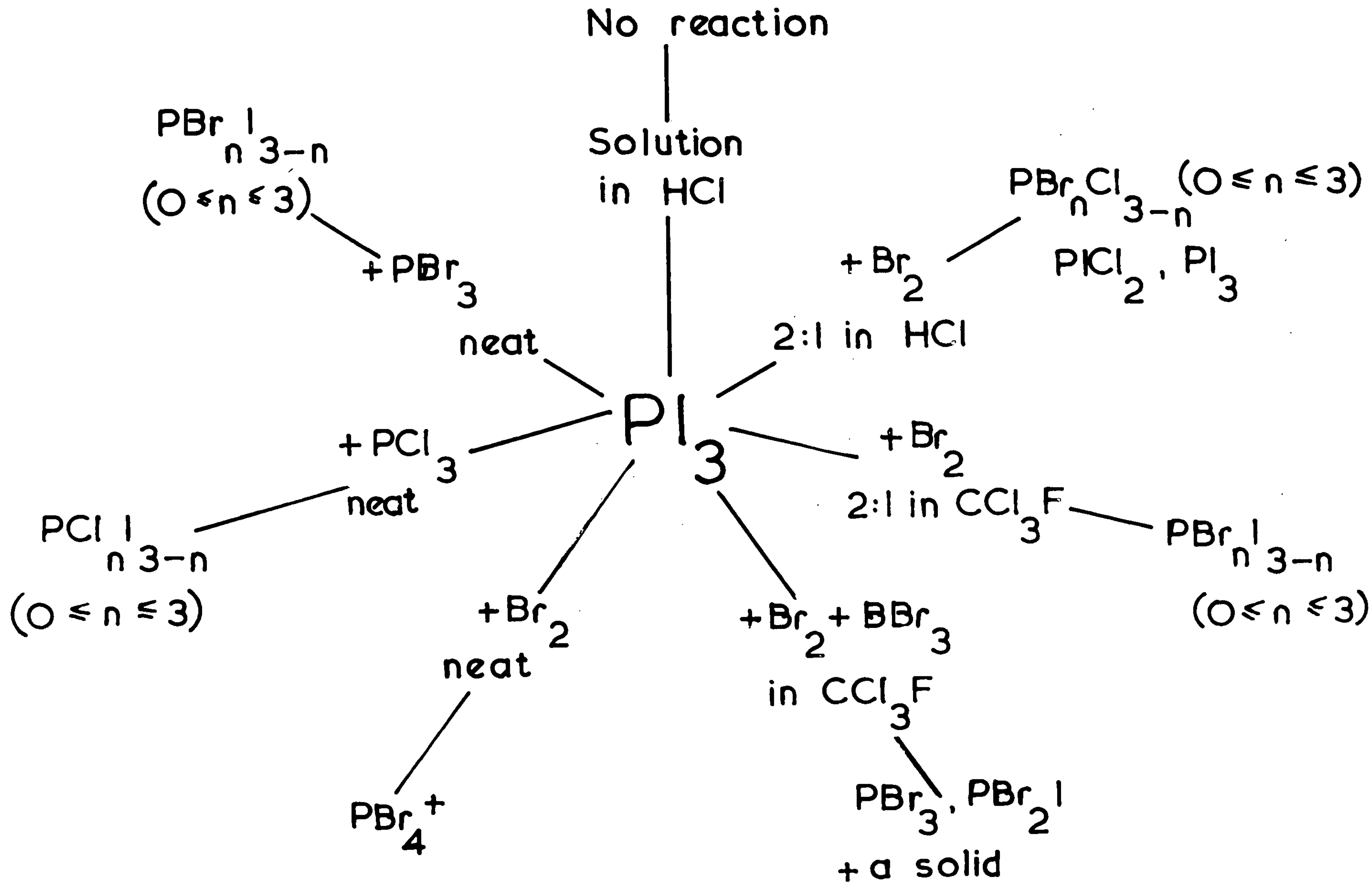
Phosphorus(III) iodide is the least soluble of the phosphorus(III) halides in liquid hydrogen chloride. Reaction with the oxidising agent bromine in the solvent and in trichlorofluoromethane resulted in the formation of phosphorus(III) exchange products. Treatment with liquid bromine did cause oxidation, the tetrabromophosphonium cation being produced.

All reactions were followed using ^{31}P n.m.r. spectroscopy, and where appropriate ^{11}B n.m.r. spectroscopy. The results of the experiments are shown in Fig.3.4.1.

Phosphorus(III) iodide is only poorly soluble in liquid hydrogen chloride at room temperature, a CAT run of 100 scans being necessary to

Fig.3.4.1

Reactions of phosphorus(III) iodide


No reaction
Solution in HCl
PI3
PBrnI3-n (0 ≤ n ≤ 3)
+PBr3 neat
+PCl3 neat
PClnI3-n (0 ≤ n ≤ 3)
+Br2 neat
PBr4+
+Br2 + BBr3 in CCl3F
PBr3, PBr2I + a solid
+Br2 2:1 in CCl3F
PBrnI3-n (0 ≤ n ≤ 3)
+Br2 2:1 in HCl
PBrnCl3-n (0 ≤ n ≤ 3)
PICl2, PI3

detect the ^{31}P n.m.r. signal from a saturated solution. The ^{31}P chemical shift, the expected singlet, occurred at -168.3 ± 0.2 p.p.m.

TABLE 3.4.1

Phosphorus(III) iodide: the variation of ^{31}P chemical shift value with solvent

Chemical shifts in p.p.m. relative to 85% H_3PO_4

Chemical shift	Solvent	Solubility	Reference
-178	-	-	119
-179	CS_2	High	145
-176 ± 1	CS_2	High	this work
-176	CH_2Cl_2, $C_2H_4Cl_2$	Moderate	165
-171 ± 1	CCl_3F	Low	this work
-168.3 ± 0.2	liquid HCl	Low	this work

The variation in the value of the chemical shift of PI_3 with solvent is shown in Table 3.4.1. It is interesting, though probably coincidental, that there is an apparent variation in shift value with solubility in the solvent. A difference of 2-3 p.p.m. is often observed between shift values in different solvents owing to differences in diamagnetic susceptibility, but the large variation, 10 p.p.m. overall, is not easily explained. The notion that PI_3 is highly soluble in CS_2 because it forms a complex, or that at least there is some strong association, may be discounted on the basis that chemical shifts of phosphorus(III) species are in general moved upfield on co-ordination.[103] The upfield shift in liquid hydrogen chloride may possibly be due to rapid exchange involving PI_3 and a protonated species. Any rapid exchange involving PI_3 and PI_xCl_{3-x} $(0 \leq x \leq 2)$ would result in a downfield shift of the PI_3 signal. A similar explanation may not be offered as explanation of the upfield shift in freon 11. Only exchange with the fluorine atom of the solvent could produce an upfield shift and such a process may be rejected owing to the strength of the C-F bond.

Before attempting oxidation or exchange reactions of PI_3 the ^{31}P n.m.r. solution spectra of neat 1:1 mixtures of PI_3 and PBr_3, PCl_3 were recorded on the instrument available in these laboratories. The results together with literature values are shown in Table 3.4.2, and ^{31}P n.m.r. spectra in Figs. 3.4.3, and 3.4.4.

The values for PBr_xI_{3-x} $(0 \leq x \leq 3)$ are in good agreement with literature values and require no further comment. Similarly the values obtained for PCl_3, $PClI_2$ and PI_3 from a 1:1 mixture of PCl_3 and PI_3 with or without a solvent are unexceptional. However, the assignment of the peak at -224.9 p.p.m. to PCl_2I does require explanation.

The values of ^{31}P chemical shifts of the mixed species PX_2Z and PXZ_2 in the series PX_3 to PZ_3 has been discussed by Van Wazer et al.[103] It is claimed that a chemical shift value is made up of both a σ and a π-contribution. Further the shift difference between that observed for a mixed species, say PX_2Z, and that calculated by interpolation between shift values for PX_3 and PZ_3 also has both σ and π contributions and is negative. The same authors deduced an empirical relationship suggesting that the negative shift differences for the mixed species should be approximately equal. (Fig.3.4.2.)

TABLE 3.4.2.

^{31}P n.m.r. chemical shift values for some phosphorus(III) halides and mixed halides

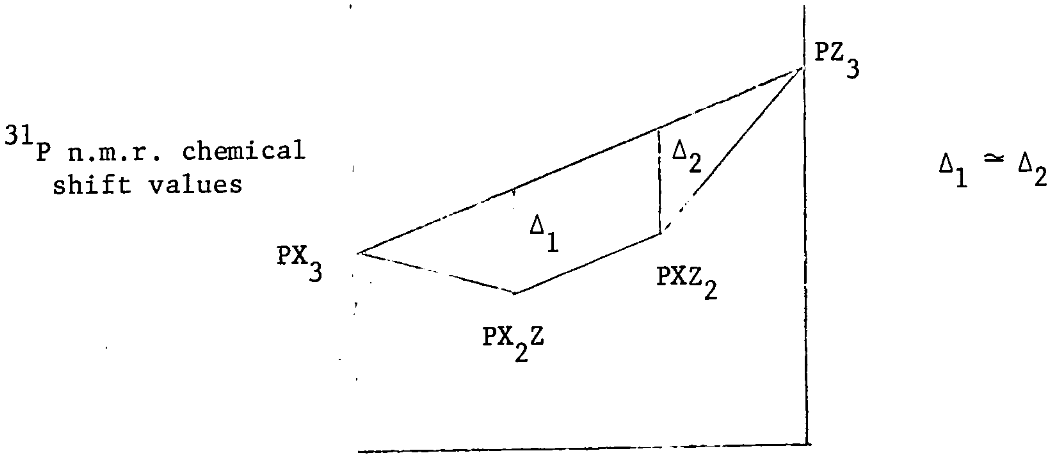
(shifts in p.p.m. rel. to 85% H_3PO_4)

PBr_3	PBr_2I	$PBrI_2$	PI_3
-228 (119)	-224 (166)	-208 (166)	-178(119)
-227 (145)	-223 (145)	-208 (145)	-184 (145)
-226.8	-221	-205	-179 (*)
PCl_3	PCl_2I	$PClI_2$	PI_3
-218 (119)	-211 (166)	-208 (166)	-178 (119)
-216.7	-224.9	-211.4	-175.2 (*)
-217	-225.2	-211.5	-176.5 (**)
-219.7	-228.6	-213.6	-174.6 (***)

(*) neat 1:1

(**) 1:1 in CS_2 solution

(***) an excess of PCl_3 added to PI_3 in $C_2H_4Cl_2$ solution.



Deviations from additivity, Δ_1 and Δ_2, in n.m.r. chemical shifts of the intermediate compounds in a substitution series

FIG.3.4.2.

Van Wazer et al calculated the σ contribution to Δ values for say X replaced by Z, showing that this contribution was equal for the two mixed species when the bond angle remained the same across the substitution series. However, the calculated value was generally less than the observed value of the deviation indicating a π contribution. Thus

$$\Delta_1 \simeq \Delta_2 = \sigma + \pi$$

where Δ_1 and Δ_2 are observed deviations, σ is the calculated σ-contribution and π is the π-contribution, obtained by subtracting the value of σ from that of Δ in any particular case.

Dillon et al[229] have assumed that π-contributions are additive, i.e. that the π-contribution for Cl replaced by I is given by the sum of contributions for Cl replaced by Br and Br replaced by I. Thus, to deduce the chemical shift value for PCl_2I, take the interpolated value from the known shifts of PCl_3 and PI_3 then subtract (a) the σ term for Cl replaced by I, (b) the π term for Cl replaced by Br and (c) that for Br replaced by I.

There are two major assumptions involved in this treatment; firstly in their calculation of σ-contributions Van Wazer et al have assumed that bond angles remained constant when X substituents in PX_3 are replaced by Z. Dillon et al in the absence of other available data have taken the assumption of Van Wazer et al and have assumed the additivity of π contributions. An empirical justification for this latter assumption is that π-effects are known to increase in the order $Cl < Br < I$.[103] Hence the replacement of Cl by I should have a bigger effect than either the replacement of Cl by Br or of Br by I. Further justification may be offered by the fact that calculated chemical shifts are in close agreement with experimentally determined values.

Table 3.4.3 shows chemical shifts for PCl_2I and $PClI_2$ (a) calculated using shift-values for PCl_3 and PI_3 alone (determined in the solvent in which the shifts of the mixed species were measured) (b) using observed chemical shift values for PCl_3 and PI_3 in a 4 peak system. The final column gives the observed shifts for the mixed species.

Although observed shifts in dichloroethane solution are rather higher than calculated values, this spectrum was obtained by adding an excess of PCl_3 to a solution of PI_3 in the solvent and recording the ^{31}P n.m.r. spectrum without delay. The most intense peak in the 4 peak system, clearly due to PCl_3, occurred at -219.7 p.p.m. which is almost 2 p.p.m.

TABLE 3.4.3

Calculated and observed ^{31}P chemical shift values for the species PCl_2I and $PClI_2$

(Chemical shifts in p.p.m. relative to 85% H_3PO_4)

Solvent	Mixed Species	Calculated shift values using method (a)	Calculated shift values using method (b)	Observed shift values
Neat*	PCl_2I	-224.5	-222.4	-224.9
	$PClI_2$	-211.5	-209.5	-211.4
Carbon disulphide	PCl_2I	-223.4	-223	-225.2
	$PClI_2$	-210.9	-210.5	-211.5
Dichloroethane	PCl_2I	-223.8	-224.2	-228.6
	$PClI_2$	-209.2	-210.1	-213.6

* The shift taken for PI_3 was that determined in carbon disulphide solution.

downfield from the normally observed shift for this species. It can be seen in Table 3.4.3 that calculated and observed shifts are usually well within 2 p.p.m. of one another. The most downfield peak in the ^{31}P n.m.r. spectrum of a 1:1 molar mixture of PCl_3 and PI_3 is thus assigned to PCl_2I (See Fig.3.4.3).

In an attempt to produce bromoiodophosphorus(V) species phosphorus (III) iodide was treated with bromine. The ^{31}P n.m.r. spectrum of a solution of PI_3 and Br_2 in 2:1 molar ratio in liquid hydrogen choride

Fig.3.4.3

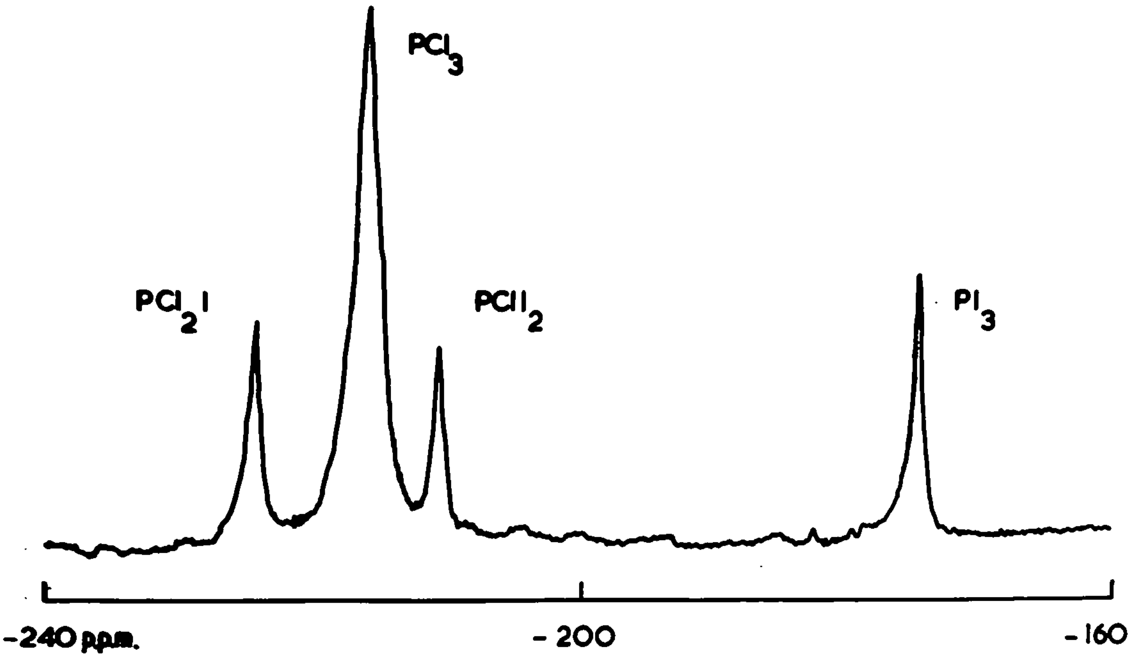
^{31}P n.m.r. solution spectrum

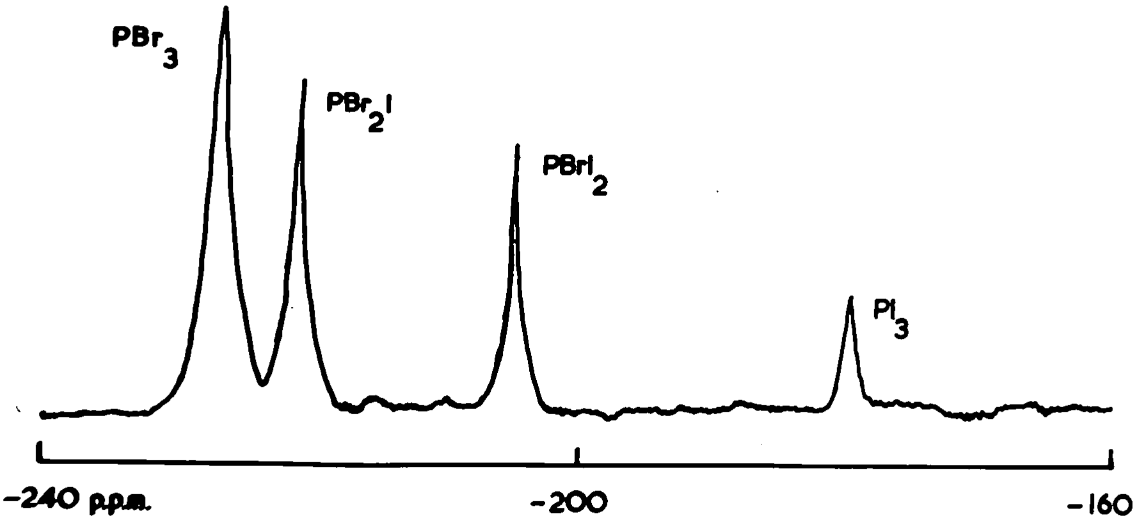
PI_3 and PCl_3 in a 1:1 molar ratio

Fig.3.4.4

^{31}P n.m.r. solution spectrum

PI_3 and PBr_3 in a 1:1 molar ratio


PCl$_3$
PCl$_2$I
PClI$_2$
PI$_3$
-240 p.p.m.
- 200
- 160


PBr$_3$
PBr$_2$I
PBrI$_2$
PI$_3$
-240 p.p.m.
-200
-160

(Fig.3.4.5) contained five signals, the most intense occurring at -185.5 p.p.m. The remaining peaks were observed at -228, -225, -218 and -209.5 p.p.m. and may be assigned to PBr_3,[119] $PBrCl_2$[136] or PCl_2I (this work), PCl_3[119] and to PI_2Cl or PI_2Br[166] respectively. The remaining signal at -185.5 p.p.m. is clearly due to a phosphorus(III) species. It is hardly consistent to assign the resonance to PI_3 since the chemical shift of this substance in the solvent has been determined as -168.5 p.p.m. (this work), yet it is difficult to postulate a previously unknown species to which the signal may be ascribed. The ^{31}P chemical shift of the unknown PBrClI has been calculated to be -232.5 ± 3.5 p.p,m.[229] and this compound may thus be ruled out. Cowley and Cohn have reported the ^{31}P n.m.r. spectrum of the liquid product obtained from a 1:1 molar mixture of P_2I_4 and Br_2 in CS_2 to contain 4 signals at -227, -223, -208 and -184 p.p.m.[145] The authors assign these peaks to PBr_3, PBr_2I, $PBrI_2$ and PI_3 respectively. They redetermined the chemical shift of PI_3 in CS_2 solution and found a value of -179 p.p.m. in agreement with the literature value of -178 p.p.m.[119] A similar spectrum to that obtained from P_2I_4 and Br_2 was obtained from a 1:1 molar mixture of PBr_3 and PI_3.[145] When the ^{31}P n.m.r. spectrum of a similar mixture was recorded in this work, however, a chemical shift value for PI_3 of -179 p.p.m. was recorded. Further work is obviously necessary to clarify the position.

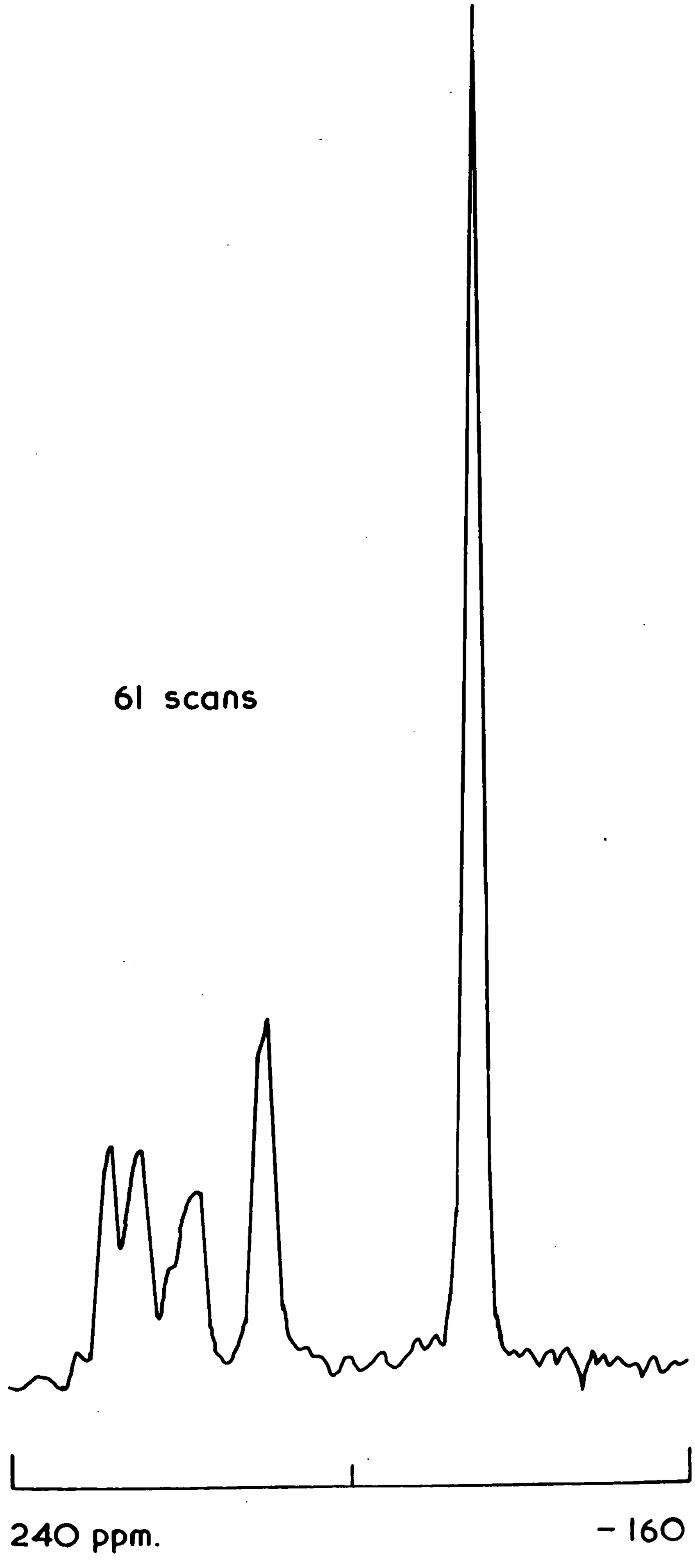
A possible mechanism accounting for the observed species in terms of exchange between PI_3 and Br_2 and subsequent solvolysis is shown in Fig.3.4.6. Phosphorus(III) species whose presence is postulated are shown underlined.

In an attempt to avoid exchange with the solvent and the production of mixed phosphorus(III) halides containing chlorine, the reaction was

Fig.3.4.5

^{31}P n.m.r. solution spectrum

PI_3 and Br_2 in a 2:1 molar ratio in liquid hydrogen chloride


61 scans
- 240 ppm.
- 160

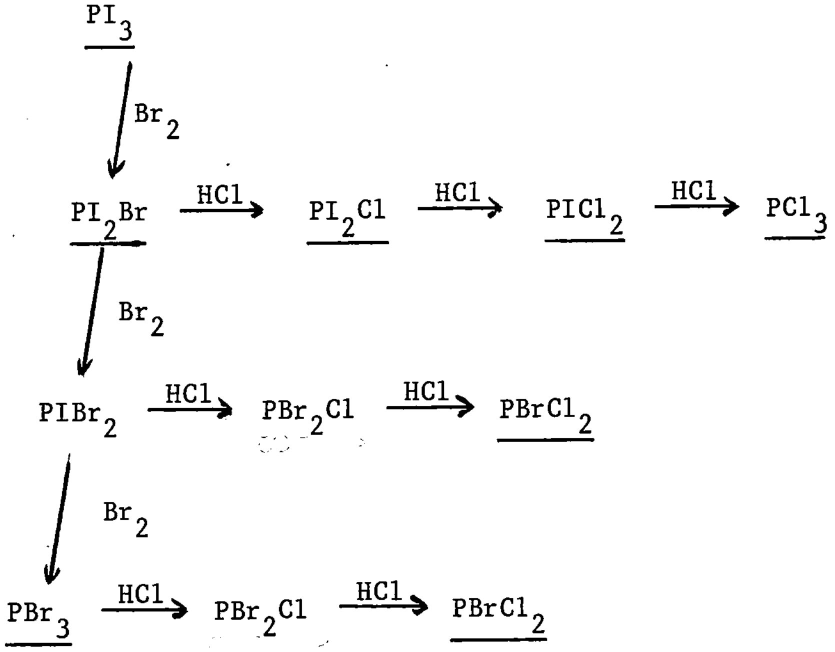


FIG.3.4.6

Possible exchange and solvolysis products from PI_3 and Br_2 in 2:1 molar ratio in liquid hydrogen chloride

repeated using freon 11 as solvent. The ^{31}P n.m.r. spectrum of this solution contained signals at -226 ± 0.5, -218, -198 and -168 p.p.m. which may be assigned to PBr_3, PBr_2I, $PBrI_2$ and PI_3 respectively. These shifts are all higher than literature values, the difference between them and those found in a neat 1:1 molar mixture of PBr_3 and PI_3 increasing from 1.5 p.p.m. for PBr_3 to 10 p.p.m. for PI_3. The chemical shift of PI_3 in freon 11 has been determined as -171 ± 1 p.p.m. in this work. Diamagnetic susceptibility changes on changing solvents may possibly account for shift differences of up to 2 p.p.m. and the markedly high value for PI_3 in this solvent has already been discussed. The higher values for PBr_2I and PBr_3 may be caused by the very high shift of PI_3.

Having established that PI_3 exchanges with Br_2 in freon 11, trichlorofluoromethane, the reaction was repeated with the addition of BBr_3 in an attempt to stabilise a bromoiodophosphorus(V) cation as its tetrabromoborate salt. The reaction between PI_3, Br_2 and BBr_3 in a 2:1:2 molar ratio in freon 11 was vigorous. A pale solid, some dark metallic looking crystals, presumably iodine, and a red solution were obtained at room temperature. The ^{31}P n.m.r. spectrum of this solution contained signals at -224.5 and -216 p.p.m. which may be assigned to PBr_3 and PBr_2I respectively. No ^{11}B n.m.r. signal could be detected from the solution, and neither ^{31}P nor ^{11}B n.m.r. signals were obtained when the spectrum of the solid was recorded. This obviously inhomogeneous reaction and products were not investigated further.

PI_3 was soluble in bromine, the ^{31}P n.m.r. spectrum of the solution consisting of a single resonance at +77.5 p.p.m. which may be understood in terms of oxidation of the phosphorus(III) to phosphorus(V) presumably to a PI_3Br^+ intermediate which then exchanges with Br_2 giving PBr_4^+. It may be that the reaction between PI_3 and Br_2 in a 1:1 molar ratio, together with an excess of Br_2, will proceed quickly to PBr_4^+; however, it may be possible with a variable temperature probe operating at low temperatures to detect the intermediate bromoiodophosphorus(V) cations. The reaction presumably proceeds in the following manner

$$PI_3 + Br_2 \rightarrow PI_3Br^+ + Br^-$$

$$PI_3Br^+ + Br_2 \rightarrow PI_2Br_2^+ + IBr$$

$$PI_2Br_2^+ + Br_2 \text{ (or IBr)} \rightarrow PIBr_3^+ + IBr \text{ (or } I_2)$$

$$PIBr_3^+ + Br_2 \text{ (or IBr)} \rightarrow PBr_4^+ + IBr \text{ (or } I_2)$$

The PBr_4^+ ions will almost certainly be stabilised by solvated Br^- ions i.e. polybromide anions.

Experimental

The behaviour of phosphorus(III) iodide in liquid hydrogen chloride

HCl (20 mmole) was condensed at -196° into an 8 mm. o.d. silica ampoule containing PI_3 (0.206 g., 0.5 mmole). The ampoule was sealed and tested in the usual manner. At room temperature the ampoule contained a pale orange solution, most of the PI_3 remaining undissolved. A CAT run of 100 scans revealed a ^{31}P n.m.r. signal at -168.3 ± 0.2 p.p.m. The literature values for PI_3 is -179 p.p.m.[119] Accordingly, the ^{31}P chemical shift of PI_3 was redetermined in CS_2, in which it is very soluble, and in freon 11 in which it is poorly soluble.

A concentrated solution of PI_3 in CS_2, contained in an 8.5 mm. o.d. pyrex n.m.r. tube, gave a ^{31}P n.m.r. signal at -176 ± 1 p.p.m.

A saturated solution of PI_3 in freon 11, contained in an 8 mm. o.d. pyrex ampoule, gave a ^{31}P n.m.r. signal at -171 ± 1 p.p.m. after a CAT run of 100 scans. Chemical shifts of -175, -176 p.p.m. have been found for PI_3 in CH_2Cl_2 and $C_2H_4Cl_2$.[146]

The reaction between phosphorus(III) iodide and phosphorus(III) bromide in the absence of a solvent

PBr_3 (1 ml., 10.5 mmole) was condensed at -196° into an 8 mm. o.d. pyrex ampoule containing PI_3 (1 g., 2.43 mmole) and the ampoule was sealed. At room temperature most of the PI_3 dissolved, but a little solid was left in the base of the ampoule. The ^{31}P n.m.r. spectrum of the solution was recorded. Three peaks could easily be seen on a single scan, at -226.8

-221 and -205 p.p.m., and a fourth at -179 p.p.m. could be seen after a short CAT run of 25 scans. These peaks may be assigned to PBr_3, PBr_2I, $PBrI_2$ and PI_3 respectively, and are in good agreement with literature values.[119,166] Signal intensity decreased on going along the series from PBr_3 to PI_3.

The reaction between phosphorus(III) iodide and phosphorus(III) chloride

(a) in the absence of a solvent

PCl_3 (0.2 ml., 2.1 mmole) was condensed at -196° into an 8 mm. o.d. pyrex ampoule containing PI_3(0.95 g., 2.3 mmole) and the ampoule was sealed. At room temperature all the PI_3 dissolved to give a dark brown solution. The ^{31}P n.m.r. spectrum of this solution consisted of 4 peaks, easily visible on a single scan, at -224.9, -216.7, -211.4 and -175.2 p.p.m.

(b) in carbon disulphide solution

The ^{31}P n.m.r. spectrum of a 1:1 molar mixture of PI_3 and PCl_3 in carbon disulphide solution was recorded. Again, 4 signals were clearly visible at -225.2, -217, -211.5 and -176.5 p.p.m.

(c) in dichloroethane solution

An excess of PCl_3 was added to a solution of PI_3 in dichloroethane solution and the ^{31}P n.m.r. spectrum was recorded without delay. 4 signals were observed at -228.6, -219.7, -213.6 and -174.6 p.p.m., that at -219.7 p.p.m. having the greatest intensity.

In all 3 caes, the peaks are assigned to PCl_2I (this work), PCl_3,[119] $PClI_2$[166] and PI_3[119] from low to high field respectively.

The reaction between phosphorus(III) iodide and bromine

Br_2 (1 ml., 18.3 mmole) was condensed at -196° into an 8 mm. o.d. pyrex ampoule containing PI_3 (1 g., 2.43 mmole). The ampoule was sealed and allowed to reach room temperature. The PI_3 dissolved in the excess of Br_2. The ^{31}P n.m.r. spectrum of the solution contained a single resonance at +77.5 p.p.m. which may be assigned at once to PBr_4^+.[131]

Thus PI_3 is oxidised by Br_2 and exchange occurs producing PBr_4^+. The reaction was then repeated in liquid hydrogen chloride.

PI_3 (0.34 g., 0.83 mmole) was placed inside an 8 mm. o.d. quartz ampoule. HCl (25 mmole) was condensed into the ampoule at -196°, followed by Br_2 (0.079 g., 0.49 mmole). The ampoule was sealed and tested in the usual manner. Signals at -228, -225, -218, -209.5 and -185.5 p.p.m. were detected in the ^{31}P n.m.r. spectrum of the solution after a CAT run of 60 scans. The signals at -185.5 and -209.5 p.p.m. could be seen on a single scan, the former being the most intense. Assignment of these signals is relatively easy in two cases; those of -228 and -218 p.p.m. are characteristic of PBr_3 and PCl_3. The peak at -225 p.p.m. may be assigned to either $PBrCl_2$ or to PCl_2I[136,229] and that at -209.5 p.p.m. to PI_2Cl or to PI_2Br.[145,166] The remaining, most intense, peak at -185.5 p.p.m. is assigned to PI_3.[145]

The reaction was repeated in trichlorofluoromethane. PI_3 (0.323 g., 0.78 mmole) was loaded into an 8 mm. o.d. pyrex ampoule. CCl_3F (1 ml.) was condensed into the ampoule at -196°, followed by Br_2 (0.064 g., 0.375 mmole). The ampoule was sealed and vigorous reaction occurred on warming to room temperature. The ^{31}P n.m.r. spectrum of the reddish-purple solution consisted of 4 signals at -226.5, -218, -198 and -168 p.p.m. These signals may be assigned to PBr_3, PBr_2I, $PBrI_2$ and PI_3

respectively. It has already been shown in this work that PI_3 has a high ^{31}P shift in freon 11. The shifts of the other species are all high, but the "highness" decreases on going along the series from PI_3 to PBr_3.

The reaction between phosphorus(III) iodide, bromine and boron tribromide

PI_3 (0.310 g., 0.75 mmole) was loaded into an 8 mm. o.d. pyrex ampoule. Freon 11 (1 ml.) was condensed into the ampoule at -196^o, followed by Br_2 (0.057 g., 0.36 mmole) and BBr_3 (0.19 g., 0.75 mmole). The ampoule was sealed, and vigorous reaction took place during warming to room temperature. The ampoule then contained a pale solid, some crystals of I_2 and a deep red solution. The ^{31}P n.m.r. spectrum of the solution contained signals at -224.5 and -216 p.p.m., which may be assigned to PBr_3 and PBr_2I. No signal could be detected when the ^{11}B n.m.r. spectrum was recorded. No solid state signal could be detected in either the ^{31}P or ^{11}B n.m.r. spectra, and the reaction was not investigated further.

3.5 Phosphine

Sheldrick recorded the solution spectrum of the phosphonium ion by dissolving phosphine in aqueous or methanolic solutions of boron trifluoride and measured the ^{31}P chemical shift as +104.5 ± 1 p.p.m.[230] The solid state value has been reported as +77.5 ± 1 p.p.m. for this ion in phosphonium iodide.[101] These values may be compared with the chemical shift for phosphine itself which has been reported as +238 p.p.m.[231] Gutowsky et al do not state whether this shift was obtained from a solution or from a gas phase spectrum. The ^{31}P n.m.r. spectrum of phosphine in liquid hydrogen chloride consisted of a sharp singlet at +245 ± 1 p.p.m. which is clearly a phosphine rather than a phosphonium ion chemical shift value. Phosphonium salts have been prepared in liquid hydrogen chloride at low temperatures and it was reported that like phosphonium iodide the salts $PH_4^+BCl_4^-$ and $PH_4^+BF_3Cl^-$ have high dissociation pressures.[206] Thus the equilibrium $PH_3 + H^+_{solv} + Cl^-_{solv} \rightleftharpoons PH_4^+ + Cl^-_{solv}$ lies firmly on the left in the solvent at room temperature. The ^{31}P chemical shift for gaseous phosphine was measured as +263 ± 1 p.p.m. in this work which is somewhat higher than the literature value of +238 p.p.m.[106] However, the observed coupling constant of 181 Hz is in excellent agreement with literature values of 180 and 182 Hz.[103] The slight downfield shift in liquid hydrogen chloride may possibly indicate some exchange between PH_3 and PH_4^+ species.

The oxidation of phosphine with chlorine was carried out in the solvent. The reaction was carried out using both 1:1 and 2:3 molar ratios of phosphine:chlorine. In both cases an orange solid precipitated out of solution and in the former reaction a ^{31}P n.m.r. signal at +245.3 p.p.m., immediately assignable to excess phosphine, was detected. No signals attributable to previously unknown chlorophosphines were observed.

The reaction between phosphine and phosphorus(III) chloride in 1:2 molar ratio was studied in the absence of a solvent. Again, an orange solid precipitated which was shown to be phosphorus by elemental analysis. A resonance at -220 p.p.m. was observed when the ^{31}P n.m.r. spectrum of the residual liquid was recorded. This signal may be immediately assigned to excess phosphorus(III) chloride.

Experimental

The behaviour of phosphine in liquid hydrogen chloride

PH_3 (5 mmole) followed by HCl (30 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule. The ampoule was sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the clear colourless solution consisted of a sharp singlet at +245 $\pm$ 1 p.p.m.

The ^{31}P n.m.r. spectrum of gaseous phosphine was then recorded. PH_3 was condensed at -196° into an 8 mm. o.d. quartz ampoule which was then sealed and tested in the usual manner. Some liquid PH_3 was present at 10°, but all was in the gas phase at 34°C. PH_3 has an S.V.P. of 38.2 atm. at 17°C[93] and it may be assumed that the gaseous pressure inside the ampoule was of the order of 40-50 atm. The ^{31}P n.m.r. spectrum of gaseous PH_3 consisted of a 1:3:3:1 quartet at +263 p.p.m. with $^1J_{^{31}P-^1H}$ 181 Hz.

The reaction between phosphine and chlorine

Cl_2 (2 mmole) followed by HCl (30 mmole) and PH_3 (2 mmole) was condensed at -196° into an 8 mm. o.d. silica ampoule. The ampoule was sealed and tested in the usual way. A bright orange solid and a clear colourless solution were present at room temperature. A sharp resonance at +245.3 p.p.m. was observed when the ^{31}P n.m.r. spectrum of the solution was recorded.

An apparently similar orange solid precipitated from a mixture of PH_3 and Cl_2 in 2:3 molar ratio in liquid hydrogen chloride. No attempt was made to record a ^{31}P n.m.r. spectrum from this ampoule.

The reaction between phosphine and phosphorus(III) chloride

PH_3 (5 mmole) followed by PCl_3 (10 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule which was sealed and tested as described previously. Much pale yellow solid formed at -78° and was orange in colour at room temperature. The ^{31}P n.m.r. spectrum of the remaining colourless liquid consisted of a sharp singlet at -220 p.p.m. which may be immediately assigned to PCl_3.[135] No signals attributable to a solid state resonance were observed. The ampoule was cracked open under dry nitrogen and the orange solid removed. This material was pumped for 2 hours at room temperature to remove traces of PCl_3 and was analysed.

Found: P, 99.6%

The orange solid may thus be assumed to be elemental phosphorus.

3.6 Reactions of triphenylphosphine and related chlorophenylphosphorus (III) compounds

Results and Discussion

Triphenylphosphine is soluble in liquid hydrogen chloride with protonation, and in liquid deuterium chloride with deuteronation. ^{31}P chemical shifts and $^{1}J_{P-H}$ and $^{1}J_{P-D}$ coupling constants were measured for the species Ph_3PH^+ and Ph_3PD^+ respectively. Oxidation of the phosphorus from the +3 to the +5 oxidation state was observed on reaction with chlorine and iodine monochloride in the solvent. The series Ph_nPCl_{3-n} $(0 \leq n \leq 3)$ can be oxidised by chlorine to $Ph_nPCl_{4-n}^+$ $(0 \leq n \leq 3)$ in liquid hydrogen chloride. Reactions were followed by ^{31}P n.m.r. spectroscopy, and the results of the experiments are shown in Table 3.6.1.

The ion Ph_3PH^+ has been detected in sulphuric acid[85] and the compound $Ph_3PH^+BCl_4^-$ has been prepared in liquid hydrogen chloride.[27] The ^{31}P n.m.r. spectrum of a solution of Ph_3P in the solvent consisted of a 1:1 doublet, with a chemical shift of -6 ± 1 p.p.m. and a P-H coupling

TABLE 3.6.1

^{31}P n.m.r. solution data for protonation, deuteronation and oxidation reactions of triphenylphosphine and related chlorophenylphosphorus(III) compounds

(^{31}P chemical shifts in p.p.m. relative to 85% H_3PO_4)

Compound	Solvent	^{31}P chemical shift values		$^{1}J_{P-X}$ Hz	Remarks
		Observed p.p.m.	Literature p.p.m.		
Ph_3P	liquid HCl	-6 ± 1	+6 (134)	505 ± 5	Ph_3PH^+. Isolated as $Ph_3PH^+HCl_2^-$
Ph_3P	liquid DCl	-5.5	+6 (134)	76.5 ± 1	Ph_3PD^+
$Ph_3P + Cl_2$ (1:1)	liquid HCl	-65 ± 1	-62, -65, -66 (177,178,183)		Ph_3PCl^+
$Ph_2PCl + Cl_2$ (1:1)	liquid HCl	-93.2	-93 (178)		$Ph_2PCl_2^+$
$PhPCl_2 + Cl_2$ (1:1)	liquid HCl	-100	-103 (178)		$PhPCl_3^+$

constant of 505 ± 5 Hz which may be immediately assigned to the protonated species Ph_3PH^+. A chemical shift of 0 p.p.m. for Ph_3PH^+ in $Ph_3PH^+Cl^-$ has been quoted,[184] and, later in this work a shift of -2.5 ± 1 p.p.m. has been measured for the species in liquid hydrogen bromide solution.

TABLE 3.6.2

The variation in ^{31}P chemical shift with counterion for the species Ph_3PH^+

(Chemical shifts in p.p.m. relative to 85% H_3PO_4, $^1J_{^{31}P-^1H}$ values in Hz)

$\delta^{31}P$	Solvent	Counterion	$^1J_{^{31}P-^1H}$	Reference
0	Not specified	Cl^-	-	184
-2.5 ± 1	Liquid HBr	Solvated Br^- ion	498	this work
-6 ± 1	Liquid HCl	Solvated Cl^- ion	510	this work

It has been shown in several instances that ^{31}P chemical shift values for phosphorus(V) cations are dependent upon counterion, generally a lower value being observed when a larger anion is present. ^{31}P chemical shifts for the tetrachlorophosphonium ion are listed in Table 3.6.3 as an example.

Thus, the variation in shift of the Ph_3PH^+ ion is totally reasonable, and it may be possible, on the basis of the lowest chemical shift being observed for the largest counterion, to postulate a higher degree of solvation for the Cl^- ion in liquid HCl than for the Br^- ion in liquid HBr.

TABLE 3.6.3

Variation in ^{31}P chemical shift with counterion for the species PCl_4^+

(^{31}P chemical shifts in p.p.m. relative to 85% H_3PO_4)

δ ^{31}P	Counterion	Solvent	Reference
-80.3	Solvated Cl^- ion	liquid HCl	this work
-87.3	Tetrahaloborate	liquid HCl	this work
-87.1	ClO_4^-	CH_2Cl_2	178
-87.9	$SbCl_6^-$	CH_2Cl_2	178
-96	PCl_6^-		167

A 1:1:1 triplet at -5.5 ± 0.5 p.p.m. with a $^1J_{P-D}$ value of 77.0 ± 2 Hz was observed when the ^{31}P n.m.r. spectrum of a solution of Ph_3P in liquid deuterium chloride was recorded. This signal is assigned to the species Ph_3PD^+. Phosphorus-deuterium spin-spin coupling was first reported by Fluck and Binder[105] in 1967. For nuclei in identical environments, the relationship between the coupling of an atom, X, with hydrogen or deuterium is given by

$$J_{XH}/J_{XD} = 6.51 \quad \text{(Ref.173)}$$

The ratio of coupling constants obtained from the species Ph_3PH^+ and Ph_3PD^+ is given by

$$J_{PH}/J_{PD} = \frac{505}{77} = 6.54$$

which is in good agreement with the theoretical value.

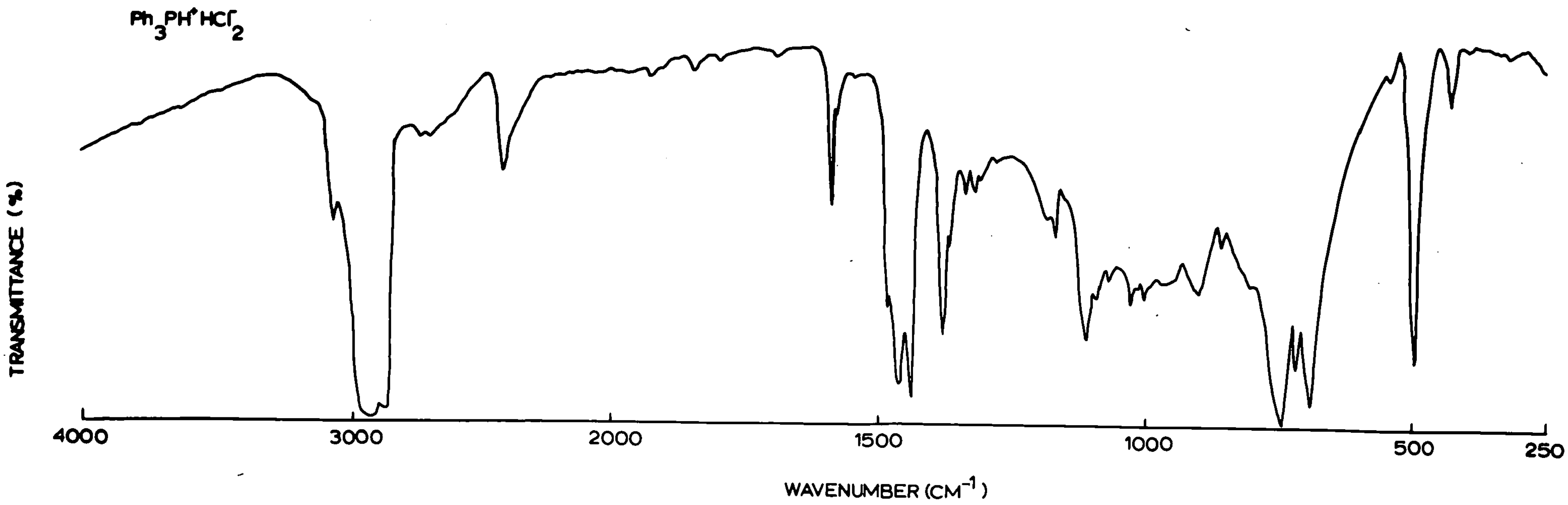
Borisenko et al have reported that the value of the ratio J_{PH}/J_{PD} slightly exceeds the theoretical value for phosphorus(V) species.[174] However, Stec et al[182] have reported values both above and below the theoretical for phosphorus(V) compounds, and so too much emphasis should not be placed on the exact value of the ratio.

On removal of the solvent from a solution of Ph_3P in liquid hydrogen chloride, much hydrogen chloride was retained above its boiling point, finally coming off at a higher temperature. Similar behaviour was observed during the preparation of tetramethylammonium hydrogendichloride in liquid hydrogen chloride.[44] The infrared spectrum of the white solid obtained from the solution of Ph_3P in liquid hydrogen chloride contained a sharp, weak absorption at 2406 cm^{-1} and a broad strong underlying band with a maximum near 750 cm^{-1} and tailing off towards 1300 cm^{-1}, in addition to absorptions characteristic of Ph_3P. The peak at 2406 cm^{-1} is assigned to ν_{P-H} in Ph_3PH^+ [175,176] and the broad peak at 750 cm^{-1} to the HCl_2^- ion.[49] Confirmation of the formulation of the compound as $Ph_3PH^+HCl_2^-$ was provided by weight analysis and elemental analysis. This compound is stable at room temperature for many months if stored under dry nitrogen. The preparation of the compound $Ph_3PH^+BCl_4^-$ has been reported.[27]

Oxidation of triphenylphosphine by chlorine in liquid hydrogen chloride and isolation of the products Ph_3PCl_2, and $Ph_3PCl^+BCl_4^-$ on addition of BCl_3, has been reported.[53] The ^{31}P n.m.r. spectrum of a solution of Ph_3P and Cl_2 in 1:10 molar ratio in the solvent contained a sharp peak at -65.1 p.p.m. which may be immediately assigned to the chlorotriphenylphosphonium ion Ph_3PCl^+.[177,178,183]

Fig.3.6.1

Infrared spectrum of triphenylphosphonium hydrogendichloride


$Ph_3PH^+HCl_2^-$
TRANSMITTANCE (%)
4000
3000
2000
1500
1000
500
250
WAVENUMBER (CM^{-1})

A conductiometric titration between Ph_3P and ICl in liquid hydrogen chloride showed an end-point at a ratio of 1:1 possibly indicating the formation of the species Ph_3PI^+.[54] The compound Ph_3PICl has been prepared and its structure in the solid state has been shown to be $Ph_3PI^+Cl^-$.[146] A solid whose composition was shown to be Ph_3PBCl_4I by elemental analysis was obtained by reaction of Ph_3P with ICl and BCl_3 in liquid hydrogen chloride. The ^{31}P n.m.r. solid state spectrum of this material contained a broad peak at -65.5 ± 2 p.p.m. which may be assigned to Ph_3PCl^+,[177,178] and not the expected Ph_3PI^+. It is shown later in this work that Ph_3PI^+ is extensively solvolysed in liquid hydrogen chloride, and the presence of a weak signal in the region of -55 p.p.m. probably due to Ph_3PI^+ (p. 113) may not be detected in a solid state spectrum whose main constituent is Ph_3PCl^+. Similarly, the ^{11}B n.m.r. solid state spectrum of the material consisted of a broad signal. The maximum of the broad peak was at +19 ± 0.7 p.p.m. The ^{11}B n.m.r. chemical shifts of BCl_4^- and BCl_3I^- are known to be +11.6 and +30.9 p.p.m. respectively[147] and it is possible that signals due to both of these anions are present in the signal from the solid. The infrared spectrum contained absorptions due to Ph_3P and also peaks at 597 cm^{-1} and 690 and 660 cm^{-1} which may be assigned to Ph_3PCl^+[53] and BCl_4^- [20f,163] respectively. It is possible to formulate the solid Ph_3PBCl_4I as consisting largely of $Ph_3PCl^+BCl_3I^-$ with some $Ph_3PI^+BCl_4^-$.

The reaction was repeated using triphenylarsine in place of triphenylphosphine. A solid, whose composition was shown to be Ph_3AsBCl_4I by analysis, was isolated. The ^{11}B n.m.r. solid state spectrum consisted of a broad peak at +11.5 ± 1 p.p.m. which may be immediately assigned to BCl_4^-.[147] Absorptions at 683 and 660 cm^{-1}, which are characteristic of the BCl_4^- ion, were present in the infrared spectrum of the material. This compound may be unambiguously formulated as $Ph_3AsI^+BCl_4^-$. The resistance to solvolysis of the Ph_3AsI^+ cation as compared with the Ph_3PI^+ cation in liquid hydrogen chloride may be a consequence of a lower degree of steric crowding around the central atom in the arsenic species producing a more stable cation.

In the series Ph_nPCl_{3-n} $(0 \leq n \leq 3)$, PCl_3 has been shown to be soluble in liquid hydrogen chloride without reaction, and Ph_3P is protonated in the solvent. The 1:1 doublet due to Ph_3PH^+ is shifted 12 p.p.m. downfield from the signal due to Ph_3P itself, recorded in benzene solution. A single peak at -90 ± 0.5 p.p.m. was observed when the ^{31}P n.m.r. spectrum of a solution of Ph_2PCl in liquid hydrogen chloride was recorded. The chemical shift of the neat liquid Ph_2PCl was determined as -82 ± 0.5 p.p.m., which is in excellent agreement with the literature value of -81.5 ± 1 p.p.m.[181] The downfield shift of 8 p.p.m. observed in liquid hydrogen chloride may be explained in terms of protonation of the Ph_2PCl. A singlet, not the doublet which might be expected from Ph_2PClH^+, is observed indicating that protonation is incomplete, and that rapid exchange with the solvent is taking place. The ^{31}P chemical shift of neat liquid $PhPCl_2$ has been reported as -161.6 p.p.m.[134] In this study a ^{31}P shift of -161.0 ± 0.5 p.p.m. was observed from a solution of $PhPCl_2$ in liquid hydrogen chloride, indicating that $PhPCl_2$, like PCl_3, dissolves without reaction in the solvent. Both Ph_2PCl and $PhPCl_2$ are oxidised by chlorine in liquid hydrogen chloride solution; ^{31}P n.m.r. solution spectra of 1:1 molar ratios of the phosphine:chlorine contains signals at -93.2 ± 0.5 and -100.3 ± 0.5 p.p.m. which are characteristic of the phosphorus(V) cations $Ph_2PCl_2^+$ and $PhPCl_3^+$ respectively.[178]

^{31}P n.m.r. data determined in this work for the species $Ph_nPCl_{4-n}^+$ ($0 \le n \le 3$) are in excellent agreement with published values. (See Table 3.6.4.).

TABLE 3.6.4

^{31}P chemical shifts for the species $Ph_nPCl_{4-n}^+$ ($0 \le n \le 3$) in the salts $Ph_nPCl_{4-n}^+X^-$

(Chemical shifts in p.p.m. relative to 85% H_3PO_4)

X	n = 0	n = 1	n = 2	n = 3	Reference
ClO_4	-87.1	-103.0	-93.2	-65.7	178
$SbCl_6$	-87.9	-102.9	-93.2	-65.0	178
Solvated Cl^- ion	-80.3	-100.3	-93.2	-65.1	this work
				-66 to -62	177

Experimental

The behaviour of triphenylphosphine in liquid hydrogen chloride

HCl (25 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing Ph_3P (0.1 g., 0.38 mmole). The ampoule was sealed and tested in the normal manner, and contained a clear colourless solution at room temperature. The ^{31}P n.m.r. spectrum of the solution consisted of a 1:1 doublet at -6 ± 1 p.p.m. with a coupling constant $^1J_{P-H}$ of 505 ± 5 Hz. This doublet may be readily assigned to the protonated species Ph_3PH^+, which has been shown to exist in liquid hydrogen chloride solution.[81]

The reaction was repeated on a larger, preparative scale. Ph_3P (0.262 g., 1 mmole) was dissolved in about 2 ml. liquid hydrogen chloride at -95° in a weight analysis cell. The clear colourless solution was allowed to equilibrate for 30 minutes at this temperature. The solvent was then removed by pumping at -95°, until with about 1/4 of the solution remaining and HCl pressure less than 1 cm. of Hg the liquid bumped and a sticky white solid was immediately obtained. Further pumping at room temperature resulted in the collapse of this sticky solid to a pure white powder, with the evolution of more gas. This gas was identified as HCl by examination of its infrared spectrum.

The weight increase during the reaction was 29.9%. That calculated for the reaction $Ph_3P \rightarrow Ph_3PH^+HCl_2^-$ is 27.8%.
Found: C, 64.42; H, 4.46; $Ph_3PH^+HCl_2^-$ requires C, 64.49; H, 5.08.
The infrared spectrum contained a sharp, weak absorption at 2406 cm^{-1} not found in the spectrum of Ph_3P, which is assigned to ν_{P-H} in Ph_3PH^+. Other workers have reported the presence of a "weak or undetectable" maximum in the region 2350-2400 cm^{-1} in the infrared spectra of Ph_3PH^+ salts.[175,176] The presence of a strong broad underlying absorption with maximum at about 750 cm^{-1} and tailing off towards 1300 cm^{-1} is indicative of HCl_2^- ion.[49]

The compound is thus identified as $Ph_3PH^+HCl_2^-$ and is stable at room temperature for several months if stored under dry nitrogen.

The reaction was also repeated in liquid deuterium chloride. DCl (30 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing Ph_3P (0.1 g., 0.38 mmole). The ampoule was sealed and tested in the usual manner, and contained a clear colourless solution at room temperature. The ^{31}P n.m.r. spectrum consisted of a 1:1:1 triplet at -5.5 p.p.m. with coupling constant $^1J_{P-D}$ of 76.5 ± 1 Hz. This signal may be readily assigned to the species Ph_3PD^+.

The reaction between triphenylphosphine and chlorine

Ph_3P (0.131 g., 0.5 mmole) was loaded into an 8 mm. o.d. silica ampoule. HCl (30 mmole) was condensed into the ampoule at -196^o, followed by Cl_2 (5 mmole). The ampoule was sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the clear green solution consisted of a readily detectable signal at -65.1 p.p.m. This may be immediately assigned to Ph_3PCl^+.[177,178,183]

The reaction between triphenylphosphine, iodine monochloride and boron trichloride

HCl was condensed at -196^o into a large reaction tube containing Ph_3P (2.62 g., 10 mmole) until a clear solution was obtained on warming to -95^o. ICl (1.828 g., 11.2 mmole) was condensed into the tube at -196^o and on warming to -95^o a brown solution was produced. 20 minutes at this temperature were allowed for equilibration. An excess of BCl_3 was condensed into the tube at -196^o, and on warming to -95^o a pale brown solid was precipitated from the hydrogen chloride solution. HCl was removed by pumping at low temperature, -95^o, and excess BCl_3 by pumping at room temperature for 12 hours. The solid was washed with dry CCl_4 until washings were colourless and then dried in vacuo.

The infrared spectrum of the ginger coloured solid contained, in addition to absorptions due to triphenylphosphine, absorptions at 597, 690 and 660 cm^{-1}. The absorption at 597 cm^{-1} may be assigned to ν_{P-Cl} in Ph_3PCl^+,[53] and those at 690 and 660 cm^{-1} are characteristic of BCl_4^-.[20f,163]

The ^{31}P n.m.r. solid state spectrum contained a broad signal at -65.5 ± 2 p.p.m. which may be assigned to Ph_3PCl^+ [178] and the ^{11}B n.m.r.

solid state spectrum contained a broad signal at +19.0 ± 0.7 p.p.m. This is high for a BCl_4^- shift, which usually lies between +11 and +12 p.p.m.,[147] but may be due to the presence of some BCl_3I^-, ^{11}B shift +30.9 p.p.m.[147]

Found: C,39.96; H,3.02; P,5.87; I,23.26; Cl,26.67. Required for $Ph_3PCl^+BCl_3I^-$, or $Ph_3PI^+BCl_4^-$; C,39.86; H,2.79; P,5.68; I,23.42; Cl,26.18.

The reaction between triphenylarsine, iodine monochloride and boron trichloride

HCl was condensed at -196° into a large reaction tube containing Ph_3As (1.29 g., 4.31 mmole) in sufficient quantity to yield a clear solution on warming to -95°. ICl (0.725 g., 4.47 mmole) was condensed into the tube at -196° and on warming to -95° the ICl dissolved with the formation of a little dark precipitate, possibly iodine. 30 minutes were allowed for equilibration at -95°. An excess of BCl_3 was condensed into the tube at -196°, and a dark solid precipitated on warming to -95°. HCl was removed by pumping at this temperature and excess BCl_3 was removed by pumping at room temperature for 18 hours. The ginger-brown solid was taken into the dry box and washed with dry CCl_4 until washings were colourless. The solid was then dried in vacuo.

In addition to absorptions due to Ph_3As, the infrared spectrum of the solid contained absorptions at 683 and 660 cm^{-1} which may be assigned to the BCl_4^- ion.[20f,163] The ^{11}B n.m.r. solid state spectrum consisted of a peak at +11.5 ± 1 p.p.m. which may be immediately assigned to BCl_4^-.[147]

Found: C,36.32; H,2.51; I,21.34; Cl,23.46. Required for $Ph_3AsI^+BCl_4^-$; C,36.91; H,2.58; I,21.66; Cl,24.20.

The behaviour of chlorodiphenylphosphorus(III) in liquid hydrogen chloride

Ph_2PCl (0.2 ml., 1.12 mmole) was syringed into an 8 mm. o.d. quartz ampoule. HCl (25 mmole) was condensed into the ampoule at -196°, which was then sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the clear colourless solution contained a single peak at -90.0 ± 0.5 p.p.m. The ^{31}P chemical shift of neat Ph_2PCl was observed to be -82 ± 0.5 p.p.m.

The reaction between chlorodiphenylphosphorus(III) and chlorine

Ph_2PCl (0.1 ml., 0.56 mmole) was syringed into an 8 mm. o.d. quartz ampoule. HCl (25 mmole) was condensed into the ampoule at -196°, followed by Cl_2 (0.56 mmole). The ampoule was sealed and tested in the usual way. The colour due to the chlorine was discharged and a clear colourless solution was obtained at room temperature. A single resonance at -93.2 ± 0.5 p.p.m. was observed, which may be immediately assigned to $Ph_2PCl_2^+$,[178] when the ^{31}P n.m.r. spectrum was recorded.

The behaviour of dichlorophenylphosphorus(III) in liquid hydrogen chloride

$PhPCl_2$ (0.2 ml., 2.6 mmole) was syringed into an 8 mm. o.d. quartz ampoule. HCl (25 mmole) was condensed into the ampoule at -196°, which was then sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the clear colourless solution contained a single peak at -161 ± 0.5 p.p.m., which may be immediately assigned to $PhPCl_2$. Literature value for neat liquid $PhPCl_2$ is -161.6 p.p.m.[134]

The reaction between dichlorophenylphosphorus(III) and chlorine

$PhPCl_2$ (0.3 ml., 3.8 mmole) was syringed into an 8 mm. o.d. quartz ampoule. HCl (25 mmole) was condensed into the ampoule at -196^o, followed by Cl_2 (3.8 mmole). The ampoule was sealed and tested in the usual way. During this process, at -45^o, the ampoule contained two liquid layers, the lower colourless and the upper green. A transient red-brown colour appeared on shaking the tube and causing the layers to mix. A clear colourless solution was obtained at room temperature. The ^{31}P n.m.r. spectrum of this solution contained a single peak at -100.3 ± 1 p.p.m. which may be assigned to $PhPCl_3^+$.[178]

3.7 The behaviour of dihalotriphenylphosphorus(V) compounds in liquid hydrogen chloride

The ^{31}P n.m.r. spectra of solutions of the dihalotriphenylphosphorus(V) compounds Ph_3PX_2 (X = Cl, Br, I) in liquid hydrogen chloride were recorded. Results are shown in Table 3.7.1.

A signal at -65.0 p.p.m. was observed in the ^{31}P n.m.r. spectrum of a solution of Ph_3PCl_2 in liquid hydrogen chloride. Values between -66 and -62 p.p.m. have been reported for the chlorotriphenylphosphonium ion in solution.[177,178]

The ^{31}P n.m.r. spectrum of a solution of Ph_3PBr_2 in the solvent contained a strong signal at -54 p.p.m. and a very weak signal at -66 p.p.m., which may be assigned to Ph_3PBr^+ [180] and Ph_3PCl^+,[177,178] respectively. The difference between the chemical shift of Ph_3PBr^+ in liquid hydrogen chloride and the literature values of -48.6 and -48.3

TABLE 3.7.1

^{31}P chemical shifts for some dihalotriphenylphosphorus(V) compounds in liquid hydrogen chloride

(chemical shifts in p.p.m. relative to 85% H_3PO_4)

Compound	δ ^{31}P	Remarks
Ph_3PCl_2	-65	Ph_3PCl^+
Ph_3PBr_2	-66, -54	Signals assigned to Ph_3PCl^+ and Ph_3PBr^+ respectively. Slight solvolysis of Ph_3PBr^+
Ph_3PI_2	-64.5, -55	Signals assigned to Ph_3PCl^+ and to Ph_3PI^+ respectively. Extensive solvolysis of Ph_3PI^+

p.p.m.,[180] solid state and $PhNO_2$ solution values respectively, may be due to a change in magnetic susceptibility, and/or to a change in counterion. Salthouse and Waddington[53] have reported the oxidation of Ph_3P with Br_2 in liquid hydrogen chloride at -95° to produce an inhomogeneous product, consisting of Ph_3PCl_2 and Ph_3PBr_2. The present study confirms that the Ph_3PBr^+ cation is solvolysed in liquid hydrogen chloride, but only slightly even at room temperature.

Two signals at -64.5 and -55 p.p.m. which may be assigned to Ph_3PCl^+ and Ph_3PI^+ respectively were observed in the ^{31}P n.m.r. spectrum of a solution of Ph_3PI_2 in liquid hydrogen chloride. The ratio of the intensities of the signals was approximately 4:1, Ph_3PCl^+:Ph_3PI^+.

A solid state ^{31}P chemical shift for Ph_3PI^+ of -42.5 p.p.m. has been reported.[180] The large difference between this value and that found in liquid hydrogen chloride solution may be due to a magnetic susceptibility or to some exchange with the solvent, or to the presence of a different counterion. Clearly Ph_3PI^+ is solvolysed to a large extent in liquid hydrogen chloride.

Experimental

Dichlorotriphenylphosphorus(V)

Ph_3PCl_2 was prepared in situ as described previously. (p.109). The ^{31}P n.m.r. solution spectrum contained a single sharp resonance at -65.1 p.p.m. which may be assigned to Ph_3PCl^+.[178]

Dibromotriphenylphosphorus(V)

HCl (30 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing Ph_3PBr_2 (0.250 g., 0.59 mmole). The ampoule was sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the clear colourless solution contained a very weak signal at -66 p.p.m. and a very strong signal at -54 p.p.m. The weak signal may be assigned to Ph_3PCl^+, formed presumably as the result of limited solvolysis. ^{31}P chemical shifts of -48.3 and -48.6 p.p.m. have been reported for the ion Ph_3PBr^+ in $PhNO_2$ solution and in the solid state respectively.[180] The signal at -54 p.p.m. is assigned to this species, the difference between the values in $PhNO_2$ and in liquid hydrogen chloride solutions presumably being due to magnetic susceptibility effects, and/or to a change in counterion.

Diiodotriphenylphosphorus(V)

HCl (30 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing Ph_3PI_2 (0.327 g., 0.58 mmole). The ampoule was sealed and tested in the usual manner. A clear orange-brown solution was obtained at room temperature. The ^{31}P n.m.r. spectrum consisted of a strong signal at -64.5 p.p.m. and a weaker signal at -55 p.p.m. The strong signal may be assigned at once to Ph_3PCl^+.[178] A solid state value of -42.5 p.p.m. for Ph_3PI^+ has been reported,[180] and the signal at -55 p.p.m. may be assigned to this species provided that an exchange with the solvent is postulated. However, it is clear that $Ph_3PI^+I^-$ is largely solvolysed in liquid hydrogen chloride.

3.8 The behaviour of phosphorus(V) halides in liquid hydrogen chloride

3.8.1. Phosphorus(V) fluoride

Results and Discussion

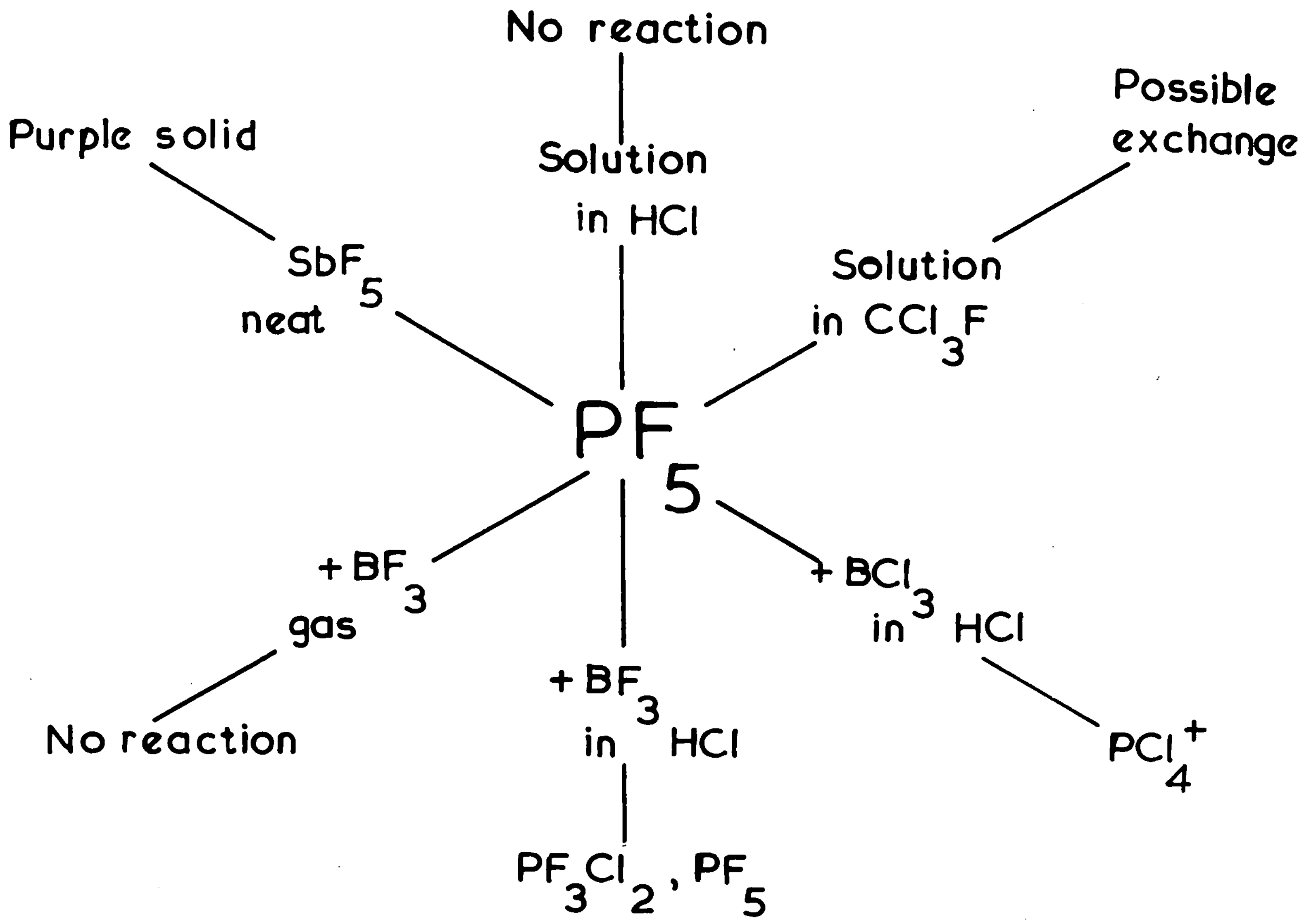
Phosphorus(V) fluoride is shown to be soluble in liquid hydrogen chloride at room temperature without reaction. Reactions with the solvoacids boron trichloride and boron trifluoride in the solvent indicate the possible formation of the tetrafluorophosphonium ion as an intermediate.

The results of the experiments are shown in Fig. 3.8.1. All reactions were followed by ^{31}P n.m.r. spectroscopy, and where appropriate ^{11}B n.m.r. spectroscopy.

Peach and Waddington[26] have reported that PF_5 is soluble in liquid hydrogen chloride at low temperatures forming a colourless solution. PF_5 acts as a source of the hexafluorophosphate ion in the presence of strong bases in the solvent according to the equation

Fig.3.8.1

Reactions of phosphorus(V) fluoride


No reaction
Purple solid
Solution
in HCl
Possible
exchange
SbF5
neat
Solution
in CCl3F
PF5
+ BF3
gas
+ BCl3
in HCl
No reaction
+ BF3
in HCl
PCl4+
PF3Cl2, PF5

$2Me_4N^+ + 2Cl^-_{solv} + 3PF_5 \xrightarrow[HCl]{liq} 2Me_4N^+PF_6^- + PF_3Cl_2$ (Ref.26)

The ^{31}P n.m.r. spectrum of a solution of PF_5 in liquid hydrogen at room temperature consisted of the expected 1:5:10:10:5:1 sextet, with a chemical shift of +81 p.p.m. and a coupling constant $^1J_{P-F}$ of 953 ± 1Hz. This is in excellent agreement with the ^{31}P n.m.r. data obtained from a gas phase spectrum; chemical shift +79.5 p.p.m., $^1J_{P-F}$ 952 Hz. It may be assumed that PF_5 is soluble in the solvent without reaction. These figures are in slight disagreement with literature data, values of +68 and +72.5 p.p.m. for the chemical shift and 930 Hz for $^1J_{P-F}$ having been reported.[133,121] The ^{31}P n.m.r. spectrum of PF_5 in the "inert" solvent CCl_3F was recorded for purposes of comparison. The peaks in this spectrum were much broader than those in the previous two spectra, possibly an indication of rapid exchange with the solvent, but the chemical shift of +80 ± 1 p.p.m. was comparable. The coupling constant was recorded as 958 ± 15 Hz. Following the observation that PF_5 dissolves unchanged in liquid hydrogen chloride, the reaction between PF_5 and BCl_3 in a 1:1 molar ratio in the solvent was investigated. Boron trichloride is a well established Lewis acid in liquid hydrogen chloride when a base is present[20e],but it is shown later in this work that in the absence of a base BCl_3 dissolves unchanged in the solvent. The ^{31}P n.m.r. spectrum of the clear colourless solution of PF_5 and BCl_3 in 1:1 molar ratio in liquid hydrogen chloride consisted of a single sharp resonance at -85.5 p.p.m. which may be immediately assigned to the tetrachlorophosphonium ion PCl_4^+.[131] The ^{11}B n.m.r. spectrum contained a single sharp peak at +11.25 p.p.m. which is characteristic of BCl_4^-.[147] Thus PF_5 and BCl_3 in liquid hydrogen chloride at room temperature react to give tetrachlorophosphonium tetrachloroborate $PCl_4^+BCl_4^-$.

$$PF_5 + BCl_3 \xrightarrow[HCl]{liquid} PCl_4^+ + BCl_4^-$$

The reaction may proceed via the formation of a tetrafluorophosphonium ion PF_4^+ and a trichlorofluoroborate ion BCl_3F^-,

$$PF_5 + BCl_3 \xrightarrow[HCl]{liquid} PF_4^+ + BCl_3F^-$$

followed by solvolysis to give the observed products. Or, involving the solvent,

$$PF_5 + HCl + BCl_3 \xrightarrow[HCl]{liquid} PF_4^+ + HF + BCl_4^-$$

again followed by solvolysis to yield the PCl_4^+ cation.

The reaction was repeated using BF_3 as the Lewis acid. BF_3 is a solvoacid in liquid hydrogen chloride, forming the BF_3Cl^- anion in the presence of a solvobase e.g. PCl_5. The compound $PCl_4^+BF_3Cl^-$ formed at -95° has been isolated and characterised at room temperature.[20b,20e] It is shown later in this work that BF_3 dissolves unchanged in liquid hydrogen chloride at room temperature. The ^{31}P n.m.r. spectrum of a 1:1 molar mixture of PF_5 and BF_3 in liquid hydrogen chloride contained two multiplets; a sextet at + 81 ± 1 p.p.m. with coupling constant $^1J_{P-F}$ of 948 Hz, and a quartet at +37 ± 0.5 p.p.m. with a P-F coupling constant of 1080 Hz. The sextet may be assigned to PF_5. The quartet is typical of a PF_3X_2 or PF_3X^+ (X = Br,Cl) species and the coupling constant of 1080 Hz is quite close to 1070 Hz observed in this work for PF_3Cl_2 in liquid hydrogen chloride. However, the ^{31}P chemical shift of PF_3Cl_2 in the solvent has been observed in the region +29.5 ± 2 p.p.m. and it is difficult to explain such a large difference in shift values. The ^{11}B n.m.r. spectrum contained a sharp resonance at +8.6 p.p.m. which may be immediately assigned to BF_3.[125] Again, the postulation of a tetracoordinate fluorophosphorus(V) cation is required to explain the observed products.

$$PF_5 + HCl + BF_3 \xrightarrow[HCl]{liquid} PF_4^+ + HF + BF_3Cl^-$$

$$PF_4^+ + HCl \rightarrow PF_3Cl^+ + HF$$

$$PF_3Cl^+ + BF_3Cl^- \rightarrow PF_3Cl_2 + BF_3$$

The overall equation may be written

$$PF_5 + 2HCl \xrightarrow[\substack{liquid\\HCl}]{BF_3} PF_3Cl_2 + 2HF$$

i.e. the solvolysis of PF_5 in "more acidic" liquid hydrogen chloride.

The reaction between PF_5 and BF_3 was repeated in the absence of a solvent. Not surprisingly the ^{31}P and ^{11}B n.m.r. spectra showed the presence of unchanged starting materials indicating that no reaction had taken place.

Phosphorus(V) fluoride was treated with an excess of the strong Lewis acid antimony(V) fluoride. Some purple solid was produced but ^{31}P n.m.r. signals could not be detected when the spectrum of this material was recorded.

3.8.2. Phosphorus(V) chloride

Phosphorus(V) chloride has been shown to be soluble in liquid hydrogen chloride producing a large increase in conductance,[20d] and there is no doubt that it behaves as a chloride ion donor in the solvent.[20e] The ^{31}P n.m.r. spectrum of a solution of PCl_5 in liquid hydrogen chloride contained a strong signal at -80.3 p.p.m. which may be assigned to the tetrachlorophosphonium ion.[131,132] The absence of signals in the region of +80 p.p.m. and +300 p.p.m. indicate the absence of the species PCl_5 and PCl_6^- respectively.[103,108] Thus, the behaviour of phosphorus(V) chloride as a chloride ion donor, i.e. a strong base, in liquid hydrogen chloride and its existence in the solvent as PCl_4^+ and solvated chloride ions is confirmed.

3.8.3. Phosphorus(V) bromide

Phosphorus(V) bromide is only slightly soluble in liquid hydrogen chloride at room temperature. The ^{31}P n.m.r. spectrum of a saturated solution contained signals at -224.7, -222.6, -218.4 and +95.3 p.p.m. The signals in the downfield region may be assigned to PBr_2Cl, $PBrCl_2$[136] and PCl_3[119] respectively, and that at +95.3 p.p.m. to PBr_4^+.[146,169] Phosphorus(V) bromide is known to exist in the solid state as $PBr_4^+Br^-$,[170] and its dissociation in solution to phosphorus(III) bromide and bromine has been reported.[171,172] The ^{31}P n.m.r. solid state spectrum of phosphorus(V) bromide was recorded and contained two strong signals at -227.5 and +104 p.p.m. The expected signal at +104 p.p.m. is in excellent agreement with the literature values of +101 and +104 $\pm$ 1 p.p.m. for PBr_4^+,[169,101] and the peak at -227.5 p.p.m. may be assigned to PBr_3.[119] Thus partial dissociation of phosphorus(V) bromide to phosphorus (III) bromide and bromine takes place even in the solid state at temperatures a little above room temperature. The PBr_3 formed as a result of dissociation will be solvolysed in liquid hydrogen chloride giving PBr_2Cl, $PBrCl_2$ and PCl_3. It has already been shown in this work that

PBr_3 is solvolysed by liquid hydrogen chloride, signals due to PBr_3, PBr_2Cl and $PBrCl_2$ being detected in the ^{31}P n.m.r. spectrum of the solution. The absence of PBr_3 in a saturated solution of phosphorus(V) bromide in the solvent is possibly due to a concentration effect.

In the reaction between phosphorus(V) bromide and an excess of boron trichloride in the solvent a clear yellow orange solution over much orange crystalline solid was observed. No signal could be detected when the ^{31}P n.m.r. spectrum of this solution was recorded, but a peak at -28.75 p.p.m., which may be assigned to BCl_3,[125] was observed in the ^{11}B n.m.r. spectrum. The orange crystalline solid was not investigated further, but it was probably $PBr_4^+BCl_3Br^-$.

^{31}P n.m.r. data from solution of the phosphorus(V) halides in liquid hydrogen chloride are summarised in Table 3.8.1.

<u>Experimental</u>

<u>The behaviour of phosphorus(V) fluoride in liquid hydrogen chloride</u>

PF_5 (2 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by HCl (25 mmole). The ampoule was sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum obtained from a CAT run of 64 scans consisted of a sharp 1:5:10:10:5:1 sextet centred at +81 p.p.m. with coupling constant $^1J_{P-F}$ of 953 ± 1 Hz. Values for PF_5 of +68 p.p.m. and 930 Hz have been reported for the ^{31}P chemical shift and P-F coupling constant respectively.[133,121]

The ^{31}P n.m.r. spectrum of PF_5 in freon 11 was also recorded. PF_5 (2 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by freon 11 (1 ml.). The ampoule was sealed and tested in the usual manner, and contained a clear colourless solution at room

TABLE 3.8.1

Behaviour and ^{31}P chemical shifts of phosphorus(V) halides in liquid hydrogen chloride

(^{31}P chemical shifts in p.p.m. relative to 85% H_3PO_4)

Compound	^{31}P chemical shift	Assignment	Remarks
PF_5	+81	PF_5	Very soluble
PCl_5	-80.3	PCl_4^+	Very soluble. Exists as PCl_4^+ and solvated Cl^- ion
PBr_5	-224.7, -222.6, -218.4, +95.3	PBr_2Cl, $PBrCl_2$, PCl_3, PBr_4^+	Slightly soluble with some dissociation $PBr_5 \rightleftharpoons PBr_3 + Br_2$, followed by exchange.

temperature. The ^{31}P n.m.r. spectrum of the solution consisted of a six line multiplet, intensities 1:5:10:10:5:1, having a chemical shift of +80 ± 1 p.p.m. and $^1J_{P-F}$ value of 958 ± 15 Hz. The peak widths in this spectrum were much broader than those in the spectrum of PF_5 in liquid hydrogen chloride, possibly due to fast exchange with fluorine of the solvent, CCl_3F.

<u>The reaction between phosphorus(V) fluoride and boron trichloride</u>

PF_5 (2 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by HCl (25 mmole) and BCl_3 (0.2 ml., 2.3 mmole). The ampoule was sealed and tested in the normal manner. At room temperature the liquid phase consisted of two clear colourless layers. The ^{31}P n.m.r. spectrum contained a single resonance at -85.5 p.p.m., which may be immediately assigned to PCl_4^+. The ^{11}B n.m.r. spectrum consisted of a single resonance at +11.25 p.p.m., which is assignable to BCl_4^-.[147]

<u>The reaction between phosphorus(V) fluoride and boron trifluoride</u>

PF_5 (2 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, followed by HCl (25 mmole) and BF_3 (2 mmole). The ampoule was sealed and tested in the normal manner. The ^{31}P n.m.r. spectrum consisted of a 1:3:3:1 quartet at +37 ± 0.5 p.p.m. with $^1J_{P-F}$ 1080 Hz and a 1:5:10:10:5:1 sextet at +81 ± 1 p.p.m. with $^1J_{P-F}$ of 948 Hz. The latter multiplet may be assigned to PF_5. The multiplicity of the former signal is indicative of PF_3X_2, or PF_3X^+, species and the P-F coupling constant, 1080 Hz, is very close to that of PF_3Cl_2. However, δ ^{31}P for PF_3Cl_2 in liquid hydrogen chloride has been shown in this work to occur in the region +29.5 ± 2 p.p.m., and the appearance of the signal at +37 p.p.m. is difficult to explain. The ^{11}B n.m.r. spectrum consisted of a single resonance at +8.6 p.p.m.

The reaction was repeated in the absence of a solvent.

PF_5 (3.5 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196° followed by BF_3 (3.5 mmole). The ampoule was sealed and tested in the usual way. At room temperature the sum of the partial pressures due to PF_5 and BF_3 was of the order of 60 atm. The ^{31}P n.m.r. spectrum consisted of a 1:5:10:10:5:1 sextet at +79.5 p.p.m. with a P-F coupling constant of 952 Hz, which may be immediately assigned to PF_5. The ^{11}B n.m.r. spectrum contained a signal at +8.6 ± 0.2 p.p.m. which, on examination using scale expansion was seen to be a 1:3:3:1 quartet with a $^{1}J_{B-F}$ value of 13 ± 0.5 Hz. This signal may be assigned to BF_3.[125,128]

The reaction between phosphorus(V) fluoride and antimony(V) fluoride

SbF_5 (0.75 ml., 10.3 mmole) was poured into an 8 mm. o.d. quartz ampoule. PF_5 (4 mmole) was condensed into the ampoule at -196°, which was then sealed and tested in the usual manner. The ampoule contained a white glassy solid, or viscous liquid, under a purple solid at room temperature. No signal was observed when the ^{31}P n.m.r. spectrum of the solid and that of the space above the solid were recorded. The ampoule was inverted and warmed using a hair dryer to effect mixing of the white and purple layers. Again signals were not observed when the ^{31}P n.m.r. spectrum of the solid and that of the space above the solid were recorded.

The behaviour of phosphorus(V) chloride in liquid hydrogen chloride

HCl (25 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196° containing PCl_5 (0.208 g., 1 mmole). The ampoule was sealed and tested in the normal manner. The ^{31}P n.m.r. spectrum of the solution contained a single resonance at -80.3 p.p.m. This signal may be assigned to PCl_4^+.[131,132] No signal was detected in the region around +300 p.p.m.;

indicating that PCl_6^- was absent.[103] Thus, PCl_5 exists totally as PCl_4^+ and solvated Cl^- ions in liquid hydrogen chloride.

The behaviour of phosphorus(V) bromide in liquid hydrogen chloride

HCl (25 mmole) was condensed into an 8 mm. o.d. quartz ampoule at -196°, containing PBr_5 (0.215 g., 0.5 mmole). The ampoule was sealed and tested in the manner previously described. The ampoule contained a pale reddish orange solution over undissolved orange crystalline PBr_5 at room temperature. The ^{31}P n.m.r. spectrum contained signals at -224.7, -222.6, -218.4 and +95.3 p.p.m., which may be assigned to PBr_2Cl, $PBrCl_2$, PCl_3[119,136] and PBr_4^+.[146,169]

The ^{31}P n.m.r. spectrum of solid PBr_5 was then recorded. A strong broad signal at +104 p.p.m. was observed, which is in excellent agreement with the literature value of 104 ± 1 p.p.m.[101] for PBr_4^+, and also a signal at -227.5 p.p.m. which may be assigned to PBr_3.[119] Both signals could be seen on a single scan.

The reaction between phosphorus(V) bromide and boron trichloride

PBr_5 (0.215 g., 0.5 mmole) was loaded into an 8 mm. o.d. quartz ampoule. HCl (25 mmole) was condensed into the ampoule at -196° followed by an excess of BCl_3. The ampoule was sealed and tested in the usual manner. A clear yellow-orange solution over an orange crystalline solid was obtained at room temperature. No signal could be detected in the ^{31}P n.m.r. spectrum of this solution, indicating that all the phosphorus was present in the solid. The ^{11}B n.m.r. spectrum of this solution contained one resonance at -28.75 p.p.m. which may be assigned to BCl_3.[125]

CHAPTER 4

REACTIONS OF PHOSPHORUS COMPLEXES OF LOW VALENT TRANSITION METALS

4.1 Platinum complexes

Results and Discussion

The quantitative reactions of tetrakis(triphenylphosphine) platinum(0) with liquid hydrogen chloride, deuterium chloride and hydrogen bromide, and of tris(triphenylphosphine)platinum(0) with liquid hydrogen chloride were investigated in situ by ^{31}P n.m.r.; the products are cis-dihalobis(triphenylphosphine)platinum(II) complexes, together with triphenylphosphonium salts and hydrogen. Trans-bis(triphenylphosphine) complexes are produced when tetrakis-(triphenylphosphine)platinum(0) is reacted with 100% sulphuric and trifluoroacetic acids. ^{31}P n.m.r. spectra are shown in the text.

The reactions of acids with complexes of transition metals in formally low oxidation states are of interest as various courses are possible. Protonation, either at the metal or at one of the ligands, may occur, without changing the oxidation state of the metal. Or, oxidation of the metal with reduction of the acid may take place. McAvoy et. al.[185] have described the reaction between tetrakis-(triphenylphosphine)platinum(0) and liquid hydrogen fluoride yielding difluorobis(triphenylphosphine)platinum(II). More recently, both this reaction, and that of tris(triphenylphosphine)platinum(0) with liquid hydrogen fluoride, have been reported to produce a compound $PtF_3(Ph_3P)_3H$, tentatively formulated as $[PtF(Ph_3P)_3][HF_2]$.[186] The ^{31}P n.m.r. solution spectrum of tetrakis(triphenylphosphine)platinum(0) in liquid hydrogen chloride is shown in fig. 4.1.1.

Fig.4.1.1

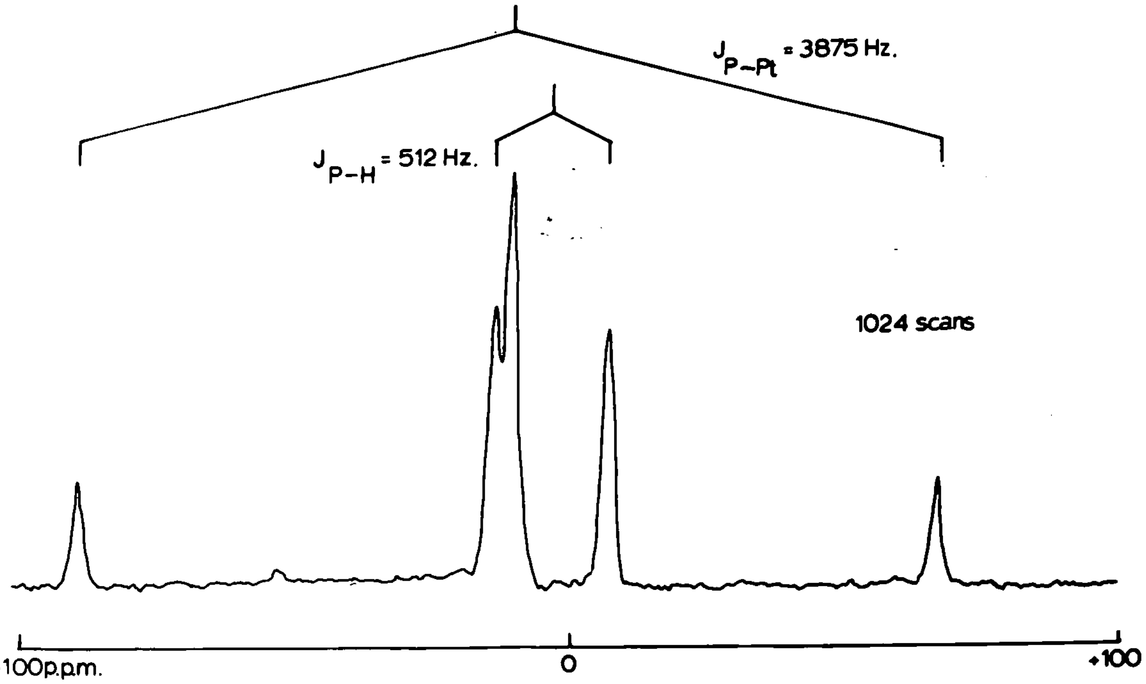
^{31}P n.m.r. solution spectra

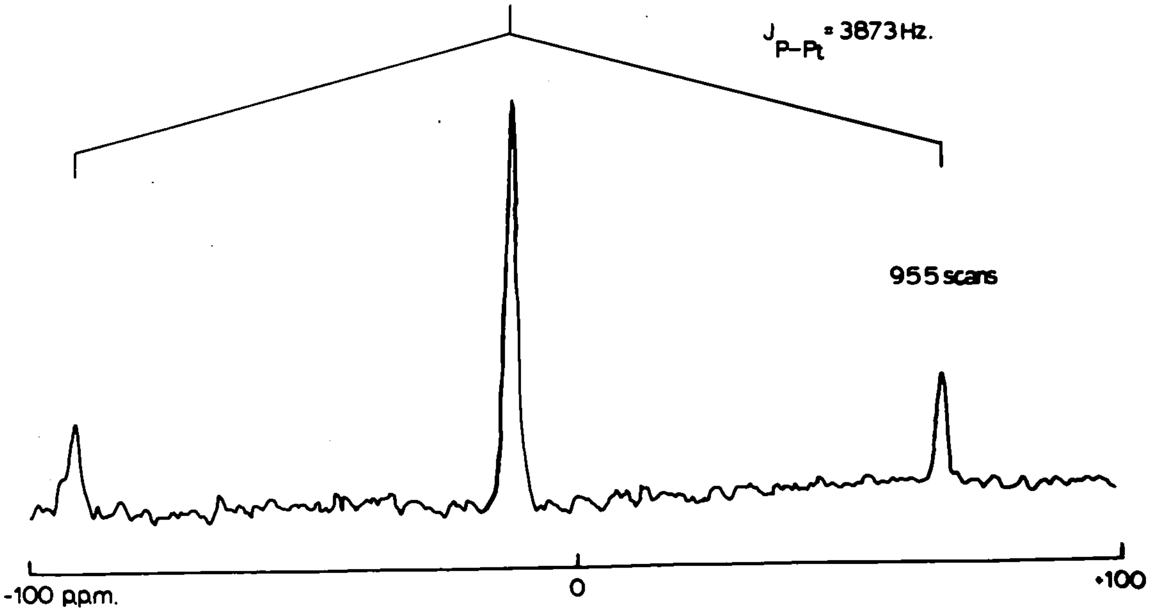
Tetrakis(triphenylphosphine)platinum(0) in liquid hydrogen chloride

Fig.4.1.2

^{31}P n.m.r. solution spectrum

cis-dichlorobis(triphenylphosphine)platinum(II) in liquid hydrogen chloride


J_{P-Pt} = 3875 Hz.
J_{P-H} = 512 Hz.
1024 scans
-100 p.p.m.
0
+100


J_{P-Pt} = 3873 Hz.
955 scans
-100 p.p.m.
0
+100

There are clearly two phosphorus species present. The 1:4:1 triplet at -11.4 p.p.m. is assigned to triphenylphosphine groups bound to platinum, the outer peaks arising from coupling with the ^{195}Pt isotope present in 33.7% abundance.[106] The magnitude of the coupling constant $^{1}J_{^{31}P-^{195}Pt}$ = 3875 ± 10Hz. indicates that the ligands are in a cis configuration.[187,188] The 1:1 doublet at -4.0 p.p.m. with $^{1}J_{^{31}P-^{1}H}$ of 512 ± 5Hz. has been shown earlier in this work to be characteristic of the species Ph_3PH^+. The intensity ratio of the multiplets is 1:1 indicating that two triphenylphosphine ligands are displaced in the reaction.

In an independent experiment it was shown that hydrogen, approximately 0.66 moles per mole of tetrakis(triphenylphosphine)platinum(0), was evolved during the reaction indicating that oxidation of the platinum from the zero to the +2 oxidation state had occurred. The most probable product to accord with the n.m.r. data would be cis-dichlorobis(triphenylphosphine)platinum(II) formed according to the equation;

$$(Ph_3P)_4Pt \ + \ 6HCl \rightarrow cis(Ph_3P)_2PtCl_2 \ + \ 2Ph_3PH^+HCl_2^- \ + \ H_2.$$

Elemental analyses on the white solid residue obtained on removal of hydrogen chloride are compatible with this stoichiometry.

The identity of the platinum-containing product was confirmed by a series of experiments. The ^{31}P n.m.r. spectrum of cis-dichlorobis(triphenylphosphine)platinum(II) in liquid hydrogen chloride, (shown in fig. 4.1.2), was recorded and consisted of a 1:4:1 triplet at -12.1 p.p.m. with $^{1}J_{^{31}P-^{195}Pt}$ of 3873Hz. Signals due to Ph_3PH^+ ions

Fig.4.1.3

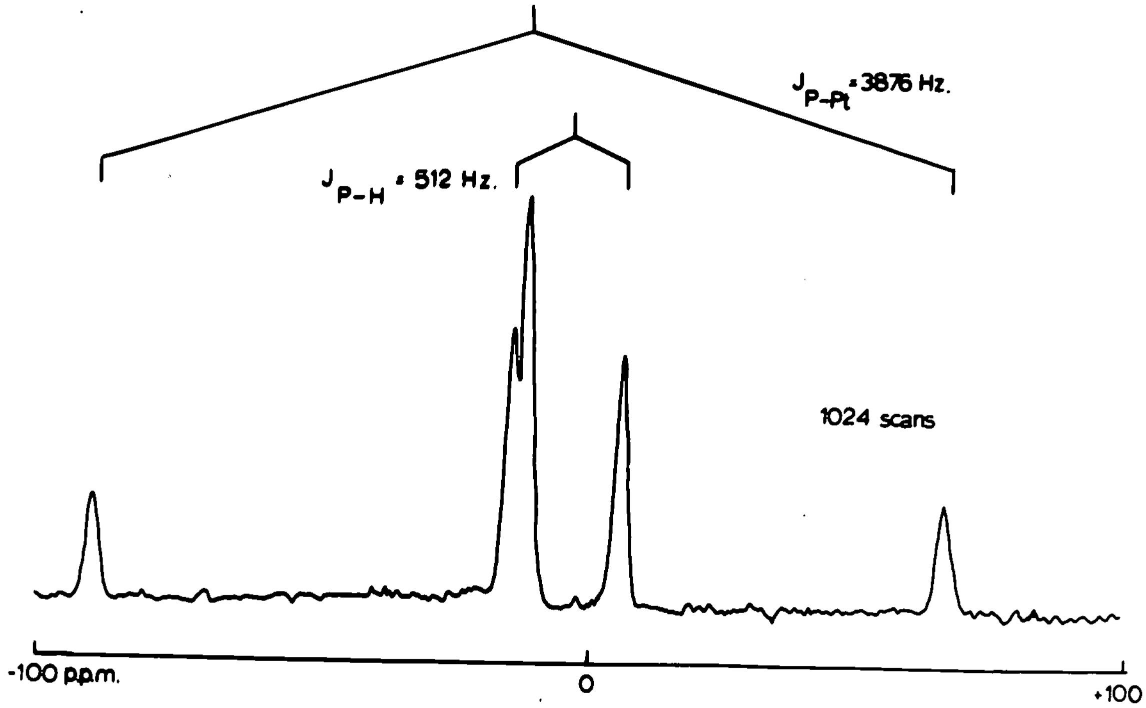
^{31}P n.m.r. solution spectrum

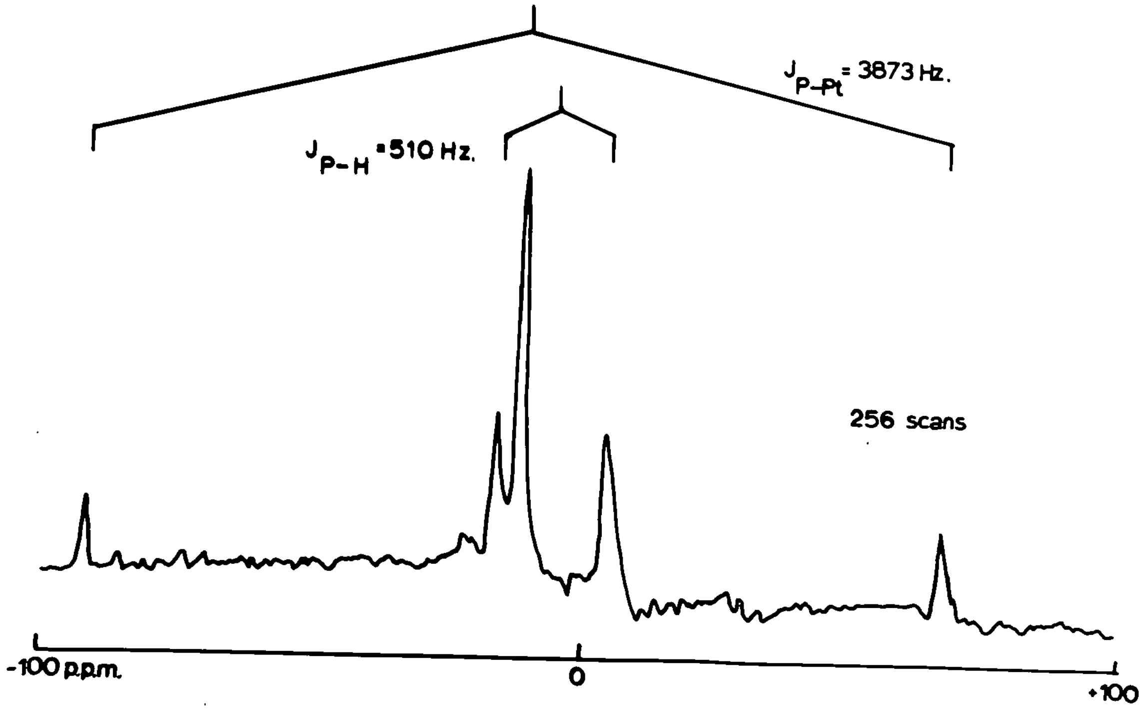
cis-dichloro(triphenylphosphine)platinum(II) and triphenylphosphine in a 1:2 molar ratio in liquid hydrogen chloride

Fig.4.1.4

^{31}P n.m.r. solution spectrum

cis-dichloro(triphenylphosphine)platinum(II) and tetrakis(triphenylphosphine)platinum(0) in a 1:1 molar ratio in liquid hydrogen chloride


J_{P-Pt} = 3876 Hz.
J_{P-H} = 512 Hz.
1024 scans
-100 p.p.m.
0
+100


J_{P-Pt} = 3873 Hz.
J_{P-H} = 510 Hz.
256 scans
-100 p.p.m.
0
+100

were absent indicating that triphenylphosphine ligands do not dissociate from the complex in liquid hydrogen chloride solution. In an independent experiment it was shown that cis-$(Ph_3P)_2PtCl_2$ is recovered unchanged from the solvent. The ^{31}P n.m.r. spectrum of triphenylphosphine and cis-dichlorobis(triphenylphosphine)platinum(II) in 2:1 molar ratio in liquid hydrogen chloride solution consisted of a 1:4:1 triplet at -10 p.p.m. with $^1J_{^{31}P-^{195}Pt}$ 3876Hz and a 1:1 doublet at -4.5 p.p.m. with $^1J_{^{31}P-^1H}$ 512 ± 1Hz. An intensity ratio of 1:1 was observed for the multiplets. (fig. 4.1.3) Finally, the ^{31}P n.m.r. spectrum of a 1:1 molar ratio of tetrakis(triphenylphosphine)-platinum(0) and cis-dichlorobis(triphenylphosphine)platinum(II) in liquid hydrogen chloride was recorded. One 1:4:1 triplet at -12.1 p.p.m., $^1J_{^{31}P-^{195}Pt}$ 3873 Hz., together with a 1:1 doublet at -4.5 p.p.m., $^1J_{^{31}P-^1H}$ 510 Hz. in 2:1 intensity ratio were observed (fig. 4.1.4).

Further evidence in favour of the postulated equation is provided by reaction between tetrakis(triphenylphosphine)platinum(0) and boron trichloride in liquid hydrogen chloride. The infrared spectrum of the white residual solid contained absorptions characteristic of cis-dichlorobis(triphenylphosphine)platinum(II) and of BCl_4^- ion.[20f,163] Elemental analysis are in good agreement with those required for a 2:1 molar mixture of $Ph_3PH^+BCl_4^-$ and cis$(Ph_3P)_2PtCl_2$. Thus, it may be assumed that the reaction proceeds as suggested, in this case the Ph_3PH^+ ions produced being stabilised as the tetrachloroborate salt.

$$(Ph_3P)_4Pt + 4HCl + 2BCl_3 \rightarrow (Ph_3P)_2PtCl_2 + 2Ph_3PH^+BCl_4^- + H_2.$$

In a very recent paper Druce et. al.[189] have reported the reactions between cis-dihalobis(tri-n-butylphosphine)platinum(II) complexes and an excess of boron trihalide to afford halogen-bridged binuclear cationic platinum(II) complexes. Thus, di-μ-chloro-tetrakis(tri-n-butylphosphine)diplatinum(II) was formed from cis-dichlorobis(tri-n-butylphosphine)platinum(II) and boron trichloride. The reaction between tetrakis(triphenylphosphine)platinum(0) and liquid hydrogen chloride has been shown in this work to yield cis-dichlorobis-(triphenylphosphine)platinum(II), triphenylphosphonium hydrogendichloride and hydrogen. Addition of an excess of boron trichloride to this reaction mixture again gave the platinum(II) complex together with triphenylphosphonium tetrachloroborate. No evidence in favour of a binuclear cationic platinum(II) complex was found. Presumably boron trichloride only reacts with cis-dichlorobis(tri-n-butylphosphine)-platinum(II) to give the reported product[189] because it is a good Lewis acid, extracting chloride ions from the platinum complex. Liquid hydrogen chloride is also a good chloride ion acceptor, yet cis-dichlorobis(triphenylphosphine)platinum(II) may be recovered unchanged from the solvent.

The reaction between tetrakis(triphenylphosphine)platinum(0) and liquid deuterium chloride is essentially similar to that between the complex and hydrogen chloride. The ^{31}P n.m.r. spectrum, shown in figure 4.1.5, contains a 1:4:1 triplet at -13.5 p.p.m. with $^{1}J_{^{31}P-^{195}Pt}$ 3873 ± 10Hz. which again may be assigned to cis$(Ph_3P)_2PtCl_2$. The 1:1 doublet has been replaced by a 1:1:1 triplet at -5.7 p.p.m.,

Fig. 4.1.5

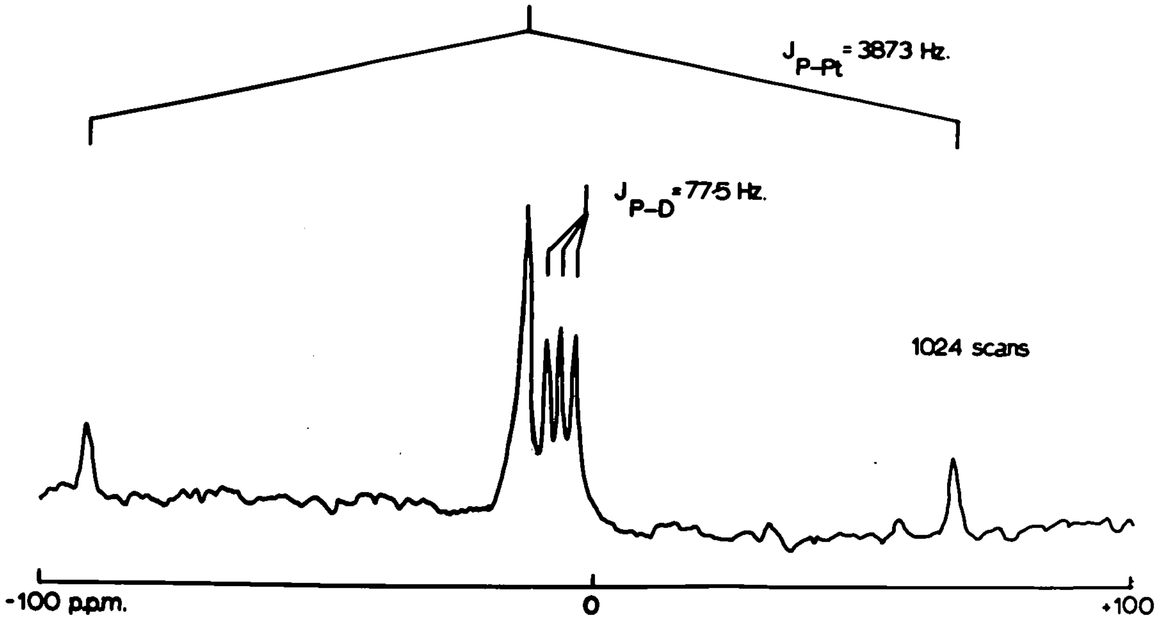
^{31}P n.m.r. solution spectrum

Tetrakis(triphenylphosphine)platinum(0) in liquid deuterium chloride

Fig.4.1.6

^{31}P n.m.r. solution spectrum

Tetrakis(triphenylphosphine)platinum(0) in liquid hydrogen bromide


J_{P-Pt} = 3873 Hz.
J_{P-D} = 77.5 Hz.
1024 scans
-100 p.p.m.
0
+100

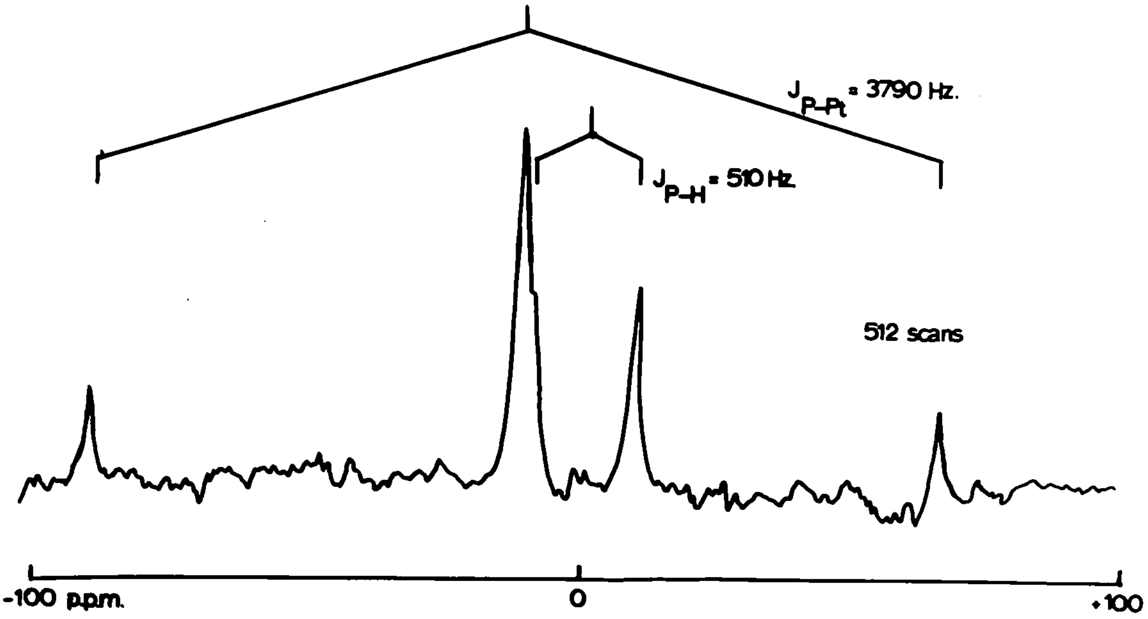

J_{P-Pt} = 3790 Hz.
J_{P-H} = 510 Hz.
512 scans
-100 p.p.m.
0
+100

Fig.4.1.7

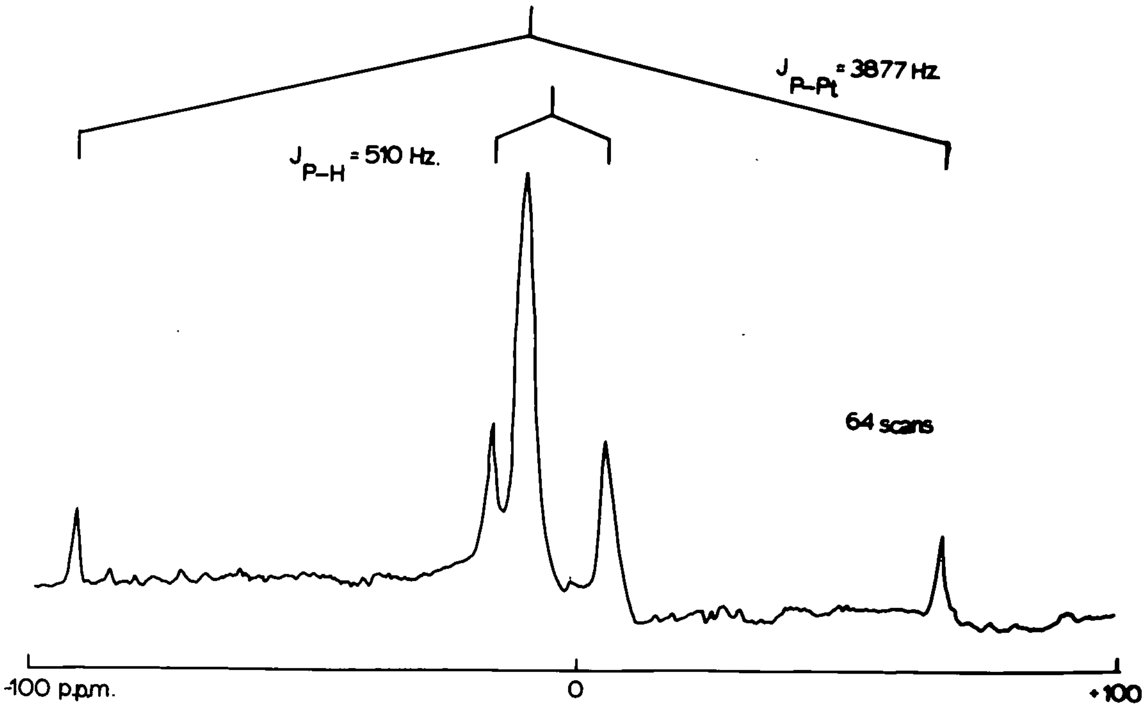
^{31}P n.m.r. solution spectrum

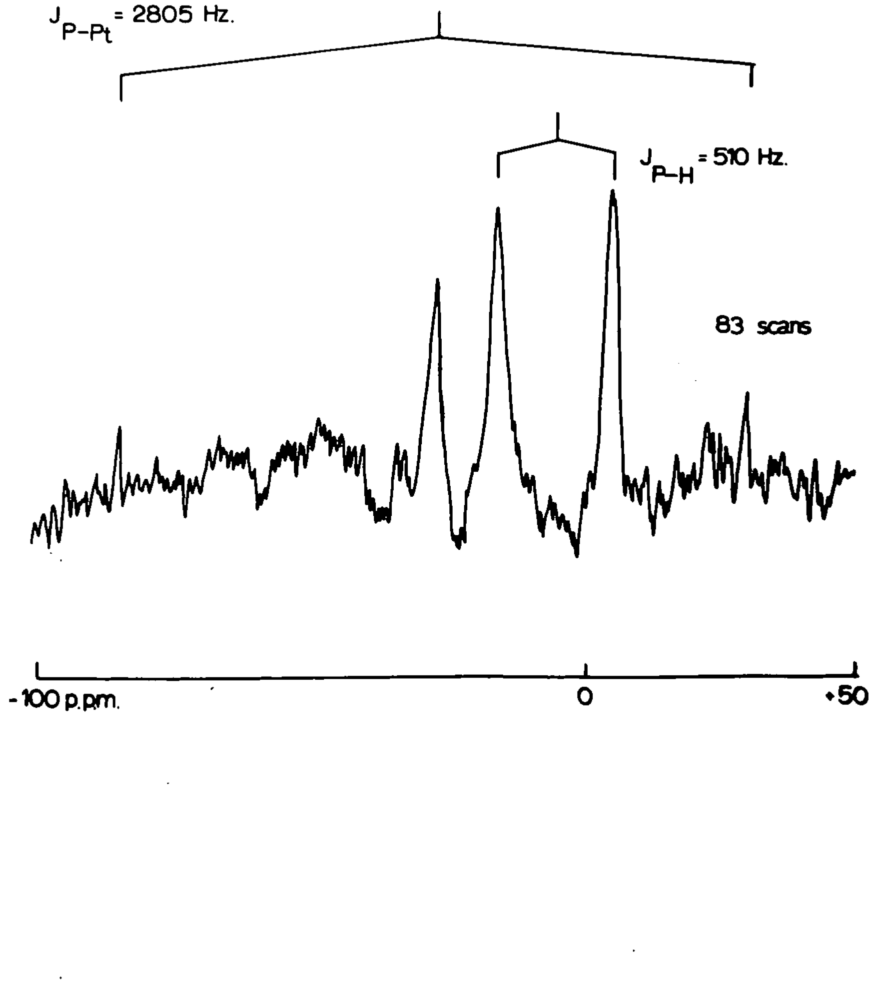
Tris(triphenylphosphine)platinum(0) in liquid hydrogen chloride

Fig.4.1.8

^{31}P n.m.r. solution spectrum

Tetrakis(triphenylphosphine)platinum(0) in 100% sulphuric acid


J_{P-Pt} = 3877 Hz
J_{P-H} = 510 Hz.
64 scans
-100 p.p.m.
0
+100


J_{P-Pt} = 2805 Hz.
J_{P-H} = 510 Hz.
83 scans
-100 p.p.m.
0
+50

$^1J_{^{31}P-^2D}$ 77.5 Hz., which has been shown earlier in this work to be characteristic of the species Ph_3PD^+. The intensity ratio of the triplets is 1:1 confirming that two triphenylphosphine ligands have been displaced during the reaction.

The ^{31}P n.m.r. spectrum of tetrakis(triphenylphosphine)platinum(0) in liquid hydrogen bromide is shown in fig. 4.1.6. There is a triplet for triphenylphosphine ligands bound to platinum at -11.5 p.p.m., $^1J_{^{31}P-^{195}Pt}$ 3790Hz., and a triphenylphosphonium doublet, one peak of which partially overlaps the central peak of the triplet, at -1.9 p.p.m. with $^1J_{^{31}P-^1H}$ 510Hz. in an overall intensity ratio of 1:1. The triplet is assigned to cis-dibromobis(triphenylphosphine)platinum(II), and the rather high chemical shift value for the Ph_3PH^+ ion may be explained in terms of changes in both diamagnetic susceptibility and counterion. An equation for the reaction may reasonably be written

$$(Ph_3P)_4Pt + xHBr \rightarrow cis(Ph_3P)_2PtBr_2 + 2Ph_3PH^+ + 2Br^-_{solv.} + H_2$$

Tris(triphenylphosphine)platinum(0) reacts with liquid hydrogen chloride in an analogous manner to the tetrakis compound. The ^{31}P n.m.r. spectrum of the tris complex in the solvent is shown in fig. 4.1.7 and is virtually identical to that of the tetrakis compound, fig. 4.1.1, save that the ratio Ph_3PH^+: $(Ph_3P)_2PtCl_2$ is now 1:2 indicating that only one triphenylphosphine ligand has been displaced during the reaction.

Cariati et. al. have reported the reactions between both tris- and tetrakis(triphenylphosphine)platinum(0) and gaseous hydrogen chloride in benzene and alcoholic solutions.[193] The nature of the product was found to depend upon the solvent; the covalent hydride $(Ph_3P)_2PtHCl$ being isolated from benzene solution, and the ionic compound $[(Ph_3P)_3PtH^+]Cl^-$ from ethanol. The same products were obtained from both the tris- and tetrakis- complexes. In this work the author was unable to repeat the reported preparation of $[(Ph_3P)_3PtH^+]Cl^-$. Elemental analyses carried out on the yellow solid product indicated that the material was not composed of a single stoichiometric compound.

The behaviour of tetrakis(triphenylphosphine)platinum(0) in benzene and its reaction with gaseous hydrogen chloride in the solvent was studied by ^{31}P n.m.r. Several authors have postulated the dissociation of triphenylphosphine ligands from tetrakis(triphenylphosphine)platinum(0) in benzene solution.[193,194,195] The ^{31}P n.m.r. spectrum of a saturated solution of the complex in benzene consisted of a singlet at -22 p.p.m. This may be interpreted as an exchange-averaged signal derived from rapidly exchanging platinum-bound and free triphenylphosphines. The absence of phosphorus-platinum satellites in the spectrum is additional evidence in favour of an exchanging system. Tris(triphenylphosphine)platinum(0) in benzene gave a singlet at -51 p.p.m. which may be interpreted in a similar manner.

A yellow solution of tetrakis(triphenylphosphine)platinum(0) in benzene did not go colourless on passage of hydrogen chloride gas as described by Cariati et. al. A yellow solid precipitated and the solution remained pale yellow in colour. A ^{31}P n.m.r. spectrum of this saturated solution was obtained only with difficulty owing to the low solubility of the material. Two equally intense signals were observed at -33 and +8 p.p.m. The upfield resonance may be assigned to triphenylphosphine and that at -33 p.p.m. to a platinum-bound triphenylphosphine ligand. The ^{31}P chemical shift of cis-dichlorobis-(triphenylphosphine)platinum(II) in liquid hydrogen chloride was recorded in this work as -12.1 p.p.m. thus the resonance at -33 p.p.m. cannot be assigned to this species and may be due to the covalent hydride $(Ph_3P)_2PtHCl$ reported by Cariati et.al.

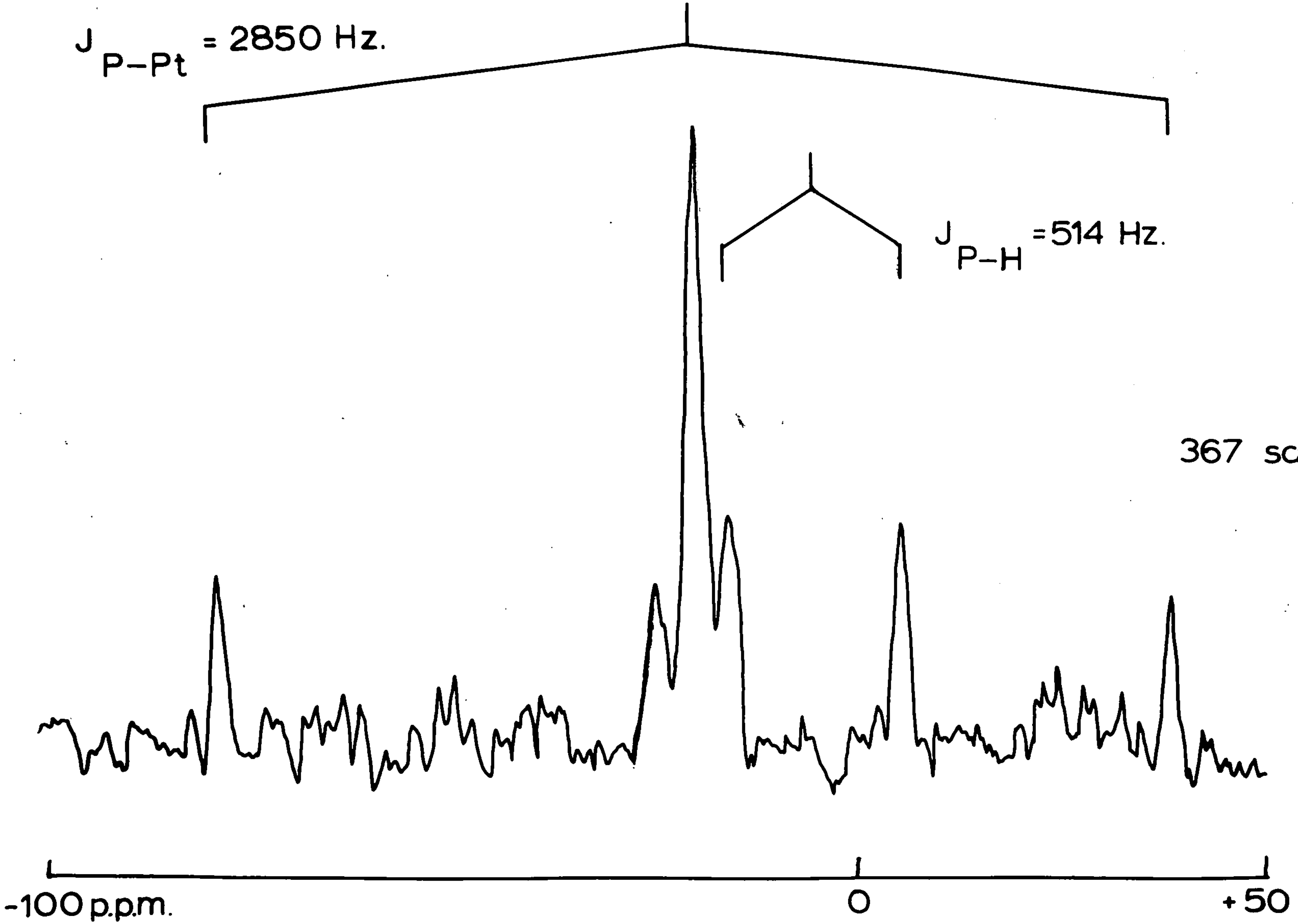
The reactions between tetrakis(triphenylphosphine)platinum(0) and the acidic room temperature solvents trifluoroacetic and 100% sulphuric acids are less easily understood than those described earlier. Figure 4.1.8 shows the ^{31}P n.m.r. solution spectrum of the complex in 100% sulphuric acid. There is a 1:4:1 triplet at -27 ± 0.5 p.p.m. which is assigned to triphenylphosphine groups bound to platinum, and a 1:1 doublet at -5.5 ± 0.5 p.p.m. with $^1J_{^{31}P-^1H}$ 510 ± 5Hz. characteristic of Ph_3PH^+. The magnitude of the coupling constant $^1J_{^{31}P-^{195}Pt}$ 2805 ± 10Hz. indicates that the phosphine ligands are in a trans-configuration.[187,188] An overall intensity ratio of 2:1, in favour of Ph_3PH^+ cations was observed. This intensity ratio probably indicates that two triphenylphosphine ligands were displaced from the tetrakis compound forming a trans-bis(triphenylphosphine)platinum(II) species which itself slowly reacts with the solvent. Dissociation of triphenylphosphine groups and subsequent protonation by the sulphuric acid would account for the high concentration of Ph_3PH^+ ion.

The ^{31}P n.m.r. spectrum of tetrakis(triphenylphosphine)platinum(0) in trifluoroacetic acid is shown in fig. 4.1.9. Three signals are present; a 1:4:1 triplet at -20 ± 0.5 p.p.m. with $^1J_{^{31}P-^{195}Pt}$ 2850 ± 3Hz., a 1:1 doublet at -5.0 ± 0.5 p.p.m. with $^1J_{^{31}P-^1H}$ 514Hz.,

Fig.4.1.9

^{31}P n.m.r. solution spectrum

Tetrakis(triphenylphosphine)platinum(0) in trifluoroacetic acid


J_{P-Pt} = 2850 Hz.
J_{P-H} =514 Hz.
367 scans
-100 p.p.m.
0
+50

and a weak singlet at -23.6 p.p.m. These signals may be assigned to a trans-bis(triphenylphosphine)platinum(II) species, triphenylphosphonium ion and possibly a second phosphorus-platinum species respectively. The intensity of the doublet increased over a period of 8 months until the intensity ratio of triplet:doublet, initially 3:1 was approximately 2:1 indicating that reaction was still proceeding.

Owing to the unpleasant nature of the solvents no attempt was made to isolate solid products from these reactions which were not studied further. In a recent publication, Thomas et.al.[190] have reported the preparation of the ionic hydride $[(Ph_3P)_3PH]^+H(CF_3COO)_2^-$ from $(Ph_3P)_4Pt$ and CF_3COOH in benzene. ^1H and ^{31}P n.m.r., infrared and analytical data are quoted and interpreted as evidence for the above formulation. A value of 160Hz. for the coupling constant arising from hydrogen-trans-phosphorus coupling was obtained from the ^1H n.m.r. spectrum of the complex in dichloromethane solution. The ^{31}P n.m.r. solution spectrum, however, consisted of a singlet at +26.6 p.p.m.

In this work no signals were observed in the region of +26.6 p.p.m. when the ^{31}P n.m.r. spectrum of $(Ph_3P)_4Pt$ in CF_3COOH was recorded. Also, the 1:4:1 triplet assigned to a trans-bis(triphenylphosphine)-platinum(II) species showed no signs of splitting. Consequently there is no evidence in this instance for the formation of a protonated platinum species.

Tetrakis(triphenylphosphine)platinum(0) reacted with liquid sulphur dioxide giving a yellow solution over a dark solid. Only signals assignable to Ph_3PS and Ph_3PO[191] were observed when the ^{31}P n.m.r. spectrum of the solution was recorded. Presumably the platinum was contained in the solid. This reaction was not studied further.

Experimental

The reaction between tetrakis(triphenylphosphine)platinum(0) and liquid hydrogen chloride

HCl (25 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing $(Ph_3P)_4Pt$ (0.110g., 0.089 mmole). The ampoule was sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the clear pale yellow solution consisted of two multiplets; a 1:4:1 triplet at -11.4 p.p.m. with $^1J_{^{31}P-^{195}Pt}$ of 3870Hz., and a 1:1 doublet at -4 p.p.m. with $^1J_{P-H}$ of 510Hz. The triplet is assigned to a bis(triphenylphosphine)platinum species,[187,188] and the doublet to the Ph_3PH^+ ion. The ratio of the intensities of the two multiplets was 1:1.

$$(Ph_3P)_4Pt + 4HCl \rightarrow 2Ph_3PH^+ + 2Cl^-(solv.) + cis\text{-}(Ph_3P)_2PtCl_2 + H_2$$

The reaction was repeated on a larger scale in order to investigate the material obtained on removal of the solvent.

HCl (200 mmole) was condensed at -196° into a 13 mm. o.d. quartz ampoule containing $(Ph_3P)_4Pt$ (0.890g., 0.716 mmole). The ampoule was sealed and brought up to room temperature in the manner previously described. The yellow solid dissolved to give a clear pale yellow solution. After 12 hours at 20° the ampoule was cooled to -196° and opened via the vacuum line to the spiral gauge. A gas (0.468 mmole) was detected having molecular weight 1 ± 1, presumably hydrogen. The ampoule was warmed to -95°, at which temperature the solvent was removed by pumping leaving a white solid. Pumping was maintained for 2 hours at room temperature to remove the last traces of HCl.

The infrared spectrum of the white solid was identical to that of an authentic sample of cis-$(Ph_3P)_2PtCl_2$ ie. absorptions due to Ph_3P ligands and two Pt-Cl stretching modes at 330 and 305cm^{-1}.[196]

Found; C, 60.1; H, 5.01; P, 8.94; Cl, 11.58;
Calculated for a mixture of $Ph_3PH^+HCl^-{}_2$: $(Ph_3P)_2PtCl_2$ in 2:1 molar ratio; C, 59.2; H, 4.35; P, 8.49; Cl, 14.6.

The low value for chlorine could be due to loss of HCl from the $Ph_3PH^+HCl_2^-$. Such a mixture would require the presence of a weak sharp absorption at about 2400cm^{-1} and a broad underlying absorption at 750cm^{-1} due to Ph_3PH^+ and HCl_2^- respectively. The infrared spectrum of a 2:1 molar ratio of authentic samples of $Ph_3PH^+HCl_2^-$ and cis-$(Ph_3P)_2PtCl_2$ was recorded. The broad absorption due to HCl_2^- was absent, and the intensity of the weak absorption at 2408cm^{-1} was of the same order as machine noise.

The reaction between tetrakis(triphenylphosphine)platinum(0) and liquid deuterium chloride.

DCl (25 mmole) was condensed at -196° into an 8mm. o.d. quartz ampoule containing $(Ph_3P)_4Pt$ (0.150g., 0.12 mmole). The ampoule was sealed and tested in the normal manner. The ^{31}P n.m.r. solution spectrum contained a 1:4:1 triplet at -14.6 p.p.m. with $^1J_{^{31}P-^{195}Pt}$ 3873Hz., and a 1:1:1 triplet at -5.7 p.p.m. with $^1J_{P-D}$ 77.5Hz which may be immediately assigned to a cis-bis(triphenylphosphine)platinum species and to the Ph_3PD^+ ion respectively. The intensities of the triplets were in the ratio 1:1.

The reaction was repeated on a larger scale.

DCl (200 mmole) was condensed at -196° into a 24mm. o.d. pyrex reaction tube containing $(Ph_3P)_4Pt$ (0.125g. 0.100 mmole). A clear yellow solution was obtained on warming to -95°. 30 minutes were allowed for equilibration and the DCl was then removed by pumping at this temperature until no liquid remained followed by 2 hours at 20°. The infrared spectrum of the white solid product was identical to that of cis$(Ph_3P)_2PtCl_2$. No absorptions due to DCl_2^- ion, or to a P-D stretching mode in the 1700cm^{-1} region, could be detected.

Found; C, 56.4; H, 4.05; P, 8.04, 9.77; Cl, 17.2;

Calculated for a 2:1 molar mixture of $Ph_3PD^+DCl_2^-$: $(Ph_3P)_2PtCl_2$;

C 59.1; H, 4.44; P, 8.47; Cl, 14.6.

The reaction between tetrakis(triphenylphosphine)platinum(0) and boron trichloride in liquid hydrogen chloride

$(Ph_3P)_4Pt$ (1.00g., 0.807 mmole) was placed inside a 13mm. o.d. quartz ampoule of type A. HCl (200 mmole) was condensed into the ampoule at -196°, followed by BCl_3 (1ml., 11.4 mmole). The ampoule was sealed and allowed to reach room temperature in the manner previously described. A clear, very pale yellow, solution was obtained. After 24 hours at 20° the ampoule was cooled to -95° and opened to the vacuum line. HCl was removed at this temperature and excess BCl_3 at room temperature by pumping for 12 hours. The infrared spectrum of the white solid product included absorptions characteristic of cis-$(Ph_3P)_2PtCl_2$ together with a broad absorption with maxima at 690 and 664cm^{-1} which may be assigned to the BCl_4^- ion.[20f,163.]

Found; C, 51.6; H, 3.91; P, 8.22; Cl, 23.2;

Calculated for a 2:1 molar mixture of $Ph_3PH^+BCl_4^-$ and $(Ph_3P)_2PtCl_2$:

C, 53.3; H, 3.95; P, 7.65; Cl, 21.9.

The ^{31}P n.m.r. spectrum of a 1:1 molar mixture of tetrakis (triphenylphosphine)platinum(0) and cis-dichlorobis(triphenylphosphine) platinum(II) in liquid hydrogen chloride.

HCl (30 mmole) was condensed at -196° into an 8mm. o.d. quartz ampoule containing $(Ph_3P)_4Pt$ (0.058g., 0.0466 mmole) and cis-$(Ph_3P)_2PtCl_2$ (0.036g., 0.0456 mmole). The ampoule was sealed and tested in the normal manner. A 1:4:1 triplet and a 1:1 doublet in a 3:1 intensity ratio were observed in the ^{31}P n.m.r. solution spectrum. The triplet at -11.5 ± 0.5 p.p.m. with $^1J_{P-Pt}$ 3873Hz., and the doublet at -6.0 ± 0.1 p.p.m. with $^1J_{P-H}$ 512 ±2Hz. may be assigned to a cis-bis-(triphenylphosphine)platinum(II) species and to the Ph_3PH^+ ion respectively.

The behaviour of cis-dichlorobis(triphenylphosphine)platinum(II) in liquid hydrogen chloride.

HCl (25 mmole) was condensed at -196° into an 8mm. o.d. quartz ampoule containing $(Ph_3P)_2PtCl_2$ (0.072g., 0.0912 mmole). The ampoule was sealed and tested in the usual manner. At room temperature there were two liquid layers in the ampoule; the upper colourless and the lower pale yellow. The ^{31}P n.m.r. spectrum consisted of a 1:4:1

triplet at -10.0 ± 1 p.p.m. with $^1J_{P-Pt}$ 3873Hz which may be immediately assigned to cis-dichlorobis(triphenylphosphine)platinum(II).[187,188]

The reaction was repeated on a larger scale:

HCl (150 mmole) was condensed at -196° into a 13mm. o.d. quartz ampoule containing cis$(Ph_3P)_2PtCl_2$ (0.240g., 0.304 mmole). The ampoule was sealed and warmed to room temperature in the normal manner; the white solid dissolving to give a clear colourless solution. After 24 hours at room temperature the ampoule was cooled to -111°, CS_2 slush bath, and opened to the vacuum line. The HCl was removed by pumping, initially at -95° and finally for 3½ hours at room temperature. The infrared spectrum of the white solid product was identical to that of the starting material.

Found; C, 52.9; H, 3.65; P, 7.98;

Required for $(Ph_3P)_2PtCl_2$; C, 54.7; H, 3.80; P, 7.85.

Thus, cis$(Ph_3P)_2PtCl_2$ is soluble in liquid hydrogen chloride without reaction and can be recovered unchanged.

The ^{31}P n.m.r. spectrum of a 2:1 molar mixture of triphenylphosphine and cis-dichlorobis(triphenylphosphine)platinum(II) in liquid hydrogen chloride.

HCl (30 mmole) was condensed at -196° into an 8mm. o.d. quartz ampoule containing Ph_3P (0.0195g., 0.0744 mmole) and cis$(Ph_3P)_2PtCl_2$ (0.0293g., 0.0371 mmole). The ampoule was sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the clear pale yellow solution was almost identical to that of $(Ph_3P)_4Pt$ in the solvent. The observed signals were: a 1:4:1 triplet at -10 p.p.m. with $^1J_{P-Pt}$ 3876Hz and a 1:1 doublet at -4.5 p.p.m. with $^1J_{P-H}$ 512 ± 1Hz., which may be immediately assigned to cis$(Ph_3P)_2PtCl_2$ and to Ph_3PH^+ respectively. The intensities of the multiplets were in a ratio of 1:1.

The behaviour of tetrakis(triphenylphosphine)platinum(0) in a range of non-aqueous solvents.

Liquid Hydrogen Bromide

HBr (25 mmole) was condensed at -196° into an 8mm. o.d. quartz ampoule containing $(Ph_3P)_4Pt$ (0.120g., 0.097 mmole). The ampoule was sealed and tested in the usual manner. All the solid dissolved at -78° giving a clear yellow solution which did not change in appearance at room temperature. $(Ph_3P)_4Pt$ is much more soluble in liquid HBr than in liquid HCl. The ^{31}P n.m.r. solution spectrum contained an obvious triplet, whose components were in the ratio approximately 1:7:1, and a singlet. The spectrum may be interpreted as a 1:4:1 triplet with the central peak superimposed on the downfield peak of a 1:1 doublet. The ^{31}P chemical shift of the triplet was -12.5 ± 1 p.p.m. with a $^1J_{P-Pt}$ value of 3790Hz., and that of the doublet was -2.5 ± 1 p.p.m. with $^1J_{P-H}$ of 510 Hz. These multiplets are assigned to cis-$(Ph_3P)_2PtBr_2$ and Ph_3PH^+ respectively.

Trifluoroacetic acid

CF_3COOH (2ml.) was added by syringe to $(Ph_3P)_4Pt$ (0.250g., 0.201 mmole) contained in an 8mm. o.d. pyrex ampoule. The ampoule was cooled to -196° evacuated to remove any non-condensible gas and sealed. The ampoule was placed inside a fume cupboard and was allowed to warm to room temperature. The ^{31}P n.m.r. spectrum of the clear colourless solution contained a 1:4:1 triplet at -20.0 ± 0.5 p.p.m. with $^1J_{P-Pt}$ 2850 ± 3Hz., a 1:1 doublet at -5.0 ± 0.5 p.p.m. with $^1J_{P-H}$ 514Hz. and a weak singlet at -23.6 p.p.m. The triplet may be assigned to a trans-bis(triphenylphosphine)platinum(II) species[187,188] and the doublet to Ph_3PH^+. An intensity ratio of approximately 3:1 was observed for the multiplets, in favour of the triplet. After 8 months the ^{31}P spectrum was again recorded, the same features being observed. The weak signal at -23.6 p.p.m. was still present and the intensity ratio triplet:doublet was now approximately 2:1

100% Sulphuric Acid

100% H_2SO_4 (2ml.) was syringed into an 8mm. o.d. pyrex ampoule containing $(Ph_3P)_4Pt$ (0.210g., 0.169 mmole). The ampoule was cooled to -196°, evacuated and sealed on the vacuum line, then allowed to reach room temperature in the atmosphere. The ^{31}P n.m.r. spectrum of the yellow viscous solution consisted of a 1:4:1 triplet at -27 ± 0.5p.p.m. with $^1J_{P-Pt}$ 2805 ± 10Hz. and a 1:1 doublet at -5.5 ± 0.5 p.p.m. with $^1J_{P-H}$ 510 ± 5Hz., which may be assigned to a trans-bis(triphenylphosphine)platinum(II) species and to Ph_3PH^+ respectively. The intensities of the multiplets were in the ratio 2:1 in favour of the Ph_3PH^+ species.

Liquid Sulphur Dioxide

SO_2 (30 mmole) was condensed at -196° into an 8mm. o.d. silica ampoule containing $(Ph_3P)_4Pt$ (0.250g., 0.201 mmole). The ampoule was sealed and tested in the normal manner, even though the saturated vapour pressure of SO_2 is much less than that of HCl at 34.2°. At room temperature the ampoule contained an intensely yellow coloured solution over a dark solid. It was impossible to obtain a ^{31}P n.m.r. spectrum initially as the R10 bridge would not remain balanced, presumably because reaction was still taking place inside the ampoule. After four days a spectrum was recorded. Two singlets were observed at -40.5 and -28.5 p.p.m. which may be assigned to Ph_3PS and Ph_3PO respectively.[191] No P-Pt peaks were observed.

Benzene

The ^{31}P n.m.r. spectrum of a saturated solution of $(Ph_3P)_4Pt$ in benzene consisted of a singlet at -22.3 p.p.m.

The reaction between tris(triphenylphosphine)platinum(0) and liquid hydrogen chloride.

HCl (30 mmole) was condensed at -196° into an 8mm. o.d. quartz tube containing $(Ph_3P)_3Pt$ (0.220g., 0.224 mmole). The ampoule was sealed and tested in the normal manner. The ^{31}P n.m.r. spectrum of the clear colourless solution consisted of a 1:4:1 triplet at -12.0 ± 0.5 p.p.m. with $^1J_{P-Pt}$ 3877 ± 2Hz. and a 1:1 doublet at -4.0 ± 0.5 p.p.m. with $^1J_{P-H}$ 510Hz., which may be assigned to cis-$(Ph_3P)_2$-$PtCl_2$ and Ph_3PH^+ respectively. The ratio of intensities of the multiplets was 2:1 in favour of the cis$(Ph_3P)_2PtCl_2$.

The behaviour of tris(triphenylphosphine)platinum(0) in benzene.

The ^{31}P n.m.r. spectrum of a saturated solution of $(Ph_3P)_3Pt$ in benzene consisted of a broad singlet at -50 ± 1 p.p.m.

4.2 Palladium

Results and Discussion

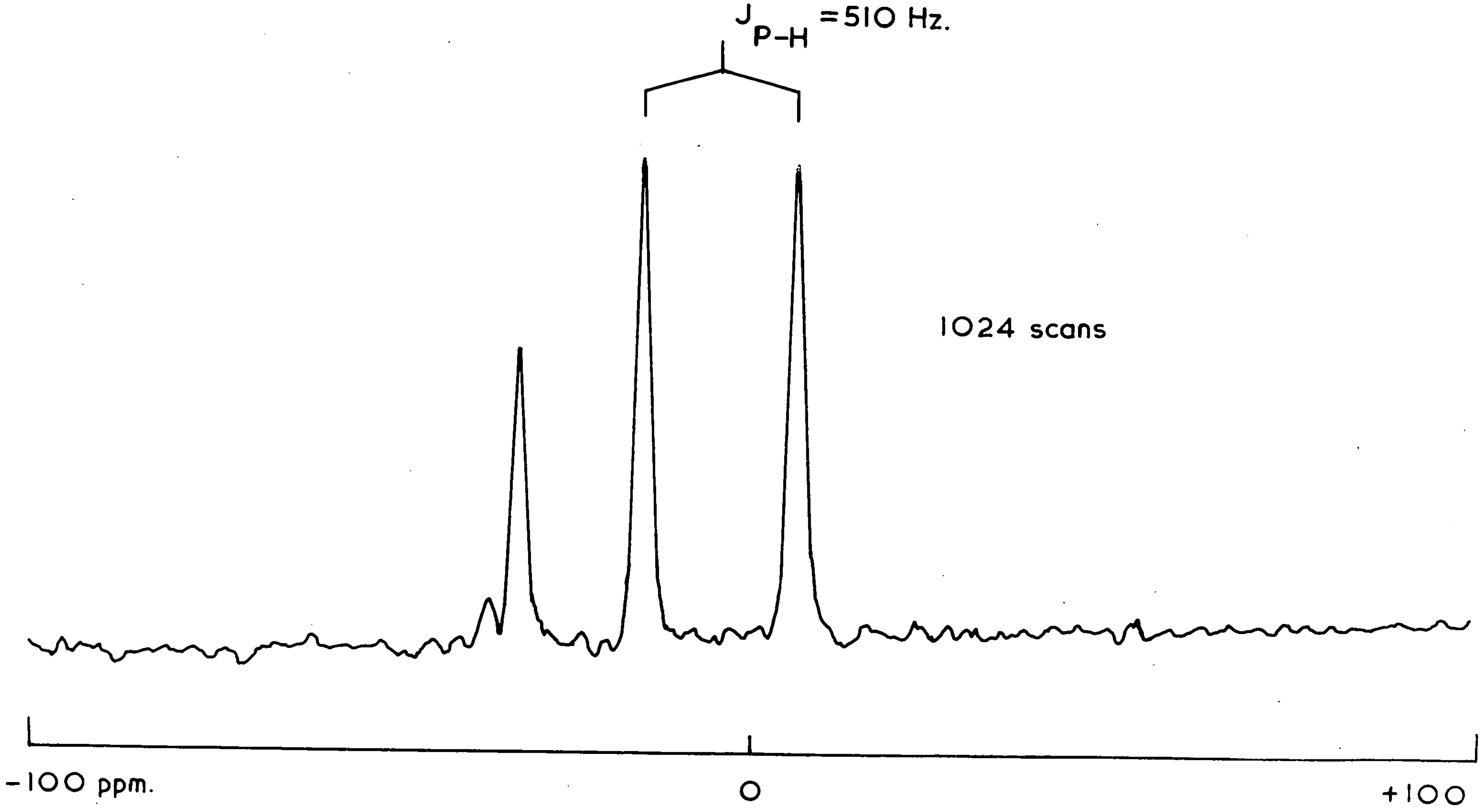
The application of ^{31}P n.m.r. to the study of phosphine complexes of palladium is seriously limited by the nuclear properties of the metal itself. ^{105}Pd present in 22.3% abundance has a spin number of $^{5}/2$ and consequently ^{31}P-^{105}Pd coupling will be difficult, if not impossible to observe owing to the low intensity of the six equal peaks in the split signal.

The ^{31}P n.m.r. spectrum of tetrakis(triphenylphosphine)palladium(0) in liquid hydrogen chloride is shown in Fig.4.2.1. Three signals are present, singlets at -35.0 and -31.0 p.p.m. and a 1:1 doublet at -3.6 p.p.m. with $^{1}J_{^{31}P-^{1}H}$ 510 Hz. The singlets are possibly due to triphenylphosphine-palladium species and the doublet is characteristic of triphenylphosphonium ion. An overall intensity ratio of 1:10:60, from low to high field, indicates that extensive dissociation of triphenylphosphine ligands has occurred. A dull yellow solid was obtained on removal of the solvent. The infrared spectrum of this material contained all the absorptions found in that of trans$(Ph_3P)_2PdCl_2$ together with a very weak band at 2400 cm^{-1} assignable to Ph_3PH^+,[175,176] and elemental analyses were very roughly compatible with a mixture of trans$(Ph_3P)_2PdCl_2$ and $Ph_3PH^+HCl_2^-$ in 1:2 molar ratio. However, such a simple formulation is difficult to correlate with the observed ^{31}P n.m.r. data and with the behaviour of trans$(Ph_3P)_2PdCl_2$ itself in liquid hydrogen chloride. This system is by no means fully understood.

Fig.4.2.1

^{31}P n.m.r. solution spectrum

Tetrakis(triphenylphosphine)palladium(0) in liquid hydrogen chloride


J_{P-H} = 510 Hz.
1024 scans
-100 ppm.
0
+100

Trans-dichlorobis(triphenylphosphine)palladium(II) slowly dissolves in liquid hydrogen chloride followed by crystallisation of a red solid, shown in plate 4.2.1. The ^{31}P n.m.r. spectrum of the yellow solution above the crystals showed a 1:1 doublet at -2.7 p.p.m. with $^{1}J_{^{31}P-^{1}H}$ 504Hz. which is characteristic of Ph_3PH^+ ions. The ^{31}P chemical shift of the complex in chloroform solution was recorded as -22.2 ± 0.5 p.p.m. which is in good agreement with shifts for other tertiary phosphines of type trans L_2PdCl_2.[192] The absence of signals in this region from the liquid hydrogen chloride solution together with the observation of a Ph_3PH^+ doublet indicates that reaction has occurred producing a triphenylphosphonium salt. Attempts to characterise the red crystalline solid product yielded somewhat confusing data. Elemental analysis clearly indicated that the compound was $(Ph_3PH^+)_2\ Pd_2Cl_6^{2-}$. Absorptions due to triphenylphosphine groups are present in the infrared spectrum of the material, but the weak band in the $2400cm^{-1}$ region, characteristic of P-H in Ph_3PH^+, was not observed. Failure to observe this absorption in the infrared spectra of authentic triphenylphosphonium compounds has already been discussed in this work. The ion $Pd_2Cl_6^{2-}$ is a known species[197,198] and Morelli et.al. have reported the infrared spectrum of the anion.[199] They ascribe absorptions at 400 and $315cm^{-1}$ to terminal and bridging Pd-Cl stretching frequencies respectively. These absorptions are not observed in the infrared spectrum of the material prepared in this work, peaks at 357, 305, 267 and 260 sh.cm^{-1} occuring in the region $400-250cm^{-1}$.

Plate 4.2.1

Crystals of $(Ph_3PH^+)_2Pd_2Cl_6^{2-}$ from a solution of trans-dichlorobis(triphenylphosphine)palladium(II) in liquid hydrogen chloride

Experimental

The reaction between tetrakis(triphenylphosphine)palladium(0) and liquid hydrogen chloride

HCl (30 mmole) was condensed at -196^o into an 8mm. o.d. quartz ampoule containing $(Ph_3P)_4Pd$ (0.102g., 0.088 mmole). The ampoule was sealed and tested in the usual manner and contained a dark yellow-brown solution at room temperature. The ^{31}P n.m.r. spectrum of the solution consisted of a very strong 1:1 doublet at -3.6 p.p.m. with $^1J_{P-H}$ 510Hz., and two singlets at -31.0 and -35.0 p.p.m. These signals may be assigned to Ph_3PH^+ and to triphenylphosphine-palladium species respectively. The ratio of the intensities of the signals, from low to high field, was approximately 1:10:60.

The reaction was repeated on a larger scale. HCl (80 mmole) was condensed at -196^o into a 13mm. o.d. quartz ampoule of type A containing $(Ph_3P)_4Pd$ (0.250g., 0.022 mmole). The ampoule was sealed and allowed to reach room temperature in the normal manner. The clear dark yellow brown solution was left at this temperature for 24 hours to equilibrate, then cooled to -112^o and the ampoule was opened to the vacuum line. HCl was removed by pumping at -95^o. The dull yellow solid residue was pumped for a further 2 hours at room temperature. The infrared spectrum of the solid contained a strong absorption at 362cm^{-1} which may be immediately assigned to a Pd-Cl stretching frequency.[196] Absorptions due to Ph_3P ligands were also present, but the strong absorption at 410cm^{-1} in the spectrum of the starting material was absent.

Found; C, 66.9; H, 4.67; P, 8.71; Cl, 14.86;

Calculated for a mixture of $Ph_3PH^+HCl_2^-$ and $(Ph_3P)_2PdCl_2$ in 2:1 molar ratio; C, 63.0; H, 4.84; P, 9.04; Cl, 15.5.

The reaction between trans-dichlorobis(triphenylphosphine)palladium(II) and liquid hydrogen chloride.

HCl (25 mmole) was condensed at -196° into an 8mm. o.d. quartz ampoule containing $(Ph_3P)_2PdCl_2$ (0.040g., 0.057 mmole). The ampoule was sealed and tested in the usual manner. The yellow solid dissolved giving a pale yellow solution from which a red solid crystallised out. The ^{31}P n.m.r. spectrum of the solution consisted of a weak 1:1 doublet at -2.7 p.p.m. with $^{1}J_{P-H}$ of 504Hz. which may be immediately assigned to the species Ph_3PH^+.

The reaction was repeated on a larger scale in order to obtain a sample of the red crystalline solid for characterisation. HCl (100 mmole) was condensed at -196° into a 13mm. o.d. quartz ampoule of type B containing $(Ph_3P)_2PdCl_2$ (0.389g., 0.55 mmole). The ampoule was sealed and warmed to room temperature in the usual manner. After 24 hours at room temperature the yellow solid had completely reacted, giving a yellow solution and beautiful shiny red crystals which were separated from the solvent in the manner previously described.

The infrared spectrum of the red crystalline solid strongly resembled that of $(Ph_3P)_2PdCl_2$, with minor changes in band positions in the regions 540-500cm^{-1} and 460-420cm^{-1}, and new absorptions at 305, 267 and 260sh.cm^{-1}. No absorption in the region 2400-2350cm^{-1}, characteristic of νP-H in Ph_3PH^+ [175] was detected. The solid was air stable.

Found; C, 45.3; H, 3.56; P, 6.58; Cl, 22.4; Pd, 24.1;

Calculated for $(Ph_3PH^+)_2Pd_2Cl_6^{2-}$; C, 45.4; H, 3.36; P, 6.51;

Cl, 22.4; Pd, 22.3.

The ^{31}P n.m.r. spectrum of trans-dichlorobis(triphenylphosphine)-palladium(II) in chloroform.

The ^{31}P n.m.r. spectrum of a saturated solution of $(Ph_3P)_2PdCl_2$ was recorded, and consisted of a sharp singlet at -22.2 ± 0.5 p.p.m. A CAT run of 68 scans gave a satisfactory spectrum.

4.3 Nickel Complexes

Results and Discussion

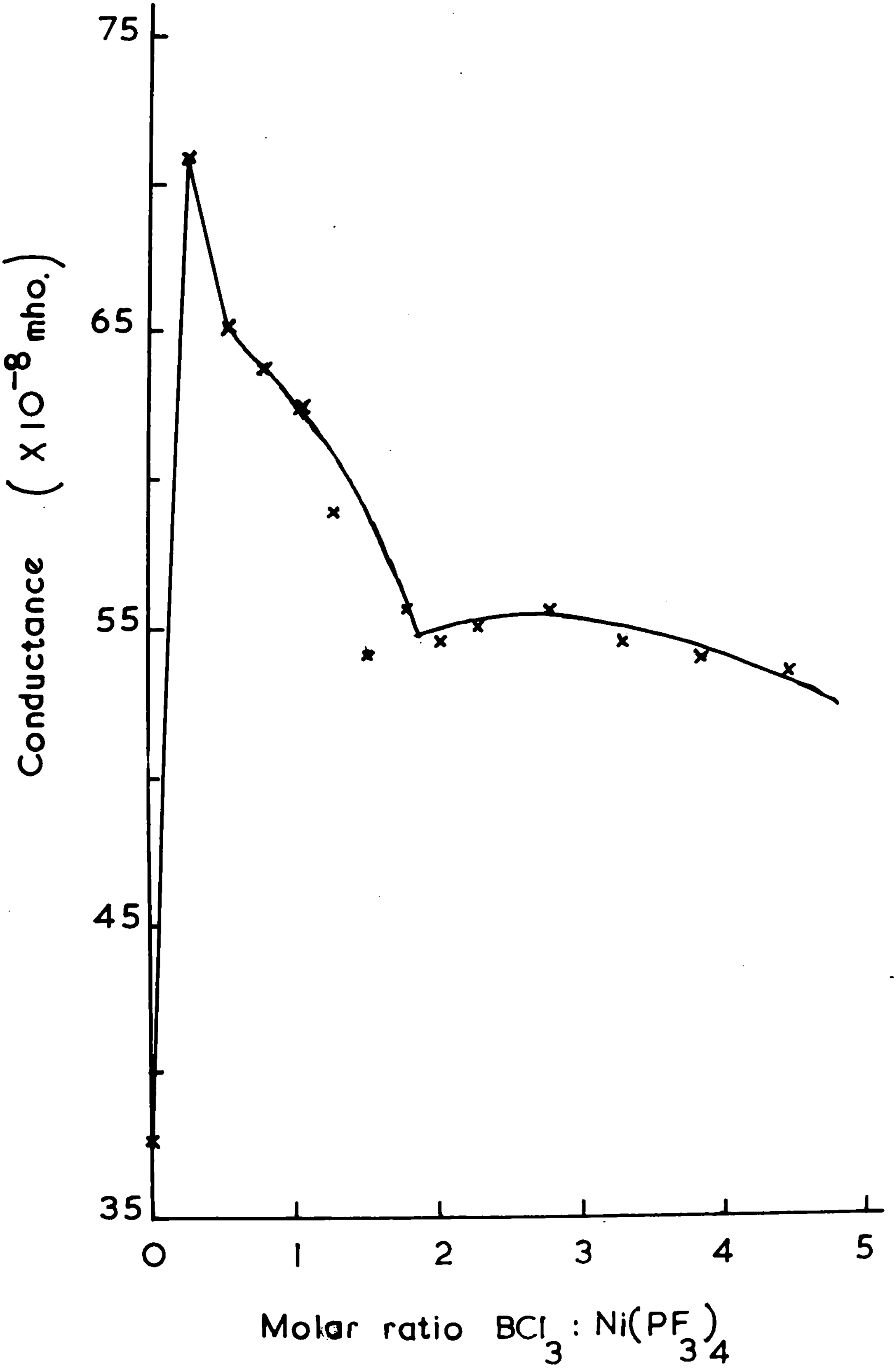
Tetracarbonylnickel has been shown to be soluble in liquid hydrogen chloride at low temperatures without evolution of gas.[57] Oxidation with chlorine at -95° yielded the compound tetrachlorotricarbonyldinickel. The behaviour of tetrakis(trifluorophosphine)-nickel(0) in liquid hydrogen chloride was studied as an extension of this work. The ^{31}P n.m.r. spectrum of the compound in liquid hydrogen chloride consisted of the expected 1:3:3:1 quartet with a chemical shift value of -37.4 ± 2 p.p.m. and $^{1}J_{P-F}$ 1346 Hz. These values are in excellent agreement with literature values for the neat liquid; it may thus be assumed that tetrakis(trifluorophosphine)nickel(0) is soluble in liquid hydrogen chloride without reaction. A conductiometric titration between the complex and boron trichloride was carried out in the solvent at -95°. The results, shown in Fig.4.3.1, indicate adduct formation rather than protonation. After a sharp rise on addition of the first aliquot of boron trichloride, the conductance fell only slightly, breaks occurring at 1:1 and 1:2 molar ratios of complex:Lewis acid. Starting materials, identified by their gas phase infrared spectra, were recovered on pumping off volatiles at low temperatures.

Oxidation of the complex in liquid hydrogen chloride with chlorine and bromine was attempted. In both cases the molar ratio of oxidising agent:complex was slightly in excess of 5:1.

This ratio was chosen in order that sufficient oxidising agent would be available if required to completely oxidise the complex i.e. to oxidise

Fig.4.3.1

Conductiometric titration, boron trichloride against tetrakis(trifluorophosphine)nickel(0)


75
65
55
45
35
Conductance (X 10^{-8} mho.)
0
1
2
3
4
5
Molar ratio $BCl_3 : Ni(PF_3)_4$

the metal from the zero to the +2 oxidation state and all the phosphorus, in the trifluorophosphine ligands, from the +3 to the +5 oxidation state. Chlorine reacted with tetrakis(trifluorophosphine)-nickel(0) to give dichlorotrifluorophosphorus(V), identified by its gas phase infrared spectrum, and nickel(II)chloride. A solid consisting largely of nickel(II) bromide was obtained from the reaction between the complex and bromine. Dichlorotrifluorophosphorus(V) was again detected, presumably formed by solvolysis of the oxidation product dibromotrifluorophosphorus(V). This behaviour, first noted by Salthouse,[81] has been discussed earlier in this work.

In their binary compounds with zerovalent nickel both carbon monoxide and phosphorus(III)fluoride function as π-acceptor, or in the Lewis sense π-acid, ligands and their abilities to behave as such are about equal.[200] Hence, the striking difference between the behaviour of tetracarbonylnickel and tetrakis(phosphorus(III)fluoride)nickel(0) on oxidation with chlorine in liquid hydrogen chloride cannot be explained in terms of significant differences between the metal-ligand bonds. A more likely explanation would seem to be that chlorine can more readily oxidise phosphorus(III)fluoride to dichlorotrifluorophosphorus(V) than carbon monoxide to phosgene. Thus the phosphorus(III)fluoride ligands would be removed, the phosphorus being oxidised from the +3 to the +5 oxidation state, as the nickel was oxidised from nickel(0) to nickel(II). The reaction may be represented by the equation

$$Ni(PF_3)_4 + 5Cl_2 \rightarrow NiCl_2 + 4PF_3Cl_2.$$

The reaction with bromine is essentially similar, save that the dibromotrifluorophosphorus(V) is solvolysed to dichlorotrifluorophosphorus(V)

$$Ni(PF_3)_4 + 5Br_2 \rightarrow NiBr_2 + 4PF_3Br_2$$
$$PF_3Br_2 + 2HCl \rightarrow PF_3Cl_2 + 2HBr.$$

Tetrakis(phosphorus(III)chloride)nickel(0) was apparently insoluble in liquid hydrogen chloride at room temperature. A buff coloured solid in addition to the yellow crystalline complex appeared in the ampoule on standing, and a signal at -217.7 p.p.m., which may be immediately assigned to phosphorus(III)chloride was detected when the ^{31}P n.m.r. solution spectrum was recorded. A preparative scale experiment which would possibly have yielded information as to the nature of the buff-coloured solid was not carried out, mainly because the reaction was slow and the likelihood of obtaining an inhomogeneous sample of the solid, contaminated with starting material, was high. The behaviour of the compound in other solvents has been reported by Irvine and Wilkinson.[201] Solutions in hydrocarbons and in carbon tetrachloride slowly decomposed, black precipitates of nickel forming on heating. The buff-coloured material was clearly not nickel, and it is possible that it was nickel(II)chloride. This would imply oxidation of the nickel by the solvent from the zero to the +2 oxidation state with consequent formation of hydrogen. It would be possible on opening the ampoule to detect hydrogen as a noncondensable gas.

The zerovalent nickel complex dicarbonylbis(triphenylphosphine) nickel(0) did not dissolve in liquid hydrogen chloride to give a clear solution. The white solid starting material increased in bulk at -78^{o} and changed colour through yellow to orange at room temperature. A 1:1 doublet at -5.5 p.p.m. with $^{1}J_{^{31}P-^{1}H}$ of 514 Hz., characteristic of triphenylphosphonium ions, was observed in the ^{31}P n.m.r. spectrum of the clear colourless liquid above the solid. On cooling to -196^{o} and opening the ampoule, a gas was detected, about 1 mole per mole of starting material. The gas phase infrared spectrum, at a pressure of 5cm. Hg in a 10cm. gas cell, showed no absorptions in the region $4000-250cm^{-1}$ suggesting that the gas could be hydrogen. However, carbon monoxide is a weak absorber in the infrared and the non-appearance of a band at $2143cm^{-1}$ in a sample at this pressure should not be taken as conclusive evidence for the absence of the gas. A pale blue solid was obtained on removal of solvent at low temperatures. The infrared spectrum of this material contained absorptions assignable to triphenylphosphonium cations, and carbonyl stretching frequencies at 2000 and $1940cm^{-1}$ indicated the presence of unreacted starting material. The pale blue colour of the material is suggestive of the presence of the blue tetrachloronickel(II)ate anion and the reaction could then be formulated as

$$(Ph_3P)_2(CO)_2Ni \; + \; 4HCl \; \rightarrow \; (Ph_3PH^+)_2NiCl_4^{2-} + H_2 \; + \; 2CO$$

However, Harriss has recently investigated the behaviour of tetraalkylammonium tetrachlorometallate salts in liquid hydrogen chloride at room temperature, including tetraethylammonium tetrachloronickel(II)ate.[202] The blue colour of the anion is completely discharged, and a buff coloured solid, presumably nickel(II) chloride, under a clear colourless solution is obtained. Thus it seems very unlikely that a tetrachloronickel(II)ate salt could be isolated from the reaction between dicarbonylbis(triphenylphosphine)-nickel(0) and liquid hydrogen chloride. Analytical data can be interpreted in terms of a mixture of starting material, nickel(II) chloride and triphenylphosphonium hydrogendichloride, but it is clearly unwise to attempt to draw firm conclusions from a patently inhomogeneous product.

Dichlorobis(triphenylphosphine)nickel(II) reacts with liquid hydrogen chloride giving a flocculent buff coloured precipitate. The clear colourless overlying solution was shown to contain triphenylphosphonium cations; a 1:1 doublet at -3.5 p.p.m. with $^{1}J_{^{31}P-^{1}H}$ 510Hz. being observed in the ^{31}P n.m.r. spectrum of the solution. The infrared spectrum of the solid material contained absorption characteristic of triphenylphosphonium ions and analytical data may be interpreted in terms of a mixture of triphenylphosphonium hydrogendichloride and nickel(II)chloride. An equation for the reaction would be

$$(Ph_3P)_2NiCl_2 \quad + \quad 4HCl \quad \rightarrow \quad 2Ph_3PH^+HCl_2^- \quad + \quad NiCl_2.$$

The behaviour of dichlorobis(triphenylphosphine)nickel(II) in liquid hydrogen chloride may be contrasted with that of cis-dichlorobis-(triphenylphosphine)platinum(II) which is recovered unchanged from the solvent.

Experimental

The behaviour of tetrakis(trifluorophosphine)nickel(0) in liquid hydrogen chloride.

$(PF_3)_4Ni$ (0.246g., 0.599 mmole) was condensed at -196° into an 8mm. o.d. quartz ampoule, followed by HCl (25 mmole). The ampoule was sealed and tested as described earlier. The ^{31}P n.m.r. spectrum of the clear colourless solution consisted of a 1:3:3:1 quartet at -137.4 ± 2 p.p.m. with $^{1}J_{P-F}$ 1346Hz. Values of -140 p.p.m. and 1300Hz. have been reported for the neat liquid.[203] It may be assumed that $(PF_3)_4Ni$ dissolves in liquid hydrogen chloride without reaction.

The reaction between tetrakis(trifluorophosphine)nickel(0) and boron trichloride.

$(PF_3)_4Ni$ (0.1107g., 0.269mmole) was condensed at -196° into a conductance cell, followed by HCl (200 mmole). This was sufficient HCl to give a clear colourless 0.0448M solution at -95°. Aliquots of BCl_3 were condensed in from the gas phase and a conductiometric titration was carried out. The results are shown graphically in fig. 4.3.1. The conductance rose markedly on addition of the first aliquot of BCl_3, but then decreased only slightly throughout the titration. Breaks in the curve occurred at 1:1 and 1:2 ratios of $(PF_3)_4Ni:BCl_3$, indicating adduct formation rather than the production of ionic species. After the titration was completed the infrared spectrum of the vapour above the liquid hydrogen chloride was recorded. Absorptions at 2880 and 965cm^{-1} due to HCl and PF_3 respectively were observed. The HCl was removed by pumping at -95° until a white glassy solid remained. The infrared spectrum of the vapour above this solid contained intense absorptions at 995 and 955cm^{-1}, which may be assigned to BCl_3,[204] and at 905, 866, 526 and 510cm^{-1} which are chateristic of $(PF_3)_4Ni$.[115] Further pumping at -63.5° and -45° removed BCl_3 and the infrared spectrum of the clear colourless liquid obtained at room temperature contained only those absorptions due to $(PF_3)_4Ni$.

The reaction between tetrakis(trifluorophosphine)nickel(0) and chlorine

$(PF_3)_4Ni$ (0.298g., 0.726mmole) was condensed at -196° into a 24mm. o.d. pyrex reaction tube followed by HCl (300mmole). The tube was warmed to -95° when a clear colourless solution was obtained. Cl_2 (3.70 mmole) was condensed into the reaction tube at -196°. On warming to -95° a copious flocculent orange precipitate was produced. After 30 minutes at this temperature the infrared spectrum of the vapour above the solution was recorded. Absorptions at 2880cm^{-1}, due to HCl, and at 980, 935, 895 and 664cm^{-1} which are characteristic of PF_3Cl_2[205] were observed. HCl was removed by pumping at -95°. The infrared spectrum of the vapour over the pale pink solid was recorded as the temperature was raised to 20°. In all cases absorptions due to PF_3Cl_2 were observed. Analytical data suggested that the solid product was largely $NiCl_2$ and the reaction was not investigated further.

The reaction between tetrakis(trifluorophosphine)nickel(0) and bromine.

$(PF_3)_4Ni$ (0.342g., 0.832 mmole) was condensed at -196° into a pyrex reaction tube, followed by HCl (400 mmole). A clear colourless solution was obtained at -95°. Br_2 (0.732g., 4.58 mmole) was condensed into the tube at -196°. A copious dull orange precipitate was produced on warming to -95°, and the colour due to Br_2 persisted. After 30 minutes at this temperature the infrared spectrum of the vapour above the solution was recorded. Absorption at 2880, 2560, 930, 905, 899 and $665cm^{-1}$ were present. The high frequency absorptions may be assigned to HCl and HBr respectively,[92] and the remaining peaks to PF_3Cl_2. Volatiles were removed by pumping at -95° and later at room temperature for 2 hours. Analytical data suggested that the dull orange solid was mainly $NiBr_2$ and the reaction was not studied further.

The behaviour of tetrakis(trichlorophosphine)nickel(0) in liquid hydrogen chloride.

HCl (30 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing yellow crystalline $(PCl_3)_4Ni$ (0.208g., 0.342 mmole). The ampoule was sealed and tested in the usual manner. At room temperature the bulk of the solid had increased and a buff coloured material was present. A CAT run of 123 scans gave a ^{31}P n.m.r. spectrum consisting of a singlet at -217.7 p.p.m. which may be immediately assigned to PCl_3.[119]

$(PCl_3)_4Ni$ was not investigated further.

The reaction between dicarbonylbis(triphenylphosphine)nickel(0) and liquid hydrogen chloride.

HCl (30 mmole) was condensed at -196° into an 8mm. o.d. quartz ampoule containing $(Ph_3P)_2(CO)_2Ni$ (0.080g., 0.125 mmole). The ampoule was sealed and tested in the usual way. The white crystalline solid gave a bulky pale orange precipitate under a clear colourless solution at room temperature. A 1:1 doublet at -5.5 p.p.m. with $^{1}J_{P-H}$ 514Hz., which may be immediately assigned to Ph_3PH^+, was observed when the ^{31}P n.m.r. spectrum of the solution was recorded. This species was present only in low concentration, a CAT run of 512 scans being required to produce a satisfactory spectrum.

The reaction was repeated on a larger scale.

HCl (140 mmole) was condensed at -196° into a 13 mm. o.d. quartz ampoule containing $(Ph_3P)_2(CO)_2Ni$ (0.650g., 1.02 mmole). The ampoule was sealed and warmed to room temperature in the normal manner. The solid increased in bulk and became yellow at -78° and orange at room temperature. At all times the liquid above the solid remained clear and colourless. After 24 hours at room temperature no further visible change had taken place. The ampoule was cooled to -196° and opened, via the vacuum line, to the spiral gauge. A gas (0.938 mmole) was detected. No absorptions in the region 4000-250cm^{-1} were detected when the infrared spectrum of the gas, 5cm. Hg pressure, was recorded. As the HCl was removed by pumping at -95° the yellow solid turned pale blue. No further colour change occurred and the solid was pumped for 2 hours at room temperature. The infrared spectrum of the pale blue solid product contained absorptions characteristic of Ph_3PH^+, identified by comparison with the spectrum of a known Ph_3PH^+ salt, $Ph_3PH^+HCl_2^-$. Weak absorptions at 2000, 1940 and 320cm^{-1} were also observed. The two high frequency bands are carbonyl stretching frequencies[206] and may be ascribed to the presence of unreacted starting material.

Found; C, 66.1; H, 4.5; P, 8.58; Cl, 16.47;

Calculated for a mixture of $NiCl_2$ and $Ph_3PH^+HCl_2^-$ in 1:2 molar ratio, C, 45.7; H, 3.59; P, 6.56; Cl, 22.5;

Calculated for $(Ph_3P)_2(CO)_2Ni$; C, 71.3; H, 4.69; P, 9.69.

This reaction was not investigated further.

The reaction between dichlorobis(triphenylphosphine)nickel(II) and liquid hydrogen chloride

HCl (25 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing $(PPh_3)_2NiCl_2$ (0.042g., 0.064 mmole). The ampoule was sealed and tested in the usual manner. The deep blue crystalline $(Ph_3P)_2NiCl_2$ reacted with the solvent to give a bulky buff coloured precipitate at room temperature and a clear colourless solution. The ^{31}P n.m.r. spectrum of the solution consisted of a weak 1:1 doublet at -3.5 p.p.m. with $^1J_{P-H}$ 510Hz., which may be immediately assigned to Ph_3PH^+.

The reaction was repeated on a larger scale.

HCl (140 mmole) was condensed at -196° into a 13 mm. o.d. quartz ampoule of type B containing $(PPh_3)_2NiCl_2$ (1.240g., 1.90 mmole). The ampoule was sealed and brought up to room temperature in the manner previously described. At -78° the crystalline solid began to dissolve and at -45° reacted to give a flocculent buff coloured solid. The solid was separated from the liquid HCl in the usual manner and was pale pink in colour at room temperature. The infrared spectrum of the solid product contained identical absorptions to those due to Ph_3PH^+ in the spectrum of an authentic sample of $Ph_3PH^+HCl_2^-$.

Found; Ni, 16.43; P, 6.46; Cl, 31.43;

Calculated for a mixture of $NiCl_2$ and $Ph_3PH^+HCl_2^-$ in 1:0.75 molar ratio;

Ni, 15.5; P, 6.2; Cl, 33.35.

This reaction was not studied further.

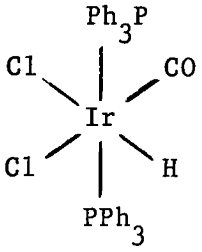
4.4 Iridium, Rhodium and Cobalt Complexes

The oxidative addition reaction occurs when a complex simultaneously shows both Lewis acidic and Lewis basic behaviour. Non-bonding electron density on the metal, two vacant coordination sites on the metal to allow the formation of two new metal-ligand bonds and a metal with oxidation states differing by two units are necessary for such reactions to proceed. Iridium(I) and Rhodium(I) complexes have been widely studied in this context, both metals having d^8 electron configurations.[207,208,209,210,211,212,213.] When there is no loss of ligand the reaction will be an equilibrium represented by

$$\mathrm{LyM}^{n} + \mathrm{XY} \rightleftharpoons \mathrm{LyM}^{n+2}\,\mathrm{XY}.$$

The position of equilibrium will be determined largely by three factors; the nature of the metal and its ligands, the nature of the added molecule XY and the M-X and M-Y bands formed, and on the reaction medium. Generally, it is observed that the higher oxidation states are more stable for the heavier metals e.g. Iridium(III) complexes are more stable than rhodium(III) complexes.[214]

The oxidative addition of a hydrogen halide HX to trans-halocarbonylbis(triphenylphosphine)iridium(I), $(Ph_3P)_2Ir(CO)Y$, (X and Y similar or dissimilar halogens) has been well studied. Vaska et. al.[215] reported the reaction between HCl and $(Ph_3P)_2Ir(CO)Cl$ in ether yielding $(Ph_3P)_2Ir(CO)HCl_2$, with one Cl trans to an H atom and the other trans to a carbonyl group. The structure of the iridium(III) complex being



Further work to elucidate the stereochemistry and mechanism of addition was carried out by Blake et. al.[216] who studied the addition of hydrogen halides to the iridium(I) complexes containing a different halogen. Their results indicated that in benzene or chloroform solution cis-HX adducts were formed. In the presence of polar solvents e.g. dimethylformamide, acetonitrile, water then mixtures of both cis- and trans- isomers were formed. The authors suggested that these isomers could result from either rapid exchange of halide ion before the addition or from exchange between halide ions in the products. It has also been suggested that in polar media the initial step involves protonation of the square complex producing a five-coordinate cationic complex, which could isomerize via an intramolecular mechanism, followed by coordination of a halide ion to give the oxidised product.[214]

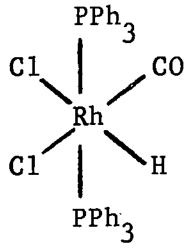
In this work an attempt was made to study the behaviour of chlorocarbonylbis(triphenylphosphine)iridium(I) in liquid hydrogen chloride using ^{31}P n.m.r. Iridium consists of two isotopes, ^{191}Ir and ^{193}Ir present in 38.5 and 61.5% abundance respectively, both having nuclear spin of 3/2. Thus, any signal due to a phosphorus atom bound to iridium would be split into eight separate signals due to P-Ir coupling. Yellow $(Ph_3P)_2Ir(CO)Cl$ reacted with hydrogen chloride gas as it was condensed into the ampoule forming a white crystalline solid which appeared to be largely insoluble in liquid hydrogen chloride. No signals were detected when the ^{31}P n.m.r. spectrum of the overlying clear colourless liquid was recorded. This is probably due to a combination of two factors; low solubility of the white iridium(III) complex produced and iridium-phosphorus coupling which would further reduce the intensity of an already weak signal. The white crystalline product was shown by elemental analysis to be hydridodichlorocarbonylbis (triphenylphosphine)iridium(III). The relative positions of the adduct H and Cl atoms were inferred from the values of Ir-Cl stretching frequencies[216] and the product was thus identical to that of Vaska,[215] shown on the preceding page.

^{103}Rh is 100% abundant and has a nuclear spin values of ½ making it a favourable nucleus for n.m.r. studies.

^{31}P n.m.r. data was obtained from the reaction between the corresponding rhodium(I) complex, chlorocarbonylbis(triphenylphosphine) rhodium(I), and liquid hydrogen chloride. Yellow crystalline $(Ph_3P)_2Rh(CO)Cl$ reacted with the solvent to give a clear yellow solution and a white crystalline solid, the nature of which will be discussed later. The ^{31}P n.m.r. spectrum of the yellow solution consisted of a 1:1 doublet at -6.0 ± 0.5 p.p.m. with $^{1}J_{^{31}P-^{1}H}$ 510 ± 5Hz. and a second 1:1 doublet at -46.6 ± 0.5 p.p.m. with $^{1}J_{^{31}P-^{103}Rh}$ 118 ± 5Hz. The former is known to be characteristic of Ph_3PH^+ and the latter may be assigned to a rhodium bound triphenylphosphine group.[217] Intensities indicated that the two phosphorus species were present in 3:2 molar ratio in favour of the triphenylphosphonium ion. During the course of several days the white solid dissolved and the solution became brown. The ^{31}P n.m.r. solution spectrum at this stage was essentially unchanged excepting that the intensity of the Ph_3PH^+ signal had increased. The study of this ampoule came to an abrupt end after 10 days when it exploded. It is possible that this was caused by the evolution of hydrogen and/or carbon monoxide from a subsequent reaction involving the white solid and the solvent.

A preparative scale experiment was performed in order to obtain a sample of the white solid product for characterisation. This material became slightly yellow green in colour as soon as the solvent was removed, and became definitely yellow over a period of days. Infrared spectra of starting material and product are shown in fig. 4.4.2.

A new peak appearing at 2047cm^{-1} in the spectrum of the product is assigned to a rhodium-hydrogen stretching frequency.[218,219.] The carbonyl band at 1940cm^{-1} in the starting material has moved to 1935cm^{-1} and there is a new peak at 270cm^{-1} which may be assigned to a rhodium chlorine stretching frequency. By analogy with the corresponding iridium complex. The peak at 318cm^{-1} in the infrared spectrum of $(Ph_3P)_2Rh(CO)Cl$ is assigned to a rhodium-chlorine stretching frequency for a Cl trans to a CO group. The second metal-halogen vibration at 270cm^{-1} may thus be ascribed to a rhodium-chlorine absorption associated with a Cl trans to an H atom. The white solid may be formulated as hydridodichlorocarbonylbis(triphenylphosphine) rhodium(III) with the structure shown below.



The rhodium(III)complex however is not stable at room temperature. Infrared spectra of the compound, which was stored under dry nitrogen, show the slow reversion to the rhodium(I) starting material. Thus the equilibrium

$$(Ph_3P)_2Rh(CO)Cl \quad + \quad HCl \quad \rightleftharpoons \quad (Ph_3P)_2RhH(CO)Cl_2$$

clearly does not lie firmly on the side of the oxidised species unlike the equilibrium for the corresponding iridium compound.

Chlorotris(triphenylphosphine)rhodium(I) has been reported to undergo oxidative-addition with elimination of one triphenylphosphine ligand on reaction with HX when X = CN, NO_3 and Cl.[212,220.] Reaction with hydrogen chloride in methylene chloride yields the unstable yellow crystalline $(PPh_3)_2RhHCl_2.0.5\ CH_2Cl_2$ which readily loses both hydrogen chloride and solvating dichloromethane. The starting material was found to be only poorly soluble in liquid hydrogen chloride at room temperature and a ^{31}P n.m.r. solution spectrum was obtained only with difficulty. Doublets corresponding to triphenylphosphonium ions and to a rhodium bound triphenylphosphine group were observed in addition to a singlet at -55 ± 0.5 p.p.m. It is difficult to suggest any assignment for this signal.

An orange solid was isolated when the reaction was carried out on a preparative scale. No noncondensable gas was detected during the preparation and it may thus be assumed that hydrogen was not evolved during the reaction. There were no absorptions in the region associated with Rh-H stretching frequencies i.e. 2100cm^{-1}, in the infrared spectrum of this solid and thus there is no evidence for the formation of a hydride. However, the absence of absorptions in this region is not to be taken as conclusive evidence that the molecule under investigation does not contain Rh-H bonds, since absorptions due to these vibrations may be very weak or even undetectable.[221] Analytical data did not conform to any clear cut pattern, and it seems likely that the orange solid is a mixture of products. Triphenylphosphoniumhydrogendichloride and hydridodichlorobis(triphenylphosphine)rhodium(III) are probably products in view of literature reports and some, but not all, analytical figures could be interpreted on this basis. ^{31}P n.m.r. and infrared spectroscopy together with elemental analysis have not provided a satisfactory explanation of the reaction between $(Ph_3P)_3RhCl$ and liquid hydrogen chloride which must be assumed to be less than simple. Further work possibly repeating the reaction using a quartz ampoule fitted with a sinter to enable filtration of the products, is necessary to clarify the situation.

Brown tricarbonyltriphenylphosphinecobalt(0) dimer dissolved in liquid hydrogen chloride at low temperatures giving a brown solution. On warming to room temperature the solution turned blue and a blue solid was precipitated. Further warming to 34.2°C, the operating temperature of the R10, resulted in discharge of the blue colour from the solution. No ^{31}P n.m.r. signals could be obtained from the colourless solution, and as a variable temperature probe was not available the coloured solutions produced at lower temperatures could not be investigated. The infrared spectrum of the turquoise solid isolated from this reaction contained absorptions characteristic of cis-dichlorobis(triphenylphosphine)cobalt(II) in addition to absorptions at 2050, 1995, 1975, 1955 and 1912cm^{-1} These absorptions are almost certainly terminal carbonyl stretching frequencies.[222] However, νCo-H in $CoH(CO)_4$ occurs at 1934cm^{-1} [223] and it is possible that one of the bands at 1955 or 1912cm^{-1} may be due to a metal-hydrogen stretching frequency. Elemental analyses carried out on the solid product were not reproducible.

The reaction was not studied further.

Experimental

The reaction between trans-chlorocarbonylbis(triphenylphosphine)iridium(I) and hydrogen chloride.

HCl was condensed at -196° into an 8mm. o.d. quartz ampoule containing $(Ph_3P)_2Ir(CO)Cl$ (0.100g., 0.013 mmole). The ampoule was sealed and tested in the usual manner. At room temperature the ampoule contained a clear colourless solution over a small quantity of white crystalline solid. No reproducible signal could be obtained when the ^{31}P n.m.r. spectrum of the solution was recorded.

The reaction was repeated on a larger scale in order to obtain a sample of the white crystalline solid for investigation. An ampoule of type B as described on p. 23 was used for this reaction.

HCl (120 mmole) was condensed at -196^{o} into a 13 mm. o.d. quartz ampoule, fitted with a sintered silica disc, containing $(Ph_3P)_2Ir(CO)Cl$ (0.973g., 1.25 mmole). The ampoule was sealed and allowed to reach room temperature in the normal manner. The yellow crystalline starting material turned white as soon as the HCl was condensed upon it, and at room temperature the ampoule contained a clear colourless solution over a white crystalline solid. The white crystals were separated from the liquid in the manner described earlier (p. 24). In addition to absorptions due to Ph_3P, the infrared spectrum of the starting material contained absorptions at 1910 and 324cm^{-1} which may be assigned to ν_{CO} and ν_{IrCl} respectively.[215] The infrared spectrum of the product contained absorptions in addition to those due to Ph_3P at 2240m, 2027s, 318w and 270w cm^{-1}. The absorptions at 2240 and 2027cm^{-1} may be assigned to ν_{IrH} and ν_{CO} respectively and those at 318 and 270cm^{-1} to IrCl absorptions[216] ν_{IrCl} at 318cm^{-1} may be assigned to a chlorine ligand trans to a carbonyl ligand, and that at 270cm^{-1} to a chlorine ligand trans to a hydride ligand.[216]

Found; C, 54.21; H, 3.68; P, 7.69; Cl, 8.6;

Required for $(Ph_3P)_2Ir(M)(CO)Cl$; C, 54.42; H, 3.80; P, 7.6; Cl, 8.7.

The compound may thus be formulated as

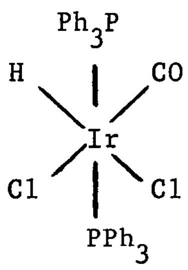
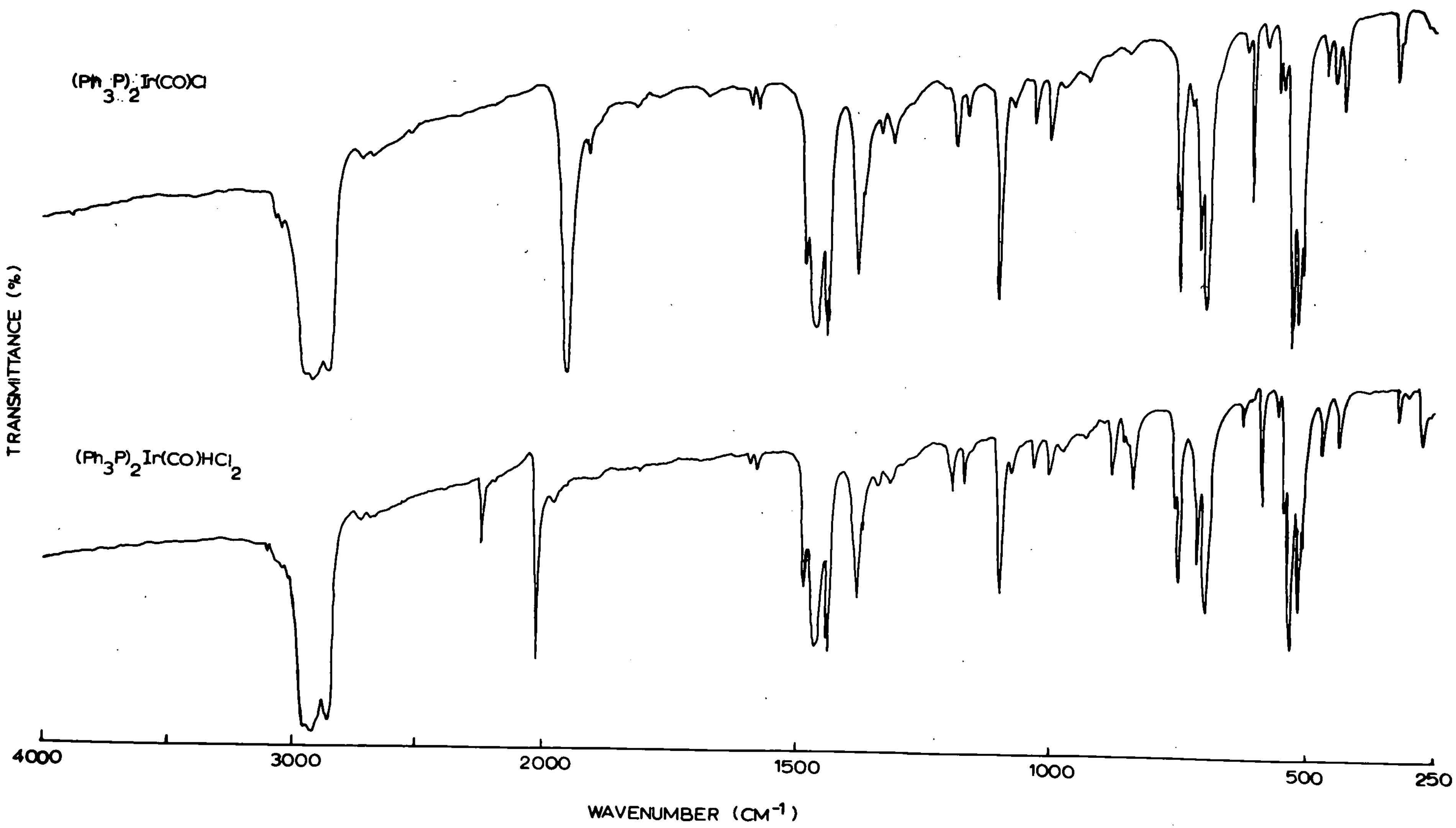


Fig.4.4.1

Infrared spectra of chlorocarbonylbis(triphenylphosphine)iridium(I) and hydridodichlorocarbonylbis(triphenylphosphine)iridium(III)


$(Ph_3P)_2Ir(CO)Cl$
$(Ph_3P)_2Ir(CO)HCl_2$
TRANSMITTANCE (%)
4000
3000
2000
1500
1000
500
250
WAVENUMBER (CM^{-1})

The reaction between trans-chlorocarbonylbis(triphenylphosphine) rhodium(I) and hydrogen chloride.

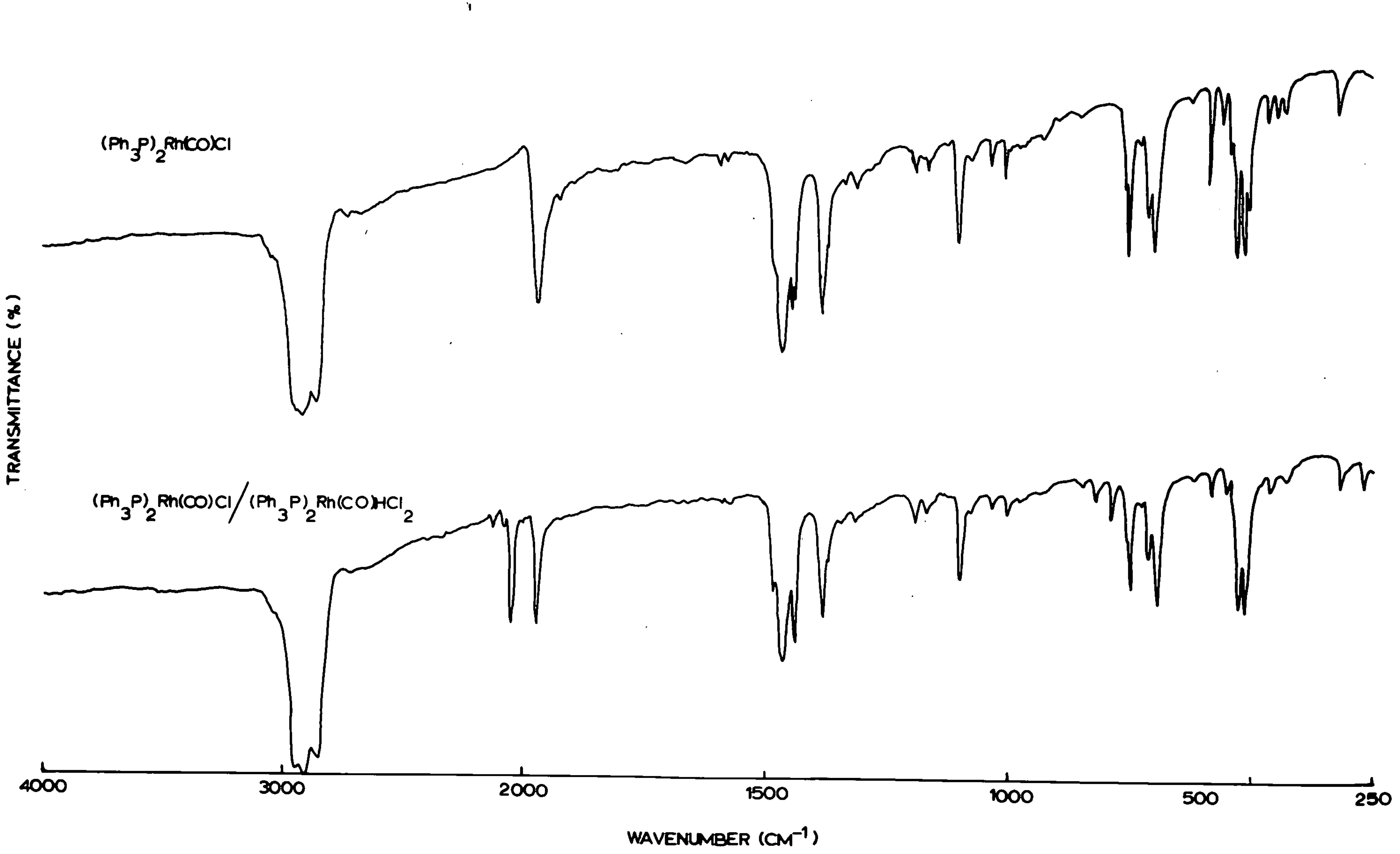
HCl (25 mmole) was condensed at -196° into an 8mm. o.d. quartz ampoule containing yellow crystalline $(Ph_3P)_2Rh(CO)Cl$ (0.060g., 0.086 mmole). The ampoule was sealed and tested in the normal manner and at room temperature contained a clear yellow solution over a white crystalline solid. The rhodium complex was only very slightly soluble in liquid hydrogen chloride, a CAT run of 900 scans being necessary to achieve a satisfactory ^{31}P n.m.r. solution spectrum. Two doublets were observed when the spectrum was recorded. The higher field doublet at -6.0 ± 0.5 p.p.m. with $^1J_{P-H}$ coupling constant 510 ± 5Hz. may be immediately assigned to Ph_3PH^+, and that at lower field, $- 46.6 \pm 0.5$ p.p.m. with $^1J_{P-Rh}$ coupling constant 118 ± 5Hz to a Ph_3P ligand bound to a rhodium atom.[217] The ratio of intensities of the doublets was approximately 3:2 in favour of the Ph_3PH^+ species. After 10 days, the white crystalline solid had dissolved forming a clear brown solution. The ^{31}P n.m.r. solution spectrum was again recorded and differed from that obtained earlier only in the fact that the ratio of intensities Ph_3PH^+:Ph_3P-Rh species was now approximately 2:1. Shortly afterwards the ampoule exploded. This was the only occasion on which an 8 mm. o.d. quartz n.m.r. ampoule exploded after successfully passing through the testing process.

The reaction was repeated on a preparative scale.

HCl (150 mmole) was condensed at -196° into a 13 mm. o.d. quartz ampoule, fitted with a sintered silica disc, containing $(Ph_3P)_2Rh(CO)Cl$ (0.500g., 0.720 mmole). The ampoule was sealed and brought up to

Fig.4.4.2

Infrared spectra of chlorocarbonylbis(triphenylphosphine)rhodium(I) and its reaction product from liquid hydrogen chloride solution


$(Ph_3P)_2Rh(CO)Cl$
$(Ph_3P)_2Rh(CO)Cl/(Ph_3P)_2Rh(CO)HCl_2$
TRANSMITTANCE (%)
4000
3000
2000
1500
1000
500
250
WAVENUMBER (CM^{-1})

room temperature in the usual manner. A yellow solution and a white crystalline solid were present at room temperature. After 12 hours the white solid was separated from the solution as described earlier, and began to turn a pale yellow-green colour as soon as all the HCl was cooled to -196°. Absorptions due to Ph_3P ligands were present in the infrared spectra of both starting material and product. New peaks appeared at 2047 and 270cm^{-1} which may be assigned to ν_{Rh-H} 218,219 and ν_{Rh-Cl} respectively. The carbonyl peak moved from 1940cm^{-1} in the starting material to 1935cm^{-1} and an absorption at 580cm^{-1} was of significantly lower intensity in the infrared spectrum of the product. After 10 days the infrared spectrum of the pale yellow-green material had altered, the absorption at 2047cm^{-1} had decreased in intensity, two carbonyl bands at 1940 and 1930cm^{-1} of equal intensities were present, the band at 580cm^{-1} had gained in intensity, and the peak at 270cm^{-1} could be detected only with the eye of faith.

Found; C, 58.5; H, 4.10; P, 7.71; Cl, 11.5; Rh, 12.9;

Required for $(Ph_3P)_2HCl_2(CO)Rh$; C, 60.8; H, 4.24; P, 8.49; Cl, 9.73; Rh, 14.11;

Required for $(Ph_3P)_2Rh(CO)Cl$; C, 64.0; H, 4.33; P, 8.94; Cl, 5.12; Rh, 15.3.

The reaction between chlorotris(triphenylphosphine)rhodium(I) and hydrogen chloride.

$(Ph_3P)_3RhCl$ was even less soluble than $(Ph_3P)_2Rh(CO)Cl$ in liquid hydrogen chloride.

HCl (30 mmole) was condensed at -196^{o} into an 8 mm. o.d. quartz ampoule containing dark red crystalline $(Ph_3P)_3RhCl$ (0.060 g., 0.063 mmole). The ampoule was sealed and tested in the usual way, and at room temperature was observed to contain a clear orange liquid over a deep red liquid and some undissolved red crystals. A ^{31}P n.m.r. spectrum of the liquid phase was obtained only with great difficulty due to the low solubility of the starting material. Five peaks were observed, a doublet at -4 ± 0.5 p.p.m. with J_{P-H} of 510 Hz, another at -45 ± 0.5 p.p.m. with a J_{P-Rh} value of 133 Hz, and a singlet at -55 ± 0.5 p.p.m. The doublets may be assigned to Ph_3PH^+ and a triphenylphosphine-rhodium system respectively.

The reaction was repeated on a preparative scale.

HCl (200 mmole) was condensed at -196^{o} into a 13 mm. o.d. quartz ampoule which contained $(Ph_3P)_3RhCl$ (0.250 g., 0.26 mmole). The ampoule was sealed and carefully brought up to room temperature in the usual manner. A clear pale orange solution was obtained at room temperature, over a little undissolved starting material and some pale orange solid. Warming to 30^{o} affected complete solution and the formation of two liquid layers, the lower being the more intensely coloured. After 24 hours the appearance of the material inside the ampoule resembled that which obtained before warming to 30^{o}. The ampoule was cooled to -196^{o} and opened via the vacuum line to the spiral gauge. No deflection was produced, i.e. no noncondensable gas, in this case hydrogen, was present. HCl was removed by pumping at -95^{o}, followed by pumping at room temperature for 2 hours. The infrared spectrum of the orange solid product contained absorptions at 330 and 342 cm^{-1} which were not present in that of the starting material. These may possibly be Rh-Cl stretching frequencies. Absorptions at 1190, 1030 and 690cm^{-1} had decreased in intensity relative absorptions at the same frequencies in the spectrum of the starting material.

Found; C, 63.5; H, 3.63; P, 8.7; Cl, 14.2; Rh, 13.3.

Required for $Ph_3PH^+HCl_2^-$, $(Ph_3P)_2RhHCl_2$; C, 62.7; H, 4.64; P, 9.00; Cl, 13.7; Rh, 9.96.

Required for $(Ph_3P)_3RhCl$; C, 70.1; H, 4.87; P, 10.1; Cl, 3.84; Rh, 11.1.

The reaction between tricarbonyltriphenylphosphinecobalt(0) dimer and hydrogen chloride.

HCl (30 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing $[Co(CO)_3PPh_3]_2$ (0.010g., 0.012 mmole). The ampoule was sealed and tested in the usual manner. The chocolate brown solid appeared to be soluble at -84°, giving a clear yellow-brown solution at -45°. At room temperature the ampoule contained a pale blue solution over a pale blue precipitate. The solution became colourless at 34.2° and it was not possible to detect any signals when the ^{31}P n.m.r. spectrum was recorded.

The reaction was reported on a larger scale in order to obtain a sample of the precipitated solid for examination.

HCl (150 mmole) was condensed into a 13 mm. o.d. type B ampoule containing $[Co(CO)_3PPh_3]_2$ (0.785g., 0.97 mmole). The ampoule was sealed and allowed to reach 0° in the manner previously described. A clear deep red-brown solution was obtained at -45°, and at 0° the ampoule contained a green solid under a green solution. After 3 hours at this temperature, the solid was filtered off, becoming pale blue in colour. The ampoule was opened in the usual manner and after pumping at room temperature the solid product turned turquoise.

The infrared spectrum of the solid contained all the absorptions found in the spectrum of $(PPh_3)_2CoCl_2$ together with peaks at 2050w, 1995m, 1975m, 1955m, 1912m, 890 br.s 720s, 345w and 310w cm^{-1}. Found; C, 33.6, 37.2; H, 4.73, 5.69; P, 6.62; Cl, 32.5; Co, 24.7.

These analytical figures are clearly inaccurate, accounting for more than 100% of the composition of the material. The turquoise solid is certainly a mixture and was not investigated further.

4.5 Iron(0) complexes

Results and Discussion.

Iqbal and Waddington[56] have reported reactions of pentacarbonyliron in liquid hydrogen chloride at -95°. The carbonyl dissolved without evolution of gas giving a conducting solution. Conductiometric titrations against the Lewis acid boron trichloride gave an end-point at a 1:1 molar ratio, interpreted as probably indicating adduct formation as well as that of the salt $[Fe(CO)_5H]^+BCl_4^-$. An end-point at a molar ratio of 1:5:1, Lewis acid: pentacarbonyliron, was obtained when pentafluorophosphorus(V) was used as the Lewis acid. This clearly indicates the formation of the salt $[Fe(CO)_5H]^+PF_6^-$ since it is known[26] that hexafluorophosphate ion is quantitatively produced from PF_5 in basic liquid hydrogen chloride solutions according to the equation

$$3PF_5 + 2Cl^-_{solv.} \longrightarrow 2PF_6^- + PF_3Cl_2.$$

The salt was in fact isolated at low temperatures but decomposed fairly rapidly at room temperature. In both the salts protonation occurred on the iron atom. Attempts to prepare the tetrachloroborate salt gave a light yellow solid at low temperatures which dissociated very rapidly at room temperature to a viscous liquid.

In this work the protonation behaviour of the series $Fe(CO)_{5-x}(PPh_3)_x$ $(0 \leq x \leq 2)$ in liquid hydrogen chloride at room temperature was studied using ^{31}P and ^{11}B n.m.r. techniques where appropriate. Both tetracarbonyltriphenylphosphineiron(0) and tricarbonylbis(triphenylphosphine)iron(0) were soluble in liquid hydrogen chloride giving clear solutions at room temperature from which it was possible to recover the unchanged starting materials. The ^{31}P n.m.r. spectrum of $Fe(CO)_4PPh_3$

in liquid hydrogen chloride solution consisted of a sharp singlet at -48 ± 0.5 p.p.m. which may be assigned to a triphenylphosphine group bound to an iron atom. There was no sign of a doublet due to triphenylphosphonium ion in the origin of -5 p.p.m. and it may be assumed that the complex dissolves without dissociation of a triphenylphosphine ligand.

Two signals at -56.1 and -55.4 p.p.m. were observed in the ^{31}P n.m.r. spectrum of $Fe(CO)_3(PPh_3)_2$ in liquid hydrogen chloride. The signals were of equal intensities so that they resembled a doublet. A possible explanation is that the signals arise from the ion $[Fe(CO)_3(Ph_3P)_2H]^+$ and that this octahedral species contains two ^{31}P nuclei in chemically different environments, one triphenylphosphine being trans to a carbonyl group and the other trans to a hydrogen atom. (See Fig. 4.5.1).

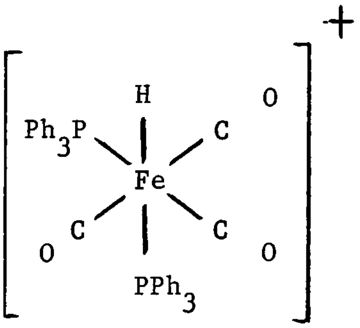


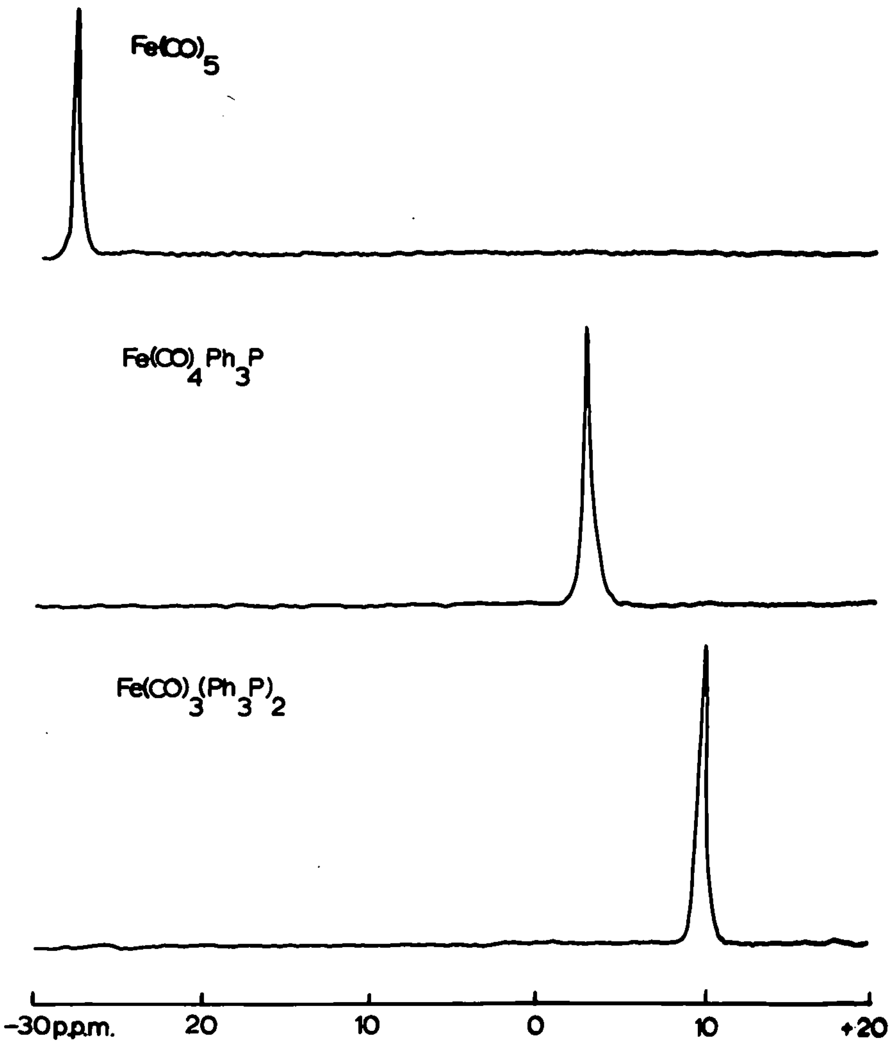
Fig. 4.5.1 A possible structure for the octahedral species $[Fe(CO)_3(Ph_3P)_2H]^+$.

The failure to observe phosphorus-hydrogen coupling may be due to a very rapid exchange of the proton with the solvent and/or the coupling constant $^2J_{P-Fe-H}$ may be unresolvably small.

Fig.4.5.2

^{11}B n.m.r. solution spectra

$Fe(CO)_{5-x}(Ph_3P)_2$ $(0 \leq x \leq 2)$ and BCl_3 in a 1:1 molar ratio in liquid hydrogen chloride


Fe(CO)5
Fe(CO)4Ph3P
Fe(CO)3(Ph3P)2
-30 p.p.m.
20
10
0
10
+20

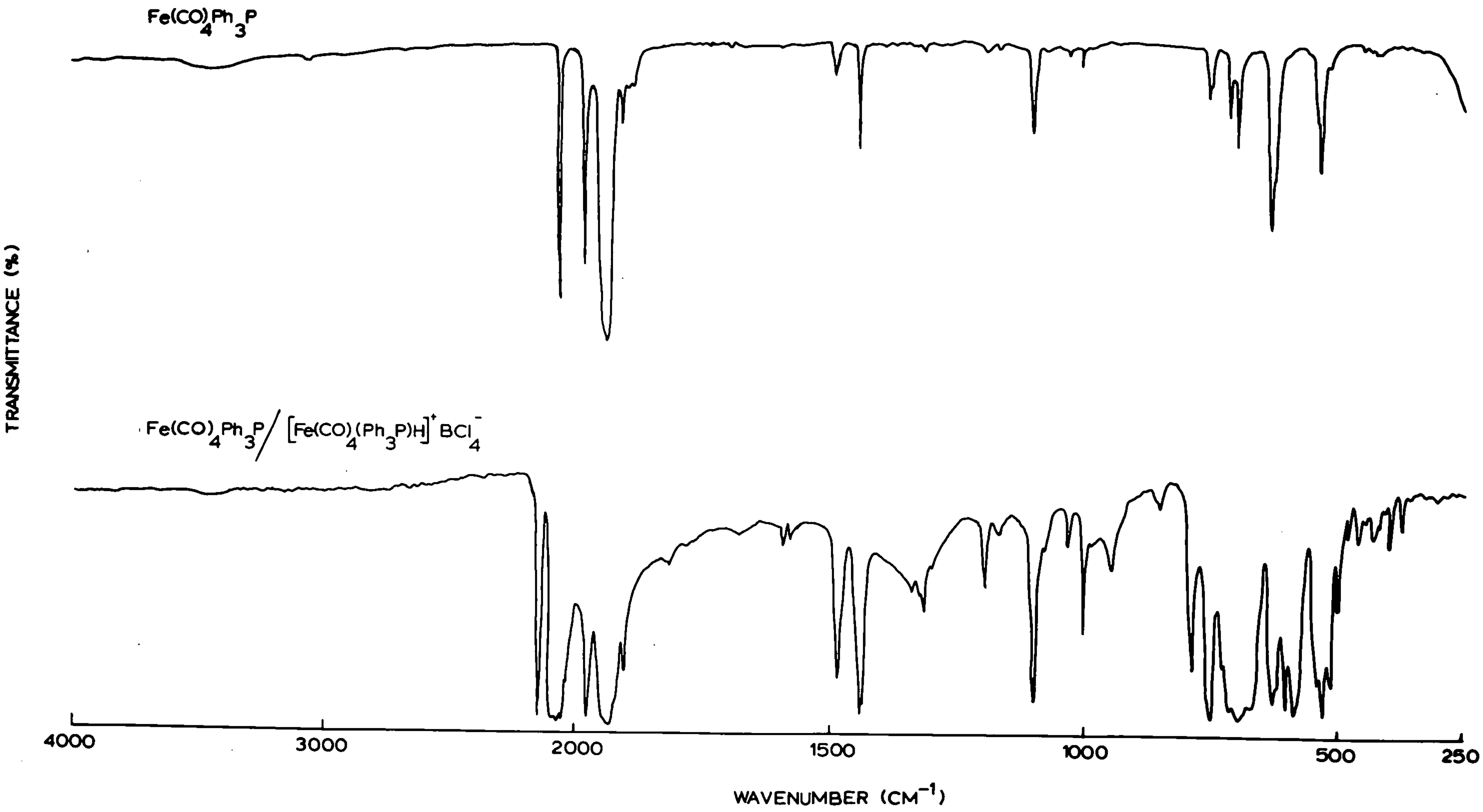
The ^{11}B n.m.r. spectra of liquid hydrogen chloride solutions of the series $Fe(CO)_{5-x}(PPh_3)_x$ $(0 \leq x \leq 2)$ and boron trichloride in 1:1 molar ratio are shown in figure 4.5.2. A clearly defined pattern of behaviour may be observed on examination of the ^{11}B chemical shifts. In all cases the spectra consist of sharp singlets which are readily assignable. The peak at -28 ± 0.5 p.p.m. in the spectrum from pentacarbonyliron(0) and boron trichloride is characteristic of boron trichloride itself.[125] There is no suggestion of an exchange averaged signal between the Lewis acid and tetrachloroborate ion and it may safely be assumed that none of the latter species are present. This would imply that pentacarbonyliron(0) is not protonated in liquid hydrogen chloride at room temperature and is in accord with the report made by earlier workers[56] who were unable to isolate a stable tetrachloroborate salt of the species $[Fe(CO)_5H]^+$ at room temperature.

The resonance at +2.5 p.p.m. in the spectrum of tetracarbonyltriphenylphosphineiron(0) and boron trichloride in the solvent is shown later in this work to be characteristic of a system with rapidly exchanging BCl_3 and BCl_4^- species. A singlet at -46.5 ± 0.5 p.p.m. was observed in the ^{31}P n.m.r. spectrum of this solution indicating that the triphenylphosphine ligand was still bound to the iron. These two results taken together may be interpreted as evidence for partial protonation of $Fe(CO)_4PPh_3$ in liquid hydrogen chloride at room temperature. Accordingly, a preparative scale experiment was carried out in an attempt to isolate a stable salt $[Fe(CO)_4(Ph_3P)H]^+BCl_4^-$. The infrared spectrum of the white solid product obtained is shown in figure 4.5.3. Davison et. al.[113] have assigned peaks at 2143 and 2075cm^{-1} in the infrared

Fig.4.5.3

Infrared Spectra

Tetracarbonyl(triphenylphosphine)iron(0) and solid product from reaction between tetracarbonyl(triphenylphosphine)iron(0) and boron trichloride in liquid hydrogen chloride


$Fe(CO)_4Ph_3P$
$Fe(CO)_4Ph_3P / [Fe(CO)_4(Ph_3P)H]^+ BCl_4^-$
TRANSMITTANCE (%)
4000
3000
2000
1500
1000
500
250
WAVENUMBER (CM^{-1})

spectrum of $Fe(CO)_4Ph_3P$ in a sulphuric acid film to carbonyl stretching frequencies in the protonated species $[Fe(CO)_4(Ph_3P)H]^+$. The strong absorptions at 2072 and $2044cm^{-1}$ in fig. 4.5.3 may thus be assigned to this species. Characteristic bands at 690 and $670cm^{-1}$ due to tetrachloroborate ions may also be discerned in a spectrum which clearly contains all absorptions found in that of the starting material. Analytical data confirmed that the white solid was a mixture of $Fe(CO)_4Ph_3P$ and $[Fe(CO)_4(Ph_3P)H]^+BCl_4^-$. The latter compound decomposed rapidly on exposure to the atmosphere, and slowly at room temperature even if stored under dry nitrogen.

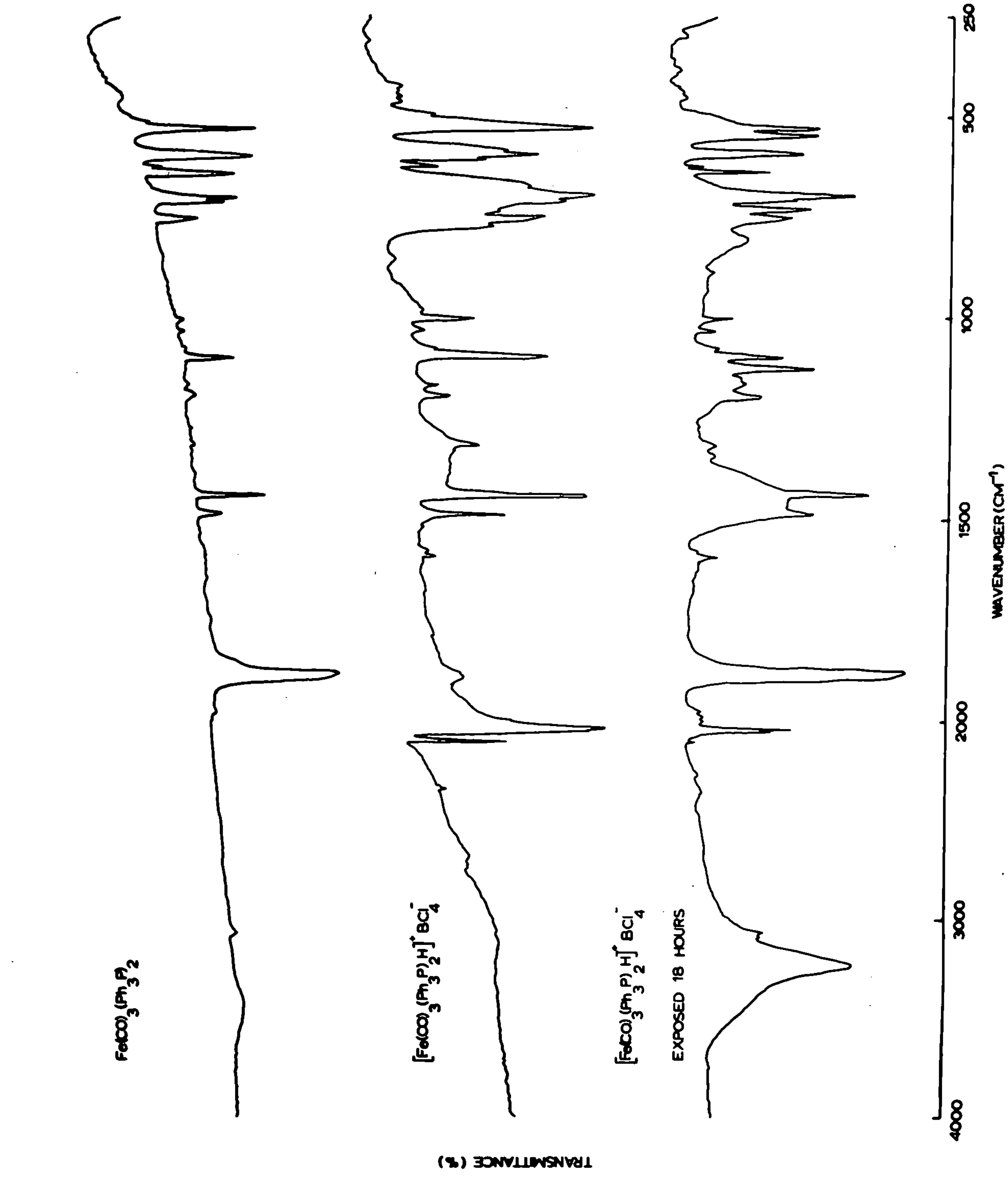
The ^{11}B n.m.r. spectrum of tricarbonylbis(triphenylphosphine)iron(0) and boron trichloride in liquid hydrogen chloride solution consisted of a sharp resonance at + 9.5 p.p.m. A ^{11}B chemical shift of + 11.6 p.p.m. for BCl_4^- has recently been reported[147] and has been determined in this work as + 10.8 p.p.m. The signal at + 9.5 p.p.m. may thus be assigned to BCl_4^-. However, the slightly low value may be due to some limited exchange with BCl_3 and this possibility cannot entirely be excluded. The ^{31}P n.m.r. spectrum of the same solution, like that of the iron compound alone in the solvent, consisted of two peaks, which may or may not be regarded as a doublet, at -55.8 and -55.0 p.p.m. Protonation of the iron atom is clearly inferred here from the observation of a tetrachloroborate chemical shift in the ^{11}B n.m.r. spectrum, and the ^{31}P n.m.r. signals could be regarded as arising from coupling between phosphorus and hydrogen atoms via the iron. If this were the case, then the magnitude of the coupling constant $^2J_{P-Fe-H}$ would be 19.4Hz.

A white solid product was isolated from a preparative scale reaction between $Fe(CO)_3(Ph_3P)_2$ and BCl_3 in liquid hydrogen chloride. Analytical data indicated that the compound was $[Fe(CO)_3(Ph_3P)_2H]^+BCl_4^-$. The

Fig.4.5.4

Infrared Spectra

Tricarbonylbis(triphenylphosphine)iron(0), hydridotricarbonylbis(triphenylphosphine)iron(0)tetrachloroborate and an exposed sample of hydridotricarbonylbis(triphenylphosphine)iron(0)tetrachloroborate


$Fe(CO)_3(Ph_3P)_2$
$[Fe(CO)_3(Ph_3P)_2H]^+ BCl_4^-$
$[Fe(CO)_3(Ph_3P)_2H]^+ BCl_4^-$
EXPOSED 18 HOURS
TRANSMITTANCE (%)
WAVENUMBER (CM^{-1})
4000
3000
2000
1500
1000
500
250

infrared spectrum, Nujol mull, of this material together with that of the parent compound is shown in fig. 4.5.4. Absorptions not found in the infrared spectrum of the starting material were observed at 2098m., 2056m.sh., 2044s., and 2030s, 1890w, 690s and 670s cm^{-1}. The latter two are characteristic of tetrachloroborate anions[20f, 163] and that at $1890cm^{-1}$ may be assigned to an Fe-H stretching frequency. The higher frequency absorptions are presumably carbonyl stretching frequencies. Davison et. al. have reported a strong absorptions at $2028cm^{-1}$ in the infrared spectrum obtained from a concentrated sulphuric acid mull of $Fe(CO)_3(Ph_3P)_2$ and have assigned this to the species $[Fe(CO)_3(Ph_3P)_2H]^+$. A very weak absorption at $1875cm^{-1}$, the position of the most intense band in the infrared spectrum of the starting material, indicates that the salt $[Fe(CO)_3(Ph_3P)_2H]^+BCl_4^-$ is not completely stable at room temperature. The compound appeared to remain unchanged if stored under dry nitrogen at -30^o. Exposure to the atmosphere resulted in rapid decomposition.

Thus of the series $Fe(CO)_{5-x}(Ph_3P)_x$ $(0 \leq x \leq 2)$, the most stable protonated species in liquid hydrogen chloride is that derived from $Fe(CO)_3(Ph_3P)_2$, and $[Fe(CO)_3(Ph_3P)_2H]^+BCl_4^-$ was the only salt which could be isolated as a stable solid at room temperature. The compound $[Fe(CO)_5H]^+PF_6^-$ has been isolated as a solid at room temperature[56], presumably because the hexafluorophosphate anion is a more effective counterion than the tetrachloroborate anion. It is anticipated that the salts $[Fe(CO)_4(Ph_3P)H]^+PF_6^-$ and $[Fe(CO)_3(Ph_3P)_2H]^+PF_6^-$ could be prepared and isolated in any future work, the reactions again being monitored using ^{31}P n.m.r. Also, should a variable temperature

^{11}B n.m.r. probe became available, the behaviour of the systems $Fe(CO)_{5-x}(Ph_3P)_x$ ($0 \leq x \leq 2$) and boron trichloride in liquid hydrogen chloride at temperatures below room temperature could be studied.

Ruthenium contains two magnetically active isotopes; ^{99}Ru with spin number of $^6/2$ and ^{101}Ru having nuclear spin $^5/2$, present in 12.81 and 16.98% abundance respectively.[106] No ^{31}P n.m.r. signals were observed when the spectrum of a saturated solution of dichlorodicarbonylbis(triphenylphosphine)ruthenium(II) in liquid hydrogen chloride was recorded. The ruthenium(II) compound recrystallised from the solvent at room temperature, and the failure to observe n.m.r. signals is probably due to the extremely low solubility of the material in the solvent.

Experimental.

The reaction between pentacarbonyliron(0) and boron trichloride

HCl (25 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing $Fe(CO)_5$ (0.474g., 2.42 mmole), followed by BCl_3 (0.283g., 2.42 mmole). The ampoule was sealed and tested in the usual manner. The ^{11}B n.m.r. spectrum of the clear yellow solution contained a single resonance at -28.5 ± 0.5 p.p.m. which may be immediately assigned to BCl_3.[125] It may thus be assumed that $Fe(CO)_5$ is not protonated in the presence of the Lewis Acid BCl_3 in liquid hydrogen chloride at 34.2°.

The behaviour of tetracarbonyltriphenylphosphineiron(0) in liquid hydrogen chloride.

HCl (25 mmole) was condensed at -196° into an 8mm. o.d. quartz ampoule containing $Fe(CO)_4Ph_3P$ (0.105g., 0.24 mmole). The ampoule was sealed and tested in the normal manner. A clear colourless solution was obtained at room temperature. The ^{31}P n.m.r. spectrum of the solution consisted of a single resonance at -48.0 ± 0.5 p.p.m. which is assigned to $Fe(CO)_4Ph_3P$. There was no sign of any signal associated with Ph_3PH^+ ions.

The experiment was repeated on a larger scale in order to examine the material obtained on removal of the solvent.

$Fe(CO)_4Ph_3P$ (0.437g., 1.02 mmole) was placed inside a 13 mm o.d. quartz ampoule of the type A described previously. HCl (150 mmole) was condensed into the ampoule at -196° whichwas then sealed and allowed to reach room temperature in the usual manner. The ampoule contained a clear faintly yellow solution at 20°. After 24 hours at room temperature the ampoule was cooled to -95 and opened to the vacuum line as described previously. The HCl was pumped off at -95°. A white solid, which turned yellow when the last of the HCl was removed, was precipitated. The solid was pumped at room temperature for 3 hours to remove any residual hydrogen chloride.

Carbonyl stretching frequencies were observed at 2050, 1976 and 1932 cm^{-1} in the infrared spectrum of the yellow solid. That of $Fe(CO)_4PPh_3$ contains absorptions at 2054, 1978 and 1934 cm^{-1}

Found: C,62.15; H, 3.4; Fe, 13.15; Required for $Fe(CO)_4Ph_3P$: C, 62.4; H, 3.8; Fe, 13.0.

The reaction between tetracarbonyltriphenylphosphineiron(0) and boron trichloride

$Fe(CO)_4Ph_3P$ (0.172 g., 0.40 mmole) was placed inside an 8 mm. o.d. quartz ampoule. HCl (25 mmole) was condensed into the ampoule at -196°, followed by BCl_3 (0.4 mmole). The ampoule was sealed and tested in the usual manner, and was observed to contain two clear liquid layers at room temperature; the lower being yellow and the upper colourless. The ^{31}P n.m.r. spectrum of the solution contained a resonance at -46.5 ± 0.5 p.p.m., and a signal at +2.5 p.p.m. was observed in the ^{11}B n.m.r. solution spectrum. The ^{11}B resonance is shown later in this work to be characteristic of a system containing exchanging BCl_3 and BCl_4^- species.

The reaction was repeated on a preparative scale. $Fe(CO)_4Ph_3P$ (1.395 g., 3.20 mmole) was placed inside a 13 mm. o.d. quartz ampoule. HCl (120 mmole) was condensed into the ampoule at -196^o, followed by BCl_3 (0.380 g., 3.23 mmole). The ampoule was sealed and allowed to reach room temperature in the usual manner. A clear yellow solution was obtained at room temperature. After 24 hours the ampoule was cooled to -95^o and opened to the vacuum line. HCl was removed by pumping at this temperature, and excess BCl_3 was similarly removed at room temperature over a period of 30 minutes. The infrared spectrum of the white solid product, shown in Figure 4.5.3, contained absorptions characteristic of the starting material together with new peaks at 2072(s), 2044(s), 690(s) and 670(s) cm^{-1}. The two high frequency absorptions may be assigned to carbonyl stretching frequencies in the species $[Fe(CO)_4(Ph_3P)H]^+$,[113] and the low frequency bands to BCl_4^-.[20f,163]

Found: C, 47.4; H, 4.6; P, 5.7; Cl, 19.5.

Calculated for $[Fe(CO)_4(Ph_3P)H]^+BCl_4^-$; C, 45.2; H, 2.74; P, 5.31; Cl, 24.3.

Calculated for $Fe(CO)_4Ph_3P$: C, 61.5; H, 3.5; P, 7.21.

The white solid was kept under dry nitrogen at room temperature for 72 hours and the infrared spectrum was again recorded. The absorptions at 2072, 2044, 690 and 670 cm^{-1} were still present but were much reduced in intensity. Exposure of a fresh sample of the white solid to the atmosphere caused rapid and complete disappearance of these bands.

The behaviour of tricarbonylbis(triphenylphosphine)iron(0) in liquid hydrogen chloride

HCl (25 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing $Fe(CO)_3(PPh_3)_2$ (0.120 g., 0.181 mmole). The ampoule was sealed and tested in the normal manner and contained a yellow solution at room temperature. The ^{31}P n.m.r. spectrum contained two signals at -56.1, and -55.4 p.p.m.

The reaction was repeated on a larger scale.

HCl (120 mmole) was condensed into a 13 mm. o.d. quartz ampoule at -196° which contained $Fe(CO)_3(PPh_3)_2$ (0.51 g., 0.76 mmole). The ampoule was sealed and allowed to reach room temperature in the usual manner. A clear pale yellow solution was obtained. After 24 hours at room temperature the ampoule was cooled to -95°, opened to the vacuum line and pumped to remove hydrogen chloride. Again, a white solid precipitated and became yellow when all the HCl was removed. The infrared spectrum of the yellow solid was identical to that of the starting material.

Found: C, 69.6; H, 4.35; Fe, 8.77;

Calculated for $Fe(CO)_3(PPh_3)_2$: C, 70.6; H, 4.6; Fe, 8.43.

The reaction between tricarbonylbis(triphenylphosphine)iron(0) and boron trichloride

$Fe(CO)_3(PPh_3)_2$ (0.170 g., 0.256 mmole) was placed inside an 8 mm. o.d. quartz ampoule. HCl (25 mmole) was condensed into the ampoule at -196°, followed by BCl_3 (0.256 mmole). The ampoule was sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the clear yellow solution contained two signals at -55.8 and -55 p.p.m. A peak at +9.5 p.p.m. was observed when the ^{11}B n.m.r. spectrum was recorded, and may be assigned to the BCl_4^- ion. Some slight exchange with BCl_3 cannot be ruled out as the literature value for the ^{11}B shift of BCl_4 is +11.6 p.p.m.[147] The presence of BCl_4^- ion and the absence of Ph_3PH^+ indicated that the iron was probably protonated.

The reaction was repeated on a preparative scale.

$Fe(CO)_3(Ph_3P)_2$ (0.910 g., 1.37 mmole) was placed inside a 13 mm. o.d. quartz ampoule. HCl (120 mmole) was condensed into the ampoule at -196°, followed by BCl_3 (0.678 g., 5.7 mmole). The ampoule was sealed and allowed to warm to room temperature in the manner previously described. A clear yellow solution was obtained at room temperature. After 48 hours the ampoule was cooled to -95° and opened to the vacuum line. HCl was removed by pumping at -95° and excess BCl_3 was similarly removed at room temperature over a period of 3 hours. The infrared spectrum of the pale yellow solid product contained, in addition to those due to Ph_3P, absorptions at 2098m, 2056msh, 2044s, 2030s and 1875 vw cm^{-1} in the $\nu_{C=O}$ region and a broad absorption with maxima at 690s and 670sh cm^{-1} which may be assigned to BCl_4^-.[20f,163] The absorption at 1875 cm^{-1} may be assigned to $Fe(CO)_3(PPh_3)_2$. A very weak absorption at 1890 cm^{-1}, possibly due to an Fe-H stretching mode was also present.

Found: C, 57.7; H, 3.85; P, 7.47; Cl, 18.5; Fe, 7.25.

Calculated for $[Fe(CO)_3(Ph_3P)_2H]^+BCl_4^-$: C, 57.2; H, 3.78; P, 7.58; Cl, 17.36; Fe, 6.84.

The compound was stored under nitrogen at -30° and appeared to be quite stable under these conditions. On exposure to air the substance readily decomposed; presumably to $Fe(CO)_3(Ph_3P)_2$, HCl and H_3BO_3. The infrared spectrum of a sample of the compound exposed to air was recorded at intervals and showed the following general trends; a broad band appeared at 3220 cm^{-1}, the ν_{CO} bands above 2000 cm^{-1} decreased in intensity relative to the band at 1878 cm^{-1} which rapidly gained in intensity, a broad band appeared around 1450 cm^{-1}, and the B-Cl absorptions in the 690 cm^{-1} region decreased in intensity. These changes may be assigned to an O-H absorption,[224] the decomposition of the protonated species and the reformation of $Fe(CO)_3(PPh_3)_2$, the presence of B-O bands,[225] and the hydrolysis of the BCl_4^- ion respectively. The variation of the infrared spectrum of the exposed material with time is shown in Fig.4.5.4.

The behaviour of dichlorodicarbonylbis(triphenylphosphine)ruthenium(II) in liquid hydrogen chloride

HCl was condensed at -196° into an 8 mm. o.d. quartz ampoule containing $(Ph_3P)_2(CO)_2RuCl_2$ (0.034 g., 0.045 mmole). The ampoule was sealed and tested in the usual manner. The white powdery starting material dissolved and white glassy crystals under a clear colourless solution were present at room temperature. No signal was observed when the ^{31}P n.m.r. spectrum of the solution was recorded.

The reaction was repeated on a larger scale in order to obtain a sample of the white glassy crystalline solid for investigation.

HCl (140 mmole) was condensed at -196° into a 13 mm. o.d. quartz ampoule of type B containing $(Ph_3P)_2(CO)_2RuCl_2$ (0.655 g., 0.871 mmole). The ampoule was sealed and warmed to room temperature in the normal manner. After 18 hours at room temperature the white glassy crystals were filtered off from the clear colourless solution as previously described. The infrared spectrum of the product was identical to that of the starting material.

Found: C, 59.6; H, 4.71;

Calculated for $(Ph_3P)_2(CO)_2RuCl_2$: C, 60.6; H, 3.99.

4.6 Gold(I) and Copper(I) Complexes

Chlorotriphenylphosphinegold(I) is very soluble in both liquid hydrogen chloride and in dichloromethane giving clear colourless solutions at room temperature. ^{31}P n.m.r. chemical shift values of -32.5 p.p.m. were obtained from solutions of the complex in these solvents. It is assumed that chlorotriphenylphosphinegold(I) dissolves in liquid hydrogen chloride without reaction. A ^{11}B chemical shift of -18 p.p.m. was observed when the n.m.r. spectrum of chlorotriphenylphosphinegold(I) and boron trichloride in 1:1 molar ratio in the solvent was recorded. This signal may be interpreted as an exchange averaged signal arising from exchange between boron trichloride and tetrachloroborate ion. Existence of the latter species implies protonation of the gold complex. The ^{31}P n.m.r. spectrum of this solution consisted of a sharp singlet at -31 $\pm$ 0.5 p.p.m. A slight upfield shift of the phosphorus signal was observed on protonation of $Fe(CO)_3(Ph_3P)_2$ in liquid hydrogen chloride in the presence of boron trichloride (see p.173). However, only starting material was isolated from mixtures of chlorotriphenylphosphinegold(I) and boron trichloride in liquid hydrogen chloride.

Chlorotris(triphenylphosphine)copper(I) dissolved in liquid hydrogen chloride at room temperature giving a pale yellow solution over a small quantity of white solid. The sole ^{31}P n.m.r. signal from this solution was a 1:1 doublet at -4.5 p.p.m. with $^{1}J_{^{31}P-^{1}H}$ 510 Hz which is immediately assignable to the triphenylphosphonium cation. Spin-spin coupling between ^{31}P and ^{63}Cu nuclei in cationic phosphite complexes of the type $[Cu(P(OMe)_3)_4]^+ClO_4^-$ has been observed.[226] The authors reported a broad four line pattern with a $^{1}J_{^{31}P-^{63}Cu}$ coupling constant of magnitude

1190 ± 30 Hz. No evidence for phosphorus-copper spin-spin coupling was found in this work. The behaviour of chlorotris(triphenylphosphine)-copper(I) in liquid hydrogen chloride may be described as dissociation of the triphenylphosphine ligands, followed by protonation to give triphenylphosphonium ions. It is thus possible that the white solid material at the base of the n.m.r. tube was copper(I) chloride. Only the signal due to triphenylphosphine, ^{31}P chemical shift +6.0 p.p.m., literature value +5.9 p.p.m.[134,135] was observed when the ^{31}P n.m.r. spectrum of a saturated solution of $(Ph_3P)_3CuCl$ in chloroform was recorded. Again, dissociation of the triphenylphosphine ligands has occurred.

Experimental

The behaviour of chlorotriphenylphosphinegold(I) in liquid hydrogen chloride

HCl (25 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing Ph_3PAuCl (0.128 g., 0.259 mmole). The ampoule was sealed and tested in the usual manner. Ph_3PAuCl is very soluble in liquid hydrogen chloride, a clear colourless solution being formed at -78°. The ^{31}P n.m.r. spectrum of this solution consisted of a sharp singlet at -32.5 p.p.m.

The ^{31}P n.m.r. spectrum of chlorotriphenylphosphinegold(I) in dichloromethane

Ph_3PAuCl is very soluble in CH_2Cl_2 at room temperature. The ^{31}P n.m.r. spectrum of a saturated solution of Ph_3PAuCl in CH_2Cl_2 consisted of a sharp singlet at -32.5 p.p.m. Thus Ph_3PAuCl may be assumed to be soluble in liquid hydrogen chloride without reaction.

The reaction between chlorotriphenylphosphinegold(I) and boron trichloride

HCl (30 mmole) followed by BCl_3 (0.73 mmole) were condensed at -196° into an 8 mm. o.d. quartz ampoule containing Ph_3PAuCl (0.360 g., 0.728 mmole). The ampoule was sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the clear colourless solution consisted of a sharp singlet at -31.0 ± 0.5 p.p.m. and the ^{11}B n.m.r. spectrum contained a single sharp resonance at -18 p.p.m. The latter values lies between those for BCl_3 and BCl_4^-, -29 and +11.6 p.p.m. respectively,[126,147] and is assigned to an exchange averaged signal arising from a rapid exchange process involving these two species. The formation of BCl_4^-, however transient, in liquid hydrogen chloride solution implies that protonation, to some extent, is occurring, possibly of the gold atom in Ph_3PAuCl.

The reaction was repeated on a larger scale.

HCl (70 mmole) followed by BCl_3 (1.5 mmole) was condensed at -196° into a 13 mm. o.d. ampoule containing Ph_3PAuCl (0.684 g., 1.38 mmole). The ampoule was sealed and placed in a dry ice/acetone bath. A clear colourless solution was obtained. 12 hours were allowed for equilibration, then the ampoule was cooled to -95° and opened to the vacuum line. HCl and BCl_3 were removed by pumping at -95° until no liquid remained, followed by 30 minutes evacuation at -84°. The infrared spectrum of the white solid product was identical to that of the starting material, and to a published spectrum of Ph_3PAuCl.[227] Absorptions at 995, 956 and 471 cm^{-1} and at 690 and 660 cm^{-1} due to BCl_3[204,228] and BCl_4^-[20f,163] respectively were totally absent. This reaction was not investigated further.

The behaviour of chlorotris(triphenylphosphine)copper(I) in liquid hydrogen chloride

HCl (30 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule containing $(Ph_3P)_3CuCl$ (0.107 g., 0.121 mmole). The ampoule was sealed and tested in the normal manner. At room temperature a clear very pale yellow solution over a small quantity of white solid was obtained. A 1:1 doublet at -4.5 p.p.m. with $^1J_{P-H}$ 510 Hz, which may be immediately assigned to Ph_3PH^+, could be seen on a single scan when the ^{31}P n.m.r. spectrum of the solution was recorded. Overnight CAT runs, with the field offset to exclude the Ph_3PH^+ signal, failed to detect any ^{63}Cu-^{31}P coupling.

The ^{31}P n.m.r. spectrum of chlorotris(triphenylphosphine)copper(I) in chloroform

The ^{31}P n.m.r. spectrum of a saturated solution of $(Ph_3P)_3CuCl$ in $CHCl_3$ consisted of a sharp singlet at +6 p.p.m., which may be immediately assigned to Ph_3P.[134,135] Again, no trace of Cu-P coupling could be observed.

$(Ph_3P)_3CuCl$ was not studied further.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The application of ^{31}P n.m.r. spectroscopy to the study of the oxidation and exchange reactions of simple phosphorus(III) compounds in liquid hydrogen chloride at room temperature has provided clear and unequivocal evidence for the course of reactions and identification of products. Only in the case of iodine containing phosphorus compounds are there difficulties in interpreting the observed ^{31}P n.m.r. spectra. Clearly, much work has yet to be done in this area before the behaviour of phosphorus-iodine compounds in liquid hydrogen chloride may be understood.

Mixed bromochlorophosphonium ions were produced by the oxidation of phosphorus(III) bromide or phosphorus(III) chloride in the presence of a boron trihalide in both liquid hydrogen chloride and liquid hydrogen bromide solutions. Attempts to generate mixed halophosphonium cations containing iodine failed, yet there seems to be no great inherent reason why such ions should not be capable of existence. The difficulties of working with liquid hydrogen iodide as a solvent are well known, and the phosphorus-iodine bond appears to be susceptible to solvolysis in liquid hydrogen chloride. Thus, the possibility of stabilising ions of the type $PI_{4-y}X_y^+$ (X = halogen, $0 \leq y \leq 4$) from mixtures of PI_3, X_2 and BX_3 in liquid hydrogen halide solution would seem to have more chance of success using liquid hydrogen bromide as solvent. The use of a variable temperature ^{31}P n.m.r. probe would obviously be of value in these studies.

Gore's conclusion that "Liquid hydrogen chloride has but a feeble solvent power for solid bodies in general" is certainly true for transition metal complexes at -95°. Working at room temperature is essential in many cases in order that solution of the complexes may be effected. The established low temperature techniques of conductiometric titration and weight analysis cannot be applied to reactions at room temperature and other physical techniques e.g. n.m.r. measurements are essential if reactions are to be followed. Even at room temperature many of the transition metal complexes were at best only poorly soluble, such that saturated solutions required spectrum accumulation in excess of 500 scans before a satisfactory ^{31}P n.m.r. spectrum could be recorded. It was observed that tetrakis(triphenylphosphine)platinum(0) was much more soluble in liquid hydrogen bromide at -84° than in liquid hydrogen chloride at the same temperature. If this is a general trend then liquid hydrogen bromide would clearly be a preferable solvent. Also, the vapour pressure of hydrogen bromide at room temperature is approximately half that of hydrogen chloride and on this basis would be a relatively "safer" solvent for room temperature use.

APPENDIX I

THE BEHAVIOUR OF SOME PHOSPHORYL COMPOUNDS IN LIQUID HYDROGEN CHLORIDE AS STUDIED BY ^{31}P N.M.R.

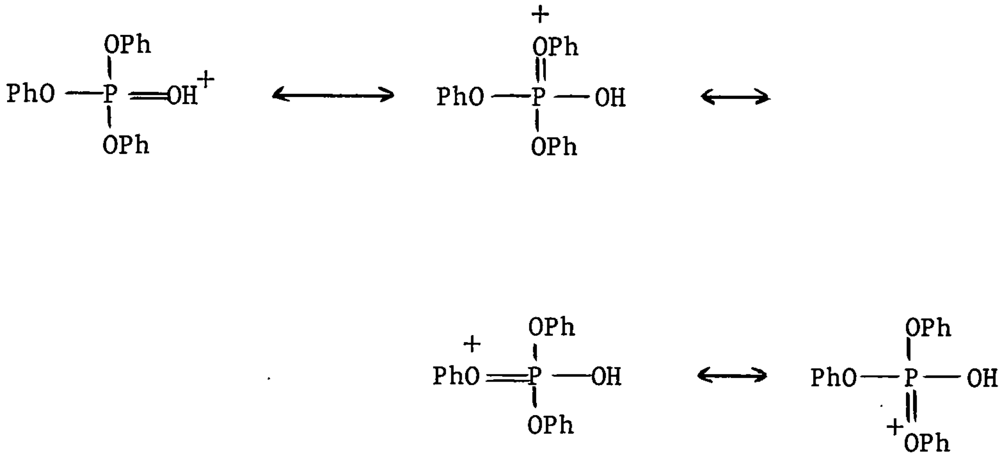
Evidence for the protonation of compounds containing the phosphoryl (P=O) group in acidic solvents has been obtained by many investigators.[103,230,233,234,235,236,237,238,239,240.] The results of conductivity measurements on solutions of triphenylphosphate in sulphuric acid have been explained in terms of protonation.[233] Gillespie et. al. deduced that triethyl phosphate is protonated in sulphuric acid solution from cryoscopic and conductivity data,[234] but that phosphoryl fluoride is not. Similar evidence for the protonation of phosphoryl chloride was reported by Paul et. al.[235]

Nuclear magnetic resonance methods have been used extensively in recent studies.[103,230,236,237,238,239,240.] Moedritzer observed ^{31}P chemical shift changes on addition of hydrochloric and perchloric acids to aqueous solutions of phosphoric and phosphonic acid derivatives.[236] Other workers have investigated protonation in systems containing hydrogen bonded directly to phosphorus by measuring $^{1}J_{P-H}$.[230,237.] Dillon and Waddington have studied by ^{31}P n.m.r. the behaviour of several inorganic phosphates in sulphuric acid, chlorosulphuric acid, and oleum solutions with varying sulphur trioxide content.[238] Recently Olah and McFarland have examined the protonation of several phosphorus compounds in fluorosulphuric acid and in fluorosulphuric acid - antimony pentafluoride solutions, using both ^{1}H and ^{31}P n.m.r.[239] Their results show that the phosphoryl compounds studied are invariably protonated at the phosphoryl oxygen, but that the ^{31}P chemical shift difference between a protonated trialkyl or -aryl phosphate and its non-protonated form is very small. Larger shift differences are observed in dialkyl phosphonates. The literature also contains chemical shift values for triphenylphosphine oxide, and its salts with hydrogen chloride and hydrogen bromide,[103] where protonation of the phosphoryl oxygen is expected.

Very recently Dillon and Waddington have investigated by means of ^{31}P n.m.r. the behaviour of some phosphoryl compounds in 100% sulphuric acid, oleum with 20% sulphur trioxide, and chlorosulphuric acid as solvents.[240] A few spectra were also recorded in oleum with 65% sulphur trioxide. With some compounds containing aryl substituents, sulphonation as well as protonation was found to occur. These workers concluded that protonation took place at the phosphoryl oxygen in all the compounds studied. In general, downfield movements of ^{31}P chemical shifts were observed on protonation. The shift differences are small in cases where phosphorus is attached to several oxygen atoms since extensive delocalisation of the positive charge is possible. Where delocalisation can take place to only a limited extent the shift differences are much larger.

In this work the ^{31}P n.m.r. spectra of a range of phosphoryl compounds in liquid hydrogen chloride solution at room temperature were recorded for two reasons. Firstly, to obtain some measure of the "acidity", or strength as a proton-donor, of liquid hydrogen chloride at room temperature by comparing the magnitude of the shift difference on protonation with those observed in other solvents for a particular phosphoryl compound. Secondly, to see whether the general trends in displacement of ^{31}P chemical shifts on protonation in acidic room temperature solvents were followed in liquid hydrogen chloride. The results are shown in table 5.1.1. ^{31}P n.m.r. chemical shifts for the parent compounds are taken from ref. 103 unless otherwise indicated and the difference Δ between δ^{31}P values for the protonated and parent species is shown in the fourth column of the table.

In agreement with earlier results the chemical shift differences are small for compounds such as triphenylphosphate where the positive charge produced by protonation can be delocalised from the phosphorus to oxygen. This may be explained using a valence bond approach in terms of contributions from phosphoryl-like structures as shown below. Alternatively, an explanation in terms of molecular orbital theory would require the donation of non-bonded electron pairs on the oxygen to vacant d-orbitals on the phosphorus with the formation of $d\pi$-$p\pi$ bonds.[239,240]



Much larger differences are observed when only limited delocalisation can take place as in the case of triphenylphosphine oxide.

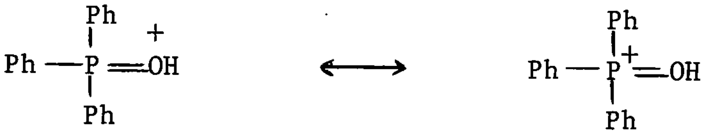
TABLE 5.1.1

^{31}P chemical shift values for some phosphoryl compounds and triphenylphosphine sulphide in liquid hydrogen chloride solution

(Chemical shifts in p.p.m. relative to 85% H_3PO_4)

Compound	Chemical Shifts		Δ
	in liquid hydrogen chloride	Parent species lit. values (103)	
$OPCl_3$	-9.1	-2.2	-6.9
$OPCl_2Ph$	-41.1	-34	-7.1
$OPClPh_2$		-42.7	
$OPPh_3$	-55.5	-25	-30.5
$OPPh_3$	-55.5	-25	-30.5
$OPPh_2OH$	-48	-25	-23
$OPPh(OH)_2$	-26.3	-18	-8.3
$OP(OH)_3$	+0.75	0	+0.75
$OPCl_3$	-9.1	-2.2	-6.9
$OPCl_2(OPh)$	-5.9	-1.5, -1.8	-4.3
$OPCl(OPh)_2$	+3.6	+6.2	-2.6
$OP(OPh)_3$	+18.2	+17.9 *	+0.3
$OP(OPh)_3$	+18.2	+17.9 *	+0.3
$OP(OPh)_2(OH)$	+12.65	+9.4	+3.25
$OP(OPh)(OH)_2$	+5.6	+4.6	+1.0
$OP(OH)_3$	+0.75	0	+0.75
$OP(OMe)_3$	-0.7	-2.1	+1.4
$OPPh_3$	-55.5	-25	-30.5
$SPPh_3$	-42.5	-43	+0.5

* reference 239.



Further evidence is provided by the shift differences produced by protonation of $OPCl_3$ and $OP(OPh)_3$. The displacement of - 6.9 p.p.m. for $OPCl_3$ is significantly larger than that of + 0.75 p.p.m. for $OP(OPh)_3$. Although the electronegativities of chlorine atoms and phenoxy groups are similar, in the former case delocalisation, by the above mechanism, of the positive charge produced by protonation is not possible.

It is also seen that although chemical shifts are usually displaced downfield on protonation of the phosphoryl compound, in cases where extensive delocalisation of the positive charge is possible e.g. in the series $P(OPh)_{4-x}(OH)_x^+$ $(1 \leq x \leq 4)$, the observed displacements are upfield. Other workers have reported slight downfield shifts of the order of 2 p.p.m. when $OP(OH)_3$ is protonated[239,240] and it is possible that the slight upfield shift in liquid hydrogen chloride is due to the different diamagnetic susceptibilities of the solvents.

Because diphenylphosphinic chloride, $OPClPh_2$, was not available the ^{31}P n.m.r. spectrum of the material in liquid hydrogen chloride could not be recorded. However, ^{31}P n.m.r. data for the other members of the series $OPCl_{3-x}Ph_x$ $(0 \leq x \leq 3)$ in the solvent was obtained. An examination of Δ values in table 5.1.1, (Δ being the displacement of the ^{31}P shift of the parent species on protonation), enables an estimate to be made of the ^{31}P chemical shift of protonated diphenylphosphinic chloride in the solvent. Taking a Δ value of -18 p.p.m. would give a ^{31}P shift of -60.7 p.p.m.

Note added in proof. The ^{31}P chemical shift of this compound in liquid hydrogen chloride has since been determined as -61.0 ± 0.1 p.p.m.[240]

The displacements of ^{31}P chemical shifts of some phosphoryl compounds on protonation in liquid hydrogen chloride solution and in several other non-aqueous acidic room temperature solvents are shown in table 5.1.2. If the observed ^{31}P resonance is regarded as an exchange-averaged signal between protonated and non-protonated species and the most downfield signal is assumed to be that of the protonated species alone, then some indication of the proton-donor strength or "acidity" of the solvent can be obtained. Only phosphoryl chloride and triphenylphosphine oxide of the compounds shown in table 5.1.2 give, for reasons already discussed, large downfield shifts on protonation.

In the case of phosphoryl chloride the order of increasing acidity, beginning with the least acidic solvent, would appear to be; liquid hydrogen chloride, 100% sulphuric acid, chlorosulphuric acid, 20% oleum and 65% oleum. At first sight it may appear that this order is not paralleled in the case of triphenylphosphine oxide. However, the shift differences in 100% H_2SO_4, 20% oleum and chlorosulphuric acid all lie within 1.8 p.p.m., a variation which could be accounted for by diamagnetic solvent susceptibility changes. It seems more likely that triphenylphosphine oxide, a much stronger base than phosphoryl chloride

TABLE 5.1.2

Displacement of ^{31}P chemical shift values of some phosphoryl compounds in acidic solvents

(displacements in p.p.m.)

Compound	$\delta\ ^{31}P$ protonated species - $\delta\ ^{31}P$ parent compound					
	Liq. HCl	100% H_2SO_4 Ref.240	20 oleum Ref.240	65 oleum Ref.240	$ClSO_2OH$ Ref.240	FSO_2OH Ref.239
$OPCl_3$	-6.9	-20.2	-34.8	-43	-22	
$OPPh_3$	-30.5	-35.5	-34		-35.8	
$OP(OH)_3$	+0.75					-2.3
$OP(OPh)_3$	+0.3	-2.4 +4.5 *	+2.9 *		+5.1 *	
$OP(OPh)_2(OH)$	+3.25	+2.9	+2.9		+3.8	
$OP(OPh)(OH)_2$	+1.0	+0.3	+1.8		+0.7	
$OP(OMe)_3$	+1.4	-0.5	-0.7	+5.9s +10.7w	0	+0.3

* fully sulphonated species, s = strong, w = weak

is completely protonated in all three solvents, liquid hydrogen chloride again being less "acidic". This is supported by literature values for the ^{31}P chemical shift of triphenylphosphine oxide in aqueous hydrochloric and hydrobromic acids.[103] Downfield displacements of -18.7 and -28.8 p.p.m. respectively are reported. Thus, the acidic solvents may be placed in order of "acidity", beginning with the least "acidic",

$$\text{aq. HCl} < \text{aq.HBr} \leq \text{liq.HCl} < 100\%\ H_2SO_4 < ClSO_2OH < 20\%\ \text{oleum} < 65\%\ \text{oleum.}$$

It is interesting to compare the behaviour of triphenylphosphine oxide and triphenylphosphine sulphide in the solvent. Both are freely soluble at room temperature giving clear colourless solutions. The ^{31}P chemical shift of Ph_3PO is moved 30.5 p.p.m. downfield indicating almost complete protonation, whereas that of Ph_3PS moves 0.5 p.p.m. upfield suggesting that protonation has taken place only to a very limited extent, if at all.

Experimental.

The phosphorus compounds used in this study were supplied by Dr K.B. Dillon. They were of the highest available grade of purity and were used without further purification. Phenyl phosphate was supplied as phenyl phosphate disodium salt. Samples were prepared and ^{31}P n.m.r. spectra recorded as described earlier in this work.

Oxidation reactions of white phosphorus in liquid hydrogen chloride solution.

The ^{31}P chemical shift of white phosphorus in liquid hydrogen chloride solution was + 518 ± 2 p.p.m. White phosphorus is only slightly soluble in the solvent at room temperature and this value was determined using a saturated solution. It may be seen that the observed chemical shift is in good agreement with published data for the shift of white phosphorus in other solvents.

Table 5.1.3

^{31}P Chemical shifts of white phosphorus in various solvents.[241]

(Chemical shifts in p.p.m. relative to 85% H_3PO_4)

Solvent	^{31}P Chemical Shift
CCl_4	+ 519[242]
$CHCl_3$	+ 521
CH_2Cl_2	+ 528
$CHClCCl_2$	+ 526
C_6H_{14}	+ 530
CS_2	+ 509[242]

The ^{31}P chemical shift of solid white phosphorus was determined as + 463 ± 2 p.p.m. which is in excellent agreement with the published value of + 460 p.p.m.[242] However, the observed shift of + 481 ± 2 p.p.m. for white phosphorus in carbon disulphide solution is below that reported by Heckmann and Fluck.[242]

White phosphorus was treated with the oxidising agent chlorine in a molar ratio P_4: Cl_2 of 1:2 in liquid hydrogen chloride solution. The ^{31}P n.m.r. spectrum contained two resonances at - 219.5 and + 522 p.p.m. which may be assigned to PCl_3 and P_4 respectively. The reaction was repeated using a molar ratio P_4: Cl_2 of 1:6. The sole resonance in the ^{31}P n.m.r. spectrum occurred at -220.2 p.p.m. and is immediately assignable to PCl_3.[134]

The ^{31}P n.m.r. spectrum of solid red phosphorus was recorded and is shown in fig. 5.1.1. Two maxima at -8 and +3 p.p.m. are superimposed on a very broad peak.

Experimental.

The reaction between white phosphorus and chlorine

(a) in 1:2 molar ratio

White phosphorus was cut into small pieces under distilled water, then washed in diethyl ether and pumped on the vacuum line for 2 hours to remove traces of ether.

HCl (30 mmole) followed by Cl_2 (1.74 mmole) was condensed at -196^o into an 8 mm. o.d. quartz ampoule containing P_4 (0.110g., 0.77mmole). The ampoule was sealed and tested as previously described. The ^{31}P n.m.r. spectrum of the colourless solution contained two signals at -219.5 and + 522 p.p.m.

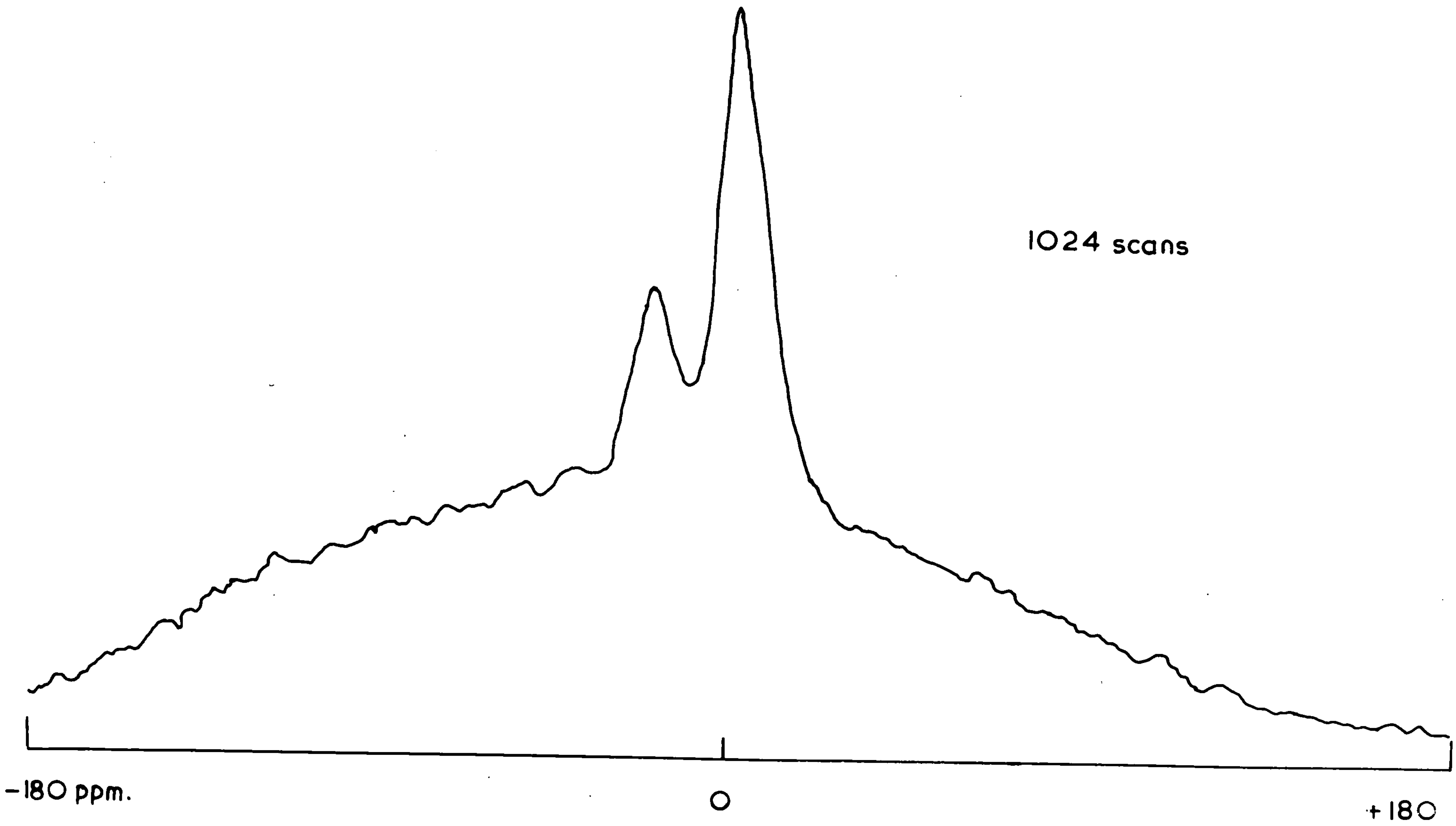
(b) <u>in 1:6 molar ratio</u>

HCl (30 mmole) followed by Cl_2 (7.8 mmole) was condensed at -196^o into an 8 mm. o.d. quartz ampoule containing P_4 (0.160g., 1.29 mmole). The ampoule was sealed and tested in the usual manner. The ^{31}P n.m.r. spectrum of the solution contained a single resonance at -220.2 p.p.m.

Fig.5.1.1

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

Red phosphorus


1024 scans
-180 ppm.
0
+180

APPENDIX II

A ^{11}B N.M.R. STUDY OF BORON TRIHALIDES AND TETRAHALOBORATE ANIONS IN LIQUID HYDROGEN CHLORIDE

The boron trihalides have been extensively used as Lewis acids in liquid hydrogen halide solvent systems.[20e,21,22,23,25,27,28,58,243]. Salts containing the tetrachloroborate and trichlorofluoroborate anions have been isolated from liquid hydrogen chloride, and tetrabromoborates and tetraiodoborates from the liquid hydrogen bromide and iodide systems respectively.

In this work the behaviour of the boron trihalides in liquid hydrogen chloride solution at room temperature was studied using ^{11}B n.m.r. Results are shown in table 5.2.1.

Table 5.2.1

^{11}B n.m.r. chemical shift values for boron trihalides in liquid hydrogen chloride at room temperature.

(Chemical shifts in p.p.m. rel. to $B(OMe)_3$).
* Gas phase determination, this work

Compound	^{11}B chemical shifts		Remarks
	Lit. value	In liquid HCl	
BF_3	+ 8.9 (126) + 8.6 ± 0.2 (*)	+ 8.6 ± 0.2	No solvolysis
BCl_3	- 29 (125) - 27.6 (126)	- 28.3	BCl_3
BBr_3	- 21.8 (125)	- 29	Solvolysis to BCl_3

Boron trifluoride dissolves unchanged in liquid hydrogen chloride whereas boron tribromide is solvolysed to boron trichloride. This behaviour is not unexpected considering the greater strength of B-F bonds compared with B-Br bonds. In no case is there any evidence for the existence of a tetracoordinated boron species in these solutions at room temperature.

TABLE 5.2.2

^{11}B chemical shifts of tetrahaloborate anions in liquid hydrogen chloride

(Chemical shifts in p.p.m. relative to $B(OMe)_3$)

Compound	^{11}B chemical shift		Remarks
	Observed in liquid HCl	Literature values[147]	
$Me_4N^+BF_4^-$	+19.8	BF_4^- + 19.9	BF_4^-
$Me_4N^+Cl^-$ + BF_3	+14.2	BF_3Cl^- + 16.6	BF_3Cl^-. Possible exchange
$Me_4N^+F^-$ + BCl_3	+11.5	$BFCl_3^-$ + 11.8	$BFCl_3^-$
$Me_4N^+Cl^-$ + BCl_3	+10.8	BCl_4^- + 11.6	BCl_4^-
$Me_4N^+Cl^-$ + $2BCl_3$	+3.5	BCl_4^- + 11.6; BCl_3 - 29, -27.6.[125,126]	Exchange averaged peak between BCl_4^-, BCl_3
$Me_4N^+Br^-$ + BCl_3	+11.3	BCl_3Br^- + 15.4	Probably BCl_4^-
$Et_4N^+I^-$ + BCl_3	+4.5	BCl_3I^- + 30.9	Exchange averaged signal

The ^{11}B chemical shifts of tetraholoborate and mixed tetraholoborate anions in liquid hydrogen chloride are shown in Table 5.2.2. The solutions were produced either by dissolving an equimolar mixture of a tetraalkylammonium salt and a boron trihalide in the solvent, or in the case of tetramethylammonium tetrafluoroborate the salt itself.

Hartman and Schrobilgen[147] have recently published ^{11}B n.m.r. data on mixed tetrahaloborate anions produced by exchange between simple tetrahaloborate anions in methylene chloride solution. Previously only the chlorotrifluoroborate anion had been well characterised.[20a, 20e.]

It is observed that the tetrafluoroborate ion is not solvolysed in liquid hydrogen chloride at room temperature. The ^{11}B chemical shift of the chlorotrifluoroborate ion is rather lower than that in methylene chloride and the possibility that the observed resonance is an exchange-averaged signal involving other chlorofluoroborate anions cannot be ruled out. The shift of the trichlorofluoroborate species is in very good agreement with the literature value and it may be assumed that this ion is not solvolysed by liquid hydrogen chloride. There is a difference of 0.8 p.p.m. between the values for the tetrachloroborate ions in the two solvents, but it seems likely that the shift obtained in liquid hydrogen chloride is characteristic of BCl_4^-.

The ^{11}B n.m.r. spectrum of a mixture of tetramethylammonium chloride and boron trichloride in 1:2 molar ratio in liquid hydrogen chloride solution consisted of a singlet at + 3.5 p.p.m. This resonance lies between those for BCl_3 and BCl_4^-, -28.3 and +10.8 p.p.m. respectively, and may be immediately assigned to an exchange averaged signal derived from both species. The molar ratio of $Me_4N^+Cl^-$: BCl_3 was made 1:2 so that the ratio of BCl_4^- ions produced to unused BCl_3 would be 1:1. The result of this experiment was frequently used in this work as a semi-quantitative guide to the extent of protonation of a species in the presence of boron trichloride in liquid hydrogen chloride. An excellent illustration of this application is provided in chapter 4.5 of this work where the study of the protonation of the series $Fe(CO)_{5-x}(Ph_3P)_x$ $(0 \leq x \leq 2)$ using ^{31}P and ^{11}B n.m.r. is described.

In a suitable solvent it could reasonably be expected to produce the bromotrichloroborate, BCl_3Br^-, anion from a 1:1 molar mixture of an alkylammonium bromide and boron trichloride. The ^{11}B chemical shift from such a solution in liquid hydrogen chloride was + 11.3 p.p.m. This is well below the reported value of + 15.4 p.p.m. for the species, and it may be assumed that extensive solvolysis has occurred. The observed resonance is possibly an exchange averaged signal derived from both the BCl_3Br^- and BCl_4^- ions.

Similarly, the ^{11}B shift of the BCl_3I^- ion, + 30.9 p.p.m.[147] was not observed in the ^{11}B n.m.r. spectrum of a 1:1 mixture of tetraethylammonium iodide and boron trichloride in liquid hydrogen chloride. Solvolysis of BCl_3I^- in the solvent is expected, but the low value, + 4.5 p.p.m., of the observed chemical shift implies that an exchange process involving 3-coordinate boron is taking place.

Experimental.

The behaviour of boron trifluoride in liquid hydrogen chloride

BF_3 (2 mmole) followed by HCl (30 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule. The ampoule was sealed and tested in the usual manner. The ^{11}B n.m.r. spectrum of the clear colourless solution obtained at room temperature consisted of a sharp singlet at + 8.6 ± 0.2 p.p.m. which may be immediately assigned to BF_3. This is in good agreement with the published value of + 8.9 p.p.m.[126] Boron-fluorine spin-spin coupling reported by Coyle and Stone, $^{1}J_{B-F}$ of 15 ± 2 Hz., was not observed.[128]

The behaviour of boron trichloride in liquid hydrogen chloride

BCl_3 (2 mmole) followed by HCl (30 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule. The ampoule was sealed and tested as described previously. The ^{11}B n.m.r. spectrum of the clear colourless solution obtained at room temperature consisted of a sharp singlet at - 28.3 p.p.m. This is in very good agreement with reported values for liquid BCl_3 of -29 and -27.6 p.p.m.[125,126]

The behaviour of boron tribromide in liquid hydrogen chloride

BBr_3 (2 mmole) followed by HCl (30 mmole) was condensed at -196° into an 8 mm. o.d. quartz ampoule which was sealed and tested in the usual manner. The ^{11}B n.m.r. spectrum of the clear colourless solution obtained at room temperature consisted of a sharp singlet at - 29 p.p.m. This may be immediately assigned to BCl_3.

The behaviour of tetramethylammonium tetrafluoroborate in liquid hydrogen chloride

$Me_4N^+BF_4^-$ (0.161g., 1 mmole) in an 8 mm. o.d. quartz ampoule was pumped overnight to remove traces of water. HCl (30 mmole) was condensed at - 196^o into the ampoule which was then sealed and tested as described previously. The ^{11}B n.m.r. spectrum of the clear colourless solution obtained at room temperature consisted of a sharp singlet at + 19.8 p.p.m. A chemical shift of + 19.9 p.p.m. has been reported for the BF_4^- ion in dichloromethane solution.[147] Thus, it may be assumed that the BF_4^- is not solvolysed by liquid hydrogen chloride at room temperature.

The reaction between tetramethylammonium chloride and boron trifluoride

HCl (30 mmole) followed by BF_3 (2 mmole) was condensed at -196^o into an 8 mm. o.d. silica ampoule containing $Me_4N^+Cl^-$ (0.219g., 2 mmole). The ampoule was sealed and tested in the usual way. The ^{11}B n.m.r. spectrum of the clear colourless solution obtained at room temperature consisted of a sharp singlet at + 14.2 p.p.m. A chemical shift of + 16.6 p.p.m. has been reported for the species BF_3Cl^-.[147]

The reaction between tetramethylammonium fluoride and boron trichloride

HCl (30 mmole) followed by BCl_3 (2 mmole) was condensed at -196^o into an 8 mm. o.d. quartz ampoule containing $Me_4N^+F^-$ (0.186g., 2 mmole). The ampoule was sealed and tested in the usual manner. The ^{11}B n.m.r. spectrum of the clear colourless solution obtained at room temperature consisted of a sharp singlet at + 11.5 p.p.m. A chemical shift of + 11.8 p.p.m. has been reported for the species $BFCl_3^-$ in dichloromethane solution.[147]

The reaction between tetramethylammonium chloride and boron trichloride

(a) $Me_4N^+Cl^-$ and BCl_3 in 1:1 molar ratio.

HCl (30 mmole) followed by BCl_3 (2 mmole) was condensed at -196° into an 8 mm. o.d. silica ampoule containing $Me_4N^+Cl^-$ (0.219g., 2 mmole). The ampoule was sealed and tested in the normal manner. The ^{11}B n.m.r. spectrum of the clear colourless solution obtained at room temperature consisted of a sharp singlet at + 10.8 p.p.m. A ^{11}B chemical shift of + 11.5 p.p.m. has been reported for the species BCl_4^- in dichloromethane solution.[147]

(b) $Me_4N^+Cl^-$ and BCl_3 in 1:2 molar ratio.

HCl (30 mmole) followed by BCl_3 (4 mmole) was condensed at -196° into an 8 mm. o.d. silica ampoule containing $Me_4N^+Cl^-$ (0.219g., 2 mmole). The ampoule was sealed and tested in the usual manner and contained a clear colourless solution at room temperature. A sharp singlet at + 3.5 p.p.m. was observed when the ^{11}B n.m.r. solution spectrum was recorded.

The reaction between tetramethylammonium bromide and boron trichloride

$Me_4N^+Br^-$ (0.131g., 0.851 mmole) contained in an 8 mm. o.d. quartz ampoule was pumped for 3 hours at room temperature to remove traces of water. HCl (30 mmole) followed by BCl_3 (0.85 mmole) was condensed into the ampoule at -196° which was then sealed and tested in the normal manner. At room temperature there were two liquid phases present; the upper being colourless and the lower layer pale yellow. The ^{11}B n.m.r. solution spectrum consisted of a sharp singlet at + 11.3 p.p.m. A ^{11}B chemical shift of + 15.4 p.p.m. has been reported for the BCl_3Br^- ion.[147]

The reaction between tetraethylammonium iodide and boron trichloride

$Et_4N^+I^-$ (0.207g., 0.806 mmole) contained in an 8 mm. o.d. silica ampoule was pumped for 3 hours at room temperature to remove traces of moisture. HCl (30 mmole) followed by BCl_3 (0.80 mmole) was condensed into the ampoule at -196° which was then sealed and tested in the usual manner. At room temperature there were two liquid phases present; the upper being colourless and the lower straw coloured. The ^{11}B n.m.r. spectrum consisted of a sharp singlet at + 4.5 p.p.m. A ^{11}B chemical shift of + 30.9 p.p.m. has been reported for the BCl_3I^- ion.[147]

The reaction between boron trichloride and sulphur dioxide

Fluck and Binder have studied the reaction between phosphorus(III) chloride and liquid sulphur dioxide using ^{31}P n.m.r. and reported the formation of phosphorus(III) oxide.[191] In this work the reaction between boron trichloride and liquid sulphur dioxide was followed using ^{11}B n.m.r.

Reaction took place slowly at room temperature with the formation of a colourless glassy solid. ^{11}B n.m.r. spectra of the reaction mixture were recorded regularly over a period of four months. The appearance of broad solid-state signals upfield from the sharp signal due to boron trichloride were observed. Typical spectra are shown in fig. 5.2.1. The three solid-state peaks had maxima at -13.5, -8 and +1 p.p.m. and are presumably due to successive replacement of chlorine by oxygen atoms in BCl_3.

A sample of the glassy solid product was obtained for analysis and was found to contain boron, chlorine, sulphur and, by difference, oxygen. No simple formulation could be fitted to the elemental composition of the solid material and it may be assumed that it is a mixture of oxygen, sulphur and chlorine containing boron compounds.

Experimental.

BCl_3(0.5 ml., 5.8 mmole) followed by SO_2 (1 ml., 22.3 mmole) was condensed into an 8 mm. o.d. silica ampoule. The ampoule was sealed and tested in the usual manner and contained a clear colourless solution at room temperature.

The ^{11}B n.m.r. spectrum of the solution, and later of the solid produced, was recorded regularly over a period of 4 months.

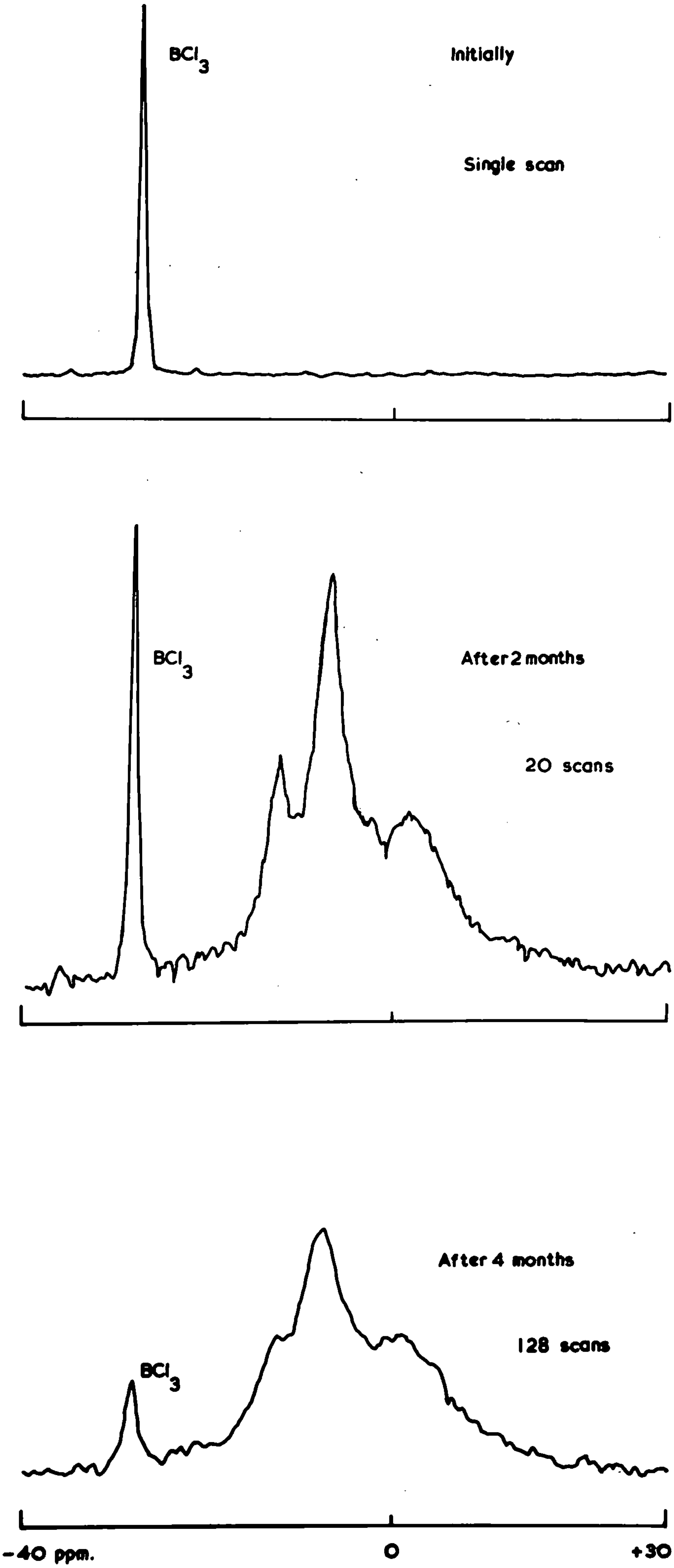
Initially the sole resonance in the ^{11}B spectrum occurred at -28 p.p.m. which is the shift of BCl_3.[125] After seven days, much weaker and broader signals, typical of signals arising from solids, were observed at -13.5, -8 and +1 p.p.m. That at -13.5 p.p.m. was the most intense of the solid-state peaks.

Spectra recorded after further time intervals all fall into the same pattern. The intensity of the sharp signal due to BCl_3 steadily

Fig. 5.2.1

^{11}B n.m.r. solution/solid state spectra

Boron trichloride in liquid sulphur dioxide


BCl3
Initially
Single scan
BCl3
After 2 months
20 scans
BCl3
After 4 months
128 scans
-40 ppm.
0
+30

decreased while the intensities of the broad solid-state signals increased. After 4 months the peak with greatest intensity was that at -8 p.p.m., the other broad peaks were of equal intensities and the sharp signal at -28 p.p.m. was the least intense. This spectrum is shown in figure 5.2.1. A large proportion of the liquid phase in the ampoule had by this time changed into a colourless glassy solid.

The reaction was repeated on a larger scale in order to obtain a sample of the glassy solid for characterisation.

BCl_3 (2.5 ml., 29 mmole) followed by SO_2 (5ml.,110 mmole) was condensed at -196^o into a 13 mm. o.d. pyrex ampoule which was then sealed and allowed to reach room temperature. The ampoule was left at this temperature for 16 months during which time much glassy solid was produced. The ampoule was cooled to -196^o and opened to the vacuum line. Using suitable cooling baths the volatile residues were pumped off at as low a temperature as possible. The infrared spectrum of the volatiles contained absorptions at; 1370, 1358, 1350, 1340, 1255, 1245, 1165, 1135, 990, 945, 858, 848, 535, 510, 500, 465, 455 cm^{-1}. Those absorptions at 990, 945, 465, 455 cm^{-1} may be assigned to BCl_3[204,228] and those at 1370, 1358, 1350, 1340, 1165, 1135, 535 and 510 cm^{-1} to SO_2.[244,245] The signals at 1255 and 1245 cm^{-1} may be tentatively assigned to $\nu S{=}O$ or to $\nu S{-}O$, those at 858 and 848 cm^{-1} to $\nu B{-}Cl$ and that at 500 cm^{-1} to $\nu S{-}Cl$.[246]

The colourless glassy solid was extremely hard and it was not possible to obtain an infrared spectrum of this material. Elemental analyses were carried out.

Found; B, 25.3; Cl, 31.7; S, 11.3.

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