# Aspects of the chemistry of some highly crowded aromatic ligands

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Straw, T. A. (1990) *Aspects of the chemistry of some highly crowded aromatic ligands*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/6215/

# Aspects of the Chemistry of some Highly Crowded Aromatic Ligands

by

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**A Thesis submitted in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy**

**Department of Chemistry**

**The University of Durham
1990**

# Statement of Copyright

# Declaration

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham between October 1987 and October 1990. All the work was my own, unless stated to the contrary, and has not previously been submitted for a degree at this or any other university.

The part of the work carried out in Toulouse was with official permission.

A Chantal, Laurent et Jonathan

# Abstract

A series of ortho-substituted arylchlorophosphoranes has been prepared. The structures of these compounds have been studied by the use of $^{35}$Cl n.q.r. and solid-state $^{31}$P n.m.r. . It has been shown that ortho substitution by groups such as $CH_3$ or $CF_3$ in phosphoranes of the type $P(Ar)Cl_4$ prevents complexation with Lewis bases, and this is also found to be the case for the derived phosphonium ions $[P(Ar)Cl_3]^+$. The bis(aryl)chlorophosphoranes with these bulky aryl groups (where it is possible for them to be formed) are found to have ionic phosphonium salt structures, regardless of the electronic properties of the aryl group. In some cases, where the aryl groups are too bulky and too electronegative, P-C bond cleavage takes place on chlorination of the bis(aryl)chlorophosphine, and the most bulky group is lost. The phosphoranes $PRCl_4$ (where R = $CH_2Cl$ or $CHCl_2$) were also prepared. For R = $CH_2Cl$, the solid phosphorane was found to have the ionic, $[PRCl_3][PRCl_5]$, structure. This is the first example of an organo-substituted chlorophosphorane to be shown to have the "phosphorus pentachloride structure" in the solid state. By contrast, $P(CHCl_2)Cl_4$ was shown by solid-state $^{31}$P n.m.r. to be a molecular, 5-coordinate species.

The generation of phosphoranides of the type $[P(Ar)(CN)_2X]^-$, with ortho-substituted aryl substituents, has also been investigated. From $^{31}$P n.m.r. it

has been shown that the 2-(methyl)phenyl group can be incorporated into such systems.

Various aryl- and aryloxy-1,3,2-dioxaphospholanes were prepared, with the aim of generating metaphosphate species via ethylene elimination. Data from mass spectrometry and from flow pyrolysis suggest that transient metaphosphates of the type $ArPO_2$ can be formed in this manner. Results would also indicate that where Ar = 2,6-$(CF_3)_2C_6H_3$ the respective metaphosphate undergoes a rearrangement via insertion into the ortho-$CF_3$ group.

It has been shown that the symmetrical diphosphene ArP=PAr (where Ar = 2,4,6-$(CF_3)_3C_6H_2$) can be formed by magnesium coupling of the aryldichlorophosphine. However, attempts to form asymmetrical diphosphines and other low-coordinate phosphorus species by DBU coupling of P(2,6-$(CF_3)_2C_6H_3$)$H_2$ with the respective chloro species were unsuccessful, due to preferred formation of Ar(H)P-P(H)Ar or ArP=PAr.

The 2,4,6-$(CF_3)_3C_6H_2$ group was successfully incorporated into various diazophosphine systems. Of particular note was the characterization of the first ever P(III)-P(III) stabilized nitrile imine. By varying the aryl groups on phosphorus in such systems ($C_6H_5$, $C_6F_5$ or 2,4,6-$(CF_3)_3C_6H_2$) it was possible to obtain further insights into the requirements for the stabilization of nitrile imines, and various trapping reaction were also performed.

# Acknowledgements

I would like to thank Dr. K. B. Dillon and Professor R. D. Chambers for their constant support and expert advice throughout my time in Durham. I would also like to express my gratitude for the invaluable technical assistance offered by the following members of staff: Dr. R. Matthews and J. Banks for n.m.r. services; Dr. M. Jones and V. McNeilly for mass spectra; Mr. B. Coult, Mrs. M. Cox and Mrs. J. Dostal for elemental analysis and Mr. R. Hart and Mr. G. Haswell for glass blowing. Many thanks are also due to Mr. T. Holmes, Mr. D. Hunter, Mr. J. Lincoln, Mr. R. Plumb and Mr. L. W. Lauchlan for regular help and advice with experimental procedure, and to all my other colleagues in the department.

I am particularly grateful to Dr. G. Bertrand of the C. N. R. S. at Toulouse for allowing me to spend three months in his laboratory and for the help and friendship of all the members of his group.

My thanks also go to my parents for their unwavering love and support through some very difficult times. Finally, I wish to thank my wife and two sons for their love, understanding and remarkable patience.

# Contents

# Chapter I

# Introduction

## 1.1 Bulky Substituents

In the past few years there has been an increasing interest in the incorporation of bulky groups into a wide range of chemical systems. Since 1981, when Yoshifuji *et al* [1] showed how the 2,4,6-tris(t-butyl)phenyl group could be used to stabilize a diphosphene to oligomerisation (see fig. 1.1), a whole host of other low-coordinate main group species has been prepared using similarly large substituents[2]. The stabilization of such low coordinate species is thus primarily achieved by the use of steric crowding. For this purpose one has a choice from a wide variety of suitable substituents. However, the nature of a given ligand may have a marked affect on the subsequent reactivity of the multiply bonded species, particularly with respect to its coordination chemistry[3].

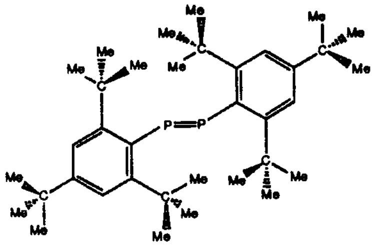
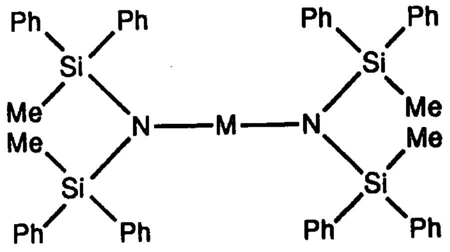


**Figure 1.1 — The First Stable Diphosphene[1]**

Other main group systems under current investigation are also reliant upon the use of highly crowded substituents. As Bertrand *et al* [4] have shown, the nitrile imine functionality may be stabilized by a combination of steric bulk and the electronic characteristics of its substituents. Organoaluminium compounds are also presently of interest due to their synthetic importance in organic chemistry[5], in particular the reactions of alkyl aluminium compounds with organic carbonyl compounds. These reactions are often complicated because of the presence of multiple reaction pathways and the dimeric nature of many organoaluminium compounds. Recent work[6–9] has focused on the use of monomeric aluminium complexes, derived from the sterically hindered 2,6-di-tert-butyl-4-methylphenol (BHT-H).

Bulky groups have also been extensively used in transition metal chemistry. For example, it has been demonstrated how bulky chelating diphosphines can be used to stabilize a tungsten-tungsten quadruple bond[10], and Chaudret *et al* [11] have recently shown how the combined incorporation of Cp* and a bulky phosphine ligand will stabilize 16-electron alkoxo complexes of ruthenium. By the use of the very crowded silylamide ligands, -$N(SiMePh_2)_2$, Power *et al* [12] have recently successfully prepared the first crystalline, two-coordinate derivatives of both iron and cobalt as the complexes $M[N(SiMePh_2)_2]_2$ (M = Co or Fe) (see fig. 1.2).



(where M = Fe or Co)

**Figure 1.2 — The First Crystalline 2-Coordinate Derivatives of Iron and Cobalt[12]**

Here, too, current interest is being extended to studying changes within a given system caused by varying the type of bulky ligand used. Notably, Toscano *et al* [13] have compared the superior stability conferred upon various organometallic complexes on replacement of bulky alkyl substituents with their corresponding perfluoro analogues.

There is also an important rôle for highly crowded ligands in organic chemistry. Olah *et al* [14] have very recently prepared the tris(1-adamantyl)methyl cation. It is the most crowded trivalent carbocation yet prepared under stable ion conditions (see fig. 1.3).

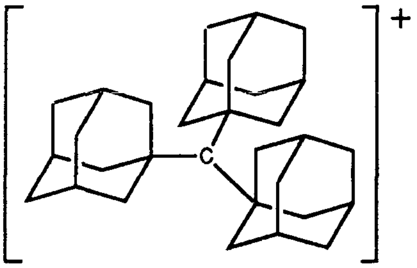


**Figure 1.3 — The Tris(1-adamantyl)methyl Cation [14]**

Its stability lies in the structural constraints of the adamantyl cage framework, resulting in a high kinetic barrier to decomposition. Another very important area of research which has benefited fron the use of bulky groups is in the development of perfluorocarbon ethers as reagents for "artificial blood". It has been shown[15] that the incorporation of perfluoroalkyl groups on carbons adjacent to the ether linkages creates holes in the liquid phase which are conducive to higher oxygen solubility, and also helps to reduce the retention time of these compounds in mammalian tissues. There has also been interest in the structure of biphenyls containing donor-acceptor chromophores and bulky substituents, which have been shown to exhibit nonlinear optical properties[16], (as such materials are of particular interest to the telecommunications industry[17]).

Other interesting and unforseen properties of bulky groups have been demonstrated. For example, Eaborn *et al* [18] discovered that the $(Me_2PhSi)_3C$- group would, when incorporated into an organomercurial, stabilize it towards unimolecular dissociation. This was attributed to the complexity, rather than simply the size, of the ligand. Having 63 bonds the $(Me_2PhSi)_3C$- group will carry much of the thermal energy in the molecule, thereby conferring a greater degree of thermal stability to the C-Hg bond.

As pointed out by Yoshifuji[19], there is a need to study the effect that changing the type of bulky group may have on a given system, even where an alteration may initially appear to be quite trivial. Hence, Yoshifuji *et al* have developed low--coordinate main group systems incorporating the 2,6-bis(t-butyl)phenyl ligand[19] or the 2,4,6-tris(t-pentyl)phenyl group[20], in order to compare with the analogous 2,4,6-tris(t-butyl)phenyl derivatives.

The use of perfluoroalkyl-substituted aromatic groups as bulky ligands is only a relatively recent development. In 1987 Escudié *et al* [21] first showed how the $2,6\text{-}(CF_3)_2C_6H_3$ group could be used to stabilize a diphosphene. In the same year, Chambers *et al* [22] demonstrated a route to the large-scale preparation of 1,3,5-tris(trifluoromethyl)benzene, the ease with which the lithio derivative could be formed and the subsequent substitution of the $2,4,6\text{-}(CF_3)_3C_6H_2$ group into a variety of organic and heteronuclear systems. It has since been shown how this ligand may be incorporated into various diphosphene and phosphaalkene derivatives[23,24]. The electronic properties of this highly fluorinated substituent can result in these systems being significantly more stable than their hydrocarbon-substituted analogues. Roesky *et al* have also recently described how the tris(trifluoromethyl)-phenoxy species can be generated, and how it may be used to form two-coordinate thallium(I) species[25].

The aim of the research presented in this thesis was to look particularly at the incorporation of the 2,4,6-$(CF_3)_3C_6H_2$ group (see fig. 1.4) into a variety of systems, and then to compare and contrast the effect that this bulky group may have in a given chemical environment with other substituents, differing in size and electronic properties. Work was concentrated on the area of phosphorus chemistry, as this offered the potential to observe the effects of bulky ligands in species varying widely in coordination state. Hence it was not only intended to study the stabilization of low-coordinate species, but also to observe the effects on the structure and chemistry involved in more highly coordinated environments, when large substituents are incorporated. Particular has been made of $^{31}P$ n.m.r. for characterization and $^{35}Cl$ n.q.r. spectroscopy has been also used extensively in the structural elucidation of organochlorophosphorane systems.

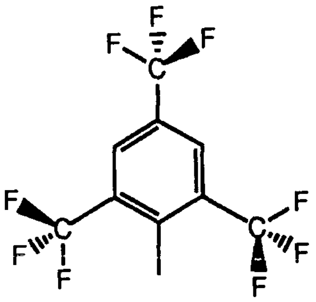


**Figure 1.4 — The 2,4,6-Tris(trifluoromethyl)phenyl Group**

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# Chapter II

# General Experimental

## 2.1 The Dry Box

Because of the air- and moisture-sensitivity of many of the compounds studied, all manipulations were carried out under an atmosphere of dry $N_2$. All of the products prepared were stored in sealed containers and kept in the dry box.

The dry box has two entry ports, a large and a small quick entry port. Before opening the inside window, the large port was purged for 30 minutes with nitrogen which had first been passed through a concentrated sulphuric acid bubbler and then a 4 Å molecular sieve tower. The quick entry port was flushed with nitrogen by means of excess internal nitrogen pressure.

The water pump was connected to a filtration apparatus inside the box through dry $CaCl_2$ to absorb any water vapour diffused into the box. A large dish containing $P_2O_5$ was exposed in the box to remove any traces of moisture present in the box atmosphere.

## 2.2 Vacuum Apparatus

For most work a standard glass combined vacuum and nitrogen line equipment was used, incorporating a two-stage, rotary oil-pump. However, for reactions involving the transfer of sulphur tetrafluoride (see below) a specially designed steel vacuum line was used, as shown in figure 2.1 a. The system was evacuated before

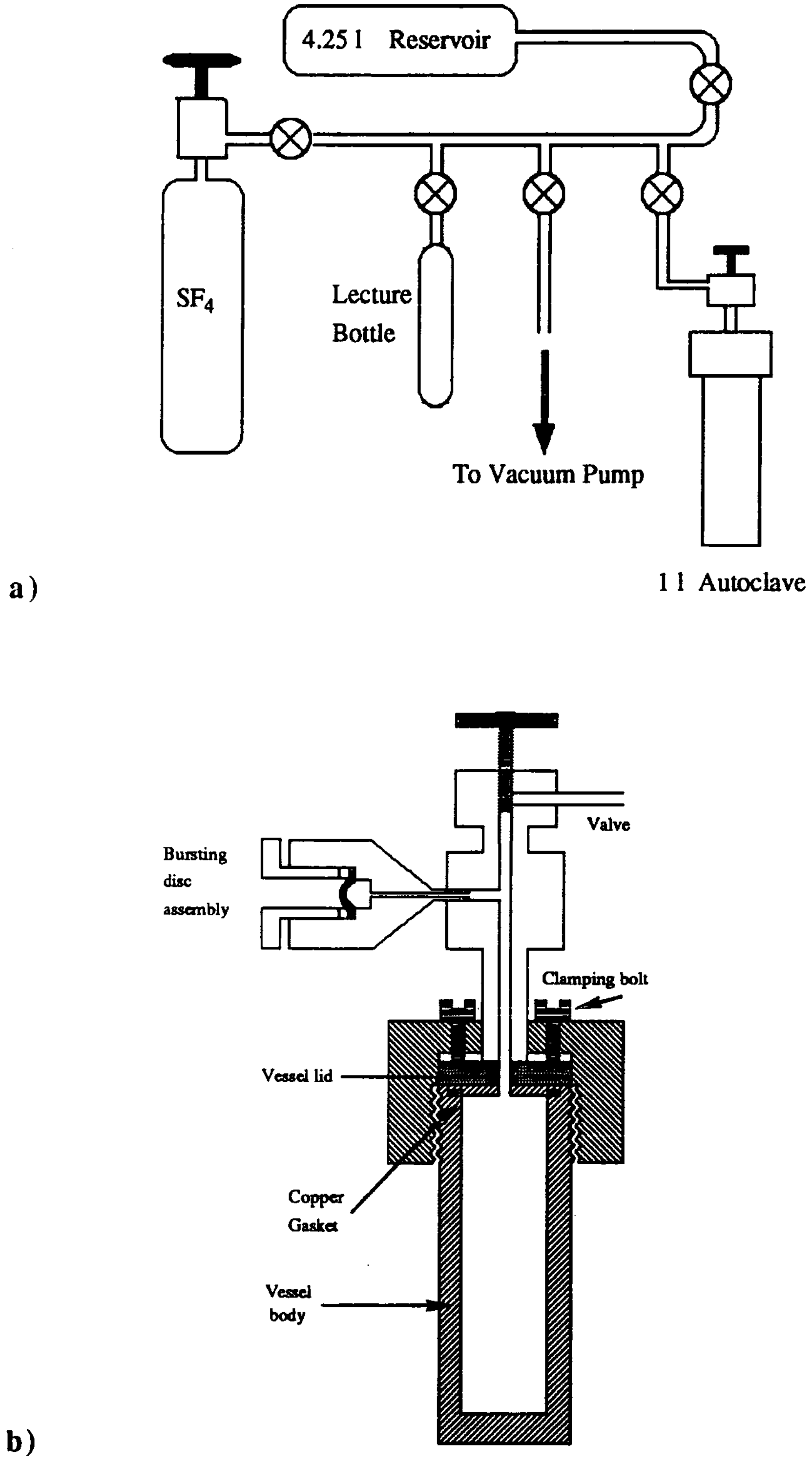

**Figure 2.1** — **a) Steel Vac. Line for SF$_4$ Transfer; b) 1 l Autoclave for SF$_4$ Fluorination Reactions.**

allowing $SF_4$ from the main cylinder to fill the upper reservoir. The gas was then condensed into small lecture bottles for weighing before being introduced into the reaction autoclave.

## 2.3 High Pressure Techniques

The $SF_4$ fluorination reactions were carried out in a 1 litre steel autoclave fitted with valve, bursting disc assembly and copper gasket seal (see fig. 2.1 b). The autoclave was first tested to 230 atmospheres pressure with nitrogen gas (calculated reaction pressure = 200 atm.), before being charged with reactants. The material to be fluorinated was placed in the autoclave. The vessel was then evacuated, cooled to -190°C with liquid air, and a weighed quantity of $SF_4$ condensed in. The autoclave was then transported (still at -190°C) to a high pressure cell before being allowed to warm to room temperature. A furnace fitted with thermocouples was then used to heat the bomb to the required temperature. The process was monitered externally by closed- cicuit T.V., and when heating was complete the bomb was allowed to cool to room temperature, before being vented in an efficient fumes hood.

## 2.4 Photochemical Reactions

Ultraviolet reactions were performed in quartz tubes with a Rayonnet photochemical reactor. All $\gamma$-ray experiments were performed using a $^{60}Co$ source (595 ci, $t_{\frac{1}{2}}$ = 5.25 years, installed 29/3/89), at 105 K Rads / hour. Reactions were carried out in sealed 5 mm n.m.r. tubes which were placed in metal sleeves during irradiation at a temperature of 18°C.

## 2.5 Chemical Analysis

C, H and N analyses were determined by micro-combustion with a Perkin-Elmer 240 instrument. Phosphorus and halogen analyses were carried out by R. Coult. For phosphorus and chlorine a weighed sample was decomposed by fusing in a nickel Parr bomb. The residue was acidified with concentrated nitric acid and made up to 100 ml with distilled water. For phosphorus a suitable aliquot was treated with ammonium molybdate / ammonium vanadate reagent and the absorbance measured at 420 $\mu$ using a Unicam SP500 spectrophotometer. Chlorine was determined by potentiometric titration against N/100 silver nitrate solution using Ag/AgCl electrodes in an acetone medium.

## 2.6 Spectroscopic Techniques

### 2.6.1 Nuclear Magnetic Resonance Spectroscopy.

Solution-state n.m.r. spectra were recorded on Bruker AC80, AC200, AC250, Varian EM360L ($^{19}$F only, operating at 56.45 MHz) and Hitachi Perkin-Elmer R-24B ($^{1}$H only, operating at 60 MHz) machines. In all cases, shifts downfield of 0 ppm have been expressed as positive. The following references were used: $^{1}$H, internal TMS; $^{11}$B, external $BF_3.Et_2O$; $^{13}$C, internal deuterated solvent; $^{19}$F, internal $CFCl_3$; $^{31}$P, external 85 % $H_3PO_4$ and $^{119}$Sn, external $SnMe_4$.

Solid-state spectra were obtained using magic angle spinning on either a Bruker CXP200 or a Varian VXR 300 machine. For air and moisture sensitive solid-state samples it was necessary to use the Kel-F, airtight rotor insert, as jointly designed by Merwin, Espidel *et al* [1]. The following references were used: $^{13}$C, external $SiMe_4$ and $^{31}$P, external "brushite" ($CaHPO_4.2H_2O$ $\delta$ $^{31}P = 1.2$ ppm).

### 2.6.2 Nuclear Quadrupole Resonance Spectroscopy

$^{35}$Cl n.q.r. spectra were obtained from a commercial mid-range Decca spectrometer using Zeeman modulation and operating between 5 and 55 MHz. Sideband suppression was used to aid the identification of closely spaced resonances. The appropriate radio-frequency coil was used, into which a 13 mm outside diameter glass sample tube was placed. Resonance frequencies were reproducible to better than than ± 10 KHz. Spectra were recorded at 77 K (liquid nitrogen), 195 K (cardice) and at room temperature. A variable temperature unit was also employed for more detailed studies.

### 2.6.3 Infrared Spectroscopy

Infrared spectra were recorded on a Perkin-Elmer 577 or 598 instrument, using a polystyrene film for calibration. The solids were prepared as Nujol mulls between KBr or CsI plates, or as a KBr disc. The liquids were recorded as thin films. Infrared spectra for solutions were obtained using 0.05 mm solution cell with a KBr window.

### 2.6.4 Mass Spectrometry

Mass spectra were obtained using a Ribermag R10 10E or VG 7070E instrument incorporating a Hewlett-Packard 5790A gas chromatograph, fitted with a 25 m cross-linked methyl silicone capillary column. Perfluorokerosene was used for referencing.

## 2.7 Preparation and Purification of Starting Materials

### 2.7.1 Treatment of Solvents

All solvents were dried and purified by standard techniques. Chlorocarbons were dried over 4 Å molecular sieve and stored under nitrogen. Hydrocarbon solvents were dried over sodium wire and then stored under nitrogen over freshly activated molecular seive. Nitrobenzene was refluxed over $P_2O_5$ and then distilled onto molecular seive.

### 2.7.2 Drying Tetraalkylammonium Halides

These compounds were dried in the established manner[2,3]. The tetra-alkylammonium halides were first dissolved in methanol. The solution was then filtered to remove any insoluble impurities. The methanol was removed under vacuum and toluene was added. The mixture was then stirred for 1 hour before the toluene was removed *in vacuo* . The salt was then heated at 373 K for 10 hours. If at this stage the salt was not a free-flowing white powder, or if from the I.R. spectrum it was evident that all the water had not been removed, then the whole proceedure was repeated. Once dried, the tetraalkylammonium chlorides in particular readily pick up moisture. Even if stored and used solely in the glove box regular redrying was required.

### 2.7.3 1,3,5-Tris(trifluoromethyl)benzene

Trimesic acid 150 g (0.7 mol) was placed in a 1 l autoclave which was then cooled in liquid nitrogen before addition of sulphur tetrafluoride 500 g (4.6 mol). The autoclave was sealed, allowed to warm to room temperature, and heated at 150°C (12 h). After venting to release unused sulphur tetrafluoride and gaseous products, the liquid contents were poured onto crushed ice to remove unreacted acid and hydrogen fluoride. The lower layer was separated, washed with sodium hydroxide solution (2 M) and dried ($MgSO_4$). Fractional distillation to remove partially fluorinated material yielded a colourless liquid, identified as 1,3,5-tris(trifluoromethyl)benzene[4] 159.5 g (80 %); B.pt. 119°C; $\delta$ $^{19}F$ = -65.3 ppm; $\delta$ $^{1}H$ = 8.1 ppm.

### 2.7.4 2,4,6-Tris(trifluoromethyl)phenyllithium

BuLi (2.5 M in hexane, 31.2 ml, 78 mmol) was added dropwise over 5 minutes to a stirred solution of 2,4,6-$(CF_3)_3C_6H_2H$ 20 g (71 mmol) in $Et_2O$ (100 ml) at -78°C. The reaction mixture was then allowed to warm to room temperature, and to stir for a further 5 hours. During this time the colour gradually changes from yellow to dark brown. The degree of lithiation can be assessed from the $^{19}F$ n.m.r. spectrum of the reaction mixture (should it be necessary more BuLi may be added). The aryllithium is believed to decompose explosively on isolation[3] and so was used *in situ*. $\delta$ $^{19}F$ / ($Et_2O$ / hexane) = -62.6 ppm (s, o-$CF_3$, 6 F), -62.8 ppm (s, p-$CF_3$, 3 F).

### 2.7.5 1,2,4,5-Tetrakis(trifluoromethyl)benzene

1,2,4,5-benzenetetracarboxylic acid 40 g (0.16 mol) was placed in a 1 l autoclave which was then cooled in liquid nitrogen before addition of sulphur tetrafluoride 200 g (1.85 mol). The autoclave was sealed, allowed to warm to room temperature, and heated at 150°C (24 h). After venting to release unused sulphur tetrafluoride and gaseous products, a small amount of crushed ice was added to remove unreacted acid and hydrogen fluoride. Chloroform (200 ml) was then added and the lower layer was separated, washed with sodium hydroxide solution (2 M) and dried

($MgSO_4$). The chloroform was then removed under reduced pressure, leaving a pale yellow solid. Vacuum sublimation (90°C, 0.1 mmHg) yielded 35.5 g (64 %) of white crystalline solid. M.pt. 69°C; $\delta$ $^{19}F$ = -60.2 ppm. However, this was shown by I.R. ($\nu$ = 1735 $cm^{-1}$) and GLC to contain approximately 3% of carbonyl-containing, partially fluorinated material. Attempts to purify further the product on a bulk scale by recrystallization or washing were unsuccessful.

Attempts to prepare a lithio derivative of this compound using a range of lithiating reagents (t-BuLi, n-BuLi, MeLi or LDA) in various solvents (hexane, diethyl ether or THF) were all unsuccessful. In all cases attempts at low temperature trapping (-78°C with $Me_3SiCl$ or $PCl_3$) produced reaction mixtures which were shown by $^{19}F$ n.m.r. to contain only starting material, and at elevated temperatures a large number of products was obtained.

Due to the cost of $SF_4$, the poor yields of product and failure to prepare a lithio derivative, no further work was carried out on this material.

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# Chapter III

# Arylchlorophosphoranes and Derived Systems.

## 3.1 Introduction.

Aryl- and alkyl-halogenophosphoranes, $PR_nX_{5-n}$, are of considerable interest since various alternative structures are possible. The compounds may be molecular trigonal bipyramids, as found for $PF_5$, they may be ionic with the structure $[PR_nX_{4-n}][PR_nX_{6-n}]$, as in the ionic form of $PCl_5$, or they may have the phosphonium salt structure $[PR_nX_{4-n}]X$,as in solid $PBr_5$. Early interest in the structure of phosphoranes of this type was fuelled by the discovery that tertiary phosphine dihalides ($PR_3X_2$) are efficient reagents for alkyl halide synthesis[2]:

$$PR_3 + X_2 \longrightarrow PR_3X_2 \overset{R'OH}{\longrightarrow} PR_3O + HX + R'X$$

In order to understand the mechanism of these reactions it was necessary to determine the structure of $PR_3X_2$. Solution-state studies[3] suggested that the conductance of triphenylphosphine dihalides approached the magnitude expected for a strong 1:1 electrolyte in methyl cyanide. Wiley *et al*[4] demonstrated how the solution state structures of organohalophosphoranes could be deduced by comparison of the $^{31}P$ n.m.r. spectrum of the phosphorane with that of its salt with a strong Lewis acid, which always had a phosphonium salt structure. As the analogy with the phosphorus pentahalides suggests, the structural possibilities are as shown by the following equation:

$$PR_3X_2 \rightleftharpoons PR_3X^+X^- \rightleftharpoons PR_3X^+PR_3X_3^-$$

Wiley's method is based on the premise that in the presence of a strong Lewis acid all of the phosphorus species will convert completely to the phosphonium salt ($PR_3X^+LX^-$) where L is the Lewis acid. This permits the spectroscopic properties of $PR_3X^+$ to be unambiguously defined. As shown in table 3.1, the similarity of the $^{31}P$ n.m.r. chemical shifts for $PPh_3Cl_2$ in acetonitrile to those of its 1:1 adducts with $AlCl_3$ or $SbCl_5$ provides strong evidence that in each case the resonance observed is that of the chlorotriphenylphosphonium ion $PPh_3Cl^+$, and hence triphenylphosphine dichloride has the phosphonium chloride structure in acetonitrile.

| Compound | Solvent | $^{31}P$ Chemical Shift |
|---|---|---|
| $PPh_3Cl_2$ | $CH_3CN$ | 62 ppm |
| $PPh_3Cl^+SbCl_6^-$ | $CH_3CN$ | 66 ppm |
| $PPh_3Cl^+AlCl_4^-$ | $PhNO_2$ | 65 ppm |

**Table 3.1 — Triphenylphosphonium ion $^{31}P$ n.m.r. shifts**

Conductimetric work by G.S. Harris and M.F. Ali[5] showed that even in the presence of a strong halide donor such as $Et_4NCl$, $PPh_3Cl_2$ does not form $PPh_3Cl_3^-$. This, together with the work of Kolditz and Hass[6], which suggests that exchange between $PR_3X^+$ and $PR_3X_3^-$ would not occur sufficiently quickly for there to be only a single signal seen in the $^{31}P$ n.m.r. spectrum, supports the phosphonium salt structure proposed by Wiley ($PPh_3Cl^+Cl^-$). Denney *et al* [7] extended these $^{31}P$ n.m.r. solution studies to cover $PPh_3Cl_2$, $PPh_2Cl_3$ and $PPhCl_4$. The latter two by comparison of the chemical shifts with those of their Lewis acid salts were shown to be molecular in nitrobenzene solution. Denney further pointed out that in preparation of phosphoranes by direct chlorination of the relevant phosphine there is the danger that over-chlorination will result in the formation of trichloride salts of the phosphorane, which would confuse structural studies. This may be one of the reasons (together with the high risk of hydrolysis) why there are anomalous results in the literature from solution studies. Holmes *et al* [8] indicated how $^{35}Cl$ n.q.r. spectroscopy could be used to distinguish axial from equatorial chlorines in the solid-state for the trigonal bipyramidal, mixed halides of phosphorus: $PCl_4F$, $PCl_3F_2$ and $PCl_2F_3$. Holmes showed (as is believed to be the general rule when the central atom is a light element[9]) that the most electronegative groups - in this case F - take up axial positions of a trigonal bipyramid. By a combination of $^{35}Cl$ n.q.r. and solid-state $^{31}P$ n.m.r. studies (n.b. without MAR the five-coordinate phosphoranes were found to have too great a chemical shift anisotropy for a signal to be seen by solid state $^{31}P$ n.m.r.) on the phosphoranes of the series $PPh_nCl_{5-n}$ (n = 1 to 3) and on their Lewis acid derivatives Dillon *et al*[1] confirmed the structures of $PPhCl_4$ and $PPh_2Cl_3$ as being covalent, five-coordinate and $PPh_3Cl_2$ as being ionic ($PPh_3Cl^+Cl^-$). Further, they showed that all alkyl-substituted chlorophosphoranes of the type $PR_nCl_{5-n}$ (n = 1 to 3, R = Me, Et) are ionic, of the form $PR_nCl^+_{4-n}Cl^-$. This is rationalized on the grounds that the phosphonium ion is stabilized by electron-supplying alkyl group(s). As even $PMeCl_4$ is ionic in the solid state it is unlikely that increase of the hydrocarbon chain length or further substitution of Cl by R will do anything other than more firmly favour the phosphonium salt structure. It should be noted, however, that if R is a sufficiently electronegative aliphatic group then a molecular phosphorane will be the preferred structure. This has been shown, for example, in the case of $P(CCl_3)Cl_4$, which is trigonal bipyramidal in the solid-state with the trichloromethyl group in an axial position[10,11,12]. $P(CF_3)Cl_4$ has also been shown to have the $\psi$tbp structure with an axial $CF_3$ group, both by Raman studies[13] and by Fild *et al* [14] using $^{35}Cl$ n.q.r.. Fild further demonstrated that, the mono- and bis-pentafluorophenylchlorophosphoranes are also molecular $\psi$tbp and that unlike $C_6H_5$, the pentafluorophenyl groups,being more electronegative than chlorine, take up axial positions. This is clear from the overall relative intensities of the equatorial to axial chlorine n.q.r. signals (table 3.2). In the general system $Ar_nCl_{5-n}$ (n = 1 to 2), for Ar = $C_6H_5$ the mono- and the bis-arylchlorophosphoranes have eq:ax intensity ratios of 2:2 and 1:2 respectively, whereas when Ar = $C_6F_5$ for the mono-arylchlorophosphorane eq:ax is 3:1, and the bis-arylchlorophosphorane gives only equatorial Cl signals, due to both axial positions being taken up by the $C_6F_5$ groups. Here it should be noted that Fild originally reported the axial $^{35}Cl$ signal for $P(C_6F_5)Cl_4$ at 27.1 MHz. This, as pointed out by Dillon and Lincoln[15], was most probably the $^{37}Cl$ equatorial signal, and since the isotopic ratio of $^{35}Cl$:$^{37}Cl$ is roughly 3:1, this by chance led to the correct structural conclusion. The signal to noise ratio for chlorine n.q.r. spectra is such that $^{37}Cl$ n.q.r. signals, being one third of the intensity of their corresponding $^{35}Cl$ signals, are often not seen. However, the $^{37}Cl$ n.q.r. spectrum can be simply calculated from the $^{35}Cl$ spectrum by dividing the frequencies by 1.2688[16]

| Compound | Av. $\nu$ $^{35}$Cl /MHz | | intensity ratio |
|---|---|---|---|
| | $\nu$ $Cl_{eq}$ | $\nu$ $Cl_{ax}$ | eq:ax |
| $P(C_6H_5)Cl_4$ | 33.66 | 25.06 | 2:2 |
| $P(C_6F_5)Cl_4$ | 34.40 | 25.30 | 3:1 |
| $P(C_6H_5)_2Cl_3$ | 33.45 | 22.34 | 1:2 |
| $P(C_6F_5)_2Cl_3$ | 35.58 | - | - |

**Table 3.2 — $^{35}$Cl n.q.r. data for phenyl- and perfluorophenyl-chlorophosphoranes**

Since Michaelis first prepared o-tolyl-$PCl_4$[17] and mesityl-$PCl_4$[18] there have been no further reports of any attempts to determine the structure of aryl-chlorophosphoranes with ortho- substituents other than hydrogen or fluorine. It would be interesting to see how increased steric crowding caused by the introduction of bulky ortho- substituents affects the type of structure adopted by the phosphorane (i.e. ionic or molecular). In the cases where the structure may be molecular, $\psi$tbp, it would be interesting to discover whether increasing the bulk of ligands in this way would have any effect on the positioning of the aryl group (axial vs. equatorial) over and above the electronic requirements already discussed. It would also be of interest to see how ortho-substitution affects the acceptor properties of the arylchlorophosphoranes and their derived phosphonium ions towards Lewis bases. The ability of phosphorus (V) chloride to accept chloride ion[19] and various pyridine bases[20] has been clearly demonstrated, and similar properties have been found in a number of organo-substituted chlorophosphoranes[21,22,23,24]. However, in chlorophosphoranes with two or more organo groups, acceptor properties of this type are not seen, though five and six-coordinate derivatives of their phosphonium ions may sometimes be formed. Further, it has been shown that the electronic nature of the organo-substituent in organochlorophosphate(V) ions has an effect upon the degree of substitution of cyanide for chloride[25,26]. The general rule seems to be that for species of the type $[PRCl_5]^-$, where R is an electron-supplying group (Me or Et), then all five chlorines can be substituted to form $[PR(CN)_5]^-$. Should R be a more electronegative substituent (Ph or $CCl_3$) then substitution stops at $[PR(CN)_3Cl_2]^-$. The rationale for this is based on the assumption that substitution proceeds via a five-coordinate phosphorus intermediate (i.e. an $S_N1$-type reaction):

$$[PRCl_{6-n}(CN)_{n-1}]^- \rightleftharpoons PRCl_{5-n}(CN)_{n-1} + Cl^-$$

$$PRCl_{5-n}(CN)_{n-1} + CN^- \longrightarrow [PRCl_{5-n}(CN)_n]^-$$

As the P-CN bond is very much stronger than the P-Cl bond then substitution by cyanide is effectively irreversible, hence substitution depends on the lability of the P-Cl bond in $[PRCl_{6-n}(CN)_{n-1}]^-$. If the R group is electronegative this will assist in delocalising the negative charge on phosphorus and in stabilising the anion to dissociation. The more difficult system to rationalize is when R = $C_6F_5$, since here even though R is more electronegative, substitution proceeds one stage further than for R = $C_6H_5$, (i.e. stops at $[P(C_6F_5)Cl(CN)_4]^-$ as opposed to $[P(C_6H_5)Cl_2(CN)_3]^-$). A possible explanation is that the more bulky $C_6F_5$ facilitates the dissociation of the chloride ion, as the increased crowding in the system favours five- rather than six-coordinate phosphorus. It would be of great interest to discover to what extent steric effects play a part in influencing the structure and reactivity of organochlorophosphoranes and their derived systems, as described above. For this work several ortho-substituted aryl-groups have been incorporated into phosphorane systems. By using a variety of solid- and solution-state spectroscopic methods, structures have been determined for these arylchlorophosphoranes and their associated phosphonium salts of Lewis acids. The acceptor properties of these species towards Lewis bases have also been studied.

Although the aim of this work was to study arylchlorophosphoranes, for comparison and as there is a lack of data in the literature, it was decided to prepare some aliphatic organochlorophosphorane systems. The alkyl phosphoranes of the series $PR_nCl_{5-n}$, (n = 1 to 3, R = Me or Et), are well known and, as explained above, have all been shown to have the phosphonium salt structure in the solid state. Some (perhaloalkyl)chlorophosphoranes (R = $CCl_3$, $C_2Cl_5$ and $CF_3$)[10 *to* 14] are also known and in this case all of the phosphoranes $PRCl_4$ have been shown to be molecular and five-coordinate, with the perhaloalkyl group taking up an axial position. There are, however, no examples in the literature of partially halogenated aliphatic groups being incorporated into such phosphorane systems. If one proposes, for example, the following series of four phosphoranes: $P(CH_3)Cl_4$, $P(CH_2Cl)Cl_4$, $P(CHCl_2)Cl_4$ and $P(CCl_3)Cl_4$, the question immediately arises as to where along the series the solid-state structure changes from ionic to molecular. In a molecular structure it would also be interesting to find whether an incompletely halogenated alkyl group takes up an axial or equatorial position.

## 3.2 Results and Discussion

### 3.2.1 $P(2\text{-}(CH_3)C_6H_4)Cl_4$

This compound was first reported by Michaelis and C. Panek[17] in 1882. Since then, however, although its 4-(methyl)phenyl isomer[27,28,29] has been extensively studied, there appear to be no further references to $P(2\text{-}(CH_3)C_6H_4)Cl_4$ in the literature. Michaelis' method for the preparation of this phosphorane was by chlorination of $P(2\text{-}(CH_3)C_6H_4)Cl_2$, which had been prepared by the action of $Hg(2\text{-}(CH_3)C_6H_4)_2$ on $PCl_3$. We found that good yields of $P(2\text{-}(CH_3)C_6H_4)Cl_2$ could be obtained using the general method of Weil *et al* [30,31] for arylphosphinous dichlorides from the reaction of an arylzinc halide with phosphorus trichloride. In Weil's method the arylzinc halide is prepared *in situ* by the addition of one equivalent of $ZnCl_2$ to the arylmagnesium bromide. We chose to use the chloro-Grignard[32] ($Mg(2\text{-}(CH_3)C_6H_4)Cl$) which, although more difficult to prepare than $Mg(2\text{-}(CH_3)C_6H_4)Br$, avoids bromine incorporation in the phosphine product.

$$Mg(2-(CH_3)C_6H_4)Cl \xrightarrow{ZnCl_2} Zn(2-(CH_3)C_6H_4)Cl \xrightarrow{PCl_3} P(2-(CH_3)C_6H_4)Cl_2$$

The phosphorane $P(2\text{-}(CH_3)C_6H_4)Cl_4$ was then prepared, in the normal way, by direct chlorination of a dichlomethane solution of $P(2\text{-}(CH_3)C_6H_4)Cl_2$ with dry chlorine gas. For the phosphorane in $CH_2Cl_2$ solution $\delta$ $^{31}P = -41.8$ ppm. This, by comparison with the $^{31}P$ chemical shift for the phosphonium ion ($P(2\text{-}(CH_3)C_6H_4)Cl_3^+$) of around 101 ppm, depending on the counter ion (see below), indicates that in dichloromethane $P(2\text{-}(CH_3)C_6H_4)Cl_4$ has a five-coordinate, molecular structure. $^{35}Cl$ n.q.r. studies (see table 3.3) on the solid phosphorane show it to be trigonal-bipyramidal. The overall intensity ratio of equatorial to axial chlorine signals is 2:2, thus the 2-(methyl)phenyl group takes up the remaining equatorial position (see fig. 3.1). At 77K, both the equatorial and axial $^{35}$Cl n.q.r. signals were split into two lines of equal intensity. This suggests that there could be crystallographic differences between each of the two equatorial and each of the two axial chlorines. Alternatively, it may be the case that there are two phosphorane molecules per asymmetric unit. Although there was the usual shift of the $^{35}$Cl n.q.r. signals to lower frequency with increase in temperature (due to increased molecular motion weakening the crystal field), there was no coalescence of the split signals on running the sample at 195 K. No signals were seen at room temperature and a variable temperature study (see fig. 3.2) showed that, on our instrument, the signals for this compound fade into the background noise at around 254 K.

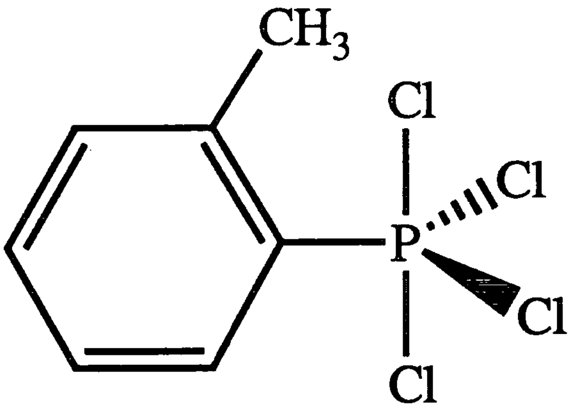


**Figure 3.1 — Deduced Structure of $P(2\text{-}(CH_3)C_6H_4)Cl_4$**

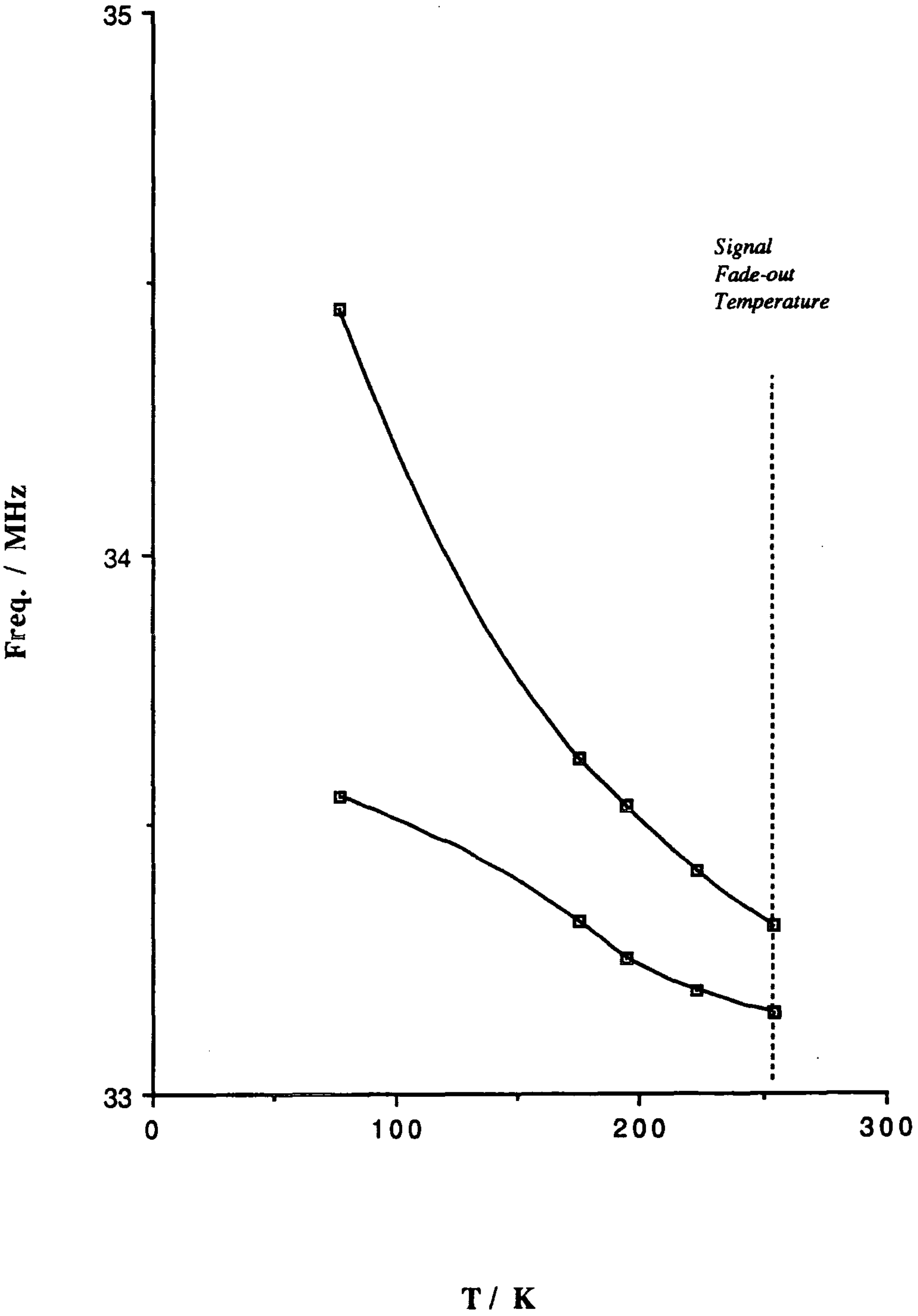


Figure 3.2 — Variable Temperature $^{35}$Cl n.q.r. Study of $\nu_{eq}$ for $P(2\text{-}(CH_3)C_6H_4)Cl_4$

| Temperature | $\nu^{35}$Cl / MHz (rel. intensity) | | intensity ratio |
|---|---|---|---|
| | $\nu_{eq}$ | $\nu_{ax}$ | eq : ax |
| 298 K | no signal seen | | - |
| 195 K | 33.26 (1) | 25.27 (1) | |
| | 33.53 (1) | 25.37 (1) | 2:2 |
| 77 K | 33.53 (1) | 25.45 (1) | |
| | 33.91 (1) | 25.67 (1) | 2:2 |

**Table 3.3 — $^{35}$Cl n.q.r. data for $P(2\text{-}(CH_3)C_6H_4)Cl_4$**

### 3.2.2 $[P(2\text{-}(CH_3)C_6H_4)Cl_3][BCl_4]$

The tetrachloroborate salt of the phosphorane $P(2\text{-}(CH_3)C_6H_4)Cl_4$, was prepared in the usual manner - by reacting one equivalent of $BCl_3$ (1M in hexanes) with the phosphorane dissolved in $CH_2Cl_2$. $\delta$ $^{31}$P / ($PhNO_2$) = 99.2 ppm, which is as expected for an aryltrichlorphosphonium ion. When this phosphonium ion is generated in solution, by the action of $SbCl_5$ on $P(2\text{-}(CH_3)C_6H_4)Cl_2$, the $^{31}$P n.m.r. chemical shift was measured at 101.7 ppm. At 77K the $^{35}$Cl n.q.r. spectrum showed two signals in the chlorophosphonium ion region, with relative intensities of 2:1. In the tetrachloroborate region two signals were seen with relative intensities 2:2 (see table 3.4). The simplest explanation is that there is one formula unit per asymmetric unit, the phosphonium ion having two chlorines equivalent and the third crystallographically inequivalent. The $BCl_4^-$ ion in this solid, at 77 K, has its four chlorine atoms equally shared between two different crystallographic environments. On warming to 195 K, a further crystallographic splitting was seen in the $BCl_4^-$ ion - three signals of relative intensities 2:1:1 were found. However, no further splitting of the phosphonium ion signals were seen. No signals were found at room temperature for this compound.

| Temperature | $\nu^{35}$Cl / MHz (rel. intensity)<br>$\nu_{P-Cl}$ | <br>$\nu_{B-Cl}$ |
|---|---|---|
| 298 K | no signal seen | |
| 195 K | 30.90 (2) | 20.74 (2) |
| | 31.20 (1) | 20.85 (1) |
| | | 21.25 (1) |
| 77 K | 31.19 (2) | 20.99 (2) |
| | 31.52 (1) | 21.54 (2) |

**Table 3.4 — $^{35}$Cl n.q.r. data for [P(2-(CH$_3$)C$_6$H$_4$)Cl$_3$][BCl$_4$]**

### 3.2.3 P(2-(CH$_3$)C$_6$H$_4$)$_2$Cl$_3$

The phosphorane, P(2-(CH$_3$)C$_6$H$_4$)$_2$Cl$_3$, is prepared by direct chlorination of the bis(aryl)phosphinous chloride in dichloromethane with dry chlorine gas. This compound does not appear to have been previously reported in the literature. In dichloromethane solution $\delta$ $^{31}$P = 88.6 ppm which is much further down-field than would be expected for a molecular phosphorane ($\delta$ $^{31}$P / (CH$_2$Cl$_2$) PPh$_2$Cl$_3$ = -32.7 ppm[28]). By comparison with the $^{31}$P n.m.r. shift for the tetrachloroborate salt of this compound (see below), it would appear that the phosphorane itself is mostly ionised in dichloromethane solution (i.e. P(2-(CH$_3$)C$_6$H$_4$)$_2$Cl$_2^+$ Cl$^-$). However, as has been explained above, this is insufficient evidence for claiming that this is also the case in the solid. Unfortunately, no n.q.r. signals were seen at any temperature in the range 20 to 40 MHz. Solid-state $^{31}P$ n.m.r. was possible, however, and two peaks (probably due to crystallographic effects[33]) were seen - $\delta$ $^{31}P$ /(solid) $P(2\text{-}(CH_3)C_6H_4)_2Cl_3$ = 90.0, 85.0 ppm. Thus, even without $^{35}Cl$ n.q.r. data, it is clear that this phosphorane has the phosphonium salt structure in the solid. There are two possible reasons for the ionic structure being preferred: i) the electron-supplying ortho-methyl group helps to stabilise the positive charge on the phosphonium ion ; ii) the increased steric crowding around phosphorus by having two ortho-substituted aryl groups favours a four- rather than five-coordinate structure. With the benefit of data from other phosphoranes of this series it seems likely that both of these factors contribute to some extent.

### 3.2.4 $[P(2\text{-}(CH_3)C_6H_4)_2Cl_2][BCl_4]$

The terachloroborate salt of the phosphorane $P(2\text{-}(CH_3)C_6H_4)_2Cl_3$ was prepared in the usual manner - by reacting one equivalent of $BCl_3$ (1M in hexanes) with the phosphorane dissolved in $CH_2Cl_2$. It was isolated as a white solid which was almost insoluble in dichloromethane. The $^{31}P$ n.m.r. chemical shift for this compound dissolved in nitrobenzene = 92.2 ppm, and in the solid-state $\delta$ $^{31}P$ = 92.3 ppm. These values are as expected for a bis(aryl)dichlorophosphonium ion and confirm the ionic structure for $P(2\text{-}(CH_3)C_6H_4)_2Cl_3$. As for the parent phosphorane, no $^{35}Cl$ n.q.r. signals were seen for this compound at room temperature or 77 K, between 18 and 40 MHz.

### 3.2.5 $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_4$

Although this compound was first reported by Michaelis in 1897[18], there appear to be no further references to it in the literature. Michaelis prepared the phosphorane ($P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_4$) in what is now the standard method for arylchlorophosphoranes i.e. by direct chlorination of the phosphinous dichloride ($P(2,4,6-(CH_3)_3C_6H_2)Cl_2$), which itself was prepared by the $AlCl_3$ catalysed reaction of mesitylene with phosphorus trichloride. By using Michaelis' method with Kharrasova's modification[34] for the phosphinous dichloride preparation (see experimental section), mesityltetrachlorophosphorane was prepared. The $^{31}P$ n.m.r. spectrum of the dichloromethane solution of $P(2,4,6-(CH_3)_3C_6H_2)Cl_4$ showed a single signal at $\delta\ ^{31}P = -40.2$ ppm, indicative of a molecular, five-coordinate structure. This is confirmed by the $^{35}Cl$ n.q.r. spectrum (see table 3.5) of this compound at 77 K, which shows just two signals of equal intensity at 34.25 MHz and 24.64 MHz, ascribed to the two equatorial and two axial chlorines respectively in a $\psi$tbp structure. The mesityl group thus takes up the remaining equatorial site (see fig. 3.3).

| Temperature | $\nu^{35}Cl$ / MHz (rel. intensity) | | intensity ratio |
|---|---|---|---|
| | $\nu_{eq}$ | $\nu_{ax}$ | eq : ax |
| 298 K | 33.53 (2) | 24.31 (2) | 2:2 |
| 195 K | 33.94 (2) | 24.43 (2) | 2:2 |
| 77 K | 34.25 (2) | 24.64 (2) | 2:2 |

**Table 3.5 — $^{35}Cl$ n.q.r. data for $P(2,4,6-(CH_3)_3C_6H_2)Cl_4$**

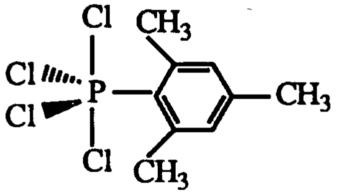


**Figure 3.3 — Deduced Structure of $P(2,4,6-(CH_3)_3C_6H_2)Cl_4$**

### 3.2.6 $[P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_3][BCl_4]$

The tetrachloroborate salt of the phosphorane $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_4$ was prepared in the usual manner - by reacting one equivalent of $BCl_3$ (1M in hexanes) with the phosphorane dissolved in $CH_2Cl_2$. It was isolated as a brown solid. The $^{31}P$ n.m.r. chemical shift for this compound dissolved in nitrobenzene of 96.1 ppm is as would be expected for the mesityltrichlorophosphonium ion, and confirms the molecular structure for $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_4$. No $^{35}Cl$ n.q.r. signals were seen for this compound at room temperature or 77 K, between 18 and 40 MHz, and elemental analysis gave very poor results, suggesting decomposition (particularly given the brown colouration of the solid).

### 3.2.7 $P(2,4,6\text{-}(CH_3)_3C_6H_2)_2Cl_3$

The bisarylphosphinous chloride, $P(2,4,6\text{-}(CH_3)_3C_6H_2)_2Cl$, was prepared by the action of two equivalents of the aryllithium reagent on $PCl_3$[35,36]. The chlorination of $P(2,4,6\text{-}(CH_3)_3C_6H_2)_2Cl$ in dichloromethane solution resulted in the precipitation of a small quantity of a pale yellow solid. On concentrating the solution under reduced pressure more of the solid was precipitated and this was then removed by filtration. After drying *in vacuo* the $^{31}P$ n.m.r. spectrum (in $CH_2Cl_2$ in which the product is sparingly soluble) showed a single peak at 88.4 ppm, and in nitrobenzene the $^{31}P$ chemical shift was found to be identical to this value. No $^{35}Cl$ n.q.r. signals were seen for this compound at room temperature or 77 K, between 18 and 40 MHz, though from the solution-state chemical shifts, and its low solubility in non-polar solvents, like the other bisarylchlorophosphoranes with bulky ortho-substituents, this compound almost certainly has the phosphonium salt structure in the solid.

### 3.2.8 $[P(2,4,6-(CH_3)_3C_6H_2)_2Cl_2][BCl_4]$

The reaction of one equivalent of $BCl_3$ (1M in hexanes) with the phosphorane suspended in $CH_2Cl_2$ produced a brown, sticky solid. The $^{31}P$ n.m.r. chemical shift for this material dissolved in nitrobenzene of 88.7 ppm confirms the phosphonium salt structure for the phosphorane (in solution). However, the appearance of the product and poor results for elemental analysis, as in the mono-aryl analogue, strongly suggest some degree of decomposition.

### 3.2.9 $P(C_6Cl_5)Cl_4$

Neither the phosphinous dichloride nor the phosphorane itself have been reported in the literature. However, $P(S)(C_6Cl_5)Cl_2$ [37] and the tertiary phosphines $P(C_6H_5)_2(C_6Cl_5)$ and $P(C_6H_5)(C_6Cl_5)_2$ are known[38,39]. The phosphinous dichloride can be prepared by the action of the aryllithium[38], arylzinc chloride[40] or arylmagnesium chloride[39,41] on $PCl_3$. The Grignard is the reagent of preference as it is stable at room temperature and can be prepared in suitably large quantities (see experimental section). Although $P(C_6Cl_5)Cl_2$ is not particularly soluble in dichloromethane, chlorination to form the phosphorane proceeds normally by bubbling chlorine gas through a suspension of the phosphinous dichloride in $CH_2Cl_2$. The product ($P(C_6Cl_5)Cl_4$) is soluble in dichloromethane and ( unlike $P(C_6Cl_5)Cl_2$) is extremely moisture sensitive - even short-term exposure to air results in rapid hydrolysis to give $P(C_6Cl_5)(O)Cl_2$ - $\delta$ $^{31}P$ ($CH_2Cl_2$) = 17.9 ppm. The $^{31}P$ n.m.r. chemical shift of -50.6 ppm for $P(C_6Cl_5)Cl_4$ in dichloromethane solution suggests that the phosphorane is molecular, and for the solid $\delta$ $^{31}P$= -50.3 ppm, which supports this deduction. It would be expected that the perchlorophenyl group would take up an axial site in a $\psi$tbp structure, as for $P(CCl_3)Cl_4$ or

$P(C_6F_5)Cl_4$. However no $^{35}$Cl n.q.r. signals were seen over the range 20 to 45 MHz at 77 K or room temperature (this should cover axial and equatorial P-Cl chlorine resonances and the perchlorophenyl C-Cl resonances). Even after recrystallisation of the phosphorane ($CH_2Cl_2$ / hexane), no $^{35}$Cl n.q.r. signals were seen. A possible explanation is that in the solid a large number of crystallographic inequivalences exist, which results in many signal splittings which would be lost in the background noise. Apart from the tetrachloroborate salt (see below), the phosphonium ion was also generated by the action of $SbCl_5$[42] on the phosphinous dichloride in dichloromethane:

$$P(C_6Cl_5)Cl_2 + 2SbCl_5 \longrightarrow P(C_6Cl_5)Cl_3^+SbCl_6^- + SbCl_3$$

The $^{31}$P n.m.r. spectrum of the solid, brown precipitate from this reaction, dissolved in $PhNO_2$, gave a single signal at 90.8 ppm - a reasonable value for $P(C_6Cl_5)Cl_3^+$ which compares well with that for the tetrachloroborate. However, although by $^{31}$P n.m.r. this reaction gives only the desired phosphonium ion, the brown solid isolated gave a very poor elemental analysis, probably due to contamination with $SbCl_3$. In general, any of the phosphinous dichlorides in this series will be oxidised to the phosphonium ion by the action of $SbCl_5$. However, none of the hexachloroantimonates formed in this way could be isolated to give reasonable elemental analyses. In short, although this provides a quick way to find the $^{31}$P n.m.r. chemical shift for the phosphonium ion, hexachloroantimonate salts ($[PR_nCl_{4-n}][SbCl_6]$) are best prepared by reacting $SbCl_5$ with the phosphorane itself.

### 3.2.10 $[P(C_6Cl_5)Cl_3][BCl_4]$

The tetrachloroborate salt of the phosphorane $P(C_6Cl_5)Cl_4$ was prepared in the usual manner - by reacting one equivalent of $BCl_3$ (1M in hexanes) with the phosphorane dissolved in $CH_2Cl_2$. Like its parent phosphorane, this tetrachloroborate salt is highly air- and moisture-sensitive. It is almost insoluble in dichloromethane. In nitrobenzene $\delta\ ^{31}P = 90.3$ ppm, which compares well with the value for the aryltrichlorophosphonium ion generated by the oxidation of $P(C_6Cl_5)Cl_2$ by $SbCl_5$ (see above), and confirms that $P(C_6Cl_5)Cl_4$ is molecular. No $^{35}Cl$ n.q.r. signals were seen in the range 18 to 45 MHz, at room temperature or 77 K, as was also the case for the phosphorane itself.

### 3.2.11 $P(C_6Cl_5)_2Cl_3$

Due to to the difficulty in obtaining the bis(aryl)phosphinous chloride in a suitably pure form it has not been possible to isolate the phosphorane itself. $P(C_6Cl_5)_2Cl$ is formed when two equivalents of $Mg(C_6Cl_5)Cl$ are added to one equivalent of $PCl_3$ in THF. When $P(C_6Cl_5)Cl_2$ is prepared in a similar manner it can be purified by subliming from the solids after the volatiles are removed, at the end of the reaction. However, it was found not to be possible to isolate $P(C_6Cl_5)_2Cl$ from the crude reaction mixture in this manner, and no solvent was found to dissolve this product selectively. Impure samples of the bis(aryl)phosphinous chloride were treated with chlorine gas, in dichloromethane. Although the results are of an impure system, which is always risky if one wishes to draw structural conclusions, they do seem to be at least partially substantiated by comparison with other phosphoranes in this series. The $^{31}P$ n.m.r. chemical shift for $P(C_6Cl_5)_2Cl$ in toluene = 76.5 ppm. After chlorinating a suspension of the crude phosphine in dichloromethane with chlorine gas, the remaining solids, when redissolved in $PhNO_2$, gave a $\delta$ $^{31}P$ of 76.1 ppm. Alone, this result would suggest that chlorination had been unsuccessful and the $^{31}P$ chemical shift was that of the starting material. However, when an excess of $SbCl_5$ was added to $P(C_6Cl_5)_2Cl$ in nitrobenzene solution the resultant mixture gave a $^{31}P$ n.m.r. shift of 76.6 ppm. It seems unlikely that $P(C_6Cl_5)_2Cl$ does not react with antimony pentachloride, or even that it should be unaffected by chlorine gas. The tentative conclusion is that the phosphorane is formed and that it is ionic in nitrobenzene solution, with a chemical shift which is fortuitously close to that of the phosphine starting material. Further, the reaction of $P(C_6Cl_5)_2Cl$ with $SbCl_5$ almost certainly produces the phosphonium hexachloroantimonate salt which, given that the phosphorane itself has the phosphonium salt structure, would be expected to give a similar $^{31}P$ n.m.r. shift. For this to be confirmed, a route to the pure phosphine starting material needs to be found.

### 3.2.12 $[P(C_6Cl_5)_2Cl_2][BCl_4]$

Due to the reasons given above for the difficulty in preparing the parent phosphorane, it was not possible to prepare its tetrachloroborate salt. There is some evidence for the hexachloroantimonate derivative (see above), and should it be possible to obtain the phosphorane in reasonable purity, there is no reason why its tetrachloroborate salt could not then be formed by the usual reaction with $BCl_3$.

### 3.2.13 $P(2\text{-}(CF_3)C_6H_4)Cl_4$

Although the phosphinous dichloride, $P(2\text{-}(CF_3)C_6H_4)Cl_2$, has been mentioned in the literature[43], together with its meta-[44] and para-isomers[45], there have been no reports of $P(2\text{-}(CF_3)C_6H_4)Cl_4$. The arylzinc chloride can be prepared *in situ* from the Grignard and $ZnCl_2$. However, the reaction is slow and requires three hours under reflux. The resultant yield of $P(2\text{-}(CF_3)C_6H_4)Cl_2$ is poor. Better results were obtained by reacting $Mg(2\text{-}(CF_3)C_6H_4)Br$ directly with $PCl_3$ at 220 K, even though this does give a mixture of products, in which there is up to 60 % Br incorporation and around 30 % $P(2\text{-}(CF_3)C_6H_4)_2X$ ($X$ = Cl or Br). The desired mono(aryl)phosphinous dihalide can be isolated by fractional distillation and chlorine for bromine exchange can be facilitated by the use of $NEt_4Cl$. The phosphorane was then prepared, in the usual way, by chlorination of $P(2\text{-}(CF_3)C_6H_4)Cl_2$ in dichloromethane with dry chlorine gas. The solution-state $^{31}P$ n.m.r. spectrun showed a single signal at -41.7 ppm in $CH_2Cl_2$. Such a relatively up-field shift is indicative of a five-coordinate, molecular phosphorane. This was confirmed by comparison with the $^{31}P$ n.m.r. shift for the phosphonium ion in the tetrachloroborate salt (see below) of 101.5 ppm. Of all the arylchlorophosphoranes in this series, $P(2\text{-}(CF_3)C_6H_4)Cl_4$ gave the $^{35}Cl$ n.q.r. spectrum with the best signal to noise ratio (see fig. 3.4) The $^{37}Cl$ signals for the equatorial chlorines were also clearly visible. It is confirmed by $^{35}Cl$ n.q.r. that the phosphorane does indeed have the five-coordinate $\psi$tbp structure with an overall equatorial to axial $^{35}Cl$ signal intensity ratio of 3:1 (see table 3.6). The aryl group is thus in an axial position as shown in fig. 3.5. The crystallographic splitting of the axial and equatorial signals at 77 K would suggest that there are at least three $P(2\text{-}(CF_3)C_6H_4)Cl_4$ molecules to the asymmetric unit. In one of the three sites there is a further crystallographic splitting of the equatorial chlorines. Thus overall there are four signals of intensity 3:2:3:1 for the equatorial chlorines, and three signals of relative intensity 1:1:1 for the axial chlorines. On warming to 195 K two of the axial signals are seen to have combined, though there remain four signals for the equatorial chlorines.

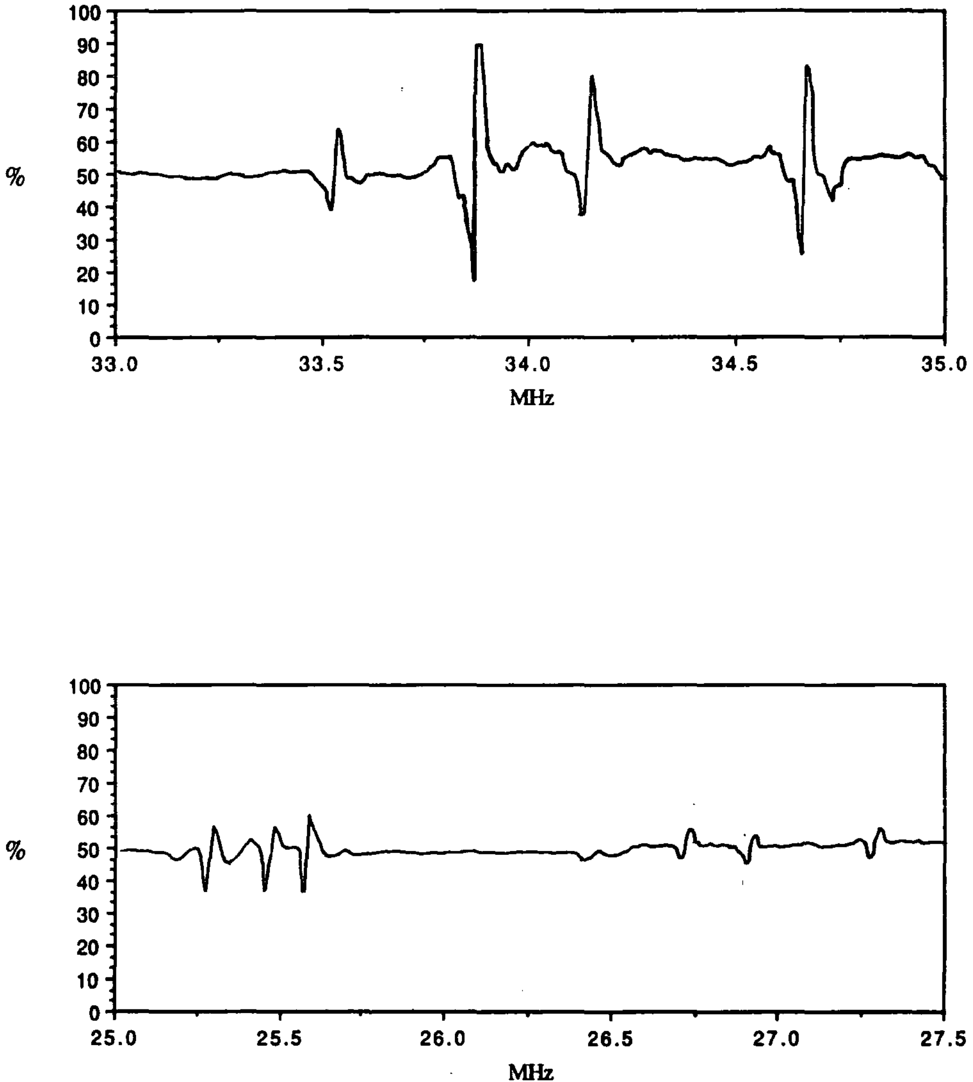


**Figure 3.4** — The 77 K $^{35}$Cl n.q.r. Spectrum of $P(2\text{-}(CF_3)C_6H_4)Cl_4$, a) $\nu_{eq}$, b) $\nu_{ax}$ with $^{37}$Cl $\nu_{eq}$ Signals.

| Temperature | $\nu$ $^{35}$Cl / MHz (rel. intensity) | | intensity ratio |
|---|---|---|---|
| | $\nu_{eq}$ | $\nu_{ax}$ | eq : ax |
| 298 K | no signal seen | | - |
| 195 K | 34.21 (3) | 25.08 (2) | |
| | 33.51 (2) | 25.31 (1) | |
| | 33.41 (3) | | |
| | 32.87 (1) | | 3:1 |
| 77 K | 34.68 (3) | 25.29 (1) | |
| | 34.59 (2) | 25.48 (1) | |
| | 33.89 (3) | 25.59 (1) | |
| | 33.53 (1) | | 3:1 |

**Table 3.6 — $^{35}$Cl n.q.r. data for $P(2\text{-}(CF_3)C_6H_4)Cl_4$**

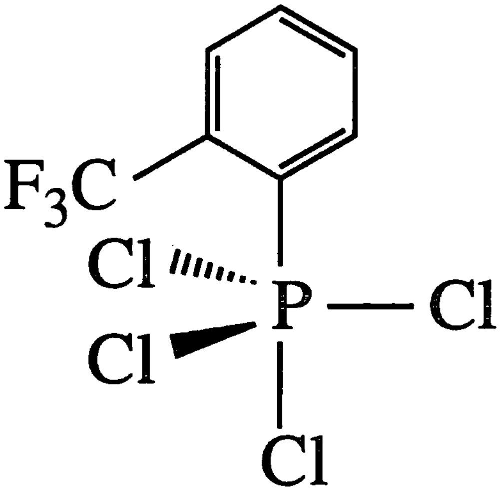


**Figure 3.5 — Deduced Structure of $P(2\text{-}(CF_3)C_6H_4)Cl_4$**

### 3.2.14 $[P(2\text{-}(CF_3)C_6H_4)Cl_3][BCl_4]$

The tetrachloroborate salt of the phosphorane $P(2\text{-}(CF_3)C_6H_4)Cl_4$ was prepared in the usual manner - by reacting one equivalent of $BCl_3$ (1M in hexanes) with the phosphorane dissolved in $CH_2Cl_2$. $[P(2\text{-}(CF_3)C_6H_4)Cl_3][BCl_4]$ is unstable at room temperature, even in a sealed tube. Over a period of days it decomposes to form a black, multi-component mixture. If refrigerated, it can be stored for a number of weeks without serious degradation, but all the chemical and physical data listed here were obtained within 24 hours of the material being prepared. The salt is insoluble in non-polar solvents and only marginally soluble in dichloromethane. $\delta\ ^{31}P$ / ($PhNO_2$) = 96.3 ppm and for the solid $\delta\ ^{31}P$ = 99.8 ppm. These are consistent with the $^{31}P$ n.m.r. chemical shift values expected for an aryltrichlorophosphonium ion. The $^{35}Cl$ n.q.r. spectrum at 77 K (see table 3.7) would suggest one formula unit per unit cell. All the chlorine atoms in both the phosphonium and the tetrachloborate ions are crystallographically inequivalent giving rise to three signals of equal intensity for $P(2\text{-}(CF_3)C_6H_4)Cl_3^+$ and four of equal intensity for $BCl_4^-$.

| Temperature | $\nu^{35}Cl$ / MHz (rel. intensity) | |
|---|---|---|
| | $\nu_{P-Cl}$ | $\nu_{B-Cl}$ |
| 77 K | 32.13 (1) | 21.65 (1) |
| | 32.02 (1) | 21.38 (1) |
| | 31.85 (1) | 21.23 (1) |
| | | 21.03 (1) |

**Table 3.7 — $^{35}Cl$ n.q.r. data for $[P(2\text{-}(CF_3)C_6H_4)Cl_3][BCl_4]$**

### 3.2.15 $P(2\text{-}(CF_3)C_6H_4)_2Cl_3$

There are no reports of this compound in the literature. It was prepared, in the usual way, by chlorination of a dichloromethane solution of the bis(aryl)-phosphinous chloride with dry chlorine gas. $P(2\text{-}(CF_3)C_6H_4)_2Cl$ was itself prepared by the action of $Mg(2\text{-}(CF_3)C_6H_4)Br$ on $PCl_3$. By $^{31}P$ n.m.r. the bis(aryl)-phosphinous halide produced in this reaction was shown to contain up to 50 % $P(2\text{-}(CF_3)C_6H_4)_2Br$. However all of the bromo-incorporated product could be easily converted to the desired chlorophosphine by treatment with $NEt_4Cl$ (see experimental). The solution-state $^{31}P$ n.m.r. chemical shift for $P(2\text{-}(CF_3)C_6H_4)_2Cl_3$ is very solvent dependent. In dichloromethane $\delta\ ^{31}P = 74.6$ ppm and the line is broad. In nitrobenzene the phosphorane gives a $^{31}P$ chemical shift at ca. 50.9 ppm, but the peak is extremely broad. This would suggest that, in solution, there are significant quantities of both molecular and ionic forms of $P(2\text{-}(CF_3)C_6H_4)_2Cl_3$ in equilibrium:

$$P(2(CF_3)C_6H_4)_2Cl_3 \rightleftharpoons P(2(CF_3)C_6H_4)_2Cl_2^+ + Cl^-$$

As a result of rapid exchange only a single, intermediate signal is seen in the $^{31}P$ n.m.r. spectrum. However, particularly in nitrobenzene where the peak is not much more than a hump on the baseline of the spectrum, it appears that exchange between the two structural forms is comparatively slow for this class of compounds. The tetrachloroborate salt of the phosphorane (see below) gives a sharp $^{31}P$ n.m.r. signal at 96.3 ppm. This confirms that in solution the phosphorane itself is not fully ionised. However, these results give little clue as to the solid-state structure of $P(2\text{-}(CF_3)C_6H_4)_2Cl_3$. Unfortunately no signals were seen by $^{35}$Cl n.q.r. at room temperature or 77 K, in the range 20 to 40 MHz. However, solid-state $^{31}$P n.m.r. was possible - $\delta$ $^{31}$P = 93.6 ppm. By comparison with the tetrachloroborate this confirms that in the solid $P(2\text{-}(CF_3)C_6H_4)_2Cl_3$ has the phosphonium salt structure. Unlike $P(2\text{-}(CH_3)C_6H_4)_2Cl_3$, this result cannot be rationalised on electronic grounds. The relatively electron-withdrawing $2\text{-}(CF_3)C_6H_4$group would not be expected to help stabilise the phosphonium ion by delocalising the positive charge - quite the opposite. The conclusion has to be that the bulky ortho-$CF_3$ group on two aromatic ligands results in a four- rather than five- coordinate structure being preferred. However, as with $PCl_5$, it may be possible to obtain the solely five-coordinate form in solution, given the right choice of solvent.

### 3.2.16 $[P(2\text{-}(CF_3)C_6H_4)_2Cl_2][BCl_4]$

The tetrachloroborate salt of the phosphorane $P(2\text{-}(CF_3)C_6H_4)_2Cl_3$ was prepared in the usual manner - by reacting one equivalent of $BCl_3$ (1M in hexanes) with the phosphorane dissolved in $CH_2Cl_2$. It was isolated as a white solid which is almost insoluble in dichloromethane. The $^{31}$P n.m.r. chemical shift for this compound dissolved in nitrobenzene = 96.3 ppm, and in the solid-state $\delta$ $^{31}$P = 99.8 ppm. These values are as expected for the bis(aryl)dichlorophosphonium ion and confirm the ionic structure in the solid-state for $P(2\text{-}(CF_3)C_6H_4)_2Cl_3$. As for the parent phosphorane, no $^{35}$Cl n.q.r. signals were seen for this compound at room temperature or 77 K, between 18 and 40 MHz.

### 3.2.17 $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_4$

There are no reports of this compound in the literature, but it can be made in the standard manner by chlorination of a dichloromethane solution of the arylphosphinous dichloride with dry chlorine gas. $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_2$[46] was prepared by the action of the aryllithium TMEDA complex on phosphorous trichloride (see experimental section). As demonstrated by Aeberli and Houlihan[47], lithiation of 1,3-bis(trifluoromethyl)benzene with butyllithium but without the presence of TMEDA resulted in an approximate 1:1 mixture of the 2,4- and $2,6\text{-}(CF_3)_2C_6H_3.Li$, which thus gave an inseparable mixture of the two arylphosphinous dichloride isomers after the reaction with $PCl_3$. The solution state $^{31}P$ n.m.r. spectrum of $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_4$ ($\delta$ $^{31}P(CH_2Cl_2)$ = -48.3 ppm) suggests a five-coordinate, molecular phosphorane. The $^{35}Cl$ n.q.r. spectrum (see table 3.8) confirms the structure as $\psi$tbp and the eqatorial : axial $^{35}Cl$ signal intensity ratio of 3:1 places the aryl group in an axial position (see fig. 3.6). Although at 77 K only one peak is seen for the axial Cl, the equatorial signal is split into two equally intense peaks, suggesting two different crystallographic sites per unit cell. On warming to cardice temperature the equatorial Cl signal splitting did decrease but there was no coalescence, and no phase change (as for the tris(trifluoromethyl) analogue) was indicated over the temperature range 77 - 195 K.

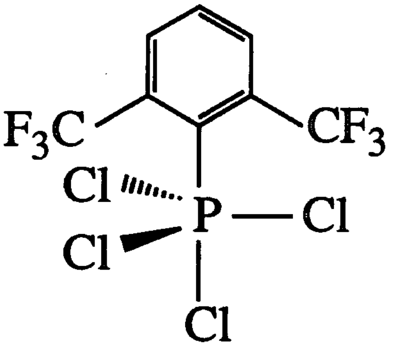


**Figure 3.6 — Deduced Structure of $P(2,6\text{-}(CF_3)_2C_6H_3)PCl_4$**

| Temperature | $\nu^{35}$Cl / MHz (rel. intensity) | | intensity ratio |
|---|---|---|---|
| | $\nu_{eq}$ | $\nu_{ax}$ | eq : ax |
| 298 K | no signal seen | | |
| 195 K | 35.03 (3) | 26.02 (2) | |
| | 34.60 (3) | | 3:1 |
| 77 K | 35.53 (3) | 26.33 (2) | |
| | 35.04 (3) | | 3:1 |

**Table 3.8 — $^{35}$Cl n.q.r. data for $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_4$**

### 3.2.18 $[P(2,6\text{-}(CF_3)_2C_6H_3)Cl_3][BCl_4]$

The tetrachloroborate salt of the phosphorane $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_4$ was prepared in the usual manner - by reacting one equivalent of $BCl_3$ (1M in hexanes) with the phosphorane dissolved in $CH_2Cl_2$. The salt is insoluble in non-polar solvents and only marginally soluble in dichloromethane. $\delta$ $^{31}$P / ($PhNO_2$) = 97.1 ppm which is as expected for an aryltrichlorophosphonium ion. The $^{35}$Cl n.q.r. spectrum at 77 K exhibits signals in the regions expected for both the phosphonium ion and the tetrachloroborate ion (see table 3.9). The relative intensities of the $^{35}$Cl signals suggest that there is some multiple of four formula units per unit cell. There appear to be two, crystallographically equivalent, and two other, inequivalent, sites for both the $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_3^+$ ion and the $BCl_4^-$ ion. Theoretically, one would expect the overall intensity ratio of the chlorine signals for the phosphonium ion to those of the tetrachloroborate ion in this compound to be 3:4. However, comparison of signal intensities between separate species in a compound can rarely be done with a good degree of accuracy. This is due to differences in relaxation times and, in this case, changes in spectrometer signal response over such a large frequency range.

| Temperature | $\nu^{35}$Cl / MHz (rel. intensity) | |
|---|---|---|
| | $\nu_{P-Cl}$ | $\nu_{B-Cl}$ |
| 77 K | 31.75 (2) | 20.81 (2) |
| | 32.12 (1) | 21.15 (1) |
| | 32.75 (1) | 21.45 (1) |

**Table 3.9** — **$^{35}$Cl n.q.r. data for [P(2,6-$(CF_3)_2C_6H_3)Cl_3$][$BCl_4$]**

### 3.2.19 P(2,6-$(CF_3)_2C_6H_3)_2Cl_3$

The bisarylphosphinous chloride, P(2,6-$(CF_3)_2C_6H_3)_2Cl$, was prepared by the action of two equivalents of the aryllithium.TMEDA complex on $PCl_3$. The chlorination of P(2,6-$(CF_3)_2C_6H_3)_2Cl$ results not in the cleavage of an aryl group from phosphororus, as is the case in the analogous 2,4,6-$(CF_3)_3C_6H_2$ system, but in the formation of the desired bisaryl phosphorane. P(2,6-$(CF_3)_2C_6H_3)_2Cl_3$ is insoluble in non-polar solvents and only marginally soluble in dichloromethane, although it can be readily dissolved in nitrobenzene. Unlike P(2-$(CF_3)C_6H_4)_2Cl_3$, $^{31}$P n.m.r. would suggest that, when in solution, P(2,6-$(CF_3)_2C_6H_3)_2Cl_3$ is more or less fully ionised - single, sharp peaks were recorded at $\delta$ $^{31}$P = 84.6 ppm in dichloromethane and 84.7 ppm in nitrobenzene. Comparison of these values with the $^{31}$P n.m.r. chemical shift of 84.7 ppm for the tetrachloroborate salt of this compound in nitrobenzene solution thus confirms that this phosphorane has the phosphonium chloride structure in solution. Solid-state $^{31}$P n.m.r. gave three signals at 86.5, 83.6 and 77.3 ppm[33]. This confirms the phosphonium salt structure for the solid phosphorane and the three signals probably represent different crystallographic environments. Unfortunately, no $^{35}Cl$ n.q.r. signals were found for this compound at room temperature or 77 K, in the range 20 to 36 MHz. However, there is no doubt about the ionic structure of this compound in either solution or solid-state. This is rationalised on the grounds that the two very bulky aryl groups favour a four-coordinate phosphonium ion over a five-coordinate molecular structure, even though these groups would be regarded as too electron-withdrawing to stabilise the resultant positive charge on phosphorus.

### 3.2.20 $[P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_2][BCl_4]$

The tetrachloroborate salt of the phosphorane $P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_3$ was prepared in the usual manner - by reacting one equivalent of $BCl_3$ (1M in hexanes) with the phosphorane dissolved in $CH_2Cl_2$. It was isolated as a white solid which is almost insoluble in dichloromethane. The $^{31}P$ n.m.r. chemical shift for this compound dissolved in nitrobenzene = 84.7 ppm. This is as would be expected for a bis(aryl)dichlorophosphonium ion and confirms the ionic structure for $P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_3$. As for the parent phosphorane, no $^{35}Cl$ n.q.r. signals were seen for this compound at room temperature or 77 K, between 18 and 40 MHz.

### 3.2.21 $[P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_2][SbCl_6]$

The hexachloroantimonate salt of the phosphorane $P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_3$ was prepared by reacting one equivalent of $SbCl_5$ in dichloromethane with the phosphorane dissolved in the same solvent at -78°C. The product precipitates from the reaction mixture as a grey powder. The $^{31}P$ n.m.r. spectrum of the product dissolved in nitrobenzene showed a single signal at 84.7 ppm, identical to the phosphorus shift for its tetrachloroborate analogue (see above), but no $^{35}$Cl n.q.r. signals were obtained over the range 18 to 40 MHz for this compound.

### 3.2.22 $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_4$

2,4,6-tris(trifluoromethyl)tetrachlorophosphorane may be readily prepared by chlorination of the arylphosphinous dichloride[48] (prepared by the action of the aryllithium[49] on $PCl_3$) with chlorine gas. In $CH_2Cl_2$ solution the $^{31}$P n.m.r. shift of -47.9 ppm for the phosphorane suggests a five-coordinate molecular structure, as is also the case in the solid - $\delta\ ^{31}P_{solid}$ = -47.9 ppm. The $^{35}$Cl n.q.r. spectrum (see table 3.10) of the solid at room temperature (298 K) shows single signals at 34.35 and 25.84 MHz in an approximately 3:1 intensity ratio, which are ascribed to the equatorial and axial chlorines respectively in a $\psi$tbp structure, with the 2,4,6-$(CF_3)_3C_6H_2$ group occupying the remaining axial position (as would be expected for such an electronegative group - fig. 3.7).

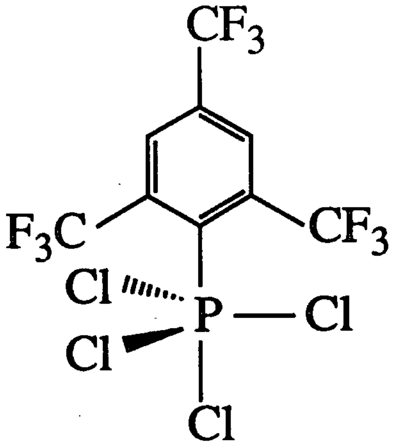


**Figure 3.7 — Deduced Structure of $P(2,4,6\text{-}(CF_3)_3C_6H_2)PCl_4$**

The $^{35}$Cl n.q.r. spectrum of $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_4$ at 77 K showed that although the equatorial : axial signal ratio was still 3:1 both signals were now split into two, suggesting that at low temperature the phosphorane molecules occupy two (see fig 3.8), slightly different, crystallographic sites. A variable temperature n.q.r. study was performed, looking at the equatorial chlorine signal (experimentally this was the most convenient having the higher signal to noise ratio), in order to discover whether the two signals seen at low temperatures gradually converge on warming the sample (i.e. a gradual averaging of the two phosphorane sites with increasing molecular vibration), or whether there is a definable phase transition temperature. Results (see fig. 3.9) show the that latter is, in fact, the case - the phase transition occurs over the range 190.5 ± 0.5 K. No evidence of hysteresis could be seen over the timescale of the experiment (i.e. approximately 20 minutes) on either warming or cooling the sample.

| Temperature | $\nu^{35}$Cl / MHz (rel. intensity) | | intensity ratio |
|---|---|---|---|
| | $\nu_{eq}$ | $\nu_{ax}$ | eq : ax |
| 298 K | 34.35 (3) | 25.84 (1) | 3:1 |
| 195 K | 34.80 (3) | 26.07 (1) | 3:1 |
| 77 K | 35.26 (3) | 25.98 (1) | |
| | 35.19 (3) | 25.91 (1) | 3:1 |

**Table 3.10 — $^{35}$Cl n.q.r. data for $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_4$**

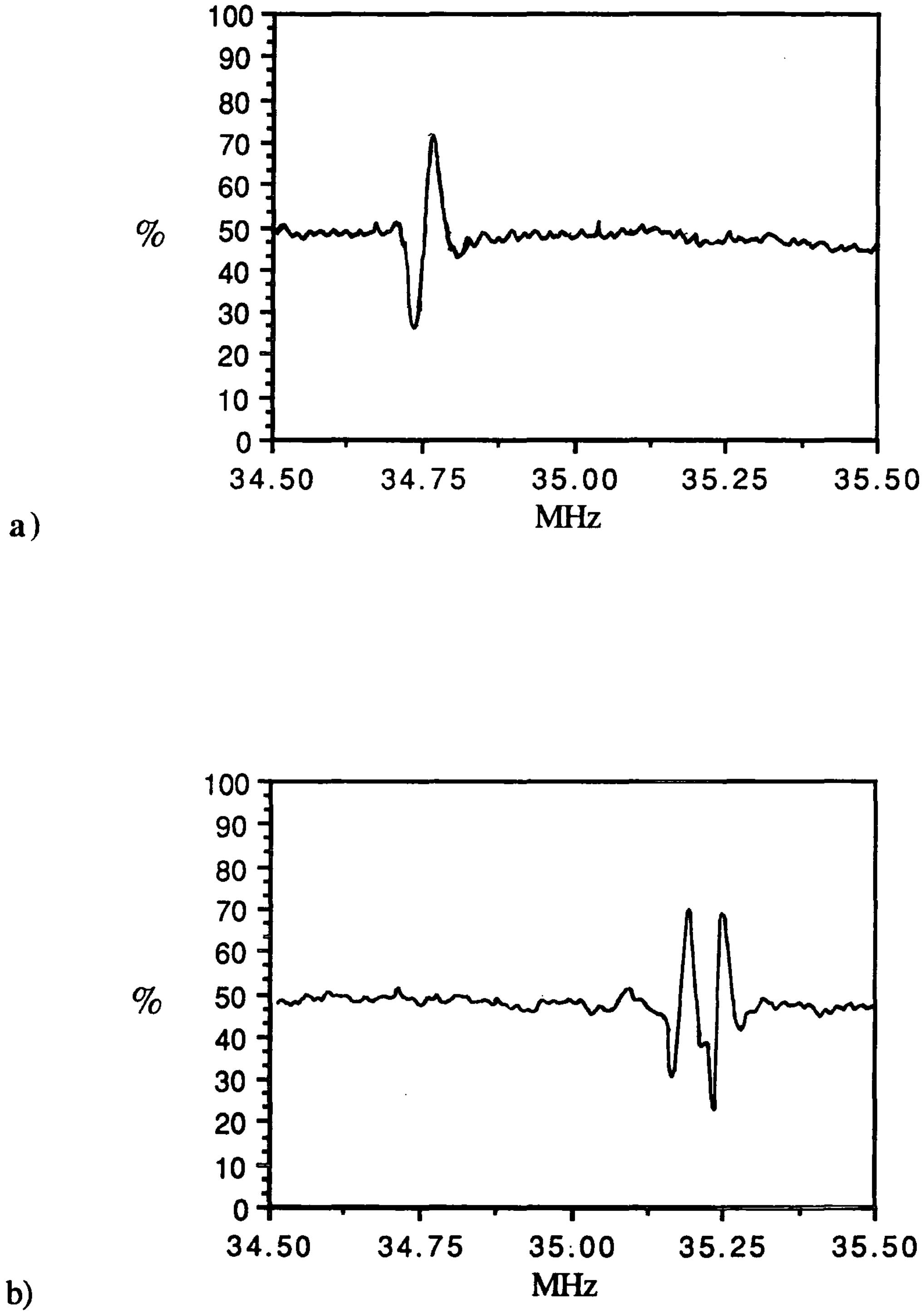


**Figure 3.8** — Equatorial $^{35}$Cl signals for $P(2,4,6-(CF_3)_3C_6H_2)Cl_4$ at a) 195 K and b) 77 K

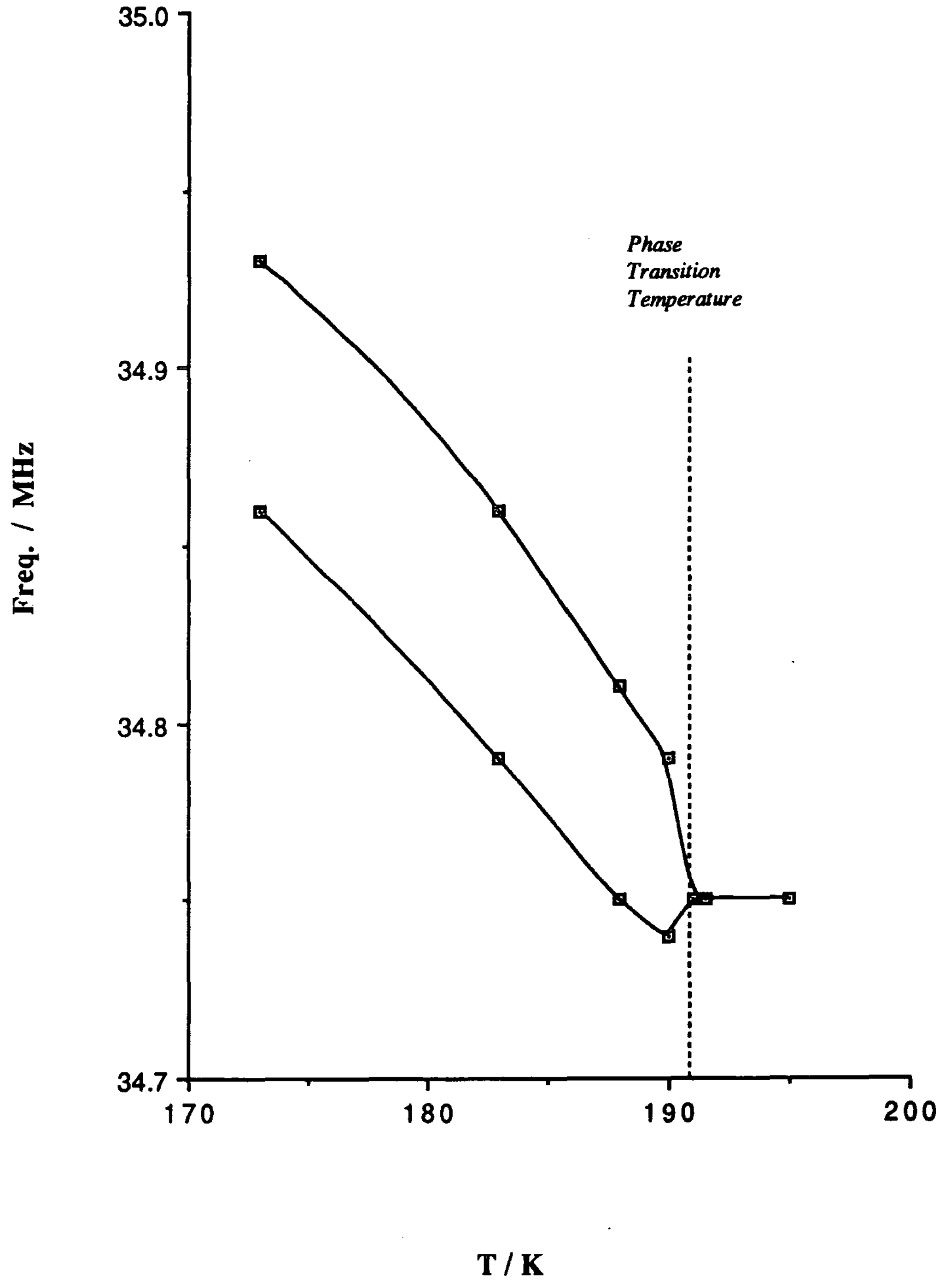


**Figure 3.9 — Variable Temperature $^{35}$Cl n.q.r. Study on $\nu_{eq}$ for $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_4$**

### 3.2.23 $[P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_3][BCl_4]$

The tetrachloroborate salt of the phosphorane $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_4$ was prepared in the usual manner - by reacting one equivalent of $BCl_3$ (1M in hexanes) with the phosphorane dissolved in $CH_2Cl_2$. Although highly air- and moisture-sensitive, when sealed in a tube under dry nitrogen this compound may be stored, indefinitely at room temperature (no noticeable change was seen in a sample more than two years after its preparation). $\delta$ $^{31}P$ ($PhNO_2$) = 97.1 ppm, which is identical to that of the $2,6\text{-}(CF_3)_2C_6H_3$ analogue and as expected for an aryltrichlorophosphonium ion. The $^{35}Cl$ n.q.r. spectrum at 77 K (see table 3.11) shows signals in the usual region for $BCl_4^-$, and the region expected for $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_3^+$. The crystallographic splittings suggest that there is some multiple of three formula units per unit cell - three equally intense signals being seen in the aryltrichlorophosphonium ion region and six equally intense signals in the tetrachloroborate ion region.

| Temperature | $\nu^{35}Cl$ / MHz (rel. intensity) | |
|---|---|---|
| | $\nu_{P-Cl}$ | $\nu_{B-Cl}$ |
| 77 K | 31.78 (1) | 20.44 (1) |
| | 31.96 (1) | 20.81 (1) |
| | 32.63 (1) | 21.51 (1) |
| | | 21.64 (1) |
| | | 21.72 (1) |
| | | 21.85 (1) |

**Table 3.11 — $^{35}Cl$ n.q.r. data for $[P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_3][BCl_4]$**

### 3.2.24 $[P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_3][SbCl_6]$

The hexachloroantimonate salt of the phosphorane $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_4$ was prepared by reacting one equivalent of $SbCl_5$ in dichloromethane with the phosphorane dissolved in the same solvent at -78°C. The product precipitates from the reaction mixture as a grey powder. The $^{31}P$ n.m.r. spectrum of the product dissolved in nitrobenzene showed a single signal at 95.9 ppm, in good agreement with its tetrachloroborate analogue (see above), but no $^{35}Cl$ n.q.r. signals were obtained over the range 18 to 40 MHz for this compound.

### 3.2.25 Chlorination of $P(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl$

The bisarylphosphinous chloride[48] was prepared by the action of two equivalents of the aryllithium on phosphorous trichloride. Bubbling an excess of dry chlorine gas through $P(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl$ in dichloromethane gave a reaction mixture which, on removal of the solvent under reduced pressure, yielded a colourless mixture, part liquid, part solid. A sample of this product in dichloromethane gave a $^{31}P$ n.m.r. spectrum with a single signal at $\delta\ ^{31}P = -47.8$ ppm. However, the $^{19}F$ n.m.r. spectrum showed there to be two $2,4,6\text{-}(CF_3)_3C_6H_2$-containing compounds (i.e. two signals in both the ortho- and para-$CF_3$ regions). Separation of this mixture. (see experimental section) was achieved by vacuum transfer of the more volatile component, which was isolated as a colourless liquid and characterised as $2,4,6\text{-}(CF_3)_3C_6H_2Cl$[50] by mass-spectroscopy, ($m/e = 316$, $M^+$) and $^{19}F$ n.m.r. , (o-$CF_3$, 6F, -65.0 ppm and p-$CF_3$, 3F, -65.4 ppm). The remaining solid was shown to be the monoaryl phosphorane $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_4$ by $^{31}P$ and $^{19}F$ n.m.r. . Although it was not possible to remove all of the aryl chloride entrained in the solid phosphorane, (hence ruling out elemental analysis), a weak

$^{35}$Cl n.q.r. spectrum at 77 K was obtained, which is identical for that already described for $P(2,4,6-(CF_3)_3C_6H_2)PCl_4$ (see above). Addition of zinc powder to a small sample of this solid in diethyl ether gave only the arylphosphinous dichloride, $P(2,4,6-(CF_3)_3C_6H_2)Cl_2$, hence confirming the previous loss of an aryl group.

$$P(2,4,6-(CF_3)_3C_6H_2)_2PCl + 2Cl_2 \longrightarrow$$

$$P(2,4,6-(CF_3)_3C_6H_2)PCl_4 + 2,4,6-(CF_3)_3C_6H_2Cl$$

Clearly, there was the possibility that the P-C cleavage was a result of the reaction of an intermediate bisaryl phosphorane with more chlorine. However, even when the reaction was carried out with a deficiency of chlorine, there was no evidence for the formation of $P(2,4,6-(CF_3)_3C_6H_2)_2Cl_3$; only the monoaryl phosphorane, the aryl chloride and unreacted bisarylphosphinous chloride were found in the product mixture on removal of the solvent. On the basis of this result it was still not clear as to whether the bisaryl phosphorane was inherently unstable, or whether it is formed as an intermediate and reacts preferentially to $P(2,4,6-(CF_3)_3C_6H_2)_2Cl$ with a second molecule of $Cl_2$. If the latter is the case it may be possible to prepare $P(2,4,6-(CF_3)_3C_6H_2)_2Cl_3$ by the use of an alternative chlorinating agent. It has been shown for phosphines of the type $PR_nCl_{3-n}$, (n = 1 to 3, R = organo group), that they can be chlorinated with $PCl_5$[51], resulting in the desired organochlorophosphorane and $PCl_3$.

$$PR_nCl_{3-n} + PCl_5 \longrightarrow PR_nCl_{5-n} + PCl_3$$

The phosphorus trichloride is then easily removed *in vacuo* with the solvent. Addition of two equivalents of $PCl_5$ to a given phosphine of this type would be normally expected to yield the hexachlorophosphate derivative of the phosphorane, $[PR_nCl_{4-n}][PCl_6]$. Unfortunately, when one equivalent of $PCl_5$ was added to $P(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl$, no reaction was observed. The two compounds coexist indefinitely in solution. It is possible that a stronger chlorinating agent would be required, for example $SbCl_5$[42]. Thus an analogous reaction to that with $PCl_5$ can be proposed:

$$PR_nCl_{3-n} + SbCl_5 \longrightarrow PR_nCl_{5-n} + SbCl_3$$

However, with $SbCl_5$, regardless of the stoichiometry of the reaction, the usual product is the hexachlorantimonate salt of the phosphorane and the presumed intermediate, $PR_nCl_{5-n}$, is not seen.

$$PR_nCl_{3-n} + 2SbCl_5 \longrightarrow PR_nCl_{4-n}^{+}SbCl_6^{-} + SbCl_3$$

The reaction of one equivalent of $SbCl_5$ with $P(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl$ resulted in a reaction mixture, which by $^{31}P$ n.m.r. contained roughly equimolar amounts of the phosphine starting material and a compound with $\delta\ ^{31}P = 84.6$ ppm. This shift does not correspond to $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_3^+$ (see above) and there was no evidence for P-C cleavage or the formation of the aryl chloride. By comparison with $P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_3$ ($\delta\ ^{31}P = 84.6$ ppm) it seems almost certain that $P(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl_2^+$ is formed in this reaction. Obviously, the $^{31}P$ n.m.r. data does not indicate whether the counter-anion is $Cl^-$ (i.e. the "free" phosphorane is formed) or, as would be indicated by only half the phosphine having reacted,

$SbCl_6^-$ (i.e. the hexachloroantimonate salt, formed preferentially by two equivalents of $SbCl_5$ reacting with one of $P(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl$). The latter seems the more likely, and when a further one equivalent of $SbCl_5$ was added to the reaction mixture only the peak at 84.6 ppm was seen by $^{31}P$ n.m.r.. Most probably because of the presence of $SbCl_3$, chemical analysis after the removal of all the volatiles showed the product to be impure. Thus there is no evidence for the formation of the molecular phosphorane, presumably because of steric interactions, and the reaction of the phosphine with chlorine gas did not indicate the presence of the ionic form. Hence there is no proof for the existence of $P(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl_3$.

### 3.2.26 Chlorination of $P(2,4,6\text{-}(CF_3)_3C_6H_2)(C_6F_5)Cl$

The phosphinous chloride, (prepared from $P(C_6F_5)Cl_2$[12] and $2,4,6\text{-}(CF_3)_3\text{-}C_6H_2Li$), was found to react with chlorine gas in a similar way to $P(2,4,6\text{-}(CF_3)_3\text{-}C_6H_2)_2Cl$. In this case there was loss of the $2,4,6\text{-}(CF_3)_3C_6H_2$ group, forming the aryl chloride (characterised as above).

$$P(C_6F_5)(Ar)Cl + 2Cl_2 \longrightarrow P(C_6F_5)Cl_4 + ArCl$$

(Ar = $2,4,6\text{-}(CF_3)_3C_6H_2$)

There was no evidence for cleavage of the $C_6F_5$ group. Thus the only phosphorus-containing product from this reaction was $P(C_6F_5)Cl_4$, clearly indicated by the single peak at -70.1 ppm (Lit. 70.9 ppm[14,24]) in the $^{31}P$ n.m.r. spectrum. This result would appear to support the theory that P-C cleavage will occur on chlorination of a bis(aryl)chlorophosphine, given that there is sufficient crowding in the system to prevent the formation of a five-coordinate, molecular phosphorane, and that the substituents are sufficiently electron-withdrawing to destabilise the resultant phosphonium ion with respect to further reaction with chlorine.

### 3.2.27 Chlorination of $P(2,4,6\text{-}(CF_3)_3C_6H_2)(C_6H_5)Cl$

The phosphinous chloride was prepared from $P(Ph)Cl_2$ and $2,4,6\text{-}(CF_3)_3\text{-}C_6H_2Li$. Due to a shortage of $SF_4$ all the results on this system were obtained from work on a single sample starting with ~ 50 mg of the diarylphosphine. A dichloromethane solution of $P(2,4,6\text{-}(CF_3)_3C_6H_2)(Ph)Cl$ was chlorinated in the usual way, with dry chlorine gas. The volatiles were then removed *in vacuo* and the solid product redissolved in $CH_2Cl_2$. The $^{31}P$ n.m.r. spectrum of this solution showed a broad peak at -12.7 ppm. On the addition of a few drops of $SbCl_5$ to the tube the resonance moved downfield to give a sharp signal at 89.1 ppm, as expected for the $[P(Ph)(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_2]^+$ ion. Although clearly there is the need for further characterisation, it would appear in the light of these preliminary results, that this system behaves similarly to that for $P(2\text{-}(CF_3)C_6H_4)_2Cl_3$ (see above). Hence there is no cleavage of the $2,4,6\text{-}(CF_3)_3C_6H_2$ group on chlorination. The diarylphosphorane is formed, and in dichloromethane solution there is an exchanging equilibrium between the molecular and phosphonium salt structures

$$P(Ar)(Ph)Cl \xrightarrow{Cl_2} P(Ar)(Ph)Cl_3 \rightleftharpoons P(Ar)(Ph)Cl_2^+ + Cl^-$$

(Ar = $2,4,6\text{-}(CF_3)_3C_6H_2$)

### 3.2.28 $P(CH_2Cl)Cl_4$

The phosphorane, $P(CH_2Cl)Cl_4$, was prepared by the chlorination of a dichloromethane solution of the alkylphosphinous dichloride by passing through dry chlorine gas. $P(CH_2Cl)Cl_2$ was prepared by the method of Prishchenko *et al* [52], which involves firstly the reaction of phosphorus trichloride with dichloromethane and aluminium trichloride, to form the (chloromethyl)trichlorophosphonium tetrachloroaluminate salt. This is subsequently reduced *in situ* to the phosphine by the action of $P(OMe)Cl_2$[53]

$$PCl_3 + CH_2Cl_2 + AlCl_3 \xrightarrow{Reflux} [P(CH_2Cl)Cl_3][AlCl_4]$$

$$[P(CH_2Cl)Cl_3][AlCl_4] \xrightarrow{P(OMe)Cl_2} P(CH_2Cl)Cl_2 + P(O)Cl_3.AlCl_3 + MeCl$$

In the aryl systems listed above, addition of excess chlorine to the phosphine would only be expected to result in the formation of trichloride, which would not be stable to elimination of chlorine under vacuum, and so would not inhibit isolation of the pure phosphorane. Whereas chlorine would not be expected to react with the aryl substituents under these conditions, one route to the preparation of $P(CCl_3)Cl_4$ is by the "exhaustive" chlorination of $P(CH_3)Cl_2$[12]. Thus, to prevent any further chlorination of the chloromethyl group, care was taken to ensure that only just sufficient chlorine was used to react with all of the phosphine to form the desired phosphorane. This was achieved by bubbling the chlorine gas through the reaction mixture a little at a time, and following the reaction between additions by $^{31}P$ n.m.r. . Removal of the solvent and any excess chlorine under vacuum left a viscous milky liquid, which slowly solidified on standing at room temperature. The broad-band $^1H$-decoupled $^{31}P$ n.m.r. spectrum of this material in $CDCl_3$ gave a single signal at -39.0 ppm. In order to try and confirm that there had been no reaction of the chloromethyl group with the chlorine gas, the $^{31}$P n.m.r. spectrum was obtained $^{1}$H-coupled. This resulted in a broadening of the signal, with two shoulders on the line suggesting an unresolved triplet (as expected for $-CH_2-P<$), with an estimated $J_{PH}$of 5 or 6 Hz. The coupling constant was more accurately obtained from the $^{1}$H n.m.r. spectrum which showed a doublet at 5.26 ppm, $J_{PH}$ = 5.3 Hz. Confirmation of the retention of the $-CH_2-$ moiety was obtained from the $^{1}$H-coupled $^{13}$C n.m.r. spectrum, of the phosphorane, which showed a triplet C-H coupling of 167.3 Hz. . There is a marked downfield displacement of the $^{13}$C chemical shift and a more than doubling of the C-P coupling constant in going from the phosphinous dichloride ($\delta$ $^{13}$C = 48.8 ppm, $J_{CP}$ = 54.5 Hz) to the tetrachlorophosphorane ($\delta$ $^{13}$C = 72.7 ppm, $J_{CP}$ = 118.5 Hz). The $^{31}$P n.m.r. spectrum of $P(CH_2Cl)Cl_4$ in nitrobenzene showed a broad signal at +50.4 ppm, suggesting that in this solvent there is at least partial ionization of the phosphorane to the phosphonium ion. Addition of $SbCl_5$ to this solution produced a sharp peak in the $^{31}$P n.m.r. spectrum at 111.0 ppm, which compares well with the value of 112.4 ppm obtained for the phosphonium ion in $[P(CH_2Cl)Cl_3][AlCl_3]$, prepared from the $PCl_3/CH_2Cl_2/AlCl_3$ reaction (see above). There is gradual decomposition of the phosphorane, even when stored in a sealed container under nitrogen. Five days after its preparation it was estimated, by comparison of the relative $^{31}$P n.m.r. peak intensities, that up to 40 % of the phosphorane had decomposed. The $^{31}$P n.m.r. spectrum of the mixture showed the decomposition products to consist of small amounts of $PCl_3$, $PCl_5$, $P(CH_2Cl)Cl_2$ and a peak at 36 ppm, assigned to $P(O)(CH_2Cl)Cl_2$ (also seen from oxidation in air of the phosphinous dichloride). By far the major decomposition product was indicated by a signal at $\delta$ $^{31}$P = -23 ppm, which remains unassigned. The solid-state $^{31}$P n.m.r. spectrum of a fresh sample of $P(CH_2Cl)Cl_4$ (i.e. two hours after its preparation), obtained at -15°C, at which temperature all the phosphorane was solid, showed two signals: at +111.1 ppm and -206.1 ppm. This would suggest that at this temperature the phosphorane has the (chloromethyl)trichlorophosphonium (chloromethyl)-pentachlorophosphate structure, $[P(CH_2Cl)Cl_3][P(CH_2Cl)Cl_5]$, in the solid. The $^{31}P$ n.m.r. chemical shift for $[P(CH_2Cl)Cl_5]^-$ was confirmed by adding an excess of $N(Et)_4Cl$ to a nitromethane solution of $P(CH_2Cl)Cl_4$. The resultant mixture gave a signal at -206.8, in good agreement with the solid state value. Thus it appears that $P(CH_2Cl)Cl_4$ is the first phosphorane of the type $PR_nCl_{5-n}$, where R is an organo-group, to be shown to have the structure, $[PR_nCl_{4-n}][PR_nCl_{6-n}]$, (i.e. analogous to $PCl_5$ in the solid). Three fairly weak $^{35}Cl$ n.q.r. signals, all of equal intensity, were observed at 31.05, 31.17 and 31.68 MHz. These were assigned to the chlorine atoms in the $[P(CH_2Cl)Cl_3]^+$ ion, and do not correspond to the known values for $P(CH_2Cl)(O)Cl_2$[54,55]. However, no other signals were observed in the region 18 to 45 MHz (i.e. all the C-Cl resonances and the P-Cl resonances from the $[P(CH_2Cl)Cl_5]^-$ anion were too weak to be detected).

### 3.2.29 $[P(CH_2Cl)Cl_3][AlCl_4]$

(Chloromethyl)trichlorophosphonium tetrachloroaluminate is formed *in situ* in the preparation given above for the phosphinous dichloride. An attempt was made to isolate the phosphonium salt by refluxing a mixture of $PCl_3$, $AlCl_3$ and $CH_2Cl_2$ for 24 hours and then removing any remaining volatile material *in vacuo* . This left a brown, sticky residue, only soluble in polar solvents such as dichloromethane and nitromethane. $^1H$, $^{13}C$ and $^{31}P$ n.m.r. indicated only the presence of the desired product, but the general appearance and elemental analysis suggested that the compound was impure, which may be due to the presence of aluminium chloride.

However, there seems to be no reason to doubt the validity of the spectroscopic data for this compound, given the absence in any of the n.m.r. spectra of other impurities. The $^{31}P$ n.m.r. spectrum for this compound dissolved in $CD_3NO_2$ showed a single signal at 112.4 ppm, corresponding to $[P(CH_2Cl)Cl_3]^+$. The broad-band $^1H$ decoupled $^{13}C$ n.m.r. spectrum consisted of a doublet at $\delta\ ^{13}C = 42.8$ ppm, $J_{CP} = 71.1$ Hz. When the $^{13}C$ spectrum was obtained proton-coupled, a further triplet splitting was observed, $J_{CH} = 163.2$ Hz. The $^1H$ n.m.r. spectrum showed only a single broad peak at 5.51 ppm, with no resolved P-H coupling. The addition of 2,2'-bipyridyl to a solution of this compound in $CD_3NO_2$, produced two new signals in the $^{31}P$ n.m.r. spectrum at -143.4 and -151.1 ppm, with a relative intensity ratio of 1:4.3. These signals were assigned to the two possible isomers of the six-coordinate, cationic complex, $[P(CH_2Cl)Cl_3.bipy]^+$. Table 3.12 compares the $^{31}P$ n.m.r. data for this system with those for $PMeCl_3^+$ and $[PMeCl_3.bipy]^+$, published by Deng and Dillon[23].

| R | $PRCl_3^+$ | $[PRCl_3.bipy]^+$ | (rel. intensities) |
|---|---|---|---|
| $CH_3$ | 119.3 | -145.1 (1) | -150.0 (1) |
| $CH_2Cl$ | 112.4 | -143.4 (1) | -151.1 (4.3) |

**Table 3.12 — $^{31}P$ n.m.r. data for $PRCl_3^+$ and $[PRCl_3.bipy]^+$**

It is worth noting that, in the case of $[PMeCl_3.bipy]^+$, for the freshly prepared complex the signal at -150.0 ppm is more intense than that at -145.1 ppm. However, there was shown to be a gradual change in the two signal intensities, until at two hours after preparation the two isomers were present in solution in roughly equal amounts. No such change was seen in the chloromethyl system, even over a period of two weeks. No $^{35}Cl$ n.q.r. signals were seen for this compound at 77K or room temperature over the frequency range 20 to 45 MHz.

### 3.2.30 $P(CHCl_2)Cl_4$

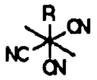
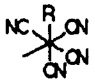
The phosphorane, $P(CHCl_2)Cl_4$, was prepared by the chlorination of a dichloromethane solution of the alkylphosphinous dichloride by passing through dry chlorine gas. $P(CHCl_2)Cl_4$ was prepared by the method of Prishchenko *et al* [52], which involves firstly the reaction of phosphorus trichloride with chloroform and aluminium trichloride, to form the (dichloromethyl)trichlorophosphonium tetrachloroaluminate salt. This can be subsequently reduced *in situ* to the phosphine by the action of $P(OMe)Cl_2$[53], though, in this case, zinc powder in diethyl ether was used as the reducing agent. The use of zinc in this way resulted in a poorer yield than quoted in the literature, but after the reduction step the phosphine in ether solution was successfully extracted from the reaction mixture by vacuum transfer. Removal of the ether by distillation then gave the pure product.

$$PCl_3 + CHCl_3 + AlCl_3 \overset{Reflux}{\longrightarrow} [P(CHCl_2)Cl_3][AlCl_4]$$

$$[P(CHCl_2)Cl_3][AlCl_4] \overset{Zn/Et_2O}{\longrightarrow} P(CHCl_2)Cl_2 + ZnCl_2.AlCl_3$$

When chlorine gas was slowly bubbled through a solution of $P(CHCl_2)Cl_2$, the desired tetrachlorophosphorane was formed, together with a small quantity of $P(CCl_3)Cl_4$[12], as indicated by $^{31}P$ n.m.r. . Carefully following the chlorination reaction by $^{31}P$ n.m.r. showed that, under these conditions, chlorination of the dichloromethyl group of the product phosphorane started to take place before chlorination of the phosphine was complete. The best result was a roughly 7:1 mixture of $P(CHCl_2)Cl_4$ and $P(CCl_3)Cl_4$ respectively, isolated as a pale yellow solid. However, apart from the fact that no $^{35}Cl$ n.q.r. spectrum could be obtained from the (dichloromethyl)tetrachlorophosphorane (possibly due to the impurity), there is no reason to doubt the validity of all other spectroscopic data obtained, particularly as $P(CCl_3)Cl_4$ is a molecular species and thus would not be expected to induce ionization of the other phosphorane. The broad-band $^1H$-decoupled $^{31}P$ n.m.r. spectrum of the phosphorane mixture in $CDCl_3$ gave signals at -34.1 ppm and -19.5 ppm for $P(CHCl_2)Cl_4$ and $P(CCl_3)Cl_4$[12] respectively. When the $^{31}P$ n.m.r. spectrum was obtained $^1H$-coupled the signal at -34.1 ppm was split to a doublet ($J_{PH}$ = 32.0 Hz), and as expected the $P(CCl_3)Cl_4$ signal showed no coupling. The $^1H$ n.m.r. spectrum showed a doublet at 6.79 ppm which confirmed the P-H coupling constant as 32.0 Hz. The broad-band $^1H$-decoupled $^{13}C$ n.m.r. spectrum of the phosphorane showed a doublet at 94.2 ppm ($J_{CP}$ = 142.1 Hz). When obtained proton-coupled, the $^{13}C$ n.m.r. signal showed a further doublet splitting ($J_{CH}$ = 194.5 Hz). As in the analogous chloromethyl system, there is a marked downfield displacement of the $^{13}C$ chemical shift and a more than doubling of the C-P coupling constant in going from the phosphinous dichloride ($\delta$ $^{13}C$ = 73.7 ppm, $J_{CP}$ = 70.5 Hz) to the tetrachlorophosphorane. No $^{13}C$ n.m.r. signals were seen for the $P(CCl_3)Cl_4$ compound in the mixture. The solid state $^{31}P$ n.m.r. spectrum gave a signal for $P(CHCl_2)Cl_4$ at -34.1 ppm, in good agreement with the solution-state value and confirming a molecular, five-coordinate structure for this phosphorane. Without $^{35}Cl$ n.q.r. data, however, the position of the dichloromethyl group in the $\psi$tbp structure (i.e equatorial or axial) remains unknown. Interestingly, the $P(CCl_3)Cl_4$ $^{31}P$ signal in this solid was recorded at 33.0 ppm. This is as would be expected given its molecular structure and by comparison with its dichloromethyl analogue. However, the solution-state $\delta$ $^{31}P$ values for this compound are all roughly in the range -19 to -20 ppm[12] showing only small variation with change in solvent[12] (not as would be expected for a molecular/ionic exchanging system). This apparent anomaly has yet to be explained.

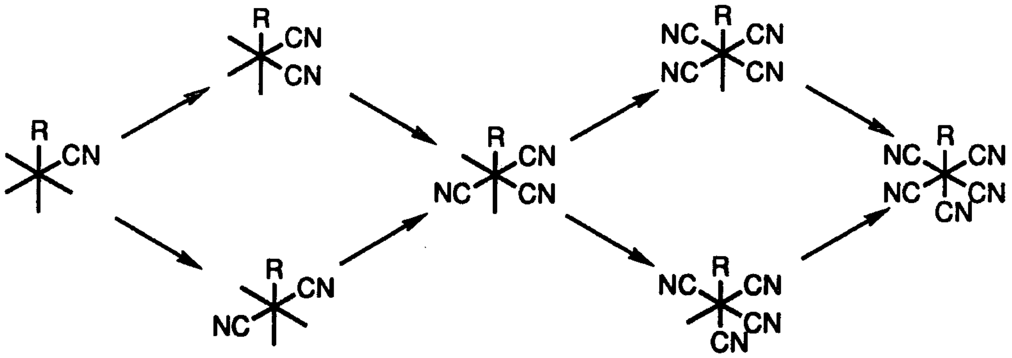
On addition of a roughly two-fold molar excess of $NEt_4Cl$ to a nitrobenzene solution of $P(CHCl_2)Cl_4$ (also containing $\sim$ 14 % of the total phosphorus in the form of $P(CCl_3)Cl_4$ - see above), the $^{31}P$ n.m.r. spectrum of the resultant mixture showed a signal at -202.2 ppm, corresponding to the limiting shift for the $[P(CHCl_2)Cl_5]^-$ ion. The formation of the $[P(CCl_3)Cl_5]^-$ ion was also evident from a resonance at -196.4 ppm, in good agreement with the already published value of -196.6 ppm[26] as the limiting shift for this species. When a small amount of AgCN was added to this solution, a new signal was discerned, attributed to one of the two possible isomers of the first substitution product $[P(CHCl_2)Cl_4CN]^-$. Addition of more AgCN caused the appearance of further upfield resonances, which could be assigned to particular members of the series $[P(CHCl_2)Cl_{5-n}(CN)_n]^-$, as shown in table 3.13. Excess AgCN ($\geq$ 5:1 molar ratio) led to three further resonances at -258.5, -260.3 and -263.4 ppm which correspond well to the known $\delta$ $^{31}P$ values for the three isomers of $[P(CCl_3)Cl_2(CN)_3]^-$ (substitution by cyanide is known to go no further in this system)[26], and to the very gradual (over some days) formation of a single resonance at -279.5 ppm, ascribed to the $[P(CHCl_2)(CN)_5]^-$ ion. Isomeric configurations were assigned to the intermediate chlorocyanophosphates by application of the method of pairwise interactions[26]. The Cl:Cl and CN:Cl terms were taken as -24.85 and -27.19 ppm respectively[26]. The $(CHCl_2)$:Cl term was then calculated from the limiting shift of $[P(CHCl_2)Cl_5]^-$ as -0.85 ppm. The ion $[P(CHCl_2)Cl_4CN]^-$ can exist in cis and

| Isomer | Ion | Calculated | Experimental |
|---|---|---|---|
| (A) |  | "-218.7" | -218.7 |
| (B) |  | -211.6 | - |
| (C) |  | -235.4 | -239.3* |
| (D) |  | -235.2 | -235.3 |
| (E) |  | -228.3 | - |
| (F) |  | -252.2 | -250.5 |
| (G) |  | -245.3 | - |
| (H) |  | -245.0 | - |
| (I) |  | -269.2 | -274.5* |
| (J) |  | -262.3 | -271.1 |
| (K) |  | "-279.5" | -279.5 |

(* = Most abundant isomer; experimental values for (A) and (K) used to calculate R:CN and CN:CN terms).

**Table 3.13 — Calculated and Experimental $^{31}$P n.m.r. Shifts (ppm) for $[P(CHCl_2)Cl_{5-n}(CN)_n]^-$**

trans forms, and since the trans isomer has no cis ($CHCl_2$):CN interactions, its shift can be calculated as -211.6 ppm. This is far from the value observed for the first cyano-substitute, which is therefore deduced to have the statistically more probable cis configuration. The ($CHCl_2$):CN term may be calculated from its shift as -10.33 ppm. Finally, the CN:CN term was calculated from the shift assigned to the $[P(CHCl_2)(CN)_5]^-$ as -29.77 ppm. The shifts of all the possible isomers in the series were then calculated, allowing assignment of the observed peaks to given species. Calculated shift values compare reasonably with those found experimentally, though there is some deviation, particularly for higher values of n. This is probably due to distortion from octahedral symmetry within the ions. It is evident from table 3.13 that not all the posible isomers for all given values of n were detected. For n = 1 to 3 those isomers which would be formed from cyanide substitution trans to the $CHCl_2$ group are apparently absent.



($R = CHCl_2$)

**Figure 3.10 — Cyanide Substitution Pathway into $[P(CHCl_2)Cl_{5-n}(CN)_n]^-$**

Although when n $< 4$ substitution trans to $CHCl_2$ is statistically less likely, the signal to noise ratio in the spectra was good enough to have detected the less intense peaks expected, assuming the site of substitution was being determined solely according to the laws of probability. Therefore it must be assumed that in this system, although complete substitution of chloride by cyanide can be achieved, substitution trans to $CHCl_2$ is disfavoured. The overall sequence of substitution is as shown in figure 3.10, and this pathway is identical to that of the previously determined $[PEtCl_{5-n}(CN)_n]^-$ system[26], and is chemically reasonable since no ionic rearrangements are necessary. As pointed out above, where $CCl_3$ is the organo group substitution goes no further than n = 3 (which was also confirmed in this experiment). This is attributed to the presence of the more electronegative trichloromethyl group, which stabilizes the 6-coordinate anion to dissociation (the expected mechanism to substitution being via the phosphorane). It appears that the $CHCl_2$ group is insufficiently electronegative to give this effect (i.e. behaves like Et).

### 3.2.31 $[P(CHCl_2)Cl_3][AlCl_4]$

(Dichloromethyl)trichlorophosphonium tetrachloroaluminate is formed *in situ* in the preparation given above for the phosphinous dichloride. The phosphonium salt was obtained as a white solid (unlike the chloromethyl analogue) on refluxing $PCl_3$, $AlCl_3$ and $CHCl_3$ for 6 hours and then removing any remaining volatile material *in vacuo* . A small quantity of this solid was then recrystallised from dichloromethane and elemental analysis was reasonable for $[P(CHCl_2)Cl_3][AlCl_4]$. The $^{31}P$ n.m.r. spectrum of this material in nitrobenzene showed a single peak at 106.7 ppm and, with $EtNO_2$ as solvent, at 108.2 ppm, as expected for the phosphonium ion. The addition of one molar equivalent of 2,2'-bipyridyl to a solution of this compound dissolved in nitrobenzene resulted in the mixture turning bright green. The $^{31}$P n.m.r. spectrum of this solution, immediately after preparation, showed two peaks of roughly equal intensity: a signal at -150.2 ppm, which was assigned to one of the two possible isomers of the six-coordinate, cationic complex, $[P(CHCl_2)Cl_3.bipy]^+$; and a peak at 148.5 ppm which corresponds to the phosphine $P(CHCl_2)Cl_2$. Addition of a further one molar equivalent of 2,2'-bipyridyl resulted in an increase in the intensity of the phosphine resonance and a corresponding decrease in the intensity of the peak at -150.2 ppm. However, at this stage a broad resonance was also observed at -200.4 ppm which is almost certainly due to the formation of the (dichloromethyl)pentachorophosphate ion, $[P(CHCl_2)Cl_5]^-$ (see above). Finally, addition of a further one equivalent of 2,2'-bipyridyl resulted in complete reduction to the phosphine, as indicated by $^{31}$P n.m.r. . The proposed pathway for this reduction, taking into account the formation of the $[P(CHCl_2)Cl_5]^-$ ion, is as follows: (*bipy* = 2,2'-bipyridyl)

a) firstly, addition of 2,2'-bipyridyl gave the six-coordinate cation:

$$bipy + [P(CHCl_2)Cl_3][AlCl_4] \longrightarrow [P(CHCl_2)Cl_3.bipy][AlCl_4]$$

b) secondly, there was transfer of 2,2'-bipyridyl from phosphorus to aluminium and chloride from aluminium to phosphorus, possibly in a stepwise process:

$$[P(CHCl_2)Cl_3.bipy][AlCl_4] \longrightarrow AlCl_3.bipy + P(CHCl_2)Cl_4$$

$$AlCl_3.bipy + P(CHCl_2)Cl_4 \longrightarrow [AlCl_2.bipy][P(CHCl_2)Cl_5]$$

c) and finally, reduction may occur via elimination of trichloride from the phosphate anion:

$$[P(CHCl_2)Cl_5]^- \xrightarrow{-Cl_3^-} P(CHCl_2)Cl_2.$$

The successive additions of 2,2'-bipyridyl were made within a few minutes of each other and the overall reaction may perhaps eventually go to completion with only one molar equivalent of 2,2'-bipyridyl. Just why $[P(CHCl_2)Cl_5]^-$ should be unstable in this system is unclear, as it can be formed from the phosphorane on addition of chloride without any immediate reduction taking place, although this may be a slow process. The (chloromethyl)pentachorophosphate ion is however believed to be inherently unstable (see above). Further, a similar reduction to the phosphine was shown to occur with $[P(CCl_3)Cl_3][SbCl_6]$ on attempting to form the relevant six-coordinate phosphorus cation[12] with 1,10-phenanthroline. However, in this case the $[P(CCl_3)Cl_5]^-$ ion was not detected, possibly because of its greater instability.

### 3.2.32 Acceptor Properties

As was explained above, one of the aims in studying arylchlorophosphoranes was to investigate their accepter properties with respect to Lewis bases. In particular, should the phosphorane accept chloride ion, then it is of interest to discover to what extent chloride can be substituted by cyanide in the resultant arylchlorophosphate ion[25,26]. It has been previously shown that $P(Ph)Cl_4$[22], as well as accepting chloride ion, will also accept various unhindered pyridines L to give molecular complexes $P(Ph)Cl_4L$ similar to those of $PCl_5$[20]. $P(C_6F_5)Cl_4$ has also been shown to complex with pyridine[24]. It should be noted, however, that phosphoranes with more than one organo group do not exhibit acceptor properties of this type. The phosphonium ion derivatives of molecular phosphoranes with strong Lewis acids[21,22,24] and those phosphoranes which have the phosphonium salt structure anyway (i.e. with alkyl substituents)[23] may accept bidentate pyridines (i.e. 1,10-phenanthroline and 2,2'-bipyridyl) to give six coordinate, cationic species (however, this is often not the case for systems with more than one organo substituent). Reactions of the quasi-phosphonium salts with pyridine can be more complex, with displacement of $Cl^-$ from the anion occurring to give the pyridine complex of the Lewis acid, the phosphorus-containing product being either the phosphorane or its pyridine adduct. Only in the case of $PCl_4^+$ salts was there clear spectroscopic evidence for the formation of the $PCl_4py_2^+$ ion as an intermediate in this process[56]. Organochlorophosphonium ions with more than one organo group also generally do not show acceptor properties, though weak addition complexes have been reported for $P(C_6F_5)_2Cl_2^+$ and even $P(C_6F_5)_3Cl^+$[24]. Surprisingly, of the compounds studied (see above), none of the aryltetrachlorophosphoranes with ortho-$CH_3$ or ortho-$CF_3$ substituents on the aryl group would accept chloride ion. When followed by $^{31}P$ n.m.r. , initial addition of the chloride donor ($NR_4Cl$, where R = ethyl, propyl or pentyl) to a solution of the phosphorane (in dichloromethane or nitrobenzene) resulted in no apparent reaction. Over a period of hours or days there was, however, a slow reduction of the phosphorane to the respective arylphosphonous dichloride. Here, reduction may be assisted by the formation of trichloride:

$$P(Ar)Cl_4 + Cl^- \longrightarrow P(Ar)Cl_2 + Cl_3^-$$

(Ar = aryl group with ortho-$CH_3$ or $CF_3$)

$P(C_6Cl_5)Cl_4$ also did not accept chloride ion and was reduced to $P(C_6Cl_5)Cl_2$.

Further, initial studies[57] would seem to suggest that even [(2-chloro)phenyl]tetrachlorophosphorane will not form the arylpentachlorophosphate ion in the presence of chloride, whereas its meta- and para-chloro isomers do. Rather than substituting into the arylpentachlorophosphate ion, it was attempted to obtain six-coordinate phosphorus species containing these bulky aryl groups by direct addition of cyanide to the respective phosphorane. However, addition of tetraalkylammonium cyanide to solutions of these phosphoranes also resulted in reduction. $^{31}P$ n.m.r. studies of the resultant reaction mixtures showed up to three products, $P(Ar)Cl_2$, $P(Ar)(CN)_2$ and $P(Ar)Cl(CN)$ (though signals attributed to the latter may have been due to cyanide substitution into species resulting from hydrolysis or oxidation). $\delta$ $^{31}P$ for $P(2\text{-}(CF_3)C_6H_4)(CN)_2$ = -71.3 ppm (quart. $J_{PF}$ = 61 Hz) and $\delta$ $^{31}P$ for $P(2,4,6\text{-}(CH_3)_3C_6H_2)(CN)_2$ = -93.1 ppm (see chap. 4 for the $^{31}P$ n.m.r. chemical shifts of other dicyanophosphines). It is not clear as to whether cyanide incorporation occurs in the reduction step (i.e. attack by cyanide ion followed by elimination of $Cl_2$), or whether it is only by simple substitution reactions into the P(V) or P(III) species. Similar results were obtained when the phosphoranes were reacted with tertiary amines (i.e. pyridine and trimethylamine) in attempts to form neutral, six-coordinate derivatives. In each case the arylphosphinous dichloride was produced. It is likely that these reactions proceed via six-coordinate intermediates, although these species are too short-lived to be observable on the n.m.r. time-scale. When the aryltrichlorophosphonium tetrachloroborates with bulky, ortho-substituted aryl groups were treated with 1,10-phenanthroline or 2,2'-bipyridyl, no reaction was observed by $^{31}P$ n.m.r. . With pyridine or trimethylamine the result was reduction to the arylphosphinousdichloride, as was also the case with cyanide. A reaction sequence, analogous to that for the phosphoranes, can be proposed with, in this case, a five-coordinate intermediate phosphonium ion - base complex which decomposes to give the phosphine, chlorine and the base, probably recomplexed with the freed Lewis acid.

$$[P(Ar)Cl_3][BCl_4] + L \longrightarrow [P(Ar)Cl_3.L][BCl_4] \xrightarrow{-Cl_2} P(Ar)Cl_2 + BCl_3.L$$

(Ar = aryl group with ortho-$CH_3$ or $CF_3$)
(L = pyridine or $NMe_3$)

In the light of these results, one must conclude that both the arylchlorophosphoranes with bulky ortho-substituents, and their associated phosphonium ions, are prevented from forming stable addition complexes with Lewis bases on the grounds of steric crowding. Instead, when treated with Lewis bases of the type listed above, the most likely reaction is reduction by elimination of $Cl_2$ or ClCN to give the relevant P(III) compound. As a result of the inability of these phosphoranes to accept chloride ion, it has not been possible subsequently to investigate cyanide substitution into the would-be arylpentachlorophosphate ions. Thus, it has not been possible to test directly the hypothesis (see introduction to this chapter) that the extent of such substitution is, in part, influenced by steric crowding in the system. However, the very fact that the inclusion of a bulky aryl group into such phosphoranes inhibits the increase of the coordination number of phosphorus adds weight to the argument that, in the $[P(C_6F_5)Cl_n(CN)_{5-n}]^-$ system, cyanide substitution is aided by the relatively bulky $C_6F_5$group destabilising the six-coordinate anion[26].

### 3.2.33 General Conclusion

To sum up, the inclusion of bulky aromatic ligands in the arylchlorophosphoranes discussed above had no effect on the general rule for ligand orientation in $\psi$tbp structures. That is to say, in those phosphoranes which take up a trigonal-bipyramidal structure, the most electronegative groups preferentially go axial, regardless of any steric considerations. All the monoaryltetrachlorophosphoranes studied were shown to have five-coordinate, molecular structures in the solid state. Though as yet no chlorophosphorane with only a single aryl substituent has been shown to have the phosphonium salt structure in the solid state, it is not inconceivable that this could be the case, given a sufficiently bulky aryl group, with (preferably) electron-supplying ortho-substituents. For example it would be interesting to prepare $P[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2]Cl_4$.

For a number of the phosphorus species discussed above, whereas in solution the $^{31}P$ n.m.r. spectra showed only single signals, in the solid two or more lines were seen. As demonstrated by Harris[33], crystallographic effects sometimes give rise to splittings of lines. In order for a particular type of phosphorus to yield a single line, all those phosphorus nuclei must be related by symmetry in the crystal. Thus, should such phosphorus atoms occupy crystallographically non-equivalent sites, they will give rise to two (or more) resonances. Such splittings are likely only to be resolvable with the use of MAR. This would explain why such features have not been noted in previous studies of phosphoranes, where solid state $^{31}P$ n.m.r. data was obtained without the use of MAR. Unfortunately, for the compounds studied above it was not possible to correlate directly crystallographic effects seen in such solid-state $^{31}P$ n.m.r. spectra with those seen in $^{35}Cl$ n.q.r. studies. Firstly, n.q.r. experiments are often conducted with the sample at much lower temperature than for solid-state n.m.r., and the crystallographic environments will often change over such a temperature range. Secondly, differences within the crystal may cause inequivalence in the chlorine sites but not the phosphorus sites.

A linear relationship between the combined $\sigma$ values for the substituents and the average axial or equatorial $^{35}$Cl n.q.r. frequencies for five-coordinate, $\psi$tbp arylchlorophosphoranes has been demonstrated by Biryukov and Diech[27]. For a phosphorane, $PR^1R^2R^3R^4Cl$ (where $R^1$ = aryl group or Cl, $R^2$ = aryl group or Cl, and $R^3 = R^4 =$ Cl), the aggregate value ($\sum \sigma_i$) is obtained from the summation of the Hammet induction constants for the substituents $R^1$, $R^2$, $R^3$ and $R^4$ For the limited amount of data available at that time it was demonstrated that the following two equations gave good agreement with $^{35}$Cl experimental values for $\nu_{eq}$ and $\nu_{ax}$:

$$\nu_{eq} = 32.90MHz + 0.08 \sum_i \sigma_i \pm 0.03$$

$$\nu_{ax} = 10.52MHz + 1.65 \sum_i \sigma_i \pm 0.29$$

Of the ortho-substituted arylchlorophosphoranes listed above, only the experimental $^{35}$Cl n.q.r. data for $P(2\text{-}(CH_3)C_6H_4)Cl_4$ fit these relationships, as shown in table 3.14. A value of $\sigma$ = 2.9 was taken for each chlorine substituent[27], and for 2-(methyl)phenyl[58], $\sigma$ = 0.292.

| Average Freq. | $\nu_{eq}$ | $\nu_{ax}$ |
|---|---|---|
| Calculated | 33.62 | 25.36 |
| Experimental | 33.72 | 25.56 |

**Table 3.14 — Calculated vs. Experimental $^{35}$Cl n.q.r. data for $P(2\text{-}(CH_3)C_6H_4)Cl_4$**

Given that $\sigma$ values for ortho-substituents are often of little use when there are steric interactions and, that Biryukov and Diech only studied phosphoranes with equatorial aryl groups, it is not surprising to find that the $^{35}$Cl n.q.r. frequencies for all the other phosphoranes listed above do not fit these relationships. For example, as shown in table 3.15, the $^{35}$Cl n.q.r. frequencies calculated for $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_4$ differ markedly from those obtained experimentally. A value of $\sigma$ for the mesityl group was estimated by a simple combinative method[59]. Thus, adding the $\sigma$ value for 4-(methyl)phenyl (-0.17)[58] to twice the value for 2-(methyl)phenyl (0.584), gives $\sigma_{mesityl} = 0.414$. If the Biryukov-Diech relationships hold, then it should be possible to use the experimental value for $\nu_{eq}$ to obtain a value for $\sum \sigma_i$ which, could then be used to predict $\nu_{ax}$, and *vice versa.* However, this relationship predicts a "cross-over point" at $\sum \sigma_i = 14.26$, where $\nu_{eq} = \nu_{ax} = 34.04$ MHz. This means for $\nu_{eq} > 34.04$ MHz, we would expect the axial chlorine signals to have an average frequency greater than that for the equatorial chlorines. Experimentally this is not the case, as is shown in the data above. With the exception of $P(2\text{-}(CH_3)C_6H_4)Cl_4$, each of the other phosphoranes which gave a $^{35}$Cl n.q.r. spectrum has an average equatorial chlorine frequency greater than 34.04 MHz, but none has $\nu_{ax}$ greater than 27 MHz.

| Average Freq. | $\nu_{eq}$ | $\nu_{ax}$ |
|---|---|---|
| Calculated | 33.63 | 25.56 |
| Experimental | 34.25 | 24.64 |

**Table 3.15 — Calculated vs. Experimental $^{35}$Cl n.q.r. data for $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_4$**

$^{35}$Cl n.q.r. studies have been used in this way to back-calculate unknown ortho-$\sigma$ values. Bray and Barnes[59] showed that for substituted chlorobenzenes the following relationship can be applied:

$$\nu_{Cl} = 34.826MHz + 1.024\sum_i \sigma_i$$

However, the predictive value of these linear relationships is at best semi-quantitative.

The chemistry of the mono-aryltetrachlorophosphoranes with bulky ortho-substituents has been discussed above. Whereas the steric bulk of a single such aryl group does not seem, at this level, to affect the general structure taken up by the phosphorane, it clearly does inhibit phosphorus from increasing its coordination number by complexing with Lewis bases.

Where it was possible for them to be prepared, all of the bis(aryl)trichlorophosphoranes incorporating bulky, ortho-substituted aromatic ligands were shown to have the phosphonium salt structure in the solid-state. Although in some cases this could have been put down to electronic considerations, where the aryl groups are clearly more electro-negative than phenyl itself the most probable explanation is that the increased steric crowding favours four- rather than five-coordinate phosphorus. Although the loss of an aryl group during the chlorination of $P(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl$ and $P(2,4,6\text{-}(CF_3)_3C_6H_2)(C_6F_5)Cl$ is without precedent for this type of reaction, it has been shown that P-C cleavage can occur in phosphorane systems due to a combination of steric and electronic effects. Poulin *et al*[60] showed that the aminolysis of $P(CF_3)_2Cl_3$ resulted in the loss of a trifluoromethyl group and the subsequent formation of the $P(CF_3)[N(CH_3)_2]_3^+$ ion:

$$P(CF_3)_2Cl_3 \xrightarrow{5NMe_2H} CHF_3 + P(CF_3)[NMe_2]_3^+ + 2NMe_2H_2^+ + 3Cl^-$$

Although the intermediate $P(CF_3)_2Cl_2[NMe_2]$ could be isolated, no additional intermediates were isolable, suggesting that the component steps occur at competitive rates. It seems reasonable to suggest that this reaction is facilitated by the increased crowding around phosphorus which accompanies the introduction of relatively bulky dimethylamino groups, and by the fact that $Cl^-$ is a good leaving group.

Although it has been shown that $PCl_2F_3$ and $PCl_3F_2$ can have the solid-state structures $[PCl_4][PCl_6]$[61] and $[PCl_4][PCl_2F_4]$[62] respectively, until now there have been no reports of organochlorophosphoranes which have an ionic structure in the solid incorporating a six-coordinate phosphate anion. Most phosphoranes of the type $PRCl_4$, where R is an organo group, will, however, accept chloride (see above) to form salts of $[PRCl_5]^-$. Where the halide donor is itself a chlorophosphorane, then a quasi-phosphonium phosphate will be produced. For example[21]:

$$PPhCl_4 + PCl_3(cat) \xrightarrow{CH_2Cl_2} [PPhCl_3][PCl_4(cat)]$$

( where cat = $O_2C_6H_4$).

However, such compounds cannot be written in the form $PRCl_4$, and are not true phosphoranes. Thus the structure determined for $P(CH_2Cl)Cl_4$ as the phosphonium phosphate is genuinely without precedent for a phosphorane of this type. The general solid-state structures for all four of the phosphoranes of the series $P(CH_nCl_{3-n})Cl_4$ (where n = 0, 1, 2 or 3) are now known (see table 3.16). However, the position of the dichloromethyl group (i.e. whether axial or equatorial) in the molecular phosphorane (n = 1) has yet to be determined. Work is continuing in this area, with the aim of using electron diffraction studies to determine the gas phase structures of the members of this series. Further it is hoped that analogous (bromo- and fluoro-substituted methyl)tetrachlorophosphorane systems could be prepared for comparison.

| Phosphorane | Solid-State Structure | Reference |
|---|---|---|
| $PMeCl_4$ | $[PMeCl_3]^+Cl^-$ | 1 |
| $P(CH_2Cl)Cl_4$ | $[P(CH_2Cl)Cl_3]^+[P(CH_2Cl)Cl_5]^-$ | This Work |
| $P(CHCl_2)PCl_4$ | 5-coordinate $P(CHCl_2)PCl_4$ | This Work |
| $P(CCl_3)Cl_4$ | $\psi$tbp $CCl_3$ axial | 10 |

**Table 3.16 — Solid-State Structures of $P(CH_nCl_{3-n})Cl_4$**

## 3.3 Experimental

### 3.3.1 General strategy

All manipulations were made under an atmosphere of dry nitrogen. All mono- and bis- arylchlorophosphines were prepared by the action of an appropriate organometallic reagent on $PCl_3$, except for $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_2$ where a Friedel-Crafts method was employed.

$$[M]Ar + PCl_3 \longrightarrow P(Ar)Cl_2$$

$$2Ar[M] + PCl_3 \longrightarrow P(Ar)_2Cl$$

$$mesitylene + PCl_3 \xrightarrow[2.pyridine]{1.\ AlCl_3} P(2,4,6-(CH_3)_3C_6H_2)Cl_2$$

It should be noted that the usefulness of the Friedel-Crafts method for arylphosphinous dichloride synthesis is limited. As has been clearly demomonstrated by Schindlbauer, alkyl benzenes when reacted with $PCl_3$ in the presence of $AlCl_3$ give a mixture of isomers. Mostly, the 1,4-isomer is produced, with a very small quantity of the 1,2-isomer, but up to 40 % of the 1,3-isomer is also formed. This means that, with the exception of mesitylene where there is clearly only one possible isomer from such electrophilic substitution, if the position of the alkyl group is an important factor, then it is better to proceed via an organometallic reagent. Halobenzenes do, however, give only small amounts of the 1,2- and 1,3-isomers, and so this method can be used to prepare phosphines of the type $P[(4\text{-}X)C_6H_4]PCl_2$ (X = F, Cl, Br) to a reasonable level of isomeric purity.

A variety of organometallic reagents was used: aryllithiums, bromo- and chlor-Grignards and arylzinc halides. The choice of which reagent to use to prepare a given phosphine was made according to the ease with which the organo-metallic reagent could be prepared, the ability to control the degree of substitution into $PCl_3$, and the yield of phosphine afforded. Where bromo- Grignards were used (and to a lesser extent when 1,2-dibromoethane was used as an initiator for chloro- Grignards) it was found that there was a high degree of bromine incorporation into the resultant arylhalophosphine. Any such >P-Br species thus formed, however, could be easily converted into >P-Cl by treating the halophosphine with dry $NEt_4Cl$ in dichloromethane.

$$P(Ar)_nX_{3-n} \xrightarrow{NEt_4Cl} P(Ar)_nCl_{3-n}$$

$$(n = 1,2; X = Cl/Br\ mixture)$$

Although there were some attempts to chlorinate phosphines using $PCl_5$ or $SbCl_5$, the general preparation of the arylchlorophosphoranes was by chlorination of the respective phosphine with dry, gaseous chlorine in dichloromethane. The solvent was then removed under reduced pressure. The solid phosphoranes were washed with a small quantity of low boiling petroleum ether and finally dried *in vacuo*. Some phosphoranes were recrystallized from pentane / dichloromethane in an attempt to improve their $^{35}Cl$ n.q.r. spectra.

$$P(Ar)_nCl_{3-n} \xrightarrow{Cl_2} P(Ar)_nCl_{5-n}$$

All the tetrachloroborate salts of the phosphoranes were prepared by adding a slight excess of a 1M solution of boron trichloride in hexanes to the phosphorane in dichloromethane solution. Where the resultant salts were insoluble and formed as a precipitate, they were filtered and washed with low boiling petroleum ether before being dried *in vacuo*. Hexachloroantimonate salts of arylchlorophosphoranes were prepared by the addition of one equivalent of antimony pentachloride to the phosphorane in a stirred solution of dichloromethane. The resultant precipitate was then filtered, washed with dichloromethane and dried *in vacuo* .

Once prepared the phosphoranes and their Lewis acid salts were characterised by elemental analysis, infrared and solution-state $^{31}$P n.m.r. . Solid-state structure determination was performed by a combination of $^{35}$Cl n.q.r. and $^{31}$P n.m.r.

### 3.3.2 Preparation of $P(2\text{-}(CH_3)C_6H_4)Cl_2$

To a 500 ml three-necked flask, fitted with dropping funnel, mechanical stirrer and reflux condenser, all being maintained under an atmosphere of dry nitrogen, was added 12.15 g (500 mmol) of magnesium turnings together with 2 ml of 1,2-dibromoethane. In the dropping funnel was placed 2-chlorotoluene 63.2 g (500 mmol) in THF (100 ml). 15 ml of the chlorotoluene-THF solution was added to the flask and the stirrer was started. The reaction mixture was heated to reflux and, with continued heating and stirring, the remaining chlorotoluene-THF solution was added over a period of about 1.5 hours. After addition was complete the reaction mixture was heated for a further 2 hours, until the magnesium was nearly all consumed. The reaction mixture was then allowed to cool to room temperature before being filtered through glass wool into a second 500 ml three-necked flask to remove any remaining magnesium. The Grignard solution was then cooled to 0 °C and anhydrous zinc chloride 68.15 g (500 mmol) in diethyl ether (100ml) was added dropwise, over a period of 45 minutes and with continuous stirring. The mixture was then heated to reflux for two hours. On cooling to room temperature the reaction mixture was transferred to an addition funnel. This arylzinc halide reagent was then added dropwise to a stirred solution of phosphorus trichloride 137.5 g (1 mol) in diethyl ether (100 ml), stirred under dry nitrogen in a 1l flask at a temperature of -78 °C. The reaction mixture was then allowed to warm to room temperature before being refluxed for 30 minutes. On cooling the salts were filtered off and the solvent with excess phosphorus trichloride was removed under reduced pressure. The product was then purified by vacuum distillation (Bpt 50°C, 0.1 mmHg).

Yield 41.6 g (43 %), $P(2\text{-}(CH_3)C_6H_4)Cl_2$.

$C_7H_7Cl_2P$ = 193.01.

Calc: C = 43.56 %, H = 3.66 %, P = 16.05 %, Cl = 36.74 %.

Found: C = 44.84 %, H = 3.99 %, P = 15.52 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 163.9 ppm.

### 3.3.3 Preparation of $P(2\text{-}(CH_3)C_6H_4)_2Cl$

To a 500 ml three-necked flask, fitted with dropping funnel, mechanical stirrer and reflux condenser, all being maintained under an atmosphere of dry nitrogen, was added 12.15 g (500 mmol) of magnesium turnings together with 2 ml of 1,2-dibromoethane. In the dropping funnel was placed 2-chlorotoluene 63.3 g (500 mmol) in THF (100 ml). 15 ml of the chlorotoluene-THF solution was added to the flask and the stirrer was started. The reaction mixture was heated to reflux and, with continued heating and stirring, the remaining chlorotoluene-THF solution was added over a period of about 1.5 hours. After addition was complete the reaction mixture was heated for a further 2 hours, until the magnesium was nearly all consumed. The reaction mixture was then allowed to cool to room temperature before being filtered through glass wool, to remove any remaining magnesium, into a dropping funnel. The Grignard solution was then added dropwise, over a period of 90 minutes, to a solution of $PCl_3$ 34.33 g (250 mmol) in anhydrous diethyl ether (200ml) contained in a 500 ml two-necked flask, under an atmosphere of dry nitrogen and at a temperature of -78 °C. When the addition was complete the reaction mixture was gradually allowed to warm to room temperature The magnesium salts were then filtered off before the solvent was removed under reduced pressure. The product was then extracted from the residue by fractional vacuum distillation (Bpt. 110°C, 0.1 mmHg).

Yield 28.6 g (23 %), $P(2\text{-}(CH_3)C_6H_4)_2Cl$.

$C_{14}H_{14}ClP = 248.69$.

Calc: C = 67.61 %, H = 5.67 %, P = 12.45 %, Cl = 14.23 %.

Found: C = 68.24 %, H = 6.35 %, Cl = 13.05 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2) = 73.6$ ppm.

### 3.3.4 Preparation of $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_2$

To a 500 ml two-necked flask fitted with mechanical stirrer, reflux condenser and maintained under an atmosphere of dry nitrogen was added phosphorus trichloride 70 g (0.51 mol), mesitylene 19.5 g (0.162 mol) and anhydrous aluminium trichloride 28 g (0.21 mol). The mixture was refluxed for three hours with continuous stirring. The flask was then cooled to 0 °C with an ice bath before pyridine 16.7 g (0.21 mol) was added dropwise, over a period of 30 minutes. The precipitate was filtered off under an atmosphere of dry nitrogen and washed with three 15 ml portions of phosphorous trichloride. The $PCl_3$ was then distilled from the filtrate and combined extracts. The product was purified from the residue by vacuum distillation (Bpt. 98 °C, 0.1mmHg).

Yield 14.2 g (40 %), $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_2$.

$C_7H_7Cl_4P = 221.07$.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2) = 168.5$ ppm.

### 3.3.5 Preparation of $P(2,4,6\text{-}(CH_3)_3C_6H_2)_2Cl$

In a 250 ml two-necked flask fitted with reflux condenser, dropping funnel and maintained under an atmosphere of dry nitrogen gas, was placed bromomesitylene 19.9 g (100 mmol) in diethyl ether (30 ml). A 2.5 M solution of n-butyllithium in hexane 52 ml was then added slowly, with continuous stirring, via the dropping funnel. When addition was complete the mixture was heated to reflux for 3 hours. A copious deposit of white, crystalline mesityllithium was produced which on cooling the reaction mixture was filtered off under nitrogen, and dried *in vacuo* . This solid was then dissolved in dry tetrahydrofuran before being added dropwise to a solution of phosphorous trichloride 6.8 g (50 mmol) in diethyl ether (100ml) contained in a 250 ml two-necked flask, under dry nitrogen and at a temperature of -78 °C. The mixture was then allowed to warm to room temperature and stirred for a further 15 hours. The solution was filtered to remove lithium salts and the solvent was removed under reduced pressure. The product was then purified by vacuum distillation (Bpt. 125 °C, 0.1 mmHg).

Yield 5.5 g (36 %), $P(2,4,6\text{-}(CH_3)_3C_6H_2)_2Cl$.

$C_{18}H_{22}ClP = 304.80$.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2) = 85.4$ ppm.

### 3.3.6 Preparation of $P(C_6Cl_5)Cl_2$

A 250-ml three-necked flask was equipped with a mechanical stirrer, a condenser and an addition funnel. Into the flask, 3.6 g (0.15 mole, 50 % excess) of magnesium turnings which had been dried in a 100°C oven, and about 6 drops of dibromoethane, were introduced. From the addition funnel, a small amount of a slurry which contained 28.5 g (0.1 mole) of hexachlorobenzene and 120 $cm^3$of sodium-dried tetrahydrofuran was added to the reaction mixture. Stirring was started, and after about 5 minutes the reaction set in as indicated by the evolution of heat and the appearance of a dark brown colour. The rest of the hexachlorobenzene/tetrahydrofuran slurry was added in small portions to maintain the reaction mixture under slow reflux. After the addition of the slurry the mixture was stirred at room temperature for three or more hours to complete the reaction. The Grignard solution was then filtered through glass wool into an addition funnel to remove any unreacted magnesium. This solution was then added dropwise, over a period of 1 hour, to a stirred solution of phosphorous trichloride 27.5 g (0.2 mole) in diethyl ether solution (100 ml), cooled to -78 °C (cardice/acetone slush bath), contained in a 500 ml two-necked flask and maintained under an atmosphere of dry nitrogen. When addition was complete the reaction mixture was allowed to warm to room temperature before the solvent and excess $PCl_3$ were removed under reduced pressure. The product was extracted from the remaining solids by vacuum sublimation (100 °C, 0.1 mmHg) to give a white solid.

Yield 9.3 g (84 %), $P(C_6Cl_5)Cl_2$.

$C_6Cl_7P$ = 351.21.

Calc: C = 20.52 %, P = 8.82 %, Cl = 70.66 %.

Found: C = 21.25 %, Cl = 72.12 %.

$^{31}P$ n.m.r. : $\delta$/(toluene) = 152.8 ppm; (solid) = 151.4, 154.3 and 159.6 ppm.

Mass Spec. m/e = 350 (major peak of $M^+$ envelope)

### 3.3.7 Preparation of $P(2\text{-}(CF_3)C_6H_4)Cl_2$ & $P(2\text{-}(CF_3)C_6H_4)_2Cl$

To a 250 ml three-necked flask, fitted with dropping funnel, mechanical stirrer and reflux condenser, all being maintained under an atmosphere of dry nitrogen, was added 2.43 g (100 mmol) of magnesium turnings together with 4 drops of 1,2-dibromoethane. In the dropping funnel was placed 2-bromo(trifluoromethyl)-benzene (100 mmol) in diethyl ether (150 ml). 15 ml of this solution was added to the flask and the reaction mixture was heated to reflux until the reaction started, at which point the heat was removed and the remaining 2-bromo(trifluoromethyl)-benzene - diethyl ether solution was added over a period of about 30 minutes - the rate of addition controlling reflux. After addition was complete the reaction mixture was stirred for 2 hours. When at room temperature the reaction mixture was filtered through glass wool to remove any remaining magnesium and transferred to a dropping funnel. The 2-(trifluoromethyl)phenylmagnesium bromide solution was then added dropwise, over 90 minutes, with continuous stirring, to a solution of phosphorus trichloride 27.5 g (200 mmol) in diethyl ether (100 ml), contained in a 250 ml two-necked flask under nitrogen and cooled to -78°C. When addition was complete the reaction mixture was allowed to warm to room temperature and to stir for a further hour. The magnesium salts were then removed by filtration and the solvent, together with excess phosphorus trichloride, was removed *in vacuo* . The residue was then treated with a sufficient quantity of tetraethylammonium chloride in dichloromethane to convert all P-Br species to P-Cl (followed by $^{31}P$ n.m.r. ). The dichloromethane was then removed *in vacuo* and diethyl ether (100 ml). The tetraethylammonium salts were removed by filtration and the ether removed under reduced pressure. Finally the residue was distilled under vacuum.

Yield 4.2 g (17 %), $P(2\text{-}(CF_3)C_6H_4)Cl_2$.

$C_7H_4Cl_2F_3P$ = 246.98.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 154.5 ppm (quart. $J_{PF}$= 84.7 Hz).

$^{19}F$ n.m.r. : $\delta/(CH_2Cl_2)$ = -56.01 ppm (d. $CF_3$, 3F)

Yield 1.8 g (10 %), $P(2\text{-}(CF_3)C_6H_4)_2Cl$.

$C_{14}H_8ClF_6P$ = 356.64.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 72.2 ppm (sept. $J_{PF}$= 66.8 Hz).

$^{19}F$ n.m.r. : $\delta/(CH_2Cl_2)$ = -57.74 ppm (d. $CF_3$, 6F)

### 3.3.8 Preparation of $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_2$

A solution of the n-butyllithium TMEDA complex (prepared from TMEDA 5.69 g (49 mmoles), 29.2 ml of a solution of n-butyllithium, 1.6 M in hexanes, (46.7 mmoles) and 10 ml of diethyl ether) was added to 10.0 g (46.7 mmoles) of 1,3-bis(trifluoromethyl)benzene in 30 ml of the same solvent at 0°C, contained in a 125 ml two-necked flask under an atmosphere of dry nitrogen. The reaction mixture became dark brown. After stirring overnight at room temperature it was transferred to a dropping funnel, before being slowly added to a solution of phosphorus trichloride 12.85 g (93.4 mmoles) in 30 ml of diethyl ether at -78 °C, contained in a 250 ml two-necked flask, under nitrogen. The reaction mixture was then allowed to warm to room temperature and 50 ml of pentane were added. After filtering off the lithium salts and elimination of the solvents *in vacuo* the product was purified by vacuum distillation (Bpt. 80°C, 0.1 mmHg).

Yield 5.3 g (35 %), $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_2$.

$C_8H_3Cl_2F_6P$ = 314.98.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 146.6 ppm (sept. $J_{PF}$= 61.0 Hz).

$^{19}F$ n.m.r. : $\delta/(CH_2Cl_2)$ = -53.14 ppm (d. $CF_3$, 6F)

### 3.3.9 Preparation of $P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl$

A solution of the n-butyllithium TMEDA complex (prepared from TMEDA 5.69 g (49 mmoles), 29.2 ml of a solution of n-butyllithium, 1.6 M in hexanes, (46.7 mmoles) and 10 ml of diethyl ether) was added to 10.0 g (46.7 mmoles) of 1,3-bis(trifluoromethyl)benzene in 30 ml of the same solvent at 0 °C. The reaction mixture became dark brown. After stirring overnight at room temperature it was slowly added to a solution of phosphorus trichloride 3.20 g (23.4 mmoles) in 30 ml of diethyl ether at -78 °C. The reaction mixture was then allowed to warm to room temperature and 50 ml of pentane were added. After filtering off the lithium salts and elimination of the solvents *in vacuo* the product was purified by vacuum distillation (Bpt. 110 °C, 0.1 mmHg).

Yield 3.8 g (33 %), $P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl$.

$C_{16}H_6ClF_{12}P$ = 492.63.

Calc: C = 39.01 %, H = 1.23 %, P = 6.29 %, Cl = 7.20 %.

Found: C = 38.62 %, H = 1.85 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 77.5 ppm (13 line mult. $J_{PF}$= 41.9 Hz).

$^{19}F$ n.m.r. : $\delta/(CH_2Cl_2)$ = -54.80 ppm (d. $CF_3$, 12F)

### 3.3.10 Preparation of $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_2$

In a two-necked, 250 ml, round-bottomed flask, fitted with dropping funnel and maintained under dry nitrogen, was placed phosphorus trichloride 19.2 g (140 mmol) in diethyl ether (100 ml). The flask was then cooled to -78°C (cardice / acetone slush bath). 2,4,6-Tris(trifluoromethyl)phenyllithium (approx 70 mmol) in diethyl ether (100 ml) was then added dropwise, with continuous stirring. When addition was complete the mixture was allowed to warm to room temperature and then left to stir for a further one hour. The lithium salts were filtered off under nitrogen and the solvent and excess phosphorus trichloride removed *in vacuo* . The residual oil was then purified by vacuum distillation (Bpt. 60 °C, 0.1 mmHg).

Yield 8.2 g (31 %), $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_2$.

$C_9H_2Cl_2F_9P$ = 382.98.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 144.4 ppm (sept. $J_{PF}$= 61.4 Hz).

$^{19}F$ n.m.r. : $\delta/(CH_2Cl_2)$ = -53.68 ppm (d. $CF_3$, 6F), -64.70 ($CF_3$, 3F).

### 3.3.11 Preparation of $P(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl$

In a two-necked, 250 ml, round-bottomed flask, fitted with dropping funnel and maintained under dry nitrogen, was placed phosphorus trichloride 4.8 g (35 mmol) in diethyl ether (100 ml). The flask was cooled to -78°C (cardice / acetone slush bath). 2,4,6-Tris(trifluoromethyl)phenyllithium (approx 70 mmol) in diethyl ether (100 $cm^3$) was then added dropwise, with continuous stirring. When addition was complete the mixture was allowed to warm to room temperature and then left to stir for a further one hour. The lithium salts were filtered off under nitrogen and the solvent removed *in vacuo* . The solid product was purified by sublimation (120°C, 0.1 mmHg).

Yield 6.1 g (28 %), $P(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl$.

$C_{18}H_4ClF_{18}P$ = 628.63.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 74.2 ppm (13 line mult. $J_{PF}$= 42.0 Hz).

$^{19}F$ n.m.r. : $\delta/(CH_2Cl_2)$ = -54.71 ppm (d. $CF_3$, 12F), -64.48 ($CF_3$, 6F).

### 3.3.12 Preparation of $P(C_6H_5)(2,4,6\text{-}(CF_3)_3C_6H_2)Cl$

In a two-necked, 250 ml, round-bottomed flask, fitted with dropping funnel and maintained under dry nitrogen, was placed phenylphosphinous dichloride 6.26

g (35 mmol) in diethyl ether (100 ml). The flask was cooled to -78°C (cardice / acetone slush bath). 2,4,6-Tris(trifluoromethyl)phenyllithium (approx 35 mmol) in diethyl ether (50 ml) was then added dropwise, with continuous stirring. When addition was complete the mixture was allowed to warm to room temperature, and then left to stir for a further one hour. The lithium salts were filtered off through dried silica under nitrogen and the solvent removed *in vacuo* . The residual oil was then purified by vacuum distillation (Bpt. 100°C, 0.1 mmHg).

Yield 11.4 g (77 %), $P(C_6H_5)(2,4,6\text{-}(CF_3)_3C_6H_2)Cl$.

$C_{15}H_7ClF_9P$ = 424.63.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 78.0 ppm (sept $J_{PF}$= 49.6 Hz).

### 3.3.13 Preparation of $P(C_6F_5)(2,4,6\text{-}(CF_3)_3C_6H_2)Cl$

To a 250 ml three-necked flask, fitted with dropping funnel, mechanical stirrer and reflux condenser, all being maintained under an atmosphere of dry nitrogen, was added 2.43 g (100 mmol) of magnesium turnings together with 4 drops of 1,2-dibromoethane. In the dropping funnel was placed bromopentafluorobenzene 24.7 g (100 mmol) in diethyl ether (150 ml). 15 ml of this solution was added to the flask and the stirrer was started. The reaction mixture was heated to reflux until the reaction started, at which point the heat was removed and the remaining bromopentafluorobenzene - diethyl ether solution was added over a period of about 30 minutes - the rate of addition controlling reflux. After addition was complete, the reaction mixture was stirred for a further 2 hours. When at room temperature, the reaction mixture was filtered through glass wool to remove any remaining magnesium and transferred to a dropping funnel. The pentafluorophenylmagnesium bromide solution was then added dropwise, over 90 minutes, with continuous stirring, to a solution of phosphorus trichloride 27.5 g (200 mmol) in diethyl ether (100 ml), contained in a 250 ml two-necked flask under nitrogen and cooled to -78°C. When addition was complete the reaction mixture was allowed to warm to room temperature and to stir for a further hour. The magnesium salts were then removed by filtration and the solvent together with excess phosphorus trichloride was removed *in vacuo* . From the residue the mixed pentafluorophenylphosphonous dihalides were distilled and treated with tetraethylammonium chloride in dichloromethane to produce solely the dichloro phosphine $P(C_6F_5)Cl_2$ 11.2 g (42 %). 9.4 g (35 mmol) of this compound was then placed in a two-necked, 250 ml, round-bottomed flask, fitted with dropping funnel and maintained under dry nitrogen. Diethyl ether (100 ml) was added and the flask was cooled to -78°C (cardice / acetone slush bath). 2,4,6-Tris(trifluoromethyl)phenyllithium (approx 35 mmol) in diethyl ether (100 ml) was then added dropwise, with continuous stirring. When addition was complete the mixture was allowed to warm to room temperature and then left to stir for a further one hour. The lithium salts were filtered off under nitrogen and the solvent removed *in vacuo* . The residual oil was then purified by vacuum distillation (Bpt. 120 °C, 0.1 mmHg).

Yield 7.6 g (42 %), $P(C_6F_5)(2,4,6\text{-}(CF_3)_3C_6H_2)Cl$.

$C_{15}H_2ClF_{14}P$ = 514.59.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 55.6 ppm ("sept." $J_{PF}$= 52.2 Hz).

$^{19}F$ n.m.r. : $\delta/(CH_2Cl_2)$ = -56.00 ppm (d. $CF_3$, 6F), -65.10 ppm ($CF_3$, 3F), -131.8 (2F), -150.2 (1F), -161.8 (2F).

A small quantity of this compound was hydrolysed by slow filtration of an ether solution through silica gel to produce $(2,4,6\text{-}(CF_3)_3C_6H_2)(C_6F_5)P(O)H$. On removal of the ether *in vacuo* the remaining white solid was characterised as follows:

$C_{15}H_3F_{14}OP$ = 496.14.

Calc: C = 36.31 %, H = 0.61 %, P = 6.24 %.

Found: C = 34.93 %, H = 0.77 %.

$^{31}$P n.m.r. : $\delta/(CH_2Cl_2)$ = 9.4 ppm (d, $J_{PH}$= 572.2 Hz).

$^{19}$F n.m.r. : $\delta/(CH_2Cl_2)$ = -55.18 ppm (s, $CF_3$, 6F), -64.80 ppm ($CF_3$, 3F), -133.4 (2F), -144.3 (1F), -159.5 (2F).

Mass Spec $CI^+$ m/e = 514 ($[M + NH_4]^+$); $CI^-$ m/e = 495 ($[M-1]^-$).

### 3.3.14 Preparation of $P(CH_2Cl)Cl_2$

To a 125 ml three-necked flask, fitted with mechanical stirrer, reflux condenser, dropping funnel and maintained under an atmosphere of dry nitrogen, were added phosphorus trichloride 10.5 g (76.5 mmol), methylene chloride 8.5 g (100 mmol), aluminium chloride 8.9 g (66.7 mmol) and methylene bromide 0.5 g (2.9 mmol). This mixture was heated to reflux for 24 hours until all the aluminium chloride had dissolved. The mixture then cooled to 0°C and methyl phosphorodichloridite 10 ml (105.8 mmol) was added, dropwise with stirring. The mixture was then heated to 70 - 80°C for 1 hour, before adding 6.0 g of finely ground, roasted potassium chloride. The mixture was again heated with stirring to 70 - 80°C for 4 hours. The solids were then filtered off and the excess phosphorus trichloride and methyl phosphorodichloridite were removed by distillation. The product was then extracted from the residue by distillation at reduced pressure, yielding $P(CH_2Cl)Cl_2$ 4.1 g (40 %) (Bpt. 45°C, 40 mmHg).

$^{31}$P n.m.r. : $\delta/(CDCl_3)$ = 159.0 ppm (t, $J_{PH}$ = 16.4 Hz).

$^{1}$H n.m.r. : $\delta/(CDCl_3)$ = 4.16 ppm (d).

$^{13}$C n.m.r. : $\delta/(CDCl_3)$ = 48.8 ppm ( t, $J_{CH}$ = 159.8 Hz; d, $J_{CP}$ = 54.5 Hz).

### 3.3.15 Preparation of $P(CHCl_2)Cl_2$

To a 125 ml three-necked flask, fitted with mechanical stirrer, reflux condenser, dropping funnel and maintained under an atmosphere of dry nitrogen, were added phosphorus trichloride 10.5 g (76.5 mmol), chloroform 11.9 g (100 mmol) and aluminium chloride 8.9 g (66.7 mmol). This mixture was heated to reflux for 6 hours until all the aluminium chloride had dissolved. The mixture was then cooled to room temperature before removal of any remaining volatiles *in vacuo* , leaving a white solid. Diethyl ether (150 ml) was then added and the mixture was cooled to -78°C. Powdered zinc metal 5.2 g (80 mmol) was added, portionwise with stirring. The mixture was then allowed gradually to warm to room temperature. The phosphine in ether was vacuum transferred from the residual solids and the ether was then removed by distillation. The product was purified by distillation at reduced pressure (Bpt. 38°C, 10 mmHg).

$^{31}P$ n.m.r. : $\delta/(CDCl_3) = 145.2$ ppm (d, $J_{PH} = 12.6$ Hz); $/(Et_2O) =$ 147.2 ppm; $/(PhNO_2) = 148.7$ ppm.

$^{1}H$ n.m.r. : $\delta/(CDCl_3) = 5.97$ ppm (d, $J_{PH} = 12.6$ Hz).

$^{13}C$ n.m.r. : $\delta/(CDCl_3) = 73.67$ ppm (d, $J_{CH} = 180.9$ Hz; d, $J_{CP} = 70.5$ Hz).

### 3.3.16 Preparation of $P(2\text{-}(CH_3)C_6H_4)Cl_4$

To a 125 ml two-necked flask, fitted with gas inlet and maintained under an atmosphere of dry nitrogen, was added $P(2\text{-}(CH_3)C_6H_4)Cl_2$ 8.1 g (42.0 mmol) and dichloromethane (50 ml). Dry chlorine gas was slowly bubbled through the solution until it just turned yellow. The reaction mixture was then allowed to stir for a further 30 minutes at room temperature. The solvent and any excess chlorine were removed *in vacuo* , leaving a white, low melting, waxy solid. The product was then washed under nitrogen with a very small quantity of low boiling petroleum ether, before being dried under vacuum.

Yield 9.3 g (84 %), $P(2\text{-}(CH_3)C_6H_4)Cl_4$.

$C_7H_7Cl_4P$ = 263.92.

Calc: C = 31.86 %, H = 2.67 %, P = 11.74 %, Cl = 53.73 %.

Found: C = 32.49 %, H = 3.03 %, P = 10.25 %, Cl = 51.60 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = -41.8 ppm.

### 3.3.17 Preparation of $P(2\text{-}(CH_3)C_6H_4)_2Cl_3$

Chlorination of $P(2\text{-}(CH_3)C_6H_4)_2Cl$, 5.0 g (20.1 mmol) in dichloromethane (50 ml) gave a pale yellow solid.

Yield 4.2 g (65 %), $P(2\text{-}(CH_3)C_6H_4)_2Cl_3$.

$C_{14}H_{14}Cl_3P$ = 319.59.

Calc: C = 52.61 %, H = 4.42 %, P = 9.69 %, Cl = 33.28 %.

Found: C = 52.17 %, H = 4.41 %, P = 9.36 %, Cl = 34.41 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 88.6 ppm, $\delta$/(solid) = 85.0, 90.0 ppm.

### 3.3.18 Preparation of $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_4$

Chlorination of $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_2$, 3.6 g (16.3 mmol) in dichloromethane (50 ml) gave a pale yellow solid.

Yield 4.2 g (88.6 %), $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_4$.

$C_9H_{11}Cl_4P$ = 291.98.

Calc: C = 37.02 %, H = 3.80 %, P = 10.61 %, Cl = 48.57 %.

Found: C = 39.80 %, H = 3.77 %, Cl = 46.89 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = -40.5 ppm, $\delta$/(solid) = -40.2 ppm.

### 3.3.19 Preparation of $P(2,4,6-(CH_3)_3C_6H_2)_2Cl_3$

Chlorination of $P(2,4,6-(CH_3)_3C_6H_2)_2Cl$, 1.2 g (3.9 mmol) in dichloromethane (50 ml) gave a pale yellow solid.

Yield 0.7 g (48 %), $P(2,4,6-(CH_3)_3C_6H_2)_2Cl_3$.

$C_{18}H_{22}Cl_3P$ = 375.70.

Calc: C = 57.55 %, H = 5.90 %, P = 8.24 %, Cl = 28.31 %.

Found: C = 58.85 %, H = 7.10 %, Cl = 26.72 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 88.4 ppm.

### 3.3.20 Preparation of $P(C_6Cl_5)Cl_4$

Chlorination of $P(C_6Cl_5)Cl_2$, 3.6 g (10.3 mmol) in dichloromethane (50 ml) gave a pale yellow solid.

Yield 2.8 g (64.7 %), $P(C_6Cl_5)Cl_4$.

$C_6Cl_9P$ = 422.12.

Calc: C = 17.07 %, P = 7.34 %, Cl = 75.59 %.

Found: C = 18.00 %, P = 6.94 %, Cl = 73.22 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = -50.6 ppm, $\delta/(solid)$ = -50.3 ppm,

### 3.3.21 Preparation of $P(2-(CF_3)C_6H_4)Cl_4$

Chlorination of $P(2-(CF_3)C_6H_4)Cl_2$, 5.2 g (21.0 mmol) in dichloromethane (50 ml) gave a colourless, transparent, low-melting solid.

Yield 5.9 g (88.2 %), $P(2-(CF_3)C_6H_4)Cl_4$.

$C_7H_4Cl_4F_3P$ = 317.89.

Calc: C = 26.45 %, H = 1.27 %, P = 9.74 %, Cl = 44.61 %.

Found: C = 27.63 %, H = 1.39 %, Cl = 43.78 %.

$^{31}$P n.m.r. : $\delta/(CH_2Cl_2)$ = -41.7 ppm.

$^{19}$F n.m.r. : $\delta/(CH_2Cl_2)$ = -57.00 ppm ($CF_3$, 3F).

### 3.3.22 Preparation of $P(2\text{-}(CF_3)C_6H_4)_2Cl_3$

Chlorination of $P(2\text{-}(CF_3)C_6H_4)_2Cl$, 3.1 g (8.7 mmol) in dichloromethane (50 ml) gave a white solid.

Yield 3.4 g (91.5 %), $P(2\text{-}(CF_3)C_6H_4)_2Cl_3$.

$C_{14}H_8Cl_3F_6P$ = 427.54.

Calc: C = 39.33 %, H = 1.89 %, P = 7.24 %, Cl = 24.88 %.

Found: C = 37.91 %, H = 1.78 %, P = 7.96 %.

$^{31}$P n.m.r. : $\delta/(CH_2Cl_2)$ = 74.6 ppm, $\delta/(PhNO_2)$ = 50.9 ppm, $\delta$/(solid) = 93.6 ppm.

$^{19}$F n.m.r. : $\delta/(CH_2Cl_2)$ = -55.06 ppm ($CF_3$, 6F).

### 3.3.23 Preparation of $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_4$

Chlorination of $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_2$, 8.3 g (26.4 mmol) in dichloromethane (50 ml) gave a white solid.

Yield 7.6 g (75 %), $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_4$.

$C_8H_3Cl_4F_6P$ = 385.89.

Calc: C = 24.90 %, H = 0.78 %, P = 8.03 %, Cl = 36.75 %.

Found: C = 23.91 %, H = 1.29 %, Cl = 35.20 %.

$^{31}$P n.m.r. : $\delta/(CH_2Cl_2)$ = -48.3 ppm.

$^{19}$F n.m.r. : $\delta/(CH_2Cl_2)$ = -52.89 ppm ($CF_3$, 6F).

### 3.3.24 Preparation of $P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_3$

Chlorination of $P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl$, 3.4 g (6.9 mmol) in dichloromethane (50 ml) gave a white solid.

Yield 3.6 g (96 %), $P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_3$.

$C_{16}H_6Cl_3F_{12}P$ = 563.53.

Calc: C = 34.10 %, H = 1.07 %, P = 5.50 %, Cl = 18.87 %.

Found: C = 35.14 %, H = 2.03 %, P = 5.15 %, Cl = 18.21 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 84.6 ppm, $\delta/$ $(PhNO_2)$ = 84.7 ppm,

$\delta/$(solid) = 77.3, 83.6, 86.5 ppm.

$^{19}F$ n.m.r. : $\delta/(CH_2Cl_2)$ = -50.78 ppm ($CF_3$, 12F).

### 3.3.25 Preparation of $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_4$

Chlorination of $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_2$, 8.0 g (20.9 mmol) in dichloromethane (50 ml) gave a white solid.

Yield 7.5 g (79 %), $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_4$.

$C_9H_2Cl_4F_9P$ = 453.89.

Calc: C = 23.82 %, H = 0.44 %, P = 6.82 %, Cl = 31.24 %.

Found: C = 24.62 %, H = 1.10 %, P = 6.44 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = -47.9 ppm.

$^{19}F$ n.m.r. : $\delta/(CH_2Cl_2)$ = -53.17 ppm ($CF_3$, 6F), -64.50 ppm ($CF_3$, 3F).

### 3.3.26 Preparation of $P(CH_2Cl)Cl_4$

Chlorination of $P(CH_2Cl)Cl_2$, 1.4 g (9.3 mmol) in dichloromethane (50 ml) gave a milky-white liquid (see text).

Yield 1.5 g (72.5 %), $P(CH_2Cl)Cl_4$.

$CH_2Cl_5P$ = 222.27.

Calc: C = 5.40 %, H = 0.91 %, P = 13.94 %, Cl = 79.75 %.

Found: Cl = 78.65 %.

$^{31}$P n.m.r. : $\delta$/($CDCl_3$) = -39.0 ppm (t).

$^{1}$H n.m.r. : $\delta$/($CDCl_3$) = 5.26 ppm (d, $J_{PH}$ = 5.3 Hz).

$^{13}$C n.m.r. : $\delta$/($CDCl_3$) = 72.7 ppm ( t, $J_{CH}$ = 167.3 Hz; d, $J_{CP}$ = 118.5 Hz).

### 3.3.27 Preparation of $P(CHCl_2)Cl_4$

Chlorination of $P(CHCl_2)Cl_2$, 1.8 g (9.6 mmol) in dichloromethane (50 ml) gave a pale yellow solid (containing ~ 14 % $P(CCl_3)Cl_4$ - see text).

Yield 1.9 g ($P(CH_2Cl)Cl_4$ ~ 75 %)

$CH_2Cl_5P$ = 222.27.

$^{31}$P n.m.r. : $\delta$/($CDCl_3$) = -34.12 ppm (d); /(solid) = -34.16 ppm.

($P(CCl_3)Cl_4$ in mixture, $\delta$ $^{31}$P /($CDCl_3$) = -19.5 ppm; /(solid) = -33.04 ppm)

$^{1}$H n.m.r. : $\delta$/($CDCl_3$) = 6.79 ppm (d, $J_{PH}$ = 32.0 Hz).

$^{13}$C n.m.r. : $\delta$/($CDCl_3$) = 94.23 ppm ( d, $J_{CH}$ = 194.5 Hz; d, $J_{CP}$ = 142.1 Hz).

### 3.3.28 Preparation of $[P(2\text{-}(CH_3)C_6H_4)Cl_3][BCl_4]$

To a 125 ml two-necked flask, fitted with dropping funnel and maintained under an atmosphere of dry nitrogen, was added $P(2\text{-}(CH_3)C_6H_4)Cl_4$ 6.2 g (23.5 mmol) and dichloromethane (50 ml). 25.0 ml (25.0 mmol) of a 1 M solution of boron trichloride in hexane was added dropwise, with stirring. The reaction mixture was then allowed stir for a further 30 minutes at room temperature. The solvent and any excess boron trichloride were removed *in vacuo* , leaving a white solid. The product was then washed under nitrogen with a small quantity of dichloromethane, before being dried under vacuum.

Yield 6.4 g (71.5 %),2[P(2-($CH_3$)$C_6H_4$)$Cl_3$][$BCl_4$].

$C_7H_7BCl_7P$ = 381.09.

Calc: C = 22.06 %, H = 1.85 %, P = 8.13 %, Cl = 65.12 %.

Found: C = 23.27 %, H = 2.29 %, Cl = 62.27 %.

$^{31}$P n.m.r. : $\delta$/($PhNO_2$) = 99.2 ppm.

### 3.3.29 Preparation of [P(2-($CH_3$)$C_6H_4$)$_2$$Cl_2$][$BCl_4$]

Reacting P(2-($CH_3$)$C_6H_4$)$_2$$Cl_3$ 4.0 g (12.5 mmol) with $BCl_3$ / hexane solution (1M) 14.0 ml (14.0 mmol) gave a white solid.

Yield 3.7 g (68 %), [P(2-($CH_3$)$C_6H_4$)$_2$$Cl_2$][$BCl_4$].

$C_{14}H_{14}BCl_6P$ = 436.76.

Calc: C = 38.50 %, H = 3.23 %, P = 7.09 %, Cl = 48.70 %.

Found: C = 39.82 %, H = 5.15 %, Cl = 46.55 %.

$^{31}$P n.m.r. : $\delta$/($PhNO_2$) = 92.2 ppm, $\delta$/(solid) = 92.3 ppm.

$^{11}$B n.m.r. : $\delta$/($PhNO_2$) = 7.75 ppm.

### 3.3.30 Preparation of [P(2,4,6-($CH_3$)$_3$$C_6H_2$)$Cl_3$][$BCl_4$]

Reacting P(2,4,6-($CH_3$)$_3$$C_6H_2$)$Cl_4$ 3.1 g (10.6 mmol) with $BCl_3$ / hexane solution (1M) 12.0 ml (12.0 mmol) gave a brown solid.

Yield 3.7 g (85 %), [P(2,4,6-($CH_3$)$_3$$C_6H_2$)$Cl_3$][$BCl_4$].

$C_9H_{11}BCl_7P$ = 409.15.

Calc: C = 26.42 %, H = 2.71 %, P = 7.57 %, Cl = 60.66 %.

Found: C = 31.44 %, H = 5.38 % (Apparent decomposition).

$^{31}$P n.m.r. : $\delta$/($PhNO_2$) = 96.1 ppm.

### 3.3.31 Preparation of [$P(2,4,6-(CH_3)_3C_6H_2)_2Cl_2$][$BCl_4$]

Reacting $P(2,4,6-(CH_3)_3C_6H_2)_2Cl_3$ 0.4 g (1.1 mmol) with $BCl_3$ / hexane solution 1.5 ml (1.5 mmol) gave a brown, sticky solid.

Yield 0.2 g (37 %), [$P(2,4,6-(CH_3)_3C_6H_2)_2Cl_2$][$BCl_4$].

$C_{18}H_{22}BCl_6P$ = 492.87.

Calc: C = 43.86 %, H = 4.50 %, P = 6.28 %, Cl = 43.16 %.

Found: C = 52.18 %, H = 7.32 % (Apparent decomposition).

$^{31}$P n.m.r. : $\delta$/($PhNO_2$) = 88.7 ppm.

### 3.3.32 Preparation of [$P(C_6Cl_5)Cl_3$][$BCl_4$]

Reacting $P(C_6Cl_5)Cl_4$ 1.8 g (5.1 mmol) with $BCl_3$ / hexane solution (1M) 6.0 ml (6.0 mmol) gave a white solid.

Yield 2.1 g (91.3 %), [$P(C_6Cl_5)Cl_3$][$BCl_4$].

$C_6BCl_{12}P$ = 539.29.

Calc: C = 13.36 %, P = 5.74 %, Cl = 78.89 %.

Found: C = 12.01 %, Cl = 78.65 %.

$^{31}$P n.m.r. : $\delta$/($PhNO_2$) = 90.3 ppm.

$^{11}$B n.m.r. : $\delta$/($PhNO_2$) = 8.24 ppm.

### 3.3.33 Preparation of [$P(2-(CF_3)C_6H_4)Cl_3$][$BCl_4$]

Reacting $P(2-(CF_3)C_6H_4)Cl_4$ 1.9 g (6.0 mmol) with $BCl_3$ / hexane solution (1M) 7.0 ml (7.0 mmol) gave a white solid.

Yield 2.2 g (84.6 %), [$P(2-(CF_3)C_6H_4)Cl_3$][$BCl_4$].

$C_7H_4BCl_7F_3P$ = 435.06.

Calc: C = 19.33 %, H = 0.93 %, P = 7.12 %, Cl = 57.04 %.

Found: C = 19.64 %, H = 2.14 %, P = 6.79 %.

$^{31}$P n.m.r. : $\delta$/($PhNO_2$) = 101.5 ppm, $\delta$/(solid) = 99.8 ppm.

$^{19}$F n.m.r. : $\delta$/($PhNO_2$) = -54.65 ppm ($CF_3$, 3F).

### 3.3.34 Preparation of $[P(2\text{-}(CF_3)C_6H_4)_2Cl_2][BCl_4]$

Reacting $P(2\text{-}(CF_3)C_6H_4)_2Cl_3$ 1.5 g (3.5 mmol) with $BCl_3$ / hexane solution (1M) 4.0 ml (4.0 mmol) gave a white solid.

Yield 1.8 g (94 %), $[P(2\text{-}(CF_3)C_6H_4)_2Cl_2][BCl_4]$.

$C_{14}H_8BCl_6F_6P$ = 544.71.

Calc: C = 30.87 %, H = 1.48 %, P = 5.69 %, Cl = 39.05 %.

Found: C = 31.56 %, H = 2.23 %, Cl = 38.41 %.

$^{31}$P n.m.r. : $\delta$/($PhNO_2$) = 96.3 ppm, $\delta$/(solid) = 99.8 ppm

$^{19}$F n.m.r. : $\delta$/($PhNO_2$) = -54.22 ppm ($CF_3$, 6F).

### 3.3.35 Preparation of $[P(2,6\text{-}(CF_3)_2C_6H_3)Cl_3][BCl_4]$

Reacting $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_4$ 4.4 g (11.4 mmol) with $BCl_3$ / hexane solution (1M) 5.0 ml (5.0 mmol) gave a white solid.

Yield 5.5 g (96 %), $[P(2,6\text{-}(CF_3)_2C_6H_3)Cl_3][BCl_4]$.

$C_8H_3BCl_7F_6P$ = 503.06.

Calc: C = 19.10 %, H = 0.60 %, P = 6.16 %, Cl = 49.33 %.

Found: C = 18.71 %, H = 0.96 %, Cl = 47.89 %.

$^{31}$P n.m.r. : $\delta$/($PhNO_2$) = 97.1 ppm.

$^{19}$F n.m.r. : $\delta$/($PhNO_2$) = -50.62 ppm ($CF_3$, 6F).

### 3.3.36 Preparation of $[P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_2][BCl_4]$

Reacting $P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_3$ 3.0 g (5.3 mmol) with $BCl_3$ / hexane solution (1M) 6.0 ml (6.0 mmol) gave a white solid.

Yield 3.3 g (91.0 %), $[P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_2][BCl_4]$.

$C_{16}H_6BCl_6F_{12}P$ = 680.70.

Calc: C = 28.23 %, H = 0.89 %, P = 4.55 %, Cl = 31.25 %.

Found: C = 28.41 %, H = 1.76 %, Cl = 29.84 %.

$^{31}P$ n.m.r. : $\delta/(PhNO_2)$ = 84.7 ppm.

$^{19}F$ n.m.r. : $\delta/(PhNO_2)$ = -50.73 ppm ($CF_3$, 12F).

### 3.3.37 Preparation of $[P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_3][BCl_4]$

Reacting $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_4$ 10.0 g (22.0 mmol) with $BCl_3$ / hexane solution (1M) 24.0 ml (24.0 mmol) gave a white solid.

Yield 11.26 g (89.5 %), $[P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_3][BCl_4]$.

$C_9H_2BCl_7F_9P$ = 571.06.

Calc: C = 18.93 %, H = 0.35 %, P = 5.42 %, Cl = 43.45 %.

Found: C = 18.66 %, H = 0.13 %, P = 5.24 %, Cl = 41.11 %.

$^{31}P$ n.m.r. : $\delta/(PhNO_2)$ = 97.1 ppm.

$^{19}F$ n.m.r. : $\delta/(PhNO_2)$ = -50.57 ppm ($CF_3$, 6F), -64.86 ppm ($CF_3$, 3F).

### 3.3.38 Preparation of $[P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_3][SbCl_6]$

To a 250 ml two-necked flask, fitted with dropping funnel and maintained under an atmosphere of dry nitrogen, were added $P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_4$ 6.0 g (13.2 mmol) and dichloromethane (50 ml). The reaction mixture was cooled to -78°C (cardice / acetone). Antimony pentachloride 4 g (13.4 mmol), in dichloromethane, was then added dropwise, with stirring. A creamy-white precipitate was formed, which was filtered off under nitrogen and washed (dichloromethane followed by pentane). The product was then dried *in vacuo* to give a whitish solid.

Yield 5.2 g (52 %), $[P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_3][SbCl_6]$.

$C_9H_2Cl_9F_9PSb = 752.91$.

Calc: C = 14.36 %, H = 0.27 %, P = 4.11 %, Cl = 42.38 %.

Found: C = 14.87 %, H = 1.32 %, P = 3.88 %, Cl = 40.94 %.

$^{31}P$ n.m.r. : $\delta/(PhNO_2) = 95.9$ ppm.

$^{19}F$ n.m.r. : $\delta/(PhNO_2) = -50.60$ ppm ($CF_3$, 6F), -64.71 ppm ($CF_3$, 3F).

### 3.3.39 Preparation of $[P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_2][SbCl_6]$

Reacting $P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_3$ 2.6 g (4.6 mmol) with $SbCl_5$ 1.4 g (4.7 mmol) in dichloromethane (100 ml) gave a grey solid.

Yield 3.6 g (42 %), $[P(2,6\text{-}(CF_3)_2C_6H_3)_2Cl_2][SbCl_6]$.

$C_{16}H_6Cl_8F_{12}PSb = 862.55$.

Calc: C = 22.28 %, H = 0.70 %, P = 3.59 %, Cl = 32.88 %.

Found: C = 23.43 %, H = 1.98 %, Cl = 31.64 %.

$^{31}P$ n.m.r. : $\delta/(PhNO_2) = 84.7$ ppm.

$^{19}F$ n.m.r. : $\delta/(PhNO_2) = -50.55$ ppm ($CF_3$, 12F).

### 3.3.40 Preparation of $[P(CH_2Cl)Cl_3][AlCl_4]$

To a 50 ml three-necked flask, fitted with mechanical stirrer, reflux condenser, dropping funnel and maintained under an atmosphere of dry nitrogen, were added phosphorus trichloride 3.5 g (25.5 mmol), methylene chloride 2.9 g (34 mmol) and aluminium chloride 2.9 g (21.7 mmol). This mixture was heated to reflux for 24 hours until all the aluminium chloride had dissolved. The remaining volatiles were removed leaving 7.3 g ("95 %") of a brown, sticky solid.

$CH_2AlCl_8P$ = 355.62.

Calc: C = 3.38 %, H = 0.57 %, P = 8.71 %, Cl = 79.75 %.

$^{31}$P n.m.r. : $\delta/(CD_3NO_2)$ = 112.4 ppm.

$^{1}$H n.m.r. : $\delta/(CD_3NO_2)$ = 5.51 ppm (s, broad).

$^{13}$C n.m.r. : $\delta/(CD_3NO_2)$ = 42.8 ppm ( t, $J_{CH}$ = 163.2 Hz; d, $J_{CP}$ = 71.1 Hz).

### 3.3.41 Preparation of $[P(CHCl_2)Cl_3][AlCl_4]$

In the preparation of $P(CHCl_2)Cl_2$ (see above), after refluxing the $PCl_3$ / $CHCl_3$ / $AlCl_3$ mixture for six hours, a large quantity of a whitish solid was formed. A small quantity (~ 3 g) of this solid was removed, recrystallised from dichloromethane and analysed as follows:

$CHAlCl_9P$ = 390.06.

Calc: C = 3.08 %, H = 0.26 %, P = 7.94 %, Cl = 81.80 %.

Found: C = 2.88 %, H = 0.48 %, Cl = 80.44 %.

$^{31}$P n.m.r. : $\delta/(PhNO_2)$ = 106.7 ppm;/$(EtNO_2)$ = 108.2 ppm.

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# Chapter IV

# Phosphoranides

## 4.1 Introduction

Phosphoranides are hypervalent (four-coordinate) phosphorus (III) compounds with a single negative charge. Early work showed that some phosphines could form weak, neutral complexes with Lewis bases[1,2]. Notably, Holmes and Wagner studied the acceptor properties of various phosphines towards $NMe_3$ and, on the basis of their results, proposed the following order of acceptor ability:

$$PCl_3 > PBr_3 \approx PMeCl_2 > PMe_3.$$

Phosphoranides had been proposed as intermediates in nucleophilic substitution in phosphorus (III) species. Wittig and Maercker[3] suggested a phosphoranide as intermediate in the reaction of (4-methyl)phenyllithium with triphenylphosphine:

$$PPh_3 + p.tolylLi \rightleftharpoons [PPh_3(p.tolyl)]^- \rightleftharpoons PPh_2(p.tolyl) + PhLi.$$

However, Kyba[4] later showed that nucleophilic substitution in tertiary phosphines is a classical $S_N2$ process, with no formation of an intermediate, but presumably the phosphoranide is present as the transition state.

The first true phosphoranide, $PBr_4^-$, was prepared by Dillon and Waddington[5] in 1969 by reacting $PBr_3$ with a saturated solution of tetra(n-propyl)ammonium bromide in 1,2-dichloro-ethane. Although $^{31}P$ n.m.r. studies showed that only a very small quantity of the $PBr_3$ complexes with bromide under these conditions, it was possible to crystallise the pure phosphoranide salt out of the reaction mixture. Dillard and Rhyne[6,7] showed that $PF_4^-$ could be formed in the gas-phase by fluoride transfer from $SF_6^-$ (generated by electron capture in a mass spectrometer) and $PF_3$;

$$SF_6 + e^- \longrightarrow SF_6^- \xrightarrow{PF_3} PF_4^-$$

Wermer and Ault[8] later trapped $Cs[PF_4]$ and $Cs[PClF_3]$ in argon matrices from the gas-phase reaction of the relative caesium halide and $PF_3$. They failed to form $Cs[PCl_4]$ in the same manner, which they claimed indicates that $PF_3$ is the stronger Lewis acid. Schmidpeter and Zwaschka[9] showed how cyano-substituted phosphoranides could be prepared, either from $P(CN)_3$ and crown-ether-sodium halide:

$$[18]crown - 6.NaX + P(CN)_3 \longrightarrow [[18]crown - 6.Na][P(CN)_3X],$$

(X = halide)

or, alternatively by the action of dihalogen on crown-ether-sodium dicyanophosphide, highlighting the comparison between phosphoranides and trihalide ions:

$$[18]crown - 6.NaP(CN)_2 + X_2 \longrightarrow [[18]crown - 6.Na][P(CN)_2X_2].$$

Sheldrick *et al* [10,11] performed X-ray crystal structure analyses on the following phosphoranides $PBr_4^-$, $P(CN)_2Br_2^-$, $P(CN)_3Br^-$ and $P(CN)_3I^-$ with either tetra-alkylammonium or crown-ether-sodium as the counter ion. $P(CN)_2Br_2^-$ was shown to have the $\psi$tbp structure as predicted by VSEPR. $P(CN)_3Br^-$ and $P(CN)_3I^-$ , on the other hand, were shown to have dimeric, $\psi$octahedral structures with symmetrical halogen-bridges, whereas $PBr_4^-$ (with $N(nPr)_4^+$ as counter ion) was shown to have a structure intermediate between the two. It is worth noting here that attempts to prepare $P(CN)_4^-$ by reacting $P(CN)_3$ with cyanide resulted in elimination of cyanogen and formation of $P(CN)_2^-$. Dillon *et al* [12] have published the X-ray crystal structures of $PCl_4^-$ and $P(CN)_3Cl^-$. Both have the VSEPR-predicted $\psi$tbp structure, yet in each case there is one very long, axial P-Cl bond, which in $PCl_4^-$ is 40 % longer than the P-Cl distance in $PCl_3$.

Although, for example, Granoth and Martin[13] reported $^{31}P$ n.m.r. evidence for the formation of a spirocyclic phosphoranide following the $LiAlH_4$ reduction of the corresponding phosphonium ion, until recently no phosphoranides with an organo group R attached to phosphorus have been described in detail. Several new phosphoranides have been reported by Deng *et al* [14] of the type $[NR_4][PR'(CN)_2X]$ (where R' = Me, Et, Ph or $C_6F_5$; X = Cl, Br, I or NCS). This work included the crystal structure of $[NEt_4][PPh(CN)_2Cl]$, which showed that the anion had a distorted $\psi$tbp structure, with the phenyl group equatorial and, again, a very long axial P-Cl bond. Bürgi[15] has shown that the shape of correlation curves derived from changes of various structural parameters for a given molecular fragment in the solid is reminiscent of the structural changes occurring along the pathways of chemical reactions. Hence, the structures of $[PPh(CN)_2Cl]^-$ and $[PCl_4]^-$ which exhibit very long axial P-Cl bonds, may be interpreted as representing "frozen intermediates" along the reaction pathway for nucleophilic addition to a phosphorus centre.

Ali and Dillon[16] have recently described how phosphoranides can be prepared with pentafluorophenyl-groups incorporated. All the phosphines of the type $P(C_6F_5)X_2$ (where X = Cl, Br or NCS) were shown to accept halide ion. This resulted in the first series of simple phosphoranides with an organo group attached to phosphorus but with no cyano-groups present. In the same work, it was shown that it is possible to form phosphoranides with two pentafluorophenyl-groups present, which represent the first phosphoranides with two organo-groups directly bound to phosphorus.

It is clear that organo-substituted phosphoranides can be formed and isolated if electron-withdrawing substituents, such as cyanide or pentafluorophenyl groups, are incorporated. However, in a recent study by Goodwin[17] it was shown that, whereas chloride addition to alkyl-substituted dicyanophosphines leads to phosphoranide formation (see above), none of the species $PCl_2(NR_2)$, $PCl(NR_2)_2$, $P(CN)_2(NR_2)$ or $P(CN)(NR_2)_2$ (where R = Et or iPr) will accept chloride ion in this way. Goodwin also demostrated how $[P(2,4,6\text{-}(CF_3)_3C_6H_2)(CN)_2Cl]^-$ could be formed by chloride addition to the dicyanophosphine. So it would seem that bulky groups can be incorporated into phosphoranides, given that they are suitably electron-withdrawing. However, the full extent to which steric bulk of substituents affects the stability of phosphoranides remains largely untested.

It has been shown that, in a similar way to the reaction of $P(CN)_3$ with $CN^-$, which results in the elimination of cyanogen and the formation of $[P(CN)_2]^-$, organo-substituted dicyanophosphines also form the respective phosphide (rather than phosphoranide) when treated with tetra(alkyl)ammonium cyanide[17,18]:

$$PR(CN)_2 + CN^- \xrightarrow{-(CN)_2} [PR(CN)]^-.$$

(where R = CN, Me, Et, Ph or $CF_3$)

The formation of phosphoranides in solution by halide addition to a phosphine is clearly indicated in $^{31}P$ n.m.r. by an upfield shift from the resonance of the precursor phosphine[19]. To illustrate this, the limiting shifts obtained by addition of excess of $X^-$ (X = Cl, Br, I, or NCS) to $PR(CN)_2$ (R = Me, Et, Ph, or $C_6F_5$) in $CH_2Cl_2$ as solvent, together with the shifts of the precursor cyanophosphines $PR(CN)_2$, are given in table 4.1[14,17]. The order of upfield displacement of the resonance of $PR(CN)_2$ by $X^-$ is: $I^- \leq NCS^- < Br^- < Cl^-$. Here it is worth noting that the NCS groups in these compounds have been shown by their I.R. spectra, to be isothiocyanate (i.e. N- rather than S-bonded[20-22]).

| | | $[PR(CN)_2X]^-$ | | | | |
|---|---|---|---|---|---|---|
| R | $PR(CN)_2$ | X = Cl | Br | NCS | I | Ref. |
| Me | -79.1 | -101.3 | -98.4 | -92.0 | -90.4 | 13 |
| Et | -61.3 | -78.0 | -70.9 | -66.2 | -66.2 | 13 |
| Ph | -72.6 | -103.3 | -90.4 | -83.8 | -77.5 | 13 |
| $C_6F_5$ | -112.9 | -154.7 | -140.2 | -135.5 | -128.9 | 13 |
| 2,4,6-$(CF_3)_3C_6H_2$ | -87.2 | -137.4 | - | - | - | 16 |

**Table 4.1 — $^{31}P$ n.m.r. data (δ/ppm) for $PR(CN)_2$ and $[PR(CN)_2X]^-$ in $CH_2Cl_2$.**

It would be interesting to study more fully the effect of choice of aryl group on the structure and stability of such phosphoranides. Of notable interest would be the steric requirements of such species, particularly with respect to the ortho-sustituents of the aryl-group.

## 4.2 Results

### 4.2.1 Acceptor Properties of $P(2\text{-}(CH_3)C_6H_4)(CN)_2$

The aryl(dicyano)phosphine, $P(2\text{-}(CH_3)C_6H_4)(CN)_2$, was prepared by the 2:1 molar ratio reaction of silver cyanide with $P(2\text{-}(CH_3)C_6H_4)Cl_2$ in acetonitrile[17]. The precursor aryldichlorophosphine was prepared by the action of the arylzinc chloride on $PCl_3$, as described in chapter 3. 2-(Methyl)phenyl(dicyano)phosphine has not previously been reported in the literature. It was isolated as a colourless oil and its $^{31}P$ n.m.r. chemical shift of -76.3 ppm is consistent with other known values for compounds of this type (see table 4.1).

In acetonitrile solution $P(2\text{-}(CH_3)C_6H_4)(CN)_2$ does appear to form phosphoranide species of the type $[P(2\text{-}(CH_3)C_6H_4)(CN)_2X]^-$ (where X = Cl, Br, I or NCS). In each case the limiting shift (i.e. the maximum upfield displacement from the $P(2\text{-}(CH_3)C_6H_4)(CN)_2$ resonance) was only achieved when a molar excess of $NR_4X$ (R = Et, Pr or Bu) was added. In the $PBr_3/Br^-$ system[5] the phosphoranide and the free phosphine show separate signals in the $^{31}P$ n.m.r. spectrum. However, as appears to be the general case for organo-substituted phosphoranides of this type[14,16,17], in the $P(2\text{-}(CH_3)C_6H_4)(CN)_2/X^-$ system a single peak was observed, even when there was a molar deficiency of $NR_4X$. This is attributable to rapid exchange in the equilibrium:

$$PAr(CN)_2 + X^- \rightleftharpoons [PAr(CN)_2X]^-$$

(where Ar = 2-($CH_3$)$C_6H_4$and $X^-$ $Cl^-$, $Br^-$, $I^-$ or $NCS^-$).

On successive additions of small amounts of $NR_4X$ to P(2-($CH_3$)$C_6H_4$)$(CN)_2$ in acetonitrile solution, a gradual increase in the upfield displacement of the signal in the $^{31}P$ n.m.r. spectrum was observed, until the limiting shift was attained, at which point further addition of $X^-$ made no noticeable change to the spectrum. The limiting shifts for the species [P(2-($CH_3$)$C_6H_4$)$(CN)_2$X]$^-$ are give in table 4.2. The choice of cation in these systems is non-trivial. Studies have shown[14] that the nature of the counter ion may have a significant influence on the $^{31}P$ chemical shift of the phosphoranide. It may well be that in solution there is ion pair formation[16]. It has been shown by Sheldrick *et al* that the solid-state structure of $PBr_4^-$ is also cation dependent: in $[N(nPr)_4][PBr_4]$[11], the phosphoranide has a bridged, $\psi$octahedral structure, whereas in $[N(Et)_4][PBr_4]$[23], the anion has a distorted, $\psi$tbp structure.

| Cation | X | $\delta$ $^{31}P$/MeCN |
|---|---|---|
| $N(Et)_4^+$ | Cl | -83.4 |
| $N(Pr)_4^+$ | Br | -83.2 |
| $N(Et)_4^+$ | I | -77.2 |
| $N(Et)_4^+$ | NCS | -77.3 |

**Table 4.2 — $^{31}P$ n.m.r. data ($\delta$/ppm) for [P(2-($CH_3$)$C_6H_4$)$(CN)_2$X]$^-$ in MeCN.**

By comparison with the analogous phenyl system (table 4.1), the much smaller difference between the $^{31}P$ n.m.r. shift for $P(2\text{-}(CH_3)C_6H_4)(CN)_2$ and the limiting shift for a given phosphoranide (table 4.2), may be partly attributable to a weaker complexation of halide or thiocyanate. This may be due to a combination of steric and electronic factors. An ortho-substituent on the aryl group would disfavour any increase in the coordination number of phosphorus, and an electron-supplying substituent, such as $CH_3$, would not be expected to have a stabilising influence on the negatively-charged phosphoranide. Attempts at low temperature crystallisation were unsuccessful in isolating any of the phosphoranides formed.

### 4.2.2 Acceptor Properties of $P(C_6Cl_5)(CN)_2$

The aryl(dicyano)phosphine, $P(C_6Cl_5)(CN)_2$, was prepared by the 2:1 molar ratio reaction of silver cyanide with $P(C_6Cl_5)Cl_2$ in acetonitrile[17]. The precursor aryldichlorophosphine was prepared by the action of the arylmagnesium chloride on $PCl_3$, as described in chapter 3. Pentachlorophenyl(dicyano)phosphine has not previously been reported in the literature. It was isolated as a white solid, which was found to be soluble in toluene or polar solvents, but not in diethyl ether or petroleum ether. The $^{31}P$ n.m.r. chemical shift for this compound was recorded in a number of solvents (see table 4.3), and the value of -79.7 ppm in dichloromethane, being intermediate to the shifts for the phenyl and pentafluorophenyl analogues (see table 4.1), is as would be expected.

| Solvent | $\delta$ $^{31}P$/ppm |
|---|---|
| $C_6H_5CH_3$ | -81.8 |
| $C_6H_5NO_2$ | -80.8 |
| $CH_3CN$ | -80.3 |
| $CH_2Cl_2$ | -79.7 |

**Table 4.3 — $^{31}P$ n.m.r. data for $P(C_6Cl_5)(CN)_2$ in various solvents.**

The reaction of $P(C_6Cl_5)(CN)_2$ with chloride gave a mixture of products. As noted from the $^{31}P$ n.m.r. spectrum, when an excess of $N(Et)_4Cl$ was added to a dichloromethane solution of $P(C_6Cl_5)(CN)_2$, three new signals were seen at -19.4 ppm, -65.2 ppm and -114.7 ppm, with approximate relative intensities of 2:1:2 respectively. When the reaction was repeated, but with nitrobenzene as solvent, again three signals were seen by $^{31}P$ n.m.r. but this time at -67.9 ppm, -87.1 ppm and -130.3 ppm, all of roughly equal intensity (a result which was shown to be reproducible). This last signal at -130.3 ppm compares well with the known value for the limiting shift for $[P(2,4,6\text{-}(CF_3)_3C_6H_2)(CN)_2Cl]^-$ ($\delta$ $^{31}P$ = -137.4)[16]). Thus, it would not seem unreasonable to assume that the phosphoranide $[P(C_6Cl_5)(CN)_2Cl]^-$ could be one of the components in this mixture. The limiting shift may well not have been achieved in the reaction in dichloromethane, due to the lower solubility of $N(Et)_4Cl$ in this solvent. It is unclear as to the identity of the other species formed in these reactions. Phosphide formation by elimination of cyanogen chloride is a possibility, though without precedent. Reaction of the pentachlorophenyl group is also possible, though it is difficult to see what exactly what form this could take.

The addition of an excess of $N(nPr)_4Br$ to a solution of $P(C_6Cl_5)(CN)_2$ in dichloromethane, also resulted in the formation of three phosphorus species, as seen by $^{31}P$ n.m.r. . Signals were recorded at -9.6 ppm, -59.3 ppm and -103.4 ppm, with the following approximate intensities 1:3:1 respectively. The signal at -103.4 ppm could be due to the formation of $[P(C_6Cl_5)(CN)_2Br]^-$, though again it is not easy to account for the presence of signals in the $^{31}P$ n.m.r. spectrum downfield of the parent dicyanophosphine, but too far upfield to be simply from hydrolysis or oxidation. Again, the results were shown to be reproducible.

### 4.2.3 Acceptor Properties of Arylphosphinous Dihalides

Most organo-substituted cyanophosphines will accept halide ion to form the respective phosphoranide, though in the case of $P(C_6Cl_5)(CN)_2$ (see above) other side reactions also appear to take place. However, as yet, the only phosphoranides derived from halide addition to organo-substituted dihalophosphines, (i.e. without cyanide substituents), are those which incorporate one or more $C_6F_5$-groups[16]. In the present work, the following phosphines (1 to 5) would not accept chloride ion, as shown by no change in the position of their $^{31}P$ n.m.r. signal when $NR_4Cl$ was added.

1. $P(2\text{-}(CH_3)C_6H_4)Cl_2$
2. $P(C_6Cl_5)Cl_2$
3. $P(2\text{-}(CF_3)C_6H_4)Cl_2$
4. $P(2,4,6\text{-}(CH_3)_3C_6H_2)Cl_2$
5. $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_2$

Also, it has been shown previously[17] that it is not possible to form the phosphoranide $[P(2,4,6\text{-}(CF_3)_3C_6H_2)Cl_3]^-$ by chloride addition to the arylphosphinous dichloride.

As explained above, it has been postulated that phosphoranides may be unstable intermediates in nucleophilic substitution reactions of anions at organophosphorus(III) centres[3,16]. As described in chapter 3, where aryl-substituted chlorophosphines are prepared by the action of an arylmagnesium bromide on $PCl_3$, there is often extensive bromo-incorporation into the resultant phosphine. Where solely the chloro-derivative is required, this can be achieved by treating the mixture of chloro- and bromo-substituted phosphines with $N(Et)_4Cl$ in dichloromethane. An example of such an experiment (the reaction of the phosphine mixture $P(2\text{-}(CF_3)C_6H_4)Br_2$, $P(2\text{-}(CF_3)C_6H_4)BrCl$ and $P(2\text{-}(CF_3)C_6H_4)Cl_2$ with $N(Et)_4Cl$) was followed by $^{31}P$ n.m.r. . On successive additions of small quantities of $N(Et)_4Cl$, all that was seen in the $^{31}P$ n.m.r. spectrum of the reaction mixture was a gradual decrease in the intensity of the resonances for the bromo-species and an increase in the intensity of the signal corresponding to $P(2\text{-}(CF_3)C_6H_4)Cl_2$. When sufficient $N(Et)_4Cl$ had been added to convert all of the bromo-substituted phosphines to the arylphosphinous dichloride, further addition of chloride resulted in no change in the $^{31}P$ n.m.r. spectrum. Any steric hindrance offered by the $CF_3$-group in this system does not appear to slow down the reaction sufficiently to prevent chloride-for-bromide exchange to occur within seconds of addition of the tetraalkylammonium chloride. Thus, should this reaction preceed via phosphoranide intermediates, they are too short-lived to be detected in this experiment, and clearly the product, $P(2\text{-}(CF_3)C_6H_4)Cl_2$, will not accept chloride to form $[P(2\text{-}(CF_3)C_6H_4)Cl_3]^-$.

## 4.3 General Conclusion

It has been demonstrated that, unlike the chlorophosphorane systems (see chapter 3), where the incorporation of aryl groups with bulky ortho-substituents prevents phosphorus from increasing its coordination number by complexation with Lewis bases, hypervalent phosphorus (III) compounds can be formed with the inclusion of such ligands. On the basis of the data presented above, the exact nature of substituents on an aryl group, Ar, to be incorporated into a phosphoranide of the type $[P(Ar)(CN)_2X]^-$ (where X = Cl, Br, I or NCS), may well be important in determining stability of such a complex. As explained above, where Ar = 2-(methyl)phenyl $^{31}P$ n.m.r. would suggest weaker complexation of $X^-$ by $P(Ar)(CN)_2$ than for when Ar = phenyl. The $C_6Cl_5$ system is more difficult to rationalize. Until the various products of the reactions of $P(C_6Cl_5)(CN)_2$ with halide can be identified, little can be said about the processes taking place. It would be of use to extend these studies to look at the acceptor properties of, for example, $P(2\text{-}(CF_3)C_6H_4)(CN)_2$ or $P(2,4,6\text{-}(CH_3)_3C_6H_2)(CN)_2$. The latter would be of particular interest, as it may well be that, due to a combination of electronic and steric effects, it may not be possible to form a stable phosphoranide of this type with the inclusion of a mesityl group.

## 4.4 Experimental

### 4.4.1 Preparation of $P(2\text{-}(CH_3)C_6H_4)(CN)_2$

To a two-necked, 250 ml round-bottomed flask, fitted with nitrogen inlet and mechanical stirrer, were added $P(2\text{-}(CH_3)C_6H_4)Cl_2$ 3.0 g (15.5 mmol) and AgCN 2.2 g (16.4 mmol), in dry acetonitrile (100 ml). The mixture was then stirred at room temperature under an atmosphere of dry nitrogen for 24 hours. If after this time the $^{31}P$ n.m.r. spectrum of the reaction mixture showed there to be any remaining phosphinous dichloride, then a little more AgCN was added as needed, and the mixture was again allowed to stir for a further 24 hours. (N.B. Due to the expense of AgCN, large excesses were not employed). When the reaction had gone to completion the solvent was removed *in vacuo* and dry, low-boiling petroleum ether (100 ml) was added. The mixture was then allowed to stir for 1 hour so that any product entrapped in the solid silver salts would be taken up into solution. The mixture was then filtered under nitrogen (the solids being retained for recla mation of silver) and the solvent removed from the filtrate *in vacuo* , leaving a colourless oil. Yield 1.9 g (70 %), $C_9H_7N_2P$ = 174.14

Calc.: C = 62.08 %, H = 4.05 %, N = 16.16 %, P = 17.77 %

Found: C = 63.14 %, H = 5.22 %, N = 15.56 %

$^{31}P$ n.m.r. : $\delta$ $^{31}P$/(MeCN) = -76.3 ppm

### 4.4.2 Preparation of $P(C_6Cl_5)(CN)_2$

To a two-necked, 250 ml round-bottomed flask, fitted with nitrogen inlet and mechanical stirrer were added $P(C_6Cl_5)Cl_2$ 3.5 g (10.0 mmol) and AgCN 1.5 g (11.2 mmol), in dry acetonitrile (100 ml). The mixture was stirred at room-temperature and under an atmosphere of dry nitrogen for 24 hours, and followed by $^{31}P$ n.m.r. . When the reaction had gone to completion the solvent was removed *in vacuo* and dry toluene (100 ml) was added. The mixture was then allowed to stir for a further 1 hour, before being filtered under nitrogen. The solvent was then removed from the filtrate *in vacuo* , leaving a white solid. Yield 1.8 g (54 %), $C_8Cl_5N_2P$ = 332.34

Calc.: C = 28.91 %, Cl = 53.34 %, N = 8.43 %, P = 9.33 %

Found: C = 28.35 %, Cl = 52.86 %, N = 8.22 %

$^{31}P$ n.m.r. : $\delta$ $^{31}P$/(MeCN) = -80.3 ppm

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# Chapter V

# Metaphosphates

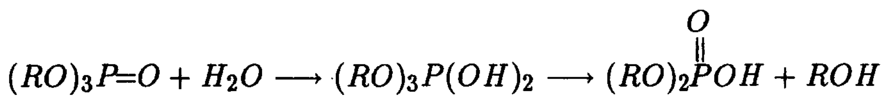
## 5.1 Introduction.

Monomeric metaphosphates have been proposed as intermediates in the hydrolysis of phosphate esters[1-7]. The coordination number of phosphorus decreases from four to three, to produce a "metaphosphate", which then adds a nucleophile to yield the product. This mechanism roughly parallels the acylium ion process for the hydrolysis of carboxylic acid esters.

$$ROPO_3H^- \longrightarrow ROH + [PO_3]^-$$

$$[PO_3]^- + H_2O \longrightarrow H_2PO_4^-$$

The other main mechanism which has been suggested for the hydrolysis of phosphate esters is where tetracoordinated phosphorus expands its coordination number to five, forming an intermediate with ψtbp structure, which then decomposes to yield the product[8-10].



$$(RO)_3P{=}O + H_2O \longrightarrow (RO)_3P(OH)_2 \longrightarrow (RO)_2\overset{\overset{\large O}{\|}}{P}OH + ROH$$

Phosphate esters are among the most important intermediary metabolites. For example, adenosine triphosphate (ATP) is the immediate transducer of biochemical energy and supplies the driving force for synthesis, muscle action, active transport and nerve action[11]. Thus the mechanisms of all reactions which involve the formation and destruction of phosphate esters, and any rôle which metaphosphates may play, are vital to the understanding of living systems.

Why monometaphosphates should be apparently so unstable has been the subject of much debate. The following equilibrium lies well to the right:

$$[PO_3]^- + H_20 \longrightarrow H_2PO_4^-.$$

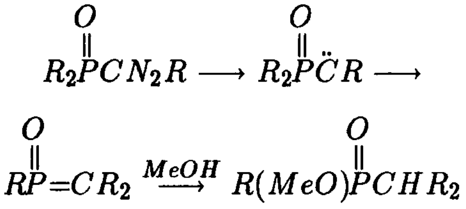
The standard free energy has been estimated at -110 kJ/mol[12,13]. and the monomeric metaphosphate ion has never been detected by any spectroscopic method in solution. By contrast, orthonitric acid is unknown; the hydrate of nitric acid has been shown by Raman spectroscopy to be hydronium nitrate[14]:

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^- \rightleftharpoons H_3NO_4.$$

It has been argued that the reason for the apparent difference in stability between nitrate and monometaphosphate is due rather to the stability of orthophosphate, and the corresponding lack of stability of orthonitrate[11]. The equilibrium between metaphosphate and orthophosphate depends on the relative strengths of single and double bonds between phosphorus and oxygen; the corresponding equilibrium in the nitrate series similarly depends on the relative strengths of single and double bonds between nitrogen and oxygen. Phosphorus to oxygen single bonds are certainly much stronger than those between nitrogen and oxygen[15] and participation from the 3d orbitals on phosphorus is believed to contribute to the greater relative stability of orthophosphate[16,17].

There has been some indication that monomeric metaphosphates can exist in the gas phase. Mass spectral peaks with masses corresponding to protonated metaphosphates have been recorded, for example $H_2PO_3^+$ and $CH_3OPO_2H^+$[18–20]. However, these species could be hydrogen phosphonates rather than metaphosphates. It was not until 1979 that Hass *et al*[21] observed $[PO_3]^-$ in the negative ion mass spectrometer. The molecular formula for the ion was confirmed by determining the accurate mass, and no structure other than metaphosphate is reasonable for $[PO_3]^-$.

Although, as yet, no stable monomeric metaphosphate has been isolated, nitrogen and carbon analogues have been prepared. Notably, Niecke *et al* have prepared[22] and obtained the X-ray structure[23] of $(Me_3Si)_2NP(=NSiMe_3)_2$. The phosphorus and three nitrogen atoms were shown to be all coplanar. They also prepared the alkylidene analogue[24], $(Me_3Si)_2NP(=NSiMe_3)(=CMe_3)$. Similar compounds have been postulated as intermediates in various chemical reactions. For example, Regitz *et al*[25–29] have have shown that the photochemical decomposition of some diazophosphonates most probably proceeds via tricoordinated pentacovalent phosphorus species as intermediates.

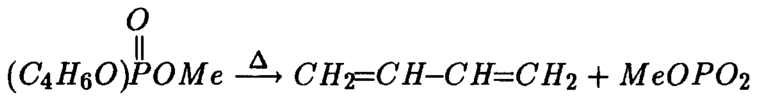


$$R_2\overset{O}{\overset{\|}{P}}CN_2R \longrightarrow R_2\overset{O}{\overset{\|}{P}}\ddot{C}R \longrightarrow$$

$$R\overset{O}{\overset{\|}{P}}=CR_2 \xrightarrow{MeOH} R(MeO)\overset{O}{\overset{\|}{P}}CHR_2$$

$(R = C_6H_5)$

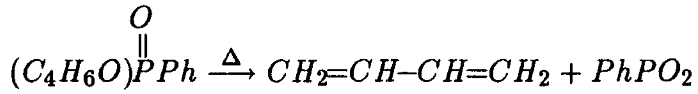
In 1974, Clapp and Westheimer[30] demonstrated that monomeric methyl metaphosphate, although unstable, could be formed by the gas-phase pyrolysis of methyl 2-butenylphosphonate, and trapped with N-methylaniline. The major product was the expected N-methylphosphoramidate.



$$(C_4H_6O)\overset{\overset{O}{\parallel}}{P}OMe \xrightarrow{\Delta} CH_2{=}CH{-}CH{=}CH_2 + MeOPO_2$$

$$MeOPO_2 + PhNHMe \longrightarrow PhN^+H(Me)PO_3^{2-}$$

Some minor products of this reaction were also found to form as a result of electrophilic attack of monomeric methyl metaphosphate on the aromatic ring. Clapp *et al*[31] showed that, depending on the other substituents at nitrogen in the aniline used, various amounts of the ortho- and para-aminobenzenephosphonic acids are also formed. Phosphonobenzene[11], the phosphorus analogue of nitrobenzene, can be formed similarly, by the pyrolysis of 1-phenyl-1-(2-butenyl)phosphinate.



$$(C_4H_6O)\overset{\overset{O}{\parallel}}{P}Ph \xrightarrow{\Delta} CH_2{=}CH{-}CH{=}CH_2 + PhPO_2$$

Metaphosphates may also be generated and trapped in solution. In the 1920s Conant and his co-workers[32–35] showed that the anions of certain $\beta$-halophosphonates and -phosphites decompose in aqueous solution to give the olefin, halide ion and phosphate, e.g.:

$$RCHXCH_2PO_3^{2-} \xrightarrow{H_2O} RCH{=}CH_2 + X^- + H_2PO_4^-.$$

In 1963, Maynard and Swann[36,37] showed both the generality of this reaction and how when, for example, the fragmentation of 2-chlorooctylphosphonate is allowed to take place in the presence of t-butyl alcohol, t-butyl phosphate is produced:

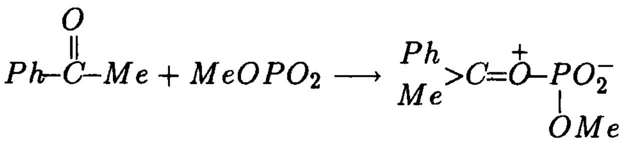
$$C_6H_{13}CHClCH_2PO_3^{2-} \xrightarrow{tBuOH} C_6H_{13}CH{=}CH_2 + tBuOPO_3H^- + Cl^-.$$

Phosphate esters of tertiary alcohols are not readily prepared by conventional means, and the simplest explanation for the preparation is that it proceeds by way of a fragmentation of the $\beta$-halophosphonate to olefin, chloride ion and $PO_3^-$, followed by electrophilic attack of the metaphosphate ion on the alcohol[11]:

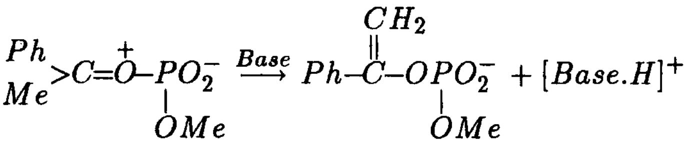
$$RCHClCH_2PO_3^{2-} \longrightarrow RCH{=}CH_2 + Cl^- + [PO_3]^-$$

The methyl ester of 1,2-dibromo-1-phenylpropane-1-phosphonic acid decomposes in a similar way in solution to form the olefin, bromide ion and the monomeric methyl metaphosphate, which can be trapped. For example, when the fragmentation is carried out in the presence of neat N-methylaniline, the major reaction products are the phosphoramidate and o- and p-(methylamino)benzenephosphonic acid[11]. As noted above, similar results were obtained from gas-phase pyrolysis preparation of $MeOPO_2$.

Metaphosphates are clearly strong electrophiles and, as has been shown by Satterthwait and Westheimer[38], will react with the unshaired electron pairs of carbonyl groups. For example, the fragmentation of the methyl ester of 1,2-dibromo--1-phenylpropylphosphonic acid in acetophenone in the presence of base leads to the formation of the methyl ester of the corresponding enol phosphate:



$$Ph{-}\overset{\overset{O}{\|}}{C}{-}Me + MeOPO_2 \longrightarrow {}^{Ph}_{Me}{>}C{=}\overset{+}{O}{-}\underset{\underset{OMe}{|}}{P}O_2^-$$

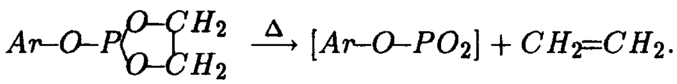


$${}^{Ph}_{Me}{>}C{=}\overset{+}{O}{-}\underset{\underset{OMe}{|}}{P}O_2^- \xrightarrow{Base} Ph{-}\overset{\overset{CH_2}{\|}}{C}{-}O\underset{\underset{OMe}{|}}{P}O_2^- + [Base.H]^+$$

(Base = 2,2,6,6-tetramethylpiperidine).

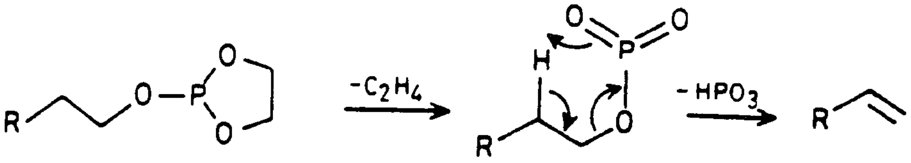
There is also evidence that metaphosphates will form zwitterionic complexes with solvents such as dioxane or acetonitrile[39]. Monomeric metaphosphate ion is isoelectronic with $SO_3$ and would be expected to add to an oxygen atom of dioxane or to the nitrogen atom of acetonitrile, just as $SO_3$ does. The adduct of $SO_3$ with dioxane is a well-known, crystalline zwitterion and mild sulphonating agent[40,41].

Apart from the intermolecular reactions of metaphosphate species as described above, Cadogan *et al* have studied the intramolecular reactions of metaphosphates with aryl substituents[42]. It was shown that 2-aryloxy-1,3,2-dioxaphospholanes break down on flash vacuum pyrolysis by a mechanism best accounted for in terms of the formation of metaphosphate moieties:



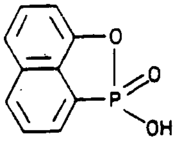
$$Ar{-}O{-}P\begin{matrix}O{-}CH_2\\ O{-}CH_2\end{matrix} \xrightarrow{\Delta} [Ar{-}O{-}PO_2] + CH_2{=}CH_2.$$

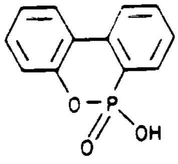
They found that if there was an abstractable $\beta$-hydrogen present on the Ar group (e.g. Ar = 2-pyridyl-$CH_2CH_2$ or $PhOCH_2CH_2$) then there was decomposition of the intermediate metaphosphate via $\beta$-elimination:

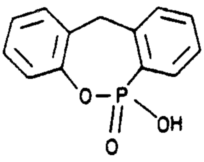


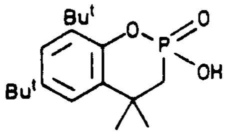
(R = pyridyl or phenoxy).

Where there was no abstractable $\beta$-hydrogen, (i.e. where Ar = $\alpha$-naphthyl, o-$PhC_6H_4$, o-$PhCH_2C_6H_4$ or 2,4,6-$tBu_3C_6H_2$), then an intramolecular C-H insertion of the metaphosphate took place, producing one of the following cyclic phosphonic monoesters:





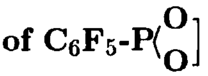




Cadogan *et al* studied the systems above which have essentially hydrocarbon Ar groups. It would be interesting to see how metaphosphates generated in a similar way, but with halocarbon aryl groups, would react. Thus the aim of this work was to prepare and study the pyrolysis of 2-aryl- and 2-aryloxy-1,3,2-dioxaphospholanes incorporating halocarbon aryl groups with varying degrees of steric crowding. It was hoped that by having $CF_3$ groups ortho to phosphorus, the product would be at least monomeric and possibly even the metaphosphate itself could be isolated. The study included flow pyrolysis of the neat, substituted 1,3,2-dioxaphospholanes and their co-pyrolysis with methanol. The mass spectra, under various conditions, (i.e. electronic ionisation, chemical ionisation and negative mode), were obtained for these starting materials, $RP(O_2C_2H_4)$, in order to see if charged metaphosphate species generated from elimination of ethylene could be detected.

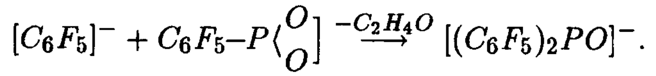
## 5.2 Results

### 5.2.1 Mass Spectrometric Study of $C_6F_5\text{-}P\langle^{O}_{O}]$



Electronic ionisation ($EI^+$) resulted in three major peaks in the mass spectrum: m/e = 91 (100 %) assigned to $[P(O_2C_2H_4)]^+$; 258 (60 %) assigned to the mass ion; and 259 (40 %), $[M+1]^+$. A minor peak, corresponding to a mass of 230 (i.e. loss of ethylene) was recorded at 1.5 % relative intesity. It would appear that, under these conditions, the preferred initial fragmentation is by P-C cleavage with susequent loss of the pentafluorophenyl group and not by elimination of ethylene, though this may occur to a small extent. Under chemical ionisation ($CI^+$), with ammonia as the ionising agent, the $[M+1]^+$ gives rise to to the dominant peak at m/e = 259 (100 %), with $M^+$ and $[M+2]^+$ at 14 % and 9 % respective relative intensities. There is much less fragmentation than in $EI^+$, with the peaks due to $[P(O_2C_2H_4)]^+$ (m/e = 91) and $[P(O_2C_2H_4).NH_3]^+$ (m/e = 108) having respective relative intensities of only 12 % and 8.5 %. There was no evidence for initial fragmentation involving elimination of ethylene. In the negative mode ($CI^-$), $[C_6F_5]^-$ gave rise to the largest peak at 167 (100 %), and the next largest peak was at m/e = 381 (33

%), probably due to $[(C_6F_5)_2PO]^-$ arising from an addition / elimination reaction inside the mass spectrometer:



$$[C_6F_5]^- + C_6F_5{-}P\left\langle\begin{smallmatrix}O\\ \\ O\end{smallmatrix}\right] \xrightarrow{-C_2H_4O} [(C_6F_5)_2PO]^-.$$

As the contributions from the mass ion and $[M+1]^-$ were both less than 1 %, it must be assumed that the preferred reaction sequence, under these conditions, is fragmentation producing the $[C_6F_5]^-$ anion, which will then react with any available starting dioxaphospholane. However, minor peaks at m/e = 230 (1.6 %) and 231 (1 %) were observed, indicating that perhaps $[C_6F_5PO_2]^-$ and $[C_6F_5PO_2H]^-$ are formed in small quantities.

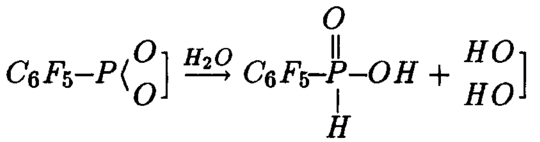
### 5.2.2 Pyrolysis of $C_6F_5\text{-}P\left\langle\begin{smallmatrix}O\\ \\ O\end{smallmatrix}\right]$

The pyrolysis of 2 g of $C_6F_5P(O_2C_2H_4)$ produced 1.7 g of a sticky white solid. The $^{31}P$ n.m.r. spectrum showed no starting material, but numerous broad peaks in the region -120 ppm to -170 ppm. The $^{19}F$ n.m.r. spectrum also showed many broad signals in the aromatic C-F region (-125 to -165 ppm), but there was also a weak doublet at -55.3 ppm ($J_{PF}$ = 1092 Hz), indicating the formation of a P-F species as a minor product. The $^{1}H$ n.m.r. spectrum showed numerous peaks in the region 3 to 6 ppm, indicating there had been incomplete, or even no, elimination of ethylene.

### 5.2.3 Co-pyrolysis of $C_6F_5\text{-}P\left\langle\begin{smallmatrix}O\\ \\ O\end{smallmatrix}\right]$ with MeOH

The co-pyrolysis of $C_6F_5P(O_2C_2H_4)$ (1 g) with methanol (5 ml) produced a mixture which, on removal of the methanol under reduced pressure, was shown to contain a roughly 1:1 mixture of ethylene glycol and $(C_6F_5)HPO(OH)$. The

$^1H$ n.m.r. spectrum of the mixture showed the ethylene glycol $CH_2$ resonance at 3.6 ppm, a doublet signal for the P-H at 7.76 ppm ($J_{PH}$ = 630 Hz) and a single signal at 10.06 ppm, assigned as the exchanging glycol and acid proton resonances. The $^{13}C$ n.m.r. spectrum gave the glycol $CH_2$ resonance at 63.8 ppm and the four signals from the pentafluorophenyl group, each being a doublet of multiplets (only the $^1J$ coupling constants were resolved) as follows: $\delta$ $^{13}C$= 107.7 ppm (C-P, $J_{CP}$ = 88.1 Hz); 138.3 ppm (C-F, $J_{CF}$ = 251.6 Hz); 144.8 ppm (C-F, $J_{CF}$ = 289.3 Hz) and 147.3 (C-F, $J_{CF}$ = 257.9 Hz). The $^{31}P$ n.m.r. spectrum, when obtained $^1H$ decoupled, gave a single signal at 5.3 ppm and, when proton coupled, the signal was split to a doublet ($J_{PH}$ = 630 Hz), in agreement with the $^1H$ n.m.r. spectrum. The formation of $(C_6F_5)HPO(OH)$ was confirmed by the mass spectrum of the two-component mixture: m/e = 232 ($M^+$, 67 %) and 65 ($[H_2PO_2]^+$, 100 %). Thus the overall reaction was formal hydrolysis of the starting dioxaphospholane:

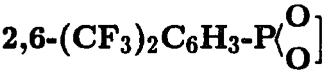


$$C_6F_5{-}P\langle{}^{O}_{O}] \xrightarrow{H_2O} C_6F_5{-}\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH + {}^{HO}_{HO}]$$

The source of the water in this reaction is unclear. The methanol had been previously dried by refluxing over sodium methoxide, followed by distillation and, as shown by $^{31}P$ n.m.r. , did not react with the starting dioxaphospholane at room temperature. It is possible that moisture was introduced to the system in the nitrogen gas or the glass wool.

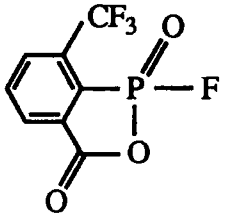
### 5.2.4 Mass Spectrometric Study of $2,6\text{-}(CF_3)_2C_6H_3\text{-}P\langle{}^{O}_{O}]$

The $EI^+$ spectrum showed the dominant peak at m/e = 91 (100 %) with only a very small contribution from the mass ion (m/e = 304 at 8.8 % intensity). There was no evidence to suggest fragmentation by initial elimination of ethylene, as it would appear that P-C cleavage is preferred, forming $[PO_2C_2H_4]^+$. With chemical ionisation ($CI^+$), the $[M+1]^+$ ion was generated (m/e = 305) and detected largely without its fragmentation. The spectrum in the negative mode was dominated by the peak resulting from the aryl anion, $[2,6\text{-}(CF_3)_2C_6H_3]^-$ (m/e = 213) at 100 %. The mass ion (m/e = 304) gave rise to a peak at 6.7 % and $[M\text{-}1]^+$ at 10.7 %. The notable features of this spectrum were the two peaks at m/e = 276 (3 %) and 277 (1.7 %), which may correspond to the species $[2,6\text{-}(CF_3)_2C_6H_3PO_2]^-$ and $[2,6\text{-}(CF_3)_2C_6H_3PO_2H]^-$, or their isomers, generated from ethylene elimination.



### 5.2.5 Pyrolysis of $2,6\text{-}(CF_3)_2C_6H_3\text{-}P\langle\begin{smallmatrix}O\\O\end{smallmatrix}]$

Pyrolysis of 2.0 g of the 2-aryl-1,3,2-dioxaphospholane yielded 1.4 g of a white, waxy solid. The solution-state, broad-band $^1H$-decoupled $^{31}P$ n.m.r. spectrum of this material in $CDCl_3$ showed two phosphorus-containing products, 'A' and 'B', with relative signal intensities of approximately 9:1 respectively. The $^{31}P$ signal for 'A' was in the form of a doublet at $\delta\ ^{31}P = 9.05$ ppm with a coupling of 1117 Hz, and for 'B', $\delta\ ^{31}P = 0.79$ ppm, a triplet with a 1115 Hz coupling. Such large couplings would indicate the formation of P-F species and the chemical shifts would suggest that both 'A' and 'B' are phosphorus (V) compounds. Two major signals were seen in the $^{19}F$ n.m.r. spectrum, both being assigned to 'A': a doublet ($J_{PF}$= 1117 Hz) at -67.6 ppm confirmed the presence of the P-F moiety for 'A', and a peak at -67.8 ppm indicated that 'A' had one $CF_3$ group. A number of other signals were also present in the region -55 to -65 ppm, but as each integrated to less than one fluorine atom with respect to the P-F or $CF_3$ signals, they were discounted as being of product 'A' and so were either from 'B', or non-phosphorus-bearing fluorinated species. The $^1H$ n.m.r. spectrum showed a group of eight lines in the aromatic region, (7.9 - 8.2 ppm), with an apparent coupling of approximately 25 Hz. As the $^1H$ n.m.r. spectrum of a 2,6-$(CF_3)_2C_6H_3$ group would be expected to show a triplet for the para proton and a single doublet for the two meta protons, it must be assumed that the rotational symmetry of the 2,6-$(CF_3)_2C_6H_3$ group about the P-C bond axis had been lost and the two meta protons were now inequivalent. This would occur if there was a barrier to rotation, or if as indicated by the fluorine spectrum, one of the $CF_3$ groups had been lost. Although there were a few other minor peaks in the aromatic region there were no other signals in the $^1H$ n.m.r. spectrum, indicating complete elimination of ethylene. The only features of the $^{13}C$ n.m.r. spectrum were an unresolved group of peaks in the region 120 - 140 ppm, the $CF_3$ / aromatic carbon region, and a very weak signal at 180.3 ppm, possibly suggesting a >C=O carbon. The mass spectrum ($EI^+$) showed a mass ion at m/e = 254 and a peak at 235, $[M-19]^+$ (i.e loss of fluorine from the mass ion), and notably, a peak at m/e = 210, $[M-44]^+$, which would indicate loss of $CO_2$ from the mass ion. The $CI^-$ mass spectrum showed a mass ion at m/e = 254 with negligible fragmentation. A mass of 254 suggests a molecular formula for 'A' of $C_8H_3F_4O_3P$. This, together with the n.m.r. data, indicates a possible structure for 'A' as follows:

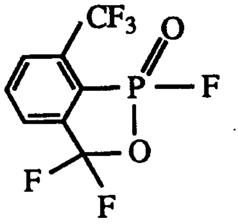


The $^{31}P$ n.m.r. and $^{19}F$ n.m.r. data compare well with those for the known compound, Ph(MeO)P(=O)F[43], as shown in table 5.1. Of note are the large P-F coupling constants, characteristic of phosphorus directly bonded to fluorine.

| n.m.r Parameter | Ph(MeO)P(=O)F | 'A' |
|---|---|---|
| $\delta$ $^{31}P$ | 17.6 ppm | 9.05 ppm |
| $\delta$ $^{19}F$ (P-F) | -66.3 ppm | -67.6 ppm |
| $J_{PF}$ | 1035 Hz | 1117 Hz |

**Table 5.1 — Comparison of n.m.r. Parameters for 'A' with Ph(MeO)P(=O)F.**

The mechanism for the formation of 'A' almost certainly proceeded via the elimination of ethylene and the initial formation of 2,6-$(CF_3)_2C_6H_3PO_2$. The metaphosphate then inserted into the C-F bond of one of the $CF_3$ groups to form the following rearranged cyclic product:



The $CF_2$ group was then most probably converted to the carbonyl by fluorine / oxygen exchange on the silica of the glass wool in the pyrolysis tube to give the final product, 'A'.

Product 'B' is clearly of the form $RP(=O)F_2$, though the exact nature of R is unclear.

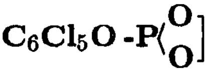
### 5.2.6 Mass Spectrometric Study of $2,4,6\text{-}(CF_3)_3C_6H_2\text{-}P\langle^{O}_{O}]$

The results for this compound were, as one might expect, very similar to those for its $2,6\text{-}(CF_3)_2C_6H_3$ analogue. The $EI^+$ spectrum showed the dominant peak at m/e = 91 (100 %) with only a very small contribution from the mass ion (m/e = 372 at 2.2 % intensity). There was no evidence to suggest fragmentation by initial elimination of ethylene, as it would appear that P-C cleavage is preferred, forming $[PO_2C_2H_4]^+$. With chemical ionisation ($CI^+$), the $[M+1]^+$ ion was generated (m/e = 373, 100 % intensity) and detected largely without its fragmentation, though the following three peaks at m/e = 91 (1.4 %), 108 (7.2 %) and 126 (21.9 %) probably correspond to $[PO_2C_2H_4]^+$, $[PO_2C_2H_4.NH_3]^+$ and $[PO_2C_2H_4.(NH_3)_2.H]^+$ respectively, indicating some P-C cleavage. The negative ion spectrum shows two major peaks, resulting from the aryl anion, $[2,4,6\text{-}(CF_3)_3C_6H_2]^-$ (m/e = 281) at 100 % and the mass ion peak (m/e = 372) at 79.8 % relative intensity. This spectrum showed two peaks at m/e = 344 (4.3 %) and 345 (1.3 %) which may correspond to the species $[2,4,6\text{-}(CF_3)_3C_6H_2PO_2]^-$ and $[2,4,6\text{-}(CF_3)_3C_6H_2PO_2H]^-$, or their isomers. The accurate (to within 5 mmu) mass for the m/e = 344 peak showed that the ion had the formula $[C_9H_2F_9O_2P]^-$, which confirms that it is either the metaphosphate anion, or some rearranged isomer.

### 5.2.7 Co-pyrolysis of $2,4,6\text{-}(CF_3)_3C_6H_2\text{-}P\langle^{O}_{O}]$ with MeOH

The co-pyrolysis of 1 g of $2,4,6\text{-}(CF_3)_3C_6H_2P(O_2C_2H_4)$ with anhydrous methanol (5 ml) produced 2 ml of a methanol solution which was shown by $^{19}F$ n.m.r. to contain many products. A large number of peaks was seen in the $CF_3$ region (-58 to -65 ppm). The $^{31}P$ n.m.r. spectrum of this solution showed the presence of no starting material, but multiple signals in the region 0 to 30 ppm. No further attempt was made to purify or extract any of the products from this mixture.

### 5.2.8 Mass Spectrometric Study of $C_6Cl_5O\text{-}P\langle^{O}_{O}]$



$C_6Cl_5O\text{-}P\langle^{O}_{O}]$

The presence of the pentachlorophenyl group in this compound gave rise to chlorine-containing fragments in the mass spectrometer, which are indicated in the spectra as multi-peak envelopes. This is due to the two chlorine isotopes, $^{35}Cl$ and $^{37}Cl$, having relative abundances of approximately 3:1. Thus assignment was aided by comparison of the relative intensities of the peaks found within an envelope with those calculated for a given ion formula. In the $EI^+$ spectrum, the most intense peak was at m/e = 91 ($[PO_2C_2H_4]^+$). There was weak detection of the mass ion, indicated by an envelope of peaks, with the most intense at 356 (2.2 %) and, as shown in table 5.2, the relative intensities of this group of peaks compare well with those calculated assuming normal isotopic abundances.

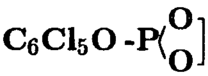
There was no indication of loss of ethylene from the mass ion, though there was shown to be successive loss of Cl and the $[C_6Cl_5OH]^+$ ion, (m/e = 266, 18.2 %), was also detected. In the $CI^+$ spectrum the $[M+1]^+$ ion was detected, which had an isotopic envelope with the most intense peak at m/e = 357 (26.3 %). Again loss of chlorine was evident, but there was no indication the the $[M+1]^+$ ion was fragmenting by loss of ethylene. The $CI^-$ spectrum indicated the ion $[M-35]^-$ (i.e the mass ion less one chlorine atom) as the highest mass fragment. Intense peak envelopes were also recorded for $[C_6Cl_5O]^-$ (m/e = 265) and for $[C_6Cl_4O]^-$ (m/e

| Mass / mmu | % Relative Intensity | |
|---|---|---|
| | Calculated | Found |
| 354 | 62.16 | 59.55 |
| 355 | 5.70 | 4.09 |
| 356 | 100 | 100 |
| 357 | 9.16 | 12.73 |
| 358 | 64.55 | 66.36 |
| 359 | 5.89 | 6.82 |
| 360 | 20.96 | 23.64 |

**Table 5.2 — Relative Intensities within the Isotopic Envelope for $[C_8H_4Cl_5O_3P]^+$ (Calculated vs. Found).**

=230). There was no detection of a mass ion or pseudo-mass ion, and no indication of fragmentation by loss of ethylene.

### 5.2.9 Pyrolysis of $C_6Cl_5O\text{-}P\langle^{O}_{O}]$



$C_6Cl_5O\text{-}P\langle^{O}_{O}]$

The attempted pyrolysis of 2.0 g of $C_6Cl_5OP(O_2C_2H_4)$ yielded 1.7 g of what was shown to be largely the starting material. The $^{31}P$ n.m.r. spectrum of the white, solid material recovered, after passing down the pyrolysis column (see experimental section for details of conditions) contained the major peak at 133.3 ppm ($C_6Cl_5OP(O_2C_2H_4)$) and two minor peaks, assigned as oxidation / hydrolysis products at 3.8 and 22.4 ppm (trace amounts of which were seen in the $^{31}P$ n.m.r. spectrum of the starting material). Thus it would appear that $C_6Cl_5OP(O_2C_2H_4)$ has higher thermal stability than 2,6-$(CF_3)_2C_6H_3P(O_2C_2H_4)$ or $C_6F_5P(O_2C_2H_4)$. It is known that perchloroaryl groups can confer high thermal stability on species into which they are incorporated[44], though it is difficult to see how that may be in this case. It could be that an aryloxy, rather than an aryl, substituent on phosphorus gives the dioxaphospholane a greater relative stability to elimination of ethylene.

### 5.2.10 General Discussion

It would appear that aryl-substituted metaphosphate species can be formed by ethylene elimination from 2-aryl-1,3,2-dioxaphospholanes, where the aryl group has trifluoromethyl substituents ortho to phosphorus. However, under the flow pyrolysis conditions used for this study, no real evidence was obtained for the formation of $C_6F_5PO_2$ or $C_6Cl_5OPO_2$. More work would need to be done in order to rationalise these results. For the compounds studied above, it would be interesting to discover how the conditions of pyrolysis (temperature, contact-time and flow-rate) affect which products are formed. Pyrolyses of dioxaphospholanes with other polyhaloaryl / aryloxy substituents could also be performed, and the incorporation of perfluoroalkyl groups could also be of interest. Finally, the availability of flash vacuum pyrolysis facilities would have allowed a closer comparison with the work of Cadogan *et al* [42].

## 5.3 Experimental

### 5.3.1 General Strategy

Ethylene chlorophosphite is commercially available (Lancaster Synthesis), but for the preparation of 2,4,6-$(CF_3)_3C_6H_2P(O_2C_2H_4)$ it was prepared acccording to the method of Lucas *et al* [45]. The 2-aryl-1,3,2-dioxaphospholanes were prepared by the method of Mukaiyama *et al* [46]: ethylene chlorophosphite was reacted with the respective aryllithium or Grignard reagent at -78°C, in diethyl ether:

$$Ar[M] + Cl\text{–}P\left\langle\begin{matrix}O\\O\end{matrix}\right] \longrightarrow Ar\text{–}P\left\langle\begin{matrix}O\\O\end{matrix}\right] + [M]Cl.$$

([M] = Li, Li.TMEDA or MgBr; Ar = aryl)

The alternative route would have been by the action of ethylene glycol on the arylphosphinous dichloride:

$$ArPCl_2 + \left.\begin{matrix}HO\\HO\end{matrix}\right] \xrightarrow{NEt_3} Ar\text{–}P\left\langle\begin{matrix}O\\O\end{matrix}\right] + 2NEt_3.HCl.$$

(Ar = aryl)

The latter of these two methods, although useful particularly if the aryl phosphinous dichloride is commercially available, was not used in this study as it would have meant a two- rather than one-pot reaction. Further, with the bulky aryl groups which we wished to incorporate, there would probably be a large amount of steric hindrance at the reaction centre.

For the preparation of 2-(pentachlorophenoxy-)1,3,2-dioxaphospholane, a similar method to that of Cadogan *et al* [42] was used: pentachlorophenol was reacted with equimolar amounts of ethylene chlorophosphite and triethylamine, with diethyl ether as solvent:

$$C_6Cl_5OH + Cl\text{–}P\left\langle\begin{matrix}O\\O\end{matrix}\right] \xrightarrow{NEt_3} C_6Cl_5O\text{–}P\left\langle\begin{matrix}O\\O\end{matrix}\right] + NEt_3.HCl.$$

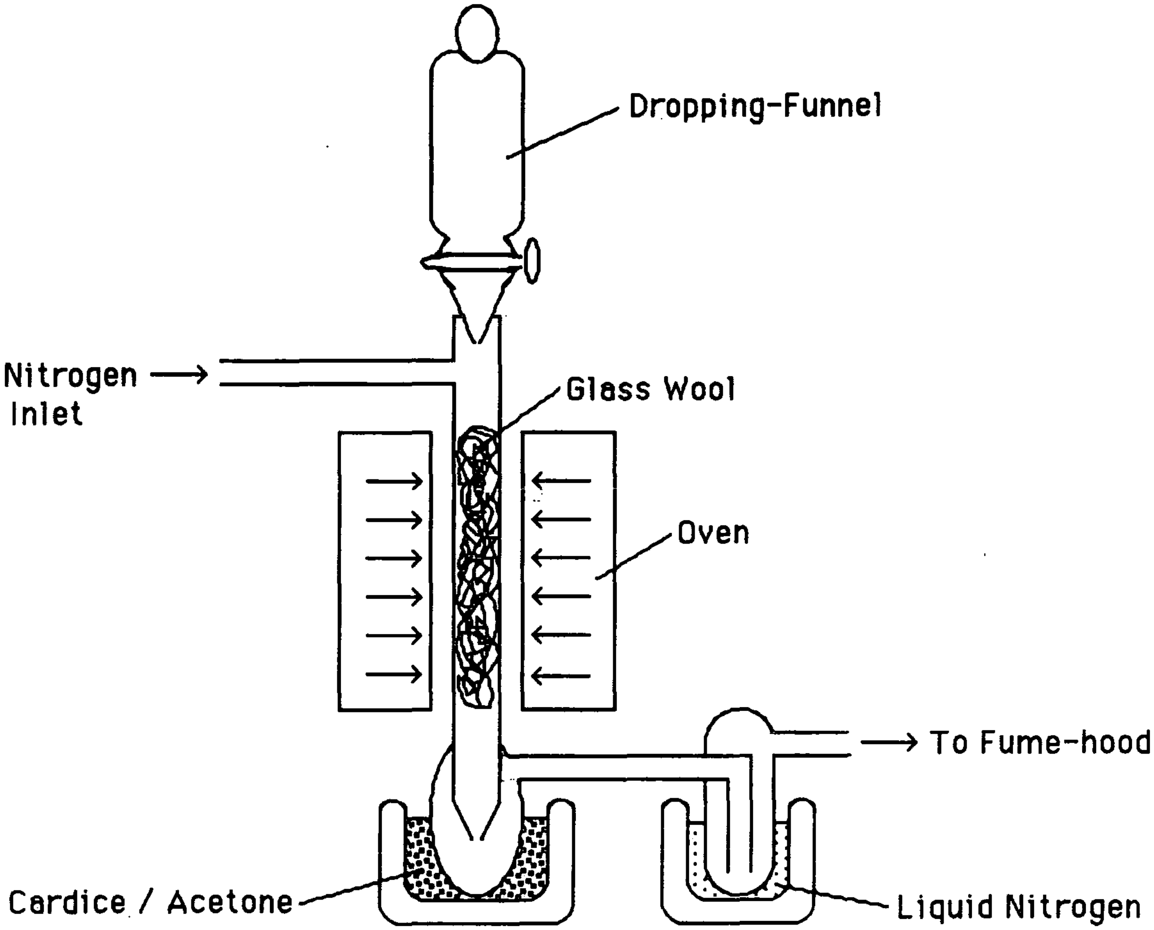
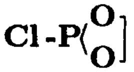


Figure 5.1 — Flow Pyrolysis Apparatus

The pyrolyses were all carried out using a nitrogen flow technique, which had been developed in Durham University Chemistry Department for ethylene elimination from fluorocarbon systems[47]. The design of the apparatus (see fig. 5.1) is particularly advantageous for the pyrolysis of materials of low volatility. The vertically mounted, quartz pyrolysis tube, contains loosely packed glass-wool, a dropping funnel and nitrogen inlet tap at the top and a system of traps at the bottom. This allows the material for pyrolysis to be dripped into the heated tube, and the resultant vapour is carried down through the tube by the flow of nitrogen gas; the product(s) from ethylene elimination are collected in the first trap, cooled with cardice, and the ethylene (together with any other gaseous products) passes into the second, liquid nitrogen-cooled trap. For all these pyrolysis experiments, the tube was heated to 440°C, (a temperature which had been shown to work well for other systems[47]). The nitrogen flow was set at approximately 220 $cm^3$ per minute. The tube volume is approximately 150 $cm^3$, thus by adding one drop of material every minute, the vapour produced from each addition should have completely passed down the column before the following drop was added. By this means, any reaction of the products of pyrolysis with the starting material was minimised. As all of the substituted 1,3,2-dioxaphospholanes prepared for these pyrolysis studies were found to be low melting solids, it was necessary for them to be liquefied by gently warming the dropping funnel with a heat-gun. For the co-pyrolysis experiments the dioxaphospholanes were dissolved in methanol; this solution was then placed in the dropping funnel and added dropwise to the pyrolysis tube, as for the neat compounds. In general, there was only a small amount of charring seen in the tube and, taking into account any elimination of ethylene, the yield (by mass) of the pyrolysis products recovered was always over 80 %.



### 5.3.2 Preparation of $\mathrm{Cl\text{-}P}\left\langle\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\right]$

To a 125 ml three-necked flask, fitted with dropping funnel, mechanical stirrer and reflux condenser, all being maintained under an atmosphere of dry nitrogen, was added 50 ml of dichloromethane and 22 ml (250 mmol) of phosphorus trichloride. To this was added with stirring 13.9 ml (250 mmol) of anhydrous ethylene glycol, the rate of addition controlling reflux. Copious amounts of hydrogen chloride were produced. When addition was complete, the dichloromethane was removed by distillation. The product was purified by distillation at reduced pressure (Bpt. 45.5 - 47.0, 15 mmHg) to give a colourless, mobile liquid.

Yield 17.4 g (55 %), $ClP(C_2H_4O_2)$.

$C_2H_4ClO_2P$ = 126.48

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2)$ = 167 ppm

### 5.3.3 Preparation of $\mathrm{C_6F_5\text{-}P}\left\langle\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\right]$

To a 250 ml three-necked flask, fitted with dropping funnel, mechanical stirrer and reflux condenser, all being maintained under an atmosphere of dry nitrogen, was added 2.43 g (100 mmol) of magnesium turnings, together with 4 drops of 1,2-dibromoethane. In the dropping funnel was placed bromopentafluorobenzene 24.7 g (100mmol) in diethyl ether (150 ml). 15 ml of this solution was added to the flask and the stirrer was started. The reaction mixture was heated to reflux until the reaction started, at which point the heat was removed and the remaining bromopentafluorobenzene - diethyl ether solution was addded over a period of about 30 minutes - the rate of addition controlling reflux. After addition was complete, the reaction mixture was stirred for a further two hours. When at room temperature, the reaction mixture was filtered through glass wool to remove any remaining magnesium and transferred to a dropping funnel. The pentafluorophenylmagnesium bromide solution was then added dropwise, over 90 minutes, with continuous stirring, to a solution of ethylene chlorophosphite 12.6 g (100 mmol) in diethyl ether (100 ml), contained in a 250 ml two-necked flask under nitrogen and cooled to -78°C. When addition was complete the reaction mixture was allowed to warm to room temperature and to stir for a further hour. The magnesium salts were then removed by filtration and the solvent was removed *in vacuo* leaving a brown, oily residue. The product was purified by vacuum distillation (Bpt 80 - 90°C, 0.1 mmHg). The product crystallized to a low-melting, colourless solid on standing at room temperature.

Yield 12.2 g (47 %), $C_6F_5P(C_2H_4O_2)$.

$C_8H_4F_5O_2P = 258.08$.

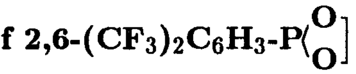
Calc: C = 37.23 %, H = 1.56 %, P = 12.00 %.

Found: C = 36.46 %, H = 1.84 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2) = 146.5$ ppm.

$^{19}F$ n.m.r. :$\delta/(CH_2Cl_2) = -137.4$ ppm (2F), -153.6 ppm (1F), -163.9 ppm (2F).

Mass spec: m/e 258 ($M^+$); 91 ($[P(O_2C_2H_4)]^+$).



### 5.3.4 Preparation of $2,6\text{-}(CF_3)_2C_6H_3\text{-}P\langle{}^{O}_{O}]$

A solution of the n-butyllithium TMEDA complex (prepared from TMEDA 5.69 g (49 mmol), 29.2 ml of a solution of n-butyllithium, 1.6 M in hexanes, (46.7 mmol) and 10 ml of diethyl ether) was added to 10.0 g (46.7 mmol) of 1,3-bis-(trifluoromethyl)benzene in 30 ml of the same solvent at 0°C, contained in a 125 ml two-necked flask under an atmosphere of dry nitrogen. After stirring overnight at room temperature the mixture was transferred to a dropping funnel, before being slowly added to a solution of ethylene chlorophosphite 6.3 g (50 mmol) in diethyl ether (50 ml) contained in a 250 ml two-necked flask, under nitrogen. The reaction mixture was then allowed to warm slowly to room temperature. After filtering off the lithium salts and removal of the solvents *in vacuo* the product was purified by vacuum distillation (Bpt. 90 - 100°C, 0.1 mmHg). The product crystallized to a low-melting, colourless solid on standing at room temperature.

Yield 8.2 g (54 %), 2,6-$(CF_3)_2C_6H_3P(C_2H_4O_2)$.

$C_{10}H_7F_6O_2P = 304.13$.

Calc: C = 39.49 %, H = 2.32 %, P = 10.18 %.

Found: C = 38.79 %, H = 2.62 %.

$^{31}P$ n.m.r. : $\delta/(CH_2Cl_2) = 155.9$ ppm (sept, $J_{PF} = 35.1$ Hz).

$^{19}F$ n.m.r. : $\delta/(CH_2Cl_2) = -55.4$ (d, $J_{PF} = 35.1$ Hz).

Mass spec: m/e 304 ($M^+$); 91 ($[P(O_2C_2H_4)]^+$).

### 5.3.5 Preparation of 2,4,6-$(CF_3)_3C_6H_2\text{-}P\langle\begin{smallmatrix}O\\O\end{smallmatrix}]$

To a two-necked, 250 ml round-bottomed flask, fitted with dropping funnel and maintained under dry nitrogen, was placed ethylene chlorophosphite 8.9 g (70 mmol) in diethyl ether (100 ml). The flask was then cooled to -78°C (cardice / acetone slush bath). 2,4,6-tris(trifluoromethyl)phenyllithium (approx 70 mmol) in diethyl ether (100 ml) was then added dropwise, with continuous stirring. When addition was complete the mixture was allowed to warm to room temperature, and then left to stir for a further one hour. The lithium salts were filtered off under nitrogen and the solvent removed *in vacuo* . The residual oil was then purified by vacuum distillation to give a colourless oil (Bpt. 100°C, 0.1 mmHg) which crystallized to a colourless solid on standing.

Yield 13.6 g (52 %), 2,4,6-$(CF_3)_3C_6H_2P(C_2H_4O_2)$.

$C_{11}H_6F_9O_2P = 372.13$.

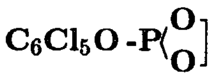
Calc: C = 35.50 %, H = 1.61 %, P = 8.32 %.

Found: C = 36.01 %, H = 2.28 %.

$^{31}$P n.m.r. : $\delta/(CH_2Cl_2)$ = 154.3 ppm (sept, $J_{PF}$ = 35.4 Hz).

$^{19}$F n.m.r. :$\delta/(CH_2Cl_2)$ = -64.2 ppm (s, 3F), -56.1 ppm (d, 6F,$J_{PF}$ = 35.4 Hz.)

Mass spec: ($CI^-$) m/e 372 ($M^-$); 281 ($[2,4,6\text{-}(CF_3)_3C_6H_2]^-$).



### 5.3.6 Preparation of $C_6Cl_5O\text{-}P\langle\overset{O}{\underset{O}{}}]$

To a 250 ml three-necked flask, fitted with dropping funnel and mechanical stirrer, all being maintained under an atmosphere of dry nitrogen, was added ethylene chlorophosphite 12.6 g (100 mmol) and anhydrous triethylamine 10.1 g (100 mmol) in diethyl ether (100 ml). The flask was cooled in an ice bath and pentachlorophenol 26.6 g (100 mmol) in diethyl ether 50 ml was then added dropwise with continuous stirring, over 30 minutes. A large quantity of triethylammonium hydrogen chloride was formed as a white precipitate. The solids were filtered off under nitrogen and washed with diethyl ether (100 ml). The combined washings were added to the initial filtrate and concentrated under reduced pressure to approximately 50 ml, whereupon the product crystallised out. The product was then removed by filtration and recrystallised from diethyl ether to give slightly yellowish white crystals.

Yield 11.6 g (33 %), $C_6Cl_5OP(C_2H_4O_2)$.

$C_8H_4Cl_5O_3P$ = 356.36.

Calc: C = 26.96 %, H = 1.13 %, P = 8.69 %, Cl = 49.74 %.

Found: C = 28.43 %, H = 1.25 %.

$^{31}$P n.m.r. : $\delta/(CH_2Cl_2)$ = 133.3 ppm

Mass spec: (see text).

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# Chapter VI

# Dicoordinate Phosphorus Compounds

## 6.1 Introduction

In the past, the many fruitless attempts to form doubly-bonded heteroatomic species gave birth to the double bond rule[1,2]. Even today, a large number of chemistry text books make reference to this theory, which states that third or fourth period elements are not able to form p$\pi$-p$\pi$ bonds between themselves, or with other second or third-row elements. Thus it was long believed that it would not be possible to form low-coordinate derivatives of elements such as silicon, germanium, phosphorus, arsenic, antimony, etc. However, over the past twenty years, studies have not only provided exceptions to this rule, but one of the reasons for the spectacular development in the chemistry of these main-group elements lies in their ability to form such unusually coordinated compounds.

In the 1960s, transient molecules with double bonds between heavier group 4A and 5A elements were detected spectroscopically, or implicated from trapping experiments. The breakthrough in this field was the isolation in 1981 of the first stable compounds with P=P, Si=C, and Si=Si double bonds. It was understood from these successful syntheses that oligomerisation could be prevented if sufficiently large ligands were utilized. However, although bulky groups may stabilize such low coordinate compounds, a wide variety of chemical reactions may still take place at the double bond. Recent reviews have summarized this field[3–7].

In the case of phosphorus, since the preparation, by Yoshifuji *et al* [8], of the first diphosphene stable at room temperature, (ArP=PAr, where Ar = 2,4,6-$tBu_3C_6H_2$), many other examples of compounds containing the -P=P- grouping have been described[9,10]. There are, however, far fewer examples of dicoordinate phosphorus forming doubly-bonded compounds with the heavier group 5A elements. The first phosphaarsene and phosphastibene were prepared by Cowley *et al* [11] from the following reaction:

$$(Me_3Si)_2CHMCl_2 + ArPH_2 \xrightarrow{DBU} ArP{=}MCH(SiMe_3)_2$$

(where DBU = 1,5-diazabicyclo[4.5.0]undec-5-ene;
Ar = 2,4,6-$tBu_3C_6H_2$; M = As, Sb)

The phosphastibene is of particular interest as, apart from having one of the lowest field $^{31}P$ n.m.r. resonances so far reported ($\delta$ 620.0 ppm), it is unstable and decomposes to the diphosphene, suggesting it to be a source of the free phosphinidene. To date, only a small number of other stable phosphaarsenes bearing only organo groups has been reported (see table 6.1)[12–15]. Recently, Weber *et al* [16–18] have demonstrated how transition-metal substituted phosphaarsenes may be prepared from the condensation reaction of a metal-substituted bis(trimethylsilyl) arsine and a phosphinous dichloride, as follows:

$$[M]{-}As(SiMe_3)_2 + ArPCl_2 \xrightarrow{-2Me_3SiCl} [M]{-}As{=}PAr$$

(where [M] = ($\eta^5$-$C_5H_4R$)(CO)($PPh_3$)Fe; R = H or Me; Ar = 2,4,6-$tBu_3C_6H_2$)

As can be seen from table 6.1, the phosphaarsene $^{31}P$ n.m.r. chemical shifts are all to very low field (typically +500 to +700 ppm).

| Phosphaarsene | $\delta$ $^{31}P$ / ppm | Ref |
|---|---|---|
| $Cp(CO)(PPh_3)Fe\text{-}As{=}P\text{-}Ar$ | +605.3 | 16 |
| $(MeCp)(CO)(PPh_3)Fe\text{-}As{=}P\text{-}Ar$ | +603.3 | 16 |
| $Ar\text{-}P{=}As\text{-}CH(SiMe_3)_2$ | +575 | 11 |
| $(Me_3Si)_2CH\text{-}P{=}As\text{-}Ar$ | +533 | 12 |
| $(Me_3Si)_3C\text{-}P{=}As\text{-}C(SiMe_3)_3$ | +668 | 13 |
| $Ar\text{-}P{=}As\text{-}N(SiMe_3)_2$ | +541 | 14 |
| $Ar\text{-}P{=}As\text{-}N[SiMe_2(tBu)]_2$ | +544 | 14 |
| $C_5Me_5\text{-}As{=}P\text{-}Ar$ | +536.8 | 15 |

**Table 6.1 — Phosphaarsene $^{31}P$ n.m.r. Chemical Shifts**

**($Ar = 2,4,6\text{-}(tBu)_3C_6H_2$)**

Grobe *et al* [19] have also recently reported the generation of phosphaarsenes using the following novel method:

$$RP(SnMe_3)_2 + F_3CAs(SMe)_2 \longrightarrow RP{=}AsCF_3 + 2Sn(Me_3)(SMe)$$

(where R = Ph, tBu)

These compounds were then trapped *in situ* as their [2 + 4] cycloadducts with either 2,3-dimethyl-1,3-butadiene or isoprene.

It has also been demonstrated that phosphorus can form doubly bonded species with the heavier group 4A elements. Stable silaphosphenes have recently been synthesized, and stabilized by means of bulky substituents on phosphorus. They were obtained by Bicklehaupt[20,21] from the reaction of ArP(H)Li and the corresponding dichlorosilanes $RR'SiCl_2$, followed by elimination of HCl:

$$RR'SiCl_2 + ArP(H)Li \longrightarrow [RR'Si(Cl)\text{–}P(H)Ar] \xrightarrow{ArP(H)Li} RR'Si{=}PAr + ArPH_2$$

(where Ar = $2,4,6\text{-}(tBu)_3C_6H_2$;
R, R' = Mes, $2,4,6\text{-}(Et)_3C_6H_2$, $2,4,6\text{-}(iPr)_3C_6H_2$;
R = $2,4,6\text{-}(iPr)_3C_6H_2$; R' = Ph, Mes, tBu.)

Again, by using substituents which have strong steric hindrance and electronic effects, Escudié *et al* have recently obtained three stable germaphosphenes[22,23]. A nearly quantitative route to the formation of these compounds was found to be dehydrofluorination of the corresponding fluorogermylphosphines by t-butyllithium at low temperature.

$$RR'GeF_2 + ArP(H)Li \longrightarrow RR'Ge(F)\text{–}P(H)Ar \xrightarrow{tBuLi} RR'Ge{=}PAr$$

(where Ar = $2,4,6\text{-}(tBu)_3C_6H_2$;
RR' = $Mes_2$[22]; Mes, t-Bu[23]; $t\text{-}Bu_2$[23].)

Using an analogous route, Escudié *et al* have also synthesized the only stannaphosphene $R_2Sn{=}PAr$ so far to be stabilized in a monomeric state[24].

$$R_2Sn(F)\text{–}P(H)Ar \xrightarrow{tBuLi} R_2Sn{=}PAr$$

(where Ar = $2,4,6\text{-}(tBu)_3C_6H_4$; R = $(Me_3Si)_2CH$)

This stannaphosphene structure was determined by n.m.r.: the $^{31}P$ chemical shift (+204.7 ppm) falls in the range of sila- and germaphosphenes. The $^{119}Sn$ n.m.r. chemical shift, at very low field (+658.3 ppm), is also a normal value for a tricoordinate $p\pi$-hybridized tin. Similar chemical shifts have been observed in stannenes[25] and distannenes[26]. Also of note are the coupling constants between phosphorus and tin ($^1J(P^{117}Sn) = 2191$, $^1J(P^{119}Sn) = 2295$ Hz). These values are much larger than for singly-bonded tin-phosphorus compounds (1150-1200 Hz), which can be attributed to a $\pi$ bond between tin and phosphorus[27].

It has been demonstrated by Escudié *et al* that the 2,6-bis(trifluoromethyl)-phenyl group can be incorporated into a symmetrical diphosphene[28] and Bigwood *et al* [29] showed how the same ligand would stabilize the stannylene, Sn(2,4,6--$(CF_3)_3C_6H_2)_2$, the first example of an organotin(II) compound with phenyltin(II) $\sigma$ bonds. Goodwin[30] has also successfully incorporated the 2,4,6-$(CF_3)_3C_6H_2$-group into various phosphaalkenes, together with the symmetrical and some asymmetrical diphosphenes. Thus hopefully it should be possible, by the incorporation of such substituents, to form both phosphaarsenes and stable stannaphosphenes. The latter would be of particular interest since the stannaphosphene of Escudié, although being unambiguously characterised by both n.m.r.[24] and by trapping reactions *in situ* [31,32], was not stable to isolation.

It would also be of interest to study the diphosphines (2,4,6-$(CF_3)_3C_6H_2P)_2$ and (2,6-$(CF_3)_2C_6H_3P)_2$, particularly with respect to the coordination chemistry of these compounds. Recent work has shown that (2,4,6-$(CF_3)_3C_6H_2P)_2$ will coordinate to transition metal centres[30,33], though Escudié had previously found (2,6-$(CF_3)_2C_6H_3P)_2$ to be inert to such complex formation[34]. As there seems to be no good rationale for these differences, further investigation is required.

## 6.2 Results

### 6.2.1 Diphosphenes from Magnesium Coupling of $P(Ar)Cl_2$

Using Yoshifuji's original method[7], (dechlorination of the dichlorophosphine by refluxing with magnesium in THF) the preparation of the symmetrical diphosphenes (A) and (B), ArP=PAr ((A) Ar = 2,6-$(CF_3)_2C_6H_3$; (B) Ar = 2,4,6-$(CF_3)_3$-$C_6H_2$) was attempted. On gently warming a THF solution of either dichlorophosphine the mixture turned from colourless through yellow to finally a muddy brown (refluxing was not required). In both cases the $^{31}P$ n.m.r. spectra of the reaction mixtures showed predominantly the formation of the desired diphosphene from the characteristic lowfield shifts ((A) $\delta$ $^{31}P$ = 477.1 ppm[28]; (B) $\delta$ $^{31}P$ = 473.8 ppm[30], together with a small amount of $ArPH_2$. Removal of the THF under reduced pressure resulted in a large degree of decomposition to form polymeric material, and the attempted separation of the diphosphenes by column chromatography over silica led only to hydrolysis products.

### .2.2 Attempted Coupling of $P(C_6Cl_5)_2Cl$

In order to discover whether the pentachlorophenyl group could be incorporated into a diphosphene, coupling of the aryldichlorophosphine was attempted by the action of magnesium in THF (see above). On gentle warming of the reaction mixture it rapidly changed from colourless to brown. $^{31}P$ n.m.r. indicated only the formation of polymeric material (many broad signals in the range 0 to 35 ppm). Attempting the coupling using the method of Goldwhite *et al* [35], which involves reacting the dichlorophosphine with 1,3,1'3'-tetraethyl-2,2'-bis(imidazolidine) in refluxing toluene, again resulted in the formation of a dark brown solution. The reaction mixture showed a major peak in the $^{31}P$ n.m.r. spectrum at 124.0 ppm, but also many other signals in the range 135 to -125 ppm. No low field signals corresponding to a possible diphosphene were detected.

### 6.2.3 Attempted Preparation of a Stannaphosphene (>Sn=P-)

$Sn(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl_2$ was prepared according to the general method described by Fjeldberg *et al*[36], by reacting two molar equivalents of the aryllithium with $SnCl_4$ in diethyl ether.

$$2ArLi + SnCl_4 \xrightarrow{-\,2\,LiCl} SnAr_2Cl_2$$

This compound was then reacted with one equivalent of $P(2,6\text{-}(CF_3)_2C_6H_3)H_2$ (prepared by the $LiAlH_4$ reduction of the dichlorophosphine[30]) and two molar equivalents of DBU, in THF at 0°C. The solution immediately turned deep brown. The $^{31}P\{^1H\}$ n.m.r. spectrum of the reaction mixture showed no lowfield signals indicative of stannaphosphene or diphosphene formation but two resonances were observed at -83.4 and -89.6 ppm with intensities of roughly 2:1 respectively and attributed (see below) to the two diastereoisomers of Ar(H)P-P(H)Ar (where Ar = $2,6\text{-}(CF_3)_2C_6H_3$). The $^{19}F$ n.m.r. spectrum, apart from showing the presence of the diphosphine ($\delta\ ^{19}F$ = -57.5 and -57.7 ppm), contained just one other peak at -64.9 ppm, assigned as $2,4,6\text{-}(CF_3)_3C_6H_2H$[37], indicating that Sn-C cleavage had also occurred. The $^{119}Sn$ n.m.r. spectrum consisted only of a broad hump on the base-line, suggesting that the tin was now contained in polymeric material.

$$2Ar_2SnCl_2 + Ar'PH_2 \xrightarrow{DBU} Ar'(H)P\text{–}P(H)Ar' + 4ArH + 2\text{"}Sn\text{"}$$

(where Ar = $2,4,6\text{-}(CF_3)_3C_6H_2$; Ar' = $2,6\text{-}(CF_3)_2C_6H_3$)

### 6.2.4 Attempted Preparation of $As(2,6\text{-}(CF_3)_2C_6H_3)Cl_2$

Using a similar route to that of Escudié for the preparation of the aryldichlorophosphine[28] (see also Chap. 3), the preparation of the analogous aryldichloroarsine was attempted. However, when a solution of 1,3-bis(trifluoromethyl)lithium-TMEDA complex was added to a slightly greater than two-fold excess of arsenic trichloride, the product isolated was the bisarylchloroarsine.

$$Ar'Li.TMEDA + AsCl_3 \overset{0^\circ C\ /\ Et_2O}{\longrightarrow} 1/2Ar'_2AsCl + 1/2AsCl_3$$

(where Ar' = $2,6\text{-}(CF_3)_2C_6H_3$)

It may be possible to produce the mono-substituted product by performing the reaction at lower temperature, or by using, for example, the arylzinc chloride in place of the aryllithium reagent. However, unlike phosphine preparation, where the degree of substitution can easily be verified by $^{31}P$ n.m.r. , in arsenic chemistry there is no such convenient tool for the assessment of products *in situ*. Furthermore, the desired arsine may not be as stable as its phosphine analogue. This was demonstrated by Cowely *et al* [12], who showed that the reaction of $2,4,6\text{-}(tBu)_3C_6H_2Li$ with $AsCl_3$ resulted in heterocycle formation rather than the desired dichloroarsine.

### 6.2.5 General Attempts at "DBU Coupling" Reactions

Apart from the reaction above with the bisaryltin dichloride, a number of other such coupling reactions with $P(2,6\text{-}(CF_3)_2C_6H_3)H_2$ were attempted. With both $P(C_6Cl_5)Cl_2$ and $As(2,6\text{-}(CF_3)_2C_6H_3)_2Cl$ the initial product was the diphosphine $(2,6\text{-}(CF_3)_2C_6H_3PH)_2$, though in both these cases there was subsequent slow conversion to the diphosphene $(2,6\text{-}(CF_3)_2C_6H_3P)_2$. Goodwin[30] also made similar observations with $P(2,4,6\text{-}(CF_3)_3C_6H_2)H_2$, in attempting to make phosphaalkenes and asymetric diphosphenes by an analogous route. It should be noted, however, that although these reactions proceed in a similar way regardless of the chloro species used, neither phosphine, $P(Ar)H_2$, (Ar = $2,6\text{-}(CF_3)_2C_6H_3$ or $2,4,6\text{-}(CF_3)_3C_6H_2$), was seen to react with DBU alone. Similar results were obtained by Escudié from the DBU dehydrohalogenation of trichlorogermylphosphines[28,38]. Escudié suggests that dehydrochlorination may result in phosphinidene intermediates (RP:) and also the radical species ($R(H)\dot{P}$), which would then couple forming the diphosphine. The precise mechanism, however, has yet to be determined.

### 6.2.6 Attempted Preparation of $P(2,6\text{-}(CF_3)_2C_6H_3)HCl$

It would be useful to prepare the species P(Ar)HCl (for Ar = $2,6\text{-}(CF_3)_2C_6H_3$ or $2,4,6\text{-}(CF_3)_3C_6H_2$) as alternative starting phosphines for coupling reactions, and as it has been demonstrated that such compounds may also be intermediates in dehydrochlorination reactions to form diphosphenes[38,39]. Generally, phosphines of the type RPHX (where X = halogen) are unstable to elimination of HX and subsequent formation of polyphosphines[40]. However, where R = $CF_3$[41] or $2,4,6\text{-}(tBu)_3C_6H_2$[42], the corresponding RPHCl phosphines are stable, suggesting that bulky or electron-withdrawing R groups will stabilize such compounds. Given that this is the case, one would expect the Ar derivatives to be stable. It was suggested that the radical reaction of $P(Ar)H_2$ with $CCl_4$ would give partial chlorination leading to P(Ar)HCl[43]. This was attempted with $P(2,6\text{-}(CF_3)_2C_6H_3)H_2$, using both chemical radical initiation (AIBN) and gamma rays. In both cases the reaction was found to be very slow and a mixture of the various possible radical recombination products was formed:

$$P(Ar)H_2 \ / \ CCl_4$$

$$\Big\downarrow \begin{array}{l} AIBN + reflux \\ or\ \gamma\text{–}rays \end{array}$$

$$P(Ar)HCl + Ar(H)P\text{–}P(H)Ar + P(Ar)(CCl_3)H + P(Ar)Cl_2$$

(Ar = 2,6-$(CF_3)_2C_6H_3$)

Under reflux, the reaction proceeds substantially more quickly than by irradiation. One week in the gamma-source was required to obtain the same degree of conversion as three hours of refluxing. The reaction was followed by $^{31}$P n.m.r. (see table 6.2).

| Compound | $\delta$ $^{31}$P / ppm | Relative Signal Intensity | |
|---|---|---|---|
| | | 1 Week in $\gamma$-source | 2 Weeks in $\gamma$-source |
| $P(Ar)H_2$ | -142.7 | 60 | 40 |
| $(Ar(H)P)_2$ | -83.4, -89.6 | 15 | 2 |
| $P(Ar)HCl$ | 10.1 | 15 | 35 |
| $P(Ar)(CCl_3)H$ | 20.6 | 10 | 20 |
| $P(Ar)Cl_2$ | 146.6 | - | 3 |

**Table 6.2 — Reaction Products of $P(2,6\text{-}(CF_3)_2C_6H_3)H_2$ with $CCl_4$**

Although none of the products was isolated from the reaction mixture, they were clearly identified *in situ* from their $^{19}$F and $^{31}$P n.m.r. spectra. The values of $\delta$ $^{31}P$ of -83.4 and -89.6 ppm (with relative intensities of 2.5:1) for the two isomers of the diphosphine are in accordance with other values found for such species[30,38]. The $^{31}P$ n.m.r. chemical shifts for $P(Ar)HCl$ and $P(Ar)(CCl_3)H$ of 10.1 and 20.6 ppm respectively, were assigned (tentatively) from the magnitude of the relative P-F coupling constants: 30 Hz for $P(Ar)HCl$ (intermediate to the values of $J_{PF}$ for $P(Ar)H_2$ and $P(Ar)Cl_2$), and 6 Hz for $P(Ar)(CCl_3)H$ (a smaller coupling, as would be expected for a diorgano-substituted phosphine - see Chap. 3 for other examples). No significant changes were seen in the relative intensities of the $^{31}P$ signals corresponding to the diphosphine isomers on heating from room temperature to 60°C.

It should be noted that in the reduction of $P(Ar)Cl_2$ to $P(Ar)H_2$ with either $LiAlH_4$ or $Sn(Bu)_3H$, there was no evidence for the intermediate formation of $P(Ar)HCl$. When one equivalent of $Sn(Bu)_3H$ was added to $P(Ar)Cl_2$ the resultant mixture was shown by $^{31}P$ n.m.r. to contain $P(Ar)Cl_2$ and $P(Ar)H_2$ in equimolar amounts.

One possible route to the isolation of $P(Ar)HCl$ may be by reaction of the trichlorogermylphosphine $ArP(H)\text{-}GeCl_3$ with one equivalent of DBU. Subsequent elimination of the complex $DBU.GeCl_2$ would lead to $P(Ar)HCl$, as indicated by Escudié as being the first step in his synthesis of the diposphene ArP=PAr[28].

## 6.3 Discussion

Although it would appear that in the examples described above the low-coordinate compounds of the type ArP=[M] (where M = As or Sn and Ar = 2,4,6-$(CF_3)_3C_6H_2$ or 2,6-$(CF_3)_2C_6H_3$) will not form by DBU coupling[11], it should not be assumed that this is necessarily due to the inherent instability of these compounds.

If a less ambiguous route to the first P-M bond formation could be found, then base-assisted dehydrochlorination would then have a better chance of giving the desired double-bonded species. Unfortunately, as previously demonstrated[30], it does not appear to be possible to form the phosphine lithio derivatives, ArP(H)Li, even at low temperature. However, perhaps it may be possible to obtain the phospha-arsene derivatives using the method of Grobe[19] (as described above). Alternatively, systems with mixed organo groups could be generated using known phosphine lithio derivatives, for example:

$$Ar'P(H)Li + Sn(Ar)_2Cl_2 \longrightarrow Ar'(H)P\text{–}Sn(Cl)(Ar)_2$$

$$Ar'(H)P\text{–}Sn(Cl)(Ar)_2 \xrightarrow{DBU} Ar'P{=}Sn(Ar)_2$$

(where Ar = 2,4,6-$(CF_3)_3C_6H_2$ or 2,6-$(CF_3)_2C_6H_3$
and Ar' = 2,4,6-$(tBu)_3C_6H_2$)

## 6.4 Experimental

### 6.4.1 General Strategy

The DBU coupling reactions were all performed by mixing 1 g (4 mmol) of $P(2,6\text{-}(CF_3)_2C_6H_3)H_2$ with 4 mmol of the relevant chloro species in THF (50 ml). This solution was then stirred under nitrogen and DBU 1.2 ml (8 mmol) in THF (20 ml) was added dropwise over a period of 5 minutes.

The $\gamma$-source was used as described in Chapter 2.

### 6.4.2 Preparation of $P(2,6\text{-}(CF_3)_2C_6H_3)H_2$ (via $LiAlH_4$)

In a 125 ml two-neck round-bottomed flask, maintained under an atmosphere of dry nitrogen, was placed $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_2$ 3.8 g (12.0 mmol) in diethyl ether (50 ml). The solution was cooled to 0°C before the drop-wise addition of a 1 M solution of $LiAlH_4$ (6.0 ml, 6.0 mmol). There was the immediate formation of a fine, white precipitate. The mixture was then allowed to warm to room temperature and to stir for a further 1 hour, before the removal of the $LiAlCl_4$ by filtration. The ether was removed by distillation and the product purified by distillation at reduced pressure (Bpt. 70°C, 20 mmHg), yielding 2.2 g (75 %) of a colourless oil.

(See below for characterisation).

### 6.4.3 Preparation of $P(2,6\text{-}(CF_3)_2C_6H_3)H_2$ (via $Bu_3SnH$)

In a 50 ml two-neck round-bottomed flask, maintained under an atmosphere of dry nitrogen, was placed $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_2$ 3.0 g (9.5 mmol) in diethyl ether (30 ml). The solution was cooled to 0°C before the drop-wise addition of a solution of $Bu_3SnH$ (5.11 ml, 19.0 mmol) in diethyl ether (10 ml). The mixture was stirred for a further 30 minutes at 0°C before warming to room temperature. The ether was then removed by distillation and the product purified by distillation at reduced pressure (Bpt. 70°C, 20 mmHg) yielding 1.9 g (81 %) of a colourless oil.

$C_8H_5F_6P$ = 246.08

$^{31}P$ n.m.r. : $\delta/(CDCl_3)$ = -142.7 ppm (t, $J_{PH}$ 214.0 Hz; sept., $J_{PF}$ = 29.4 Hz).

$^{19}F$ n.m.r. : $\delta/(CDCl_3)$ = -61.5 ppm (d, $J_{PF}$ 29.4 Hz; t, $J_{FH}$ = 5.1 Hz).

$^{1}H$ n.m.r. : $\delta/(CDCl_3)$ = 3.9 ppm (d, $J_{PH}$ 214.0 Hz; sept., $J_{FH}$ = 5.1 Hz, P-H, 2 H);

7.52 ppm (t, $J_{HH}$ = 7.9 Hz p-Ar-H, 1H); 7.89 ppm (d, $J_{HH}$ = 7.9 Hz, m- Ar-H, 2 H).

I.R.: 2370 $cm^{-1}$ (P-H stretch).

### 6.4.4 Preparation of $Sn(2,4,6\text{-}(CF_3)_3C_6H_2)_2Cl_2$

In a two-necked, 250 ml, round-bottomed flask, fitted with dropping funnel and maintained under dry nitrogen, was placed tin tetrachloride 2.6 g (10 mmol) in diethyl ether (50 ml). The flask was cooled to -78°C (cardice / acetone slush bath). 2,4,6-Tris(trifluoromethyl)phenyllithium (approx 20 mmol) in diethyl ether (30 ml) was then added dropwise, with continuous stirring. When addition was complete the mixture was allowed to warm to room temperature, and then left to stir for a further one hour. The lithium salts were filtered off under nitrogen and the solution concentrated to 15 ml under reduced pressure. A pale yellow solid precipitated out and this was filtered off, washed with a small quantity of ether and dried under vacuum yielding 3.6 g (48 %). A small quantity for analysis was then recrystallised from pentane to give small, white, flakey crystals.

$C_{18}H_4Cl_2F_{18}Sn$ = 751.80.

Calc: C = 28.76 %, H = 0.54 %, Sn = 15.79 %, Cl = 9.43 %.

Found: C = 26.29 %, H = 0.54 %, Cl = 9.85 %.

$^{19}$F n.m.r. : $\delta$/($CDCl_3$) = -54.71 ppm (s.$CF_3$, 12F), -64.12 ($CF_3$, 6F).

$^{1}$H n.m.r. : $\delta$/($CDCl_3$) = 8.19 ppm (s).

$^{119}$Sn n.m.r. : $\delta$/($CDCl_3$) = -146.5 ppm; /(THF) -147.8 ppm.

Mass Spec.: m/e = 733 ($[M - 19]^+$), 717 ($[Ar_2SnCl]^+$), 471 ($[ArSnCl_2]^+$).

### 6.4.5 Preparation of $As(2,6\text{-}(CF_3)_2C_6H_3)_2Cl$

* *n.b. This was the attempted preparation of* $As(2,6\text{-}(CF_3)_2C_6H_3)Cl_2$.

A solution of the n-butyllithium TMEDA complex (prepared from TMEDA 2.85 g (25 mmoles), 14.6 ml of a solution of n-butyllithium, 1.6 M in hexanes, (23.4 mmoles) and 10 ml of diethyl ether) was added to 5.0 g (23.4 mmoles) of 1,3-bis(trifluoromethyl)benzene in 30 ml of the same solvent at 0°C, contained in a 125 ml two-necked flask under an atmosphere of dry nitrogen. After stirring overnight at room temperature it was transferred to a dropping funnel, before being slowly added to a solution of arsenic trichloride 9.1 g (50.2 mmoles) in 30 ml of diethyl ether at -78 °C, contained in a 250 ml two-necked flask, under nitrogen. The reaction mixture was then allowed to warm to room temperature and 50 ml of pentane were added. After filtering off the lithium salts the solution was concentrated to 15 ml, upon which a yellow solid was precipitated. The product was filtered off and dried under vacuum. Vacuum sublimation (90°C, 0.1 mmHg) yielded 3.2 g (51 %) of a pale yellow crystalline solid, a small amount of which was recrystallised from dichloromethane for analysis.

$C_{16}H_6ClF_{12}As$ = 536.58.

Calc: C = 35.82 %, H = 1.13 %, As = 13.96 %, Cl = 7.62 %.

Found: C = 35.25 %, H = 0.98 %, Cl = 6.61 %.

$^{19}$F n.m.r. : $\delta$/(CDCl$_3$) = -54.40 ppm (s. CF$_3$).

$^1$H n.m.r. : $\delta$/(CDCl$_3$) = 7.59 ppm (t, $J_{HH}$ = 7.9 Hz, p-Ar-H, 1 H); 7.81 ppm (d, $J_{HH}$ = 7.9 Hz m-Ar-H, 2H)

$^{13}$C n.m.r. : $\delta$/(CDCl$_3$) = 123.7 ppm (q, $J_{CF}$ = 276.8 Hz, CF$_3$); 130.4 ppm (s, p-CH); 131.3 ppm (s, m-CH); 134.5 ppm (q, $J_{CF}$ = 33.5 Hz, C-CF$_3$); 142.9 ppm (s, C-As).

Mass Spec.: m/e = 536 (M$^+$), 501 ([AsAr$_2$]$^+$).

### 6.4.6 Preparation of 1,3,1',3'-Tetraethyl-2,2'-bis(imidazolidine)

N,N-dimethylformamide dimethylacetal (17.9 g, 20 ml, 151 mmol) was added in one portion to a stirred solution of N,N'-diethylethylene diamine (15.1 g, 18.3 ml, 130 mmol) in dry benzene (35 ml). The reaction mixture was heated in a distillation vessel to 110°C for 3 hours, and the remaining benzene was removed *in vacuo* . The residue was distilled under vacuum to give the low melting solid (Mpt. 48°C), 1,3,1',3'-Tetraethyl-2,2'-bis(imidazolidine). Yield 11.7 g (71 %); Bpt. 87-88°C (3 mmHg).

### 6.4.7 Reaction of P(2,6-(CF$_3$)$_2$C$_6$H$_3$)H$_2$ with CCl$_4$

To P(2,6-(CF$_3$)$_2$C$_6$H$_3$)H$_2$ 1.4 g (5.7 mmol) was added carbon tetrachloride (25 ml). 0.5 ml of this solution was then placed in a 5 mm n.m.r. tube and degassed before sealing and placing in the gamma-source (see Chap. 2). To the remainder of the solution was added a catalytic quantity of AIBN before reluxing under nitrogen. The same products were observed by both methods (see text) and were characterised by n.m.r as follows:

$(P(2,6\text{-}(CF_3)_2C_6H_3)H)_2$ (two isomers (A) and (B))

(A):

$^{31}P$ n.m.r. : $\delta$ = -83.4 ppm (d, $J_{PH}$ = 192.4 Hz; mult, $J_{PF}$ = 25 Hz).

$^{19}F$ n.m.r. : $\delta$ = -57.7 ppm (t, $J_{PF}$ = 25 Hz; d $J_{FH}$ = 3 Hz).

(B):

$^{31}P$ n.m.r. : $\delta$ = -89.6 ppm (d, $J_{PH}$ = 174.3 Hz; mult, $J_{PF}$ = 25 Hz).

$^{19}F$ n.m.r. : $\delta$ = -57.5 ppm (t, $J_{PF}$ = 25 Hz; d $J_{FH}$ = 3 Hz).

$P(2,6\text{-}(CF_3)_2C_6H_3)HCl$

$^{31}P$ n.m.r. : $\delta$ = 10.1 ppm (d, $J_{PH}$ = 213.5 Hz; sept, $J_{PF}$ = 30 Hz).

$^{19}F$ n.m.r. : $\delta$ = -56.5 ppm (d, $J_{PF}$ = 30 Hz; d $J_{FH}$ = 3.5 Hz).

$P(2,6\text{-}(CF_3)_2C_6H_3)(CCl_3)Cl$

$^{31}P$ n.m.r. : $\delta$ = 20.6 ppm (d, $J_{PH}$ = 243.1 Hz; sept, $J_{PF}$ = 6 Hz).

$^{19}F$ n.m.r. : $\delta$ = -55.6 ppm (d, $J_{PF}$ = 6 Hz; d $J_{FH}$ = 4.5 Hz).

(see above for $P(2,6\text{-}(CF_3)_2C_6H_3)H_2$ and Chap. 3. for $P(2,6\text{-}(CF_3)_2C_6H_3)Cl_2$).

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# Chapter VII

# Diazophosphines and Related Systems

## 7.1 Introduction

### 7.1.1 Nitrile Imines

As shown in fig 7.1, diazomethane (A) is unique among small molecules in potentially having six structural isomers (B - G)[1]. Of these isomers , diazirene (B) and cyanamide (C) are stable at room temperature, and derivatives of isocyanamide (D) and carbodiimide (E) have been reported. The synthesis and structure of the first derivative of isodiazirene (F) has recently been reported by Niecke *et al* [2] but until recently only transient derivatives had been reported for the last isomer, nitrile imine (G), the first having been prepared by Huisgen *et al* in 1959[3]. They have been widely used in organic synthesis, in regioselective 1,3 dipolar cycloadditions[4]. Although nitrile imines had been observed by I.R. and U.V. in a matrix at 85 K [5–7], or by mass[7] or real time photoelectron spectroscopy in the gas phase[8], it was not until 1988 that Sicard *et al* (in the research group of Dr. G. Bertrand, CNRS, Toulouse) prepared the first stable species of this kind[9].

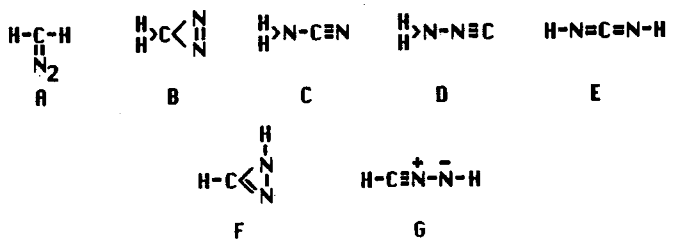
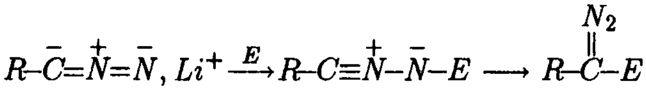


Figure 7.1 — Diazomethane and its Isomers

Transient nitrile imines have commonly been prepared by dehydrohalogenation of hydrazonoyl halides, dehydrogenation of aldehyde hydrazones, and thermolysis or photolysis of tetrazoles or related heterocycles[4]. The approach of Bertrand's group is totally different and consists of the attack of an electrophile at the terminal nitrogen atom of diazolithium salts. Although this would generally lead to the respective diazo derivative, it has been postulated that the first step of such reactions is the formation of the nitrile imine, which susequently rearranges[10–16],



$$R\text{–}\overset{-}{C}{=}\overset{+}{N}{=}\overset{-}{N},\, Li^{+} \xrightarrow{E} R\text{–}C{\equiv}\overset{+}{N}\text{–}\overset{-}{N}\text{–}E \longrightarrow R\text{–}\overset{\overset{N_2}{\|}}{C}\text{–}E$$

and the first real evidence for such a reaction pathway was obtained by Granier *et al* in 1988[17] Thus by reacting the lithium salts of various phosphorus-substituted diazomethanes at low temperature with chlorophosphines of the type $R_2PCl$, it was shown that, depending on the nature of both the electrophiles and diazolithium salts, diazo derivatives or alternatively nitrile imines were obtained (summarised in table 7.1)[18].

These results have been rationalized on the grounds that bulky substituents will increase the energy barrier of the 1,3 shift from the nitrogen substituent to the carbon in the nitrile imine / diazo rearrangement. However, although there is clearly a need for bulky substituents in the stabilisation of nitrile imines, this does not explain why, of the two species (A and B) below, A is stable indefinitely at room temperature as a solid or in solution, whereas B has not even been detected at -78°C. This might be explained by electronic factors and it has been postulated that the "push-pull" effect of substituents may be a strong stabilizing factor[18].

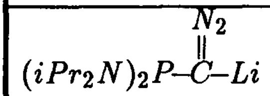
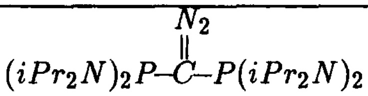
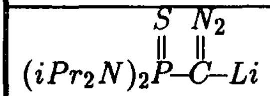
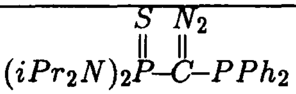
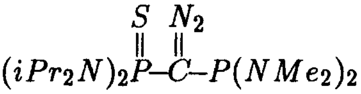
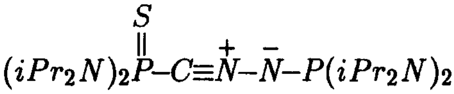
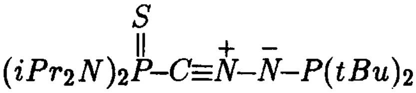
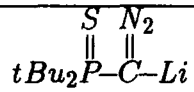
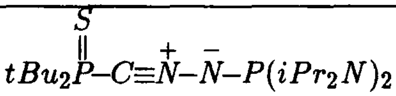
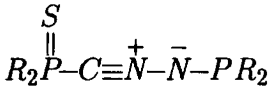
| Diazo lithium salt | Chlorophosphine | Product |
|---|---|---|
|  $(iPr_2N)_2P\text{–}\overset{N_2}{\overset{\|}{C}}\text{–}Li$ | $(iPr_2N)_2PCl$ |  $(iPr_2N)_2P\text{–}\overset{N_2}{\overset{\|}{C}}\text{–}P(iPr_2N)_2$ |
|  $(iPr_2N)_2\overset{S}{\overset{\|}{P}}\text{–}\overset{N_2}{\overset{\|}{C}}\text{–}Li$ | $Ph_2PCl$<br>$(Me_2N)_2PCl$<br>$(iPr_2N)_2PCl$<br>$tBu_2PCl$ |  $(iPr_2N)_2\overset{S}{\overset{\|}{P}}\text{–}\overset{N_2}{\overset{\|}{C}}\text{–}PPh_2$<br> $(iPr_2N)_2\overset{S}{\overset{\|}{P}}\text{–}\overset{N_2}{\overset{\|}{C}}\text{–}P(NMe_2)_2$<br> $(iPr_2N)_2\overset{S}{\overset{\|}{P}}\text{–}C\equiv\overset{+}{N}\text{–}\overset{-}{N}\text{–}P(iPr_2N)_2$<br> $(iPr_2N)_2\overset{S}{\overset{\|}{P}}\text{–}C\equiv\overset{+}{N}\text{–}\overset{-}{N}\text{–}P(tBu)_2$ |
|  $tBu_2\overset{S}{\overset{\|}{P}}\text{–}\overset{N_2}{\overset{\|}{C}}\text{–}Li$ | $(iPr_2N)_2PCl$ |  $tBu_2\overset{S}{\overset{\|}{P}}\text{–}C\equiv\overset{+}{N}\text{–}\overset{-}{N}\text{–}P(iPr_2N)_2$ |

**Table 7.1 — Reactivity of Diazolithium salts with various Chlorophosphines**


$R_2\overset{S}{\overset{\|}{P}}\text{–}C\equiv\overset{+}{N}\text{–}\overset{-}{N}\text{–}PR_2$

(A)

$R_2P\text{–}C\equiv\overset{+}{N}\text{–}\overset{-}{N}\text{–}PR_2$

(B)

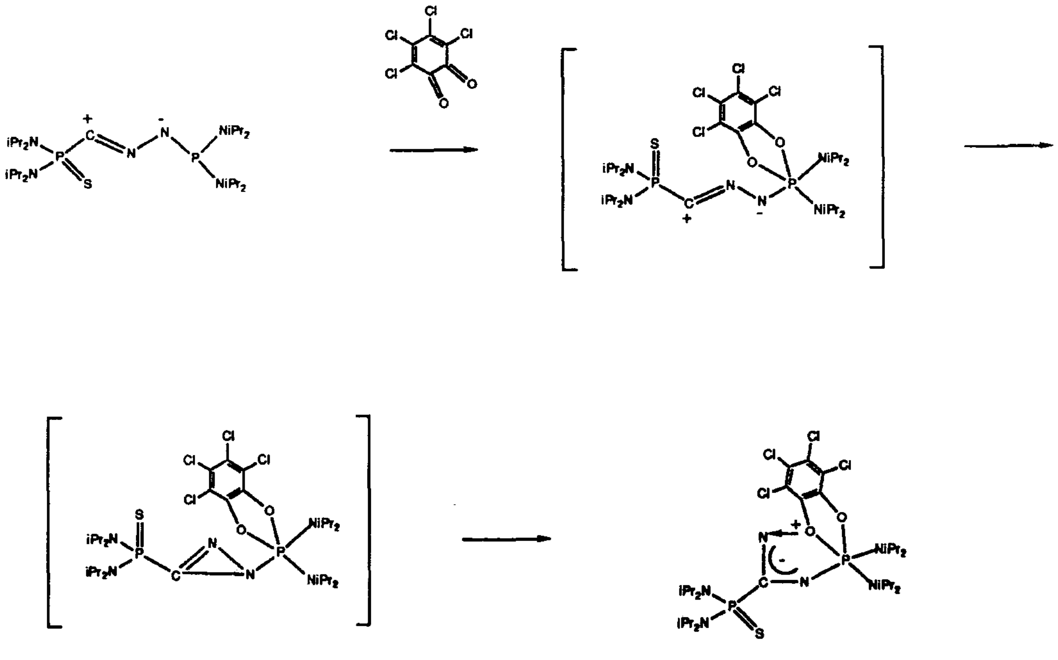
(R = iPr$_2$N)

This would seem to be supported by the fact that the boron analogue to B has been shown by Goodwin[19] to be a relatively stable nitrile imine, though this was attributed to the degree of crowding around boron.

$$R_2P\text{–}C\equiv\overset{+}{N}\text{–}\overset{-}{N}\text{–}BR_2$$

(R = iPr$_2$N)

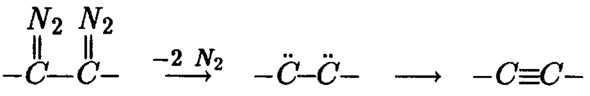
In purely phosphorus-substituted systems, however, it is at least clear that the hybridization state of P is of importance to the stability of the nitrile imine. As quinones are well-known to react with phosphines to give the corresponding pentacoordinated phosphoranes[20], Granier *et al* [21] attempted to prepare a P(V) - P(V) substituted nitrile imine by reacting A with tetrachloroorthoquinone (TCOQ). Although this reaction was believed to proceed via a transient new nitrile imine, this rearranged to form the imidoylnitrene/oxonium complex, possibly via the isodiazirene, as follows:



The stabilization of nitrenes by coordination with nitrogen is well known[22], but had only previously been postulated for oxygen.[23]

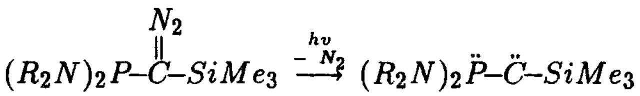
### 7.1.2 Phosphinocarbenes

Over a century ago Curtius[24] had shown how shown how an $\alpha$,$\alpha$'-biscarbene was an alkyne:



$$-\overset{N_2}{\overset{\|}{C}}-\overset{N_2}{\overset{\|}{C}}- \xrightarrow{-2\,N_2} -\ddot{C}-\ddot{C}- \longrightarrow -C\equiv C-$$

The phosphorus atom in a phosphine may act as a nucleophile, via its lone pair of electrons, or as an electrophile, by donation into vacant d orbitals. Such characteristics are similar to those of carbenes. It was thus demonstrated by Igau *et al* [25] how a system analogous to that above could be generated by elimination of nitrogen from a diazophosphine, resulting in a $\lambda^3$-phosphinocarbene:



$$(R_2N)_2P-\overset{N_2}{\overset{\|}{C}}-SiMe_3 \xrightarrow[-N_2]{h\nu} (R_2N)_2\ddot{P}-\ddot{C}-SiMe_3$$

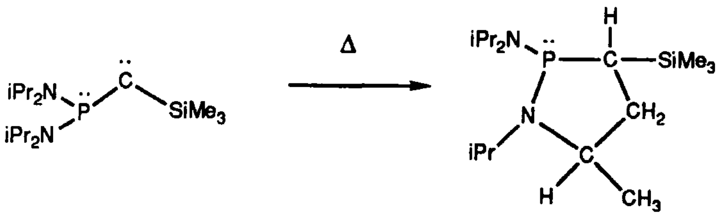
(R = iPr)

Such a species is stabilized by the vinyl ylide and $\lambda^5\sigma^3$-phosphaalkyne resonance forms:

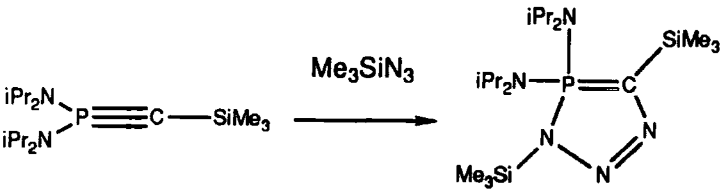
$$>\ddot{P}-\ddot{C}- \longleftrightarrow >\overset{+}{P}=\overset{-}{C}- \longleftrightarrow >P\equiv C-$$

Experimental results would seem to support theoretical calculations that predict all three resonance forms to be energetically very close[26].

Thus phosphinocarbenes may behave as "normal" carbenes, by, for example performing insertion-type reactions:



or as phosphaalkynes by taking part in [2 + 3] cycloaddition reactions:

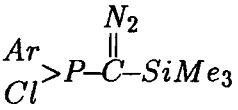


The aim of the following work was to attempt to generate analogous systems as described above, but to replace the commonly-used $iPr_2N$ substituents with bulky electron-withdrawing aromatic ligands, such as 2,4,6-$(CF_3)_3C_6H_2$ or 2,6-$(CF_3)_2C_6H_3$. In such a way it was hoped to gain a better understanding of the factors involved in the formation, stabilization and reactivity of nitrile imines and phosphinocarbenes.

## 7.2 Results

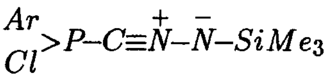
### 7.2.1 2,6-$(CF_3)_2C_6H_3PCl_2$ + Li-C($N_2$)-$SiMe_3$

A stoichiometric amount of Li-C($N_2$)-$SiMe_3$ (generated with LDA in THF at -78°C) was added to a THF solution of 2,6-$(CF_3)_2C_6H_3PCl_2$, in an attempt to form a diazophosphine or nitrile imine with chlorine as one of the phosphorus substituents, i.e.



$$\begin{matrix}Ar\\Cl\end{matrix}\!>\!P\!-\!\overset{\overset{N_2}{\|}}{C}\!-\!SiMe_3$$

or



$$\begin{matrix}Ar\\Cl\end{matrix}\!>\!P\!-\!C\!\equiv\!\overset{+}{N}\!-\!\overset{-}{N}\!-\!SiMe_3$$

(Ar = 2,6-$(CF_3)_2C_6H_3$)

The $^{31}P$ n.m.r. spectrum of the reaction mixture showed a single signal, with no observable coupling ($\delta\ ^{31}P = -4.8$ ppm) and no diazo stretching band was seen in the I.R. spectrum. After removal of the THF *in vacuo* it was found that the phosphorus-containing product was not soluble in low polarity solvents (i.e. pentane or hexane) and as it decomposed over a period of 2 or 3 hours to give a mixture of products, further direct characterisation was not possible. On the assumption that the product may be the phosphaalkyne 2,6-$(CF_3)_2C_6H_3$-CP[27] (formed by elimination of nitrogen and trimethylsilyl chloride), a trapping experiment was attempted by the addition of one molar equivalent of trimethylsilyl azide to the reaction mixture. Initially a single product was observed by $^{31}P$ n.m.r. at $\delta\ ^{31}P =$ -1 ppm, though this is unlikely to be due to a triazaphosphole[27], and this new product also decomposed within hours, to give a complex mixture.

It was also shown that when 2,6-$(CF_3)_2C_6H_3PCl_2$ was added to LDA at -78°C then, as indicated by $^{31}P$ n.m.r. , the sole phosphorus-containing product (apart from a little oxidation / hydrolysis) was the symmetric diphosphene.

$$2ArPCl_2 \xrightarrow{LDA} ArP{=}PAr$$

(where Ar = 2,6-$(CF_3)_2C_6H_3$).

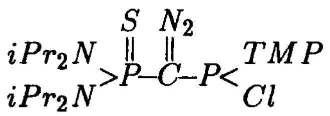
This suggests that the product with $\delta$ $^{31}P$ = -4.8 is a result of the dichlorophosphine reacting with the diazomethyllithium and not with LDA.

### 7.2.2 2,4,6-$(CF_3)_3C_6H_2PCl_2$ + $(iPr_2N)_2P$-$C(N_2)$-Li

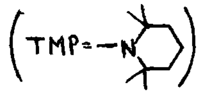
A stoichiometric amount of the lithium salt of $(iPr_2N)_2P$-$C(N_2)$-H, generated with LDA in THF at -78°C, was added to a THF solution of the aryldichlorophosphine. The $^{31}P$ n.m.r. spectrum of the reaction mixture showed a large number of products and the I.R. spectrum showed the presence of no new diazo or nitrile imine products, only a small amount of $(iPr_2N)_2P$-$C(N_2)$-H.

### 7.2.3 TMP-$PCl_2$ + $(iPr_2N)_2P(S)$-$C(N_2)$-Li

A stoichiometric amount of a solution of the lithium salt of $(iPr_2N)_2P(S)$-$C(N_2)$-H, prepared with LDA in THF, was added via canule to a THF solution of TMP-$PCl_2$. Although by $^{31}P$ n.m.r. there were seen to be a number of side products, it appeared that the major product of the reaction was the diazophosphine:



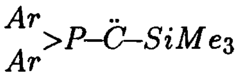
$$\begin{array}{l}iPr_2N\\ iPr_2N\end{array}\!\!>\overset{\overset{S}{\|}}{P}-\overset{\overset{N_2}{\|}}{C}-P<\begin{array}{l}TMP\\ Cl\end{array}$$



$\delta$ $^{31}P$ = 64.4 ppm (d, 172 Hz, >P(S)-) and 94.8 ppm (d, 172 Hz, TMP(Cl)P-); I.R. 2095 $cm^{-1}$ (-$C(N_2)$-). An attempt to abstract chloride ion by the addition of one molar equivalent of trimethylsilyl triflate (in ether at -78°C) to the reaction mixture produced a complex mixture, as indicated by $^{31}P$ n.m.r.

### 7.2.4 $[2,4,6\text{-}(CF_3)_3C_6H_2]_2PCl + Li\text{-}C(N_2)\text{-}SiMe_3$

The 1:1 reaction of the lithium salt of $H\text{-}C(N_2)\text{-}SiMe_3$ (generated in THF with LDA at -78°C) with $[2,4,6\text{-}(CF_3)_3C_6H_2]_2PCl$ gave a deep blue solution containing a number of products. The I.R. solution spectrum of the reaction mixture showed diazo stretching bands at 2040 and 2090 $cm^{-1}$ and a nitrile imine stretch at 2140 $cm^{-1}$. The $^{31}P$ n.m.r. spectrum showed a number of products, including a septet signal at -70 ppm ($J_{PF} =$ 40 Hz). Septet signals with a similar coupling (though not fully resolved) were recorded at $\delta\ ^{31}P = -5$ and $+77$ ppm, which are tentatively assigned to the diazophosphine and nitrile imine respectively. Unfortunately, attempts at product separation by TLC were unsuccessful. In a previous study of this reaction[19] it was suggested that the signal seen in the $^{31}P$ n.m.r. spectrum at -70 ppm may be due to the carbene:



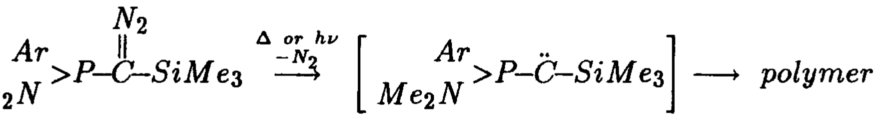
$$\begin{matrix} Ar & \\ & >P\text{–}\ddot{C}\text{–}SiMe_3 \\ Ar & \end{matrix}$$

(where Ar = $2,4,6\text{-}(CF_3)_3C_6H_2$).

However, when under the same conditions $[2,4,6\text{-}(CF_3)_3C_6H_2]_2PCl$ is reacted with an equimolar amount of LDA alone, a deep blue solution is also formed. The blue colour persists for approximately 24 hours at room temperature, before gradually turning brown. The $^{31}P$ n.m.r. spectrum of the blue solution showed it to contain $[2,4,6\text{-}(CF_3)_3C_6H_2]_2PCl$ and a further signal at -70 ppm (sept, $J_{PF} =$ -40 Hz), assumed to correspond to the phosphide anion $[2,4,6\text{-}(CF_3)_3C_6H_2]_2P^-$.

### 7.2.5 2,4,6-$(CF_3)_3C_6H_2P(NMe_2)Cl$ + Li-$C(N_2)$-$SiMe_3$

The diazophosphine 2,4,6-$(CF_3)_3C_6H_2P(NMe_2)$-$C(N_2)$-$SiMe_3$ ($\delta$ $^{31}P$ / (PhMe) = 63.8 ppm, sept, $J_{PF}$ = 35 Hz; I.R. 2060 $cm^{-1}$, -$C(N_2)$-) was formed by the reaction of the aryl(dimethylamino)chlorophosphine with one molar equivalent of the lithium salt of trimethylsilyldiazomethane. Attempted distillation of the product saw elimination of nitrogen, with the production of polymeric material (as indicated by multiple, broad signals in the $^{31}P$ n.m.r. spectrum). U.V. irradiation of a toluene solution of the diazophosphine for one hour at 300 nm also resulted in the visible evolution of nitrogen and the production of a polymer. A similar result was obtained by simply warming the solution to 40°C for a few minutes. Although this process may proceed via an intemediate carbene, when the decomposition of the diazophosphine was followed by $^{31}P$ n.m.r. , only signals corresponding to the starting material and the final polymeric product were found. Thus any carbene species formed was probably very short-lived.



$$\begin{matrix}Ar\\Me_2N\end{matrix}\!>\!P\!-\!\overset{N_2}{\overset{\|}{C}}\!-\!SiMe_3 \xrightarrow[-N_2]{\Delta\ or\ h\nu} \left[\begin{matrix}Ar\\Me_2N\end{matrix}\!>\!P\!-\!\ddot{C}\!-\!SiMe_3\right] \longrightarrow polymer$$

(where Ar = 2,4,6-$(CF_3)_3C_6H_2$).

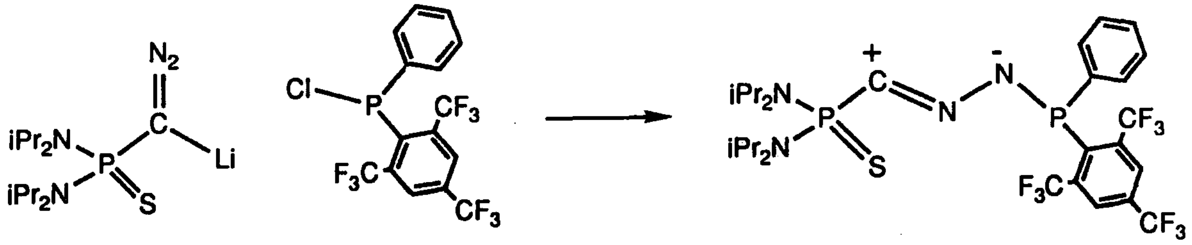
### 7.2.6 2,4,6-$(CF_3)_3C_6H_2P(NPr^i_2)Cl$ + Li-$C(N_2)$-$SiMe_3$

The 1:1 reaction of $P(NPr^i_2)Cl$ with the lithium salt of trimethylsilyldiazomethane (generated with LDA in THF at -78°C) did not produce the desired diazophosphine but, as shown by the $^{31}P$ n.m.r. spectrum of the reaction mixture, a complex array of products. As has been shown previously[19], organo lithium reagents may attack the $CF_3$ groups in compounds incorporating the 2,4,6-$(CF_3)_3$-

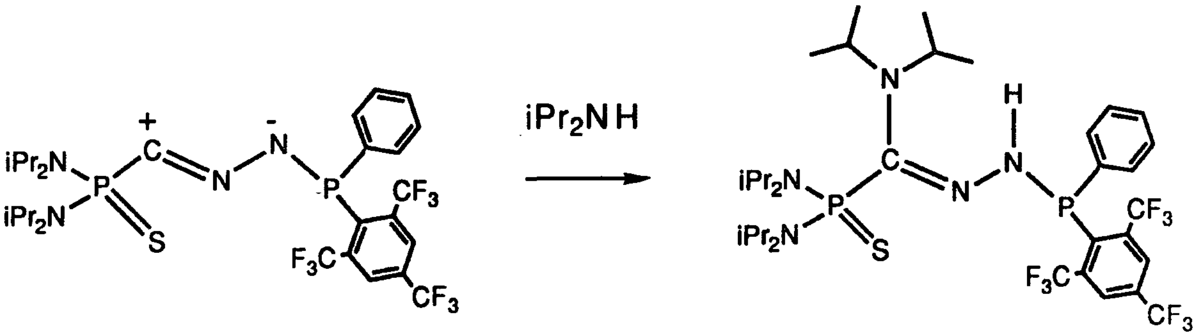
$C_6H_2$ ligand in preference to giving straightforward substitution or metalation reactions. This would seem to have been the case in this reaction, where a number of quartets in the $^{31}P$ n.m.r. spectrum can most easily be explained by the loss of a trifluoromethyl group, giving rise to a wide range of products, including polymeric material.

### 7.2.7 2,4,6-$(CF_3)_3C_6H_2(Ph)PCl$ + Li-$C(N_2)$-P(S)$(NPr^i{}_2)_2$

When the lithium salt of H-$C(N_2)$-P(S)$(NPr^i{}_2)_2$, generated with LDA at -78°C, was reacted with an equimolar amount of the diarylchlorophosphine, 2,4,6-$(CF_3)_3$-$C_6H_2$(Ph)PCl, the initial product was the nitrile imine, as indicated in the I.R. spectrum of the reaction mixture by a characteristic, broad band at 2130 $cm^{-1}$. The $^{31}P$ n.m.r. spectrum of the reaction mixture was also consistant with the formation of the nitrile imine, with two signals: $\delta\ ^{31}P = 27.9$ ppm (s, $(iPr_2N)_2P(S)$-)) and 70.6 ppm (sept, $J_{PF} = 41.5$ Hz, 2,4,6-$(CF_3)_3C_6H_2$(Ph)P-). Thus:



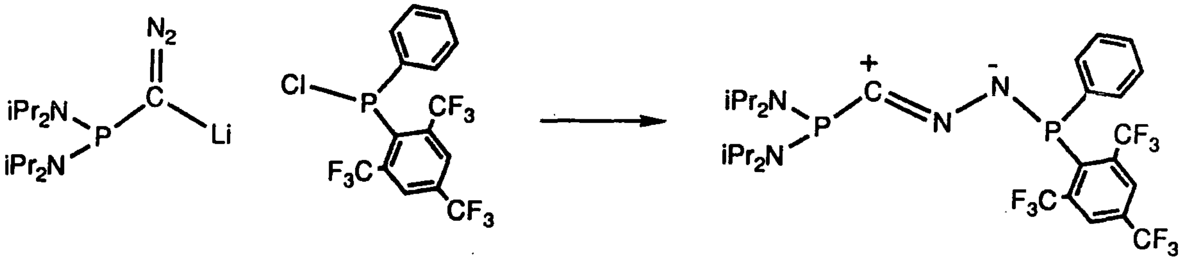
However, over a period of about 40 hours at room temperature, the nitrile imine reacted quantitatively with the diisopropylamine liberated in the initial LDA lithiation of the diazophosphine as follows:



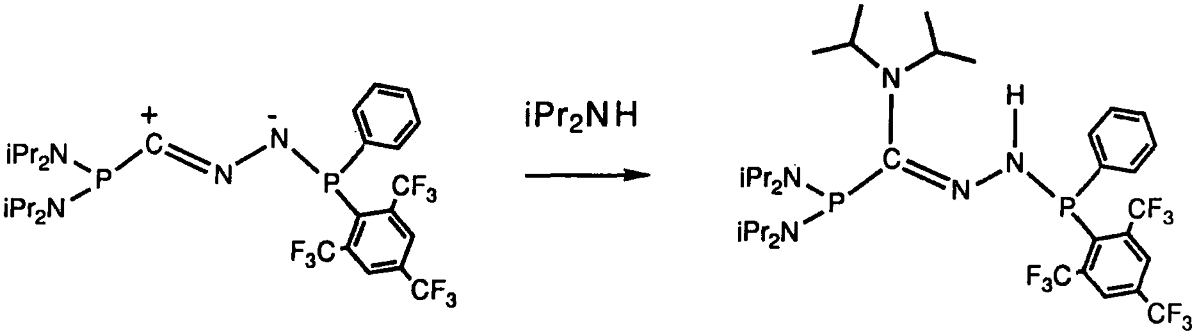
This reaction can be followed by $^{31}P$ n.m.r. : the resonance corresponding to the $(iPr_2N)_2P(S)$- group at 27.9 ppm in the nitrile imine diminished with the appearance of a new signal for this group at 67.8 ppm (s). By contrast the signal for the 2,4,6-$(CF_3)_3C_6H_2(Ph)P$- group moved upfield from 70.6 ppm in the nitrile imine to give rise to a new septet at 39.9 ppm ($J_{PF}$ = 45 Hz) for the product. The hydrazonoyl amide is air-stable and may be purified by column chromatography over silica gel. It has been clearly characterised by $^{1}H$, $^{13}C$, and $^{31}P$ n.m.r. spectroscopy (see 7.5.11). When the lithiation of $(iPr_2N)_2P(S)$-$C(N_2)$-H was performed with BuLi rather than LDA, the nitrile imine was formed as the final product and derivatives were formed by the addition of suitable trapping agents (see below). However, no attempt has been made as yet to isolate the nitrile imine itself (though this may be possible).

### 7.2.8 $2,4,6-(CF_3)_3C_6H_2(Ph)PCl$ + $(iPr_2N)_2P-C(N_2)-Li$

When the lithium salt of $(iPr_2N)_2P-C(N_2)-H$, generated with LDA at -78°C, was reacted with an equimolar amount of the diarylchlorophosphine, $2,4,6-(CF_3)_3-C_6H_2(Ph)PCl$, the initial product was the nitrile imine, as indicated in the I.R. spectrum of the reaction mixture by a characteristic, broad band at 2130 $cm^{-1}$. The $^{31}P$ n.m.r. spectrum of the reaction mixture was also consistent with the formation of the nitrile imine, with two signals: $\delta\ ^{31}P = 43.7$ ppm (s, $(iPr_2N)_2P-$)) and 73.2 ppm (sept, $J_{PF} = 41.5$ Hz, $2,4,6-(CF_3)_3C_6H_2(Ph)P-$). This is the first ever example of the formation of a nitrile imine stabilised by a P(III) substituent at both carbon and nitrogen:



Like the thiophosphoryl analogue (see above) the nitrile imine, once formed, reacted over a period of a few hours with diisopropylamine (liberated in the initial lithiation of the diazophosphine) to form the corresponding hydrazonoyl amide: $\delta\ ^{31}P = 34.2$ ppm (s, $(iPr_2N)_2P-$), 40.0 ppm (sept, $J_{PF} = 45$ Hz, $2,4,6-(CF_3)_3-C_6H_2(Ph)P-$). The I.R. spectrum showed no diazo or nitrile imine stretching bands.

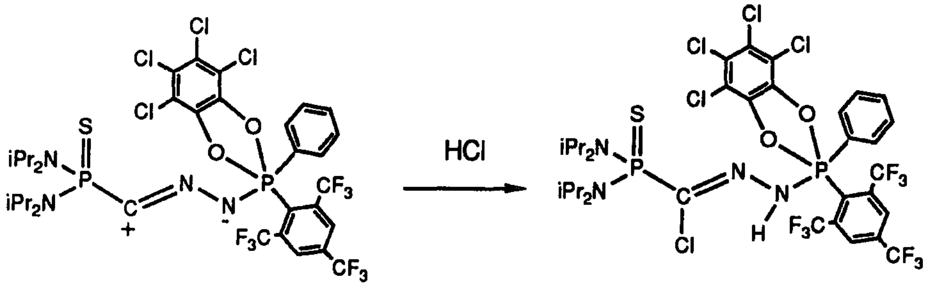


However, in this case isolation of the product was unsuccessful due to the air-/moisture-sensitivity of the $(iPr_2N)_2P$- sustituent. By contrast the 2,4,6--$(CF_3)_3C_6H_2(Ph)P$- group is remarkably stable to oxidation (and 2,4,6-$(CF_3)_3$-$C_6H_2(Ph)PCl$ may be washed with water with only a very small amount of hydrolysis taking place).

### 7.2.9 2,4,6-$(CF_3)_3C_6H_2(Ph)P$-NNC-$P(S)(NPr^i{}_2)_2$ + TCOQ

When the reaction mixture containing the nitrile imine, 2,4,6-$(CF_3)_3C_6H_2$-(Ph)P-NNC-$P(S)(NPr^i{}_2)_2$, was cooled to -10°C and tetrachloroorthoquinone was added in a 30 % molar excess, three products were evident from $^{31}P$ n.m.r. . The products were the new P(V)-P(V)-substituted nitrile imine, formed by simple addition of TCOQ to the lone pair on the phosphorus of the 2,4,6-$(CF_3)_3C_6H_2$-(Ph)P- group, and its isomer, the oxonium-stabilised nitrene (these two products being formed in relative 4:1 amounts). The third product was the hydrazonoyl chloride, formed by formal HCl addition to the product P(V)-P(V) nitrile imine, and is believed to be due to impurities in the TCOQ, (as when the reaction was first carried out, a large excess of TCOQ was used and the hydrazonoyl chloride was produced as the sole product).

Hence:



Slow filtration of the reacton mixture through silica gel resulted in dehydrochlorination of the hydrazonoyl chloride to its parent nitrile imine. The nitrile imine and its oxonium-nitrene isomer were then successfully separated and isolated by column chromatography. Thus, with pure TCOQ one would expect the reaction to produce these two products only (see fig. 7.2). Mass spectroscopy showed mass ions for both products, confirming that they were isomers. I.R. spectroscopy gave a characteristic broad band at 2162 $cm^{-1}$ for the nitrile imine. $^{31}P$ n.m.r. showed two doublet signals for the nitrile imine at 27.8 ppm (>P(S)-) and -24.5 ppm (P(V)) with $J_{PP}$ = 8.6 Hz. The oxonium nitrene also showed two doublets in the $^{31}P$ n.m.r. spectrum, at 48.4 ppm (>P(S)-) and -32.1 ppm (P(V)) with $J_{PP}$ = 5.1 Hz. The absence of infra-red absorption above 2000 $cm^{-1}$ rules out the carbodiimide (i.e. P(V)-N=C=N-P(V)') as a possible structure. The hydrazonoyl chloride was isolated by reconverting the nitrile imine product. A slight molar excess of a 1 M diethyl ether solution of HCl was added to a THF solution of the nitrile imine at room temperature. Removal of the solvent and any excess HCl *in vacuo* yielded a white solid. The $^{31}P$ n.m.r. spectrum showed the two phosphorus signals at $\delta\ ^{31}P$ /(THF) = 61.0 ppm (>P(S)-, d) and -22.9 Hz (P(V), d), $J_{PP}$ = 4.7 Hz. This product was recrystallised from acetonitrile/pentane and the X-ray crystal structure was subsequently obtained (see below) which confirmed the hydrazonoyl chloride structure.

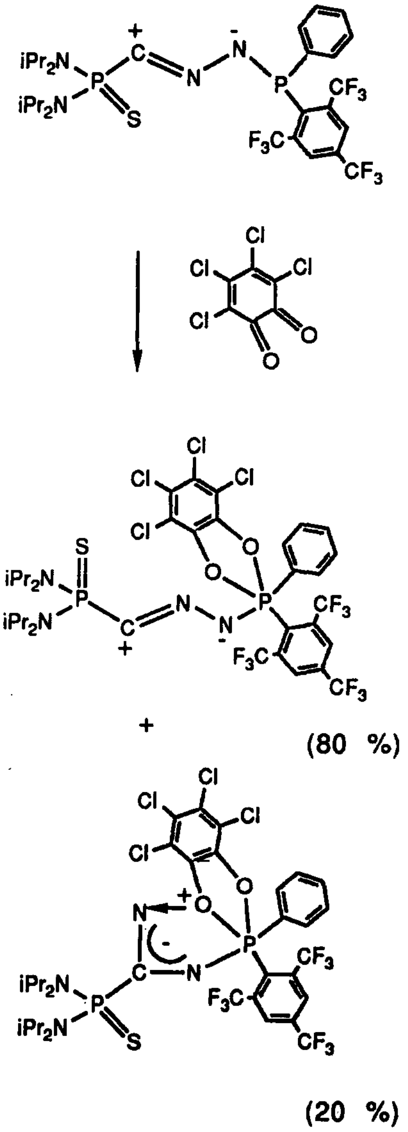
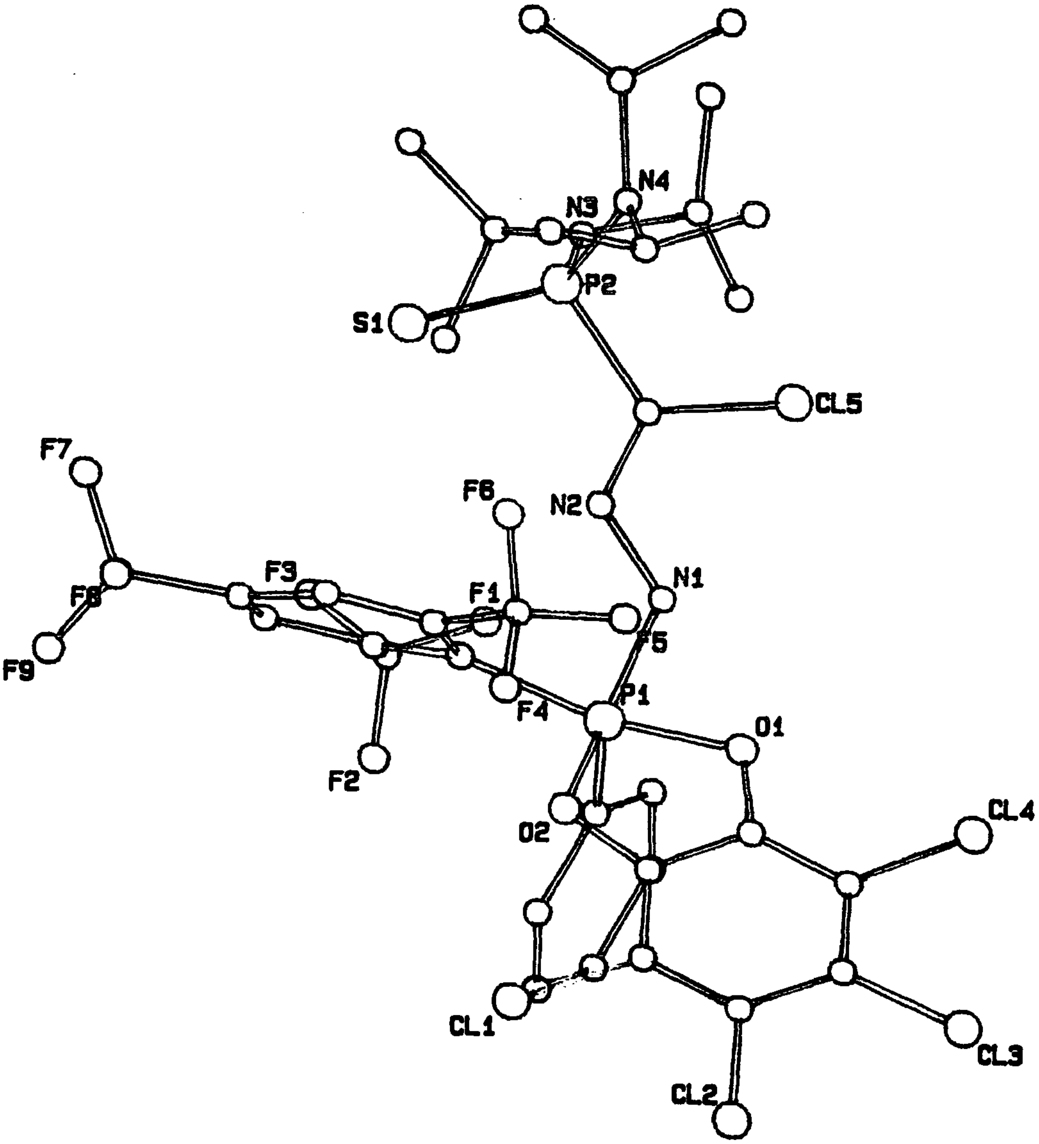


**Figure 7.2 — 2,4,6-$(CF_3)_3C_6H_2$(Ph)P-NNC-P(S)$(NiPr_2)_2$ + TCOQ**

### 7.2.10 X-ray Crystal Structure of the Hydrazonoyl Chloride



| Bond | Å(S.D.) | Bond | Å(S.D.) |
|---|---|---|---|
| P(1)-O(1) | 1.748(2) | P(1)-O(2) | 1.706(2) |
| P(1)-C(7) | 1.794(3) | P(1)-C(13) | 1.913(3) |
| O(1)-C(1) | 1.348(4) | O(2)-C(2) | 1.357(4) |
| C(1)-C(2) | 1.374(4) | C(4)-C(5) | 1.385(4) |
| C(2)-C(3) | 1.379(5) | C(5)-C(6) | 1.401(5) |
| C(3)-C(4) | 1.392(5) | C(6)-C(1) | 1.364(5) |
| C(3)-Cl(1) | 1.714(3) | C(5)-Cl(3) | 1.717(4) |
| C(4)-Cl(2) | 1.723(4) | C(6)-Cl(4) | 1.714(3) |
| C(7)-C(8) | 1.387(5) | C(10)-C(11) | 1.372(6) |
| C(8)-C(9) | 1.376(5) | C(11)-C(12) | 1.376(5) |
| C(9)-C(10) | 1.368(5) | C(12)-C(7) | 1.387(4) |
| C(13)-C(14) | 1.404(4) | C(16)-C(17) | 1.369(4) |
| C(14)-C(15) | 1.387(4) | C(17)-C(18) | 1.387(4) |
| C(15)-C(16) | 1.374(4) | C(18)-C(13) | 1.405(4) |
| C(14)-C(19) | 1.509(4) | C(16)-C(21) | 1.503(5) |
| C(18)-C(20) | 1.495(4) | | |
| C(19)-F(1) | 1.328(4) | C(21)-F(7) | 1.24(2) |
| C(19)-F(2) | 1.331(5) | C(21)-F(8) | 1.409(9) |
| C(19)-F(3) | 1.333(5) | C(21)-F(9) | 1.23(1) |
| C(20)-F(4) | 1.328(5) | C(21)-F(7)' | 1.22(2) |
| C(20)-F(5) | 1.331(4) | C(21)-F(8)' | 1.26(1) |
| C(20)-F(6) | 1.325(5) | C(21)-F(9)' | 1.347(9) |
| N(1)-N(2) | 1.354(4) | N(2)-C(22) | 1.258(4) |
| N(1)-H(N1) | 0.97 | C(22)-Cl(5) | 1.768(3) |
| P(2)-C(22) | 1.854(4) | P(2)-N(3) | 1.656(2) |
| P(2)-S | 1.929(1) | P(2)-N(4) | 1.662(2) |
| N(3)-C(23) | 1.491(4) | N(4)-C(29) | 1.494(4) |
| N(3)-C(26) | 1.483(4) | N(4)-C(32) | 1.487(5) |
| C(23)-C(24) | 1.525(5) | C(29)-C(30) | 1.530(5) |
| C(23)-C(25) | 1.532(6) | C(29)-C(31) | 1.513(4) |
| C(26)-C(27) | 1.508(7) | C(32)-C(33) | 1.508(6) |
| C(26)-C(28) | 1.494(8) | C(32)-C(34) | 1.511(6) |

**Table 7.2 — Bond Lengths for the Hydrazonoyl Chloride**

| Bond Angle | deg(S.D.) | Bond Angle | deg(S.D.) |
|---|---|---|---|
| N(1)-P(1)-O(1) | 81.6(1) | O(1)-P(1)-C(7) | 96.8(1) |
| N(1)-P(1)-O(2) | 149.4(1) | O(1)-P(1)-C(13) | 153.5(1) |
| N(1)-P(1)-C(7) | 110.5(1) | O(2)-P(1)-C(7) | 99.2(1) |
| N(1)-P(1)-C(13) | 93.2(1) | O(2)-P(1)-C(13) | 83.5(1) |
| O(1)-P(1)-O(2) | 88.0(1) | C(7)-P(1)-C(13) | 103.4(1) |
| P(1)-O(1)-C(1) | 112.6(2) | P(1)-O(2)-C(2) | 113.1(2) |
| C(6)-C(1)-C(2) | 121.8(3) | C(3)-C(4)-C(5) | 121.0(3) |
| O(1)-C(1)-C(6) | 126.2(3) | Cl(2)-C(4)-C(3) | 119.3(2) |
| O(1)-C(1)-C(2) | 111.9(3) | Cl(2)-C(4)-C(5) | 119.7(3) |
| O(1)-C(2)-C(3) | 121.3(3) | C(4)-C(5)-C(6) | 120.3(3) |
| O(2)-C(2)-C(1) | 112.6(3) | Cl(3)-C(5)-C(4) | 120.7(3) |
| O(2)-C(2)-C(3) | 126.1(2) | Cl(3)-C(5)-C(6) | 119.0(2) |
| C(2)-C(3)-C(4) | 117.6(3) | C(5)-C(6)-C(1) | 117.9(3) |
| Cl(1)-C(3)-C(2) | 119.4(3) | Cl(4)-C(6)-C(5) | 122.4(3) |
| Cl(1)-C(3)-C(4) | 123.0(3) | Cl(4)-C(6)-C(1) | 119.7(3) |
| P(1)-C(7)-C(8) | 119.7(2) | P(1)-C(7)-C(12) | 121.4(2) |
| C(12)-C(7)-C(8) | 118.7(3) | C(9)-C(10)-C(11) | 119.4(4) |
| C(7)-C(8)-C(9) | 120.5(3) | C(10)-C(11)-C(12) | 121.0(3) |
| C(8)-C(9)-C(10) | 120.5(4) | C(11)-C(12)-C(7) | 119.9(3) |
| P(1)-C(13)-C(14) | 126.4(2) | P(1)-C(13)-C(18) | 117.9(2) |
| C(18)-C(13)-C(14) | 115.6(3) | C(15)-C(16)-C(17) | 119.0(3) |
| C(13)-C(14)-C(15) | 121.3(2) | C(16)-C(17)-C(18) | 120.3(3) |
| C(14)-C(15)-C(16) | 121.0(3) | C(17)-C(18)-C(13) | 122.1(3) |
| C(19)-C(14)-C(13) | 124.8(3) | C(20)-C(18)-C(13) | 124.6(3) |
| C(19)-C(14)-C(15) | 113.9(3) | C(21)-C(16)-C(15) | 120.7(3) |
| C(20)-C(18)-C(17) | 113.2(2) | C(21)-C(16)-C(17) | 120.3(3) |

Continued next page:

**Table 7.3 — Bond Angles for the Hydrazonoyl Chloride**

Cont.

| Bond Angle | deg(S.D.) | Bond Angle | deg(S.D.) |
|---|---|---|---|
| C(14)-C(19)-F(1) | 113.7(2) | C(16)-C(21)-F(7) | 115.5(7) |
| C(14)-C(19)-F(2) | 113.0(3) | C(16)-C(21)-F(8) | 110.9(5) |
| C(14)-C(19)-F(3) | 110.9(3) | C(16)-C(21)-F(9) | 114.6(9) |
| F(1)-C(19)-F(2) | 106.7(3) | F(7)-C(21)-F(8) | 99.1(1) |
| F(1)-C(19)-F(3) | 105.8(3) | F(7)-C(21)-F(9) | 111.1(1) |
| F(2)-C(19)-F(3) | 106.2(2) | F(8)-C(21)-F(9) | 103.7(9) |
| C(18)-C(20)-F(4) | 112.9(3) | C(16)-C(21)-F(7)' | 114.4(8) |
| C(18)-C(20)-F(5) | 115.0(2) | C(16)-C(21)-F(8)' | 112.0(1) |
| C(18)-C(20)-F(6) | 110.6(3) | C(16)-C(21)-F(9)' | 110.4(6) |
| F(4)-C(20)-F(5) | 106.0(3) | F(7)'-C(21)-F(8)' | 113.1(1) |
| F(4)-C(20)-F(6) | 106.9(3) | F(7)'-C(21)-F(9)' | 105.1(1) |
| F(5)-C(20)-F(6) | 104.9(3) | F(8)'-C(21)-F(9)' | 102.1(1) |
| P(1)-N(1)-N(2) | 120.9(2) | N(2)-C(22)-Cl(5) | 120.6(3) |
| P(1)-N(1)-H(N1) | 119.6 | N(2)-C(22)-P(2) | 119.4(2) |
| N(2)-N(1)-H(N1) | 119.6 | Cl(5)-C(22)-P(2) | 120.0(2) |
| N(1)-N(2)-C(22) | 120.4(2) | | |
| C(22)-P(2)-S | 107.92(9) | S-P(2)-N(3) | 115.36(9) |
| C(22)-P(2)-N(3) | 105.6(1) | S-P(2)-N(4) | 117.47(9) |
| C(22)-P(2)-N(4) | 101.7(1) | N(3)-P(2)-N(4) | 107.3(1) |
| P(2)-N(3)-C(23) | 119.8(2) | P(2)-N(4)-C(29) | 114.9(2) |
| P(2)-N(3)-C(26) | 124.0(2) | P(2)-N(4)-C(32) | 118.4(2) |
| C(23)-N(3)-C(26) | 115.3(2) | C(29)-N(4)-C(32) | 121.3(2) |
| N(3)-C(23)-C(24) | 112.3(3) | N(4)-C(29)-C(30) | 116.2(3) |
| N(3)-C(23)-C(25) | 112.3(3) | N(4)-C(29)-C(31) | 112.5(3) |
| C(24)-C(23)-C(25) | 109.9(3) | C(30)-C(29)-C(31) | 110.5(3) |
| N(3)-C(26)-C(27) | 115.2(4) | N(4)-C(32)-C(33) | 116.1(3) |
| N(3)-C(26)-C(28) | 112.8(3) | N(4)-C(32)-C(34) | 113.2(3) |
| C(27)-C(26)-C(28) | 113.8(3) | C(33)-C(32)-C(34) | 110.6(3) |

## 7.3 Follow-up Work

Work on this project area has been continued by workers in Dr. G. Bertrand's group at the Laboratoire de Chimie de Coordination, CNRS, Toulouse. The 2,4,6-$(CF_3)_3C_6H_2(Ph)P$- nitrile imine system has been further investigated and the area of study has been expanded by the generation of systems incorporating $(C_6F_5)_2P$- and 2,4,6-$(CF_3)_3C_6H_2(C_6F_5)P$- substituents. The diarylchlorophosphine starting materials for this purpose were prepared in Durham as part of this work (see Chapter 3). Here in outline are the results to date.

### 7.3.1 2,4,6-$(CF_3)_3C_6H_2(Ph)(C_6Cl_4O_2)P$-NNC-$P(S)(NPr^i{}_2)_2$

The reactivity of the nitrile imine formed by the addition of TCOQ to 2,4,6--$(CF_3)_3C_6H_2(Ph)(C_6Cl_4O_2)P$-NNC-$P(S)(NPr^i{}_2)_2$ has been studied (see fig. 7.3). Although unreactive towards methanol, as has already been shown, this nitrile imine will react with HCl to form the hydrazonoyl chloride. In a similar way, addition of diisopropylamine produced the hydrazonoyl amide, though unlike the hydrazonoyl chloride this failed to regenerate the nitrile imine by passage over silica gel. This same hydrazonoyl amide was formed when TCOQ was added to the hydrazonoyl chloride formed by the action of the LDA generated lithium salt of H-$C(N_2)$-$P(NPr^i{}_2)_2$ on 2,4,6-$(CF_3)_3C_6H_2(Ph)PCl$. Thus the order of addition of TCOQ and $iPr_2NH$ to the initial P(V)-P(III) substituted nitrile imine is not important.

### 7.3.2 2,4,6-$(CF_3)_3C_6H_2(C_6F_5)PCl$ + Li-$C(N_2)$-$P(S)(NPr^i{}_2)_2$

When the lithium salt of H-$C(N_2)$-$P(S)(NPr^i{}_2)_2$, generated with LDA at -78°C, was reacted with an equimolar amount of the diarylchlorophosphine, 2,4,6-$(CF_3)_3$-

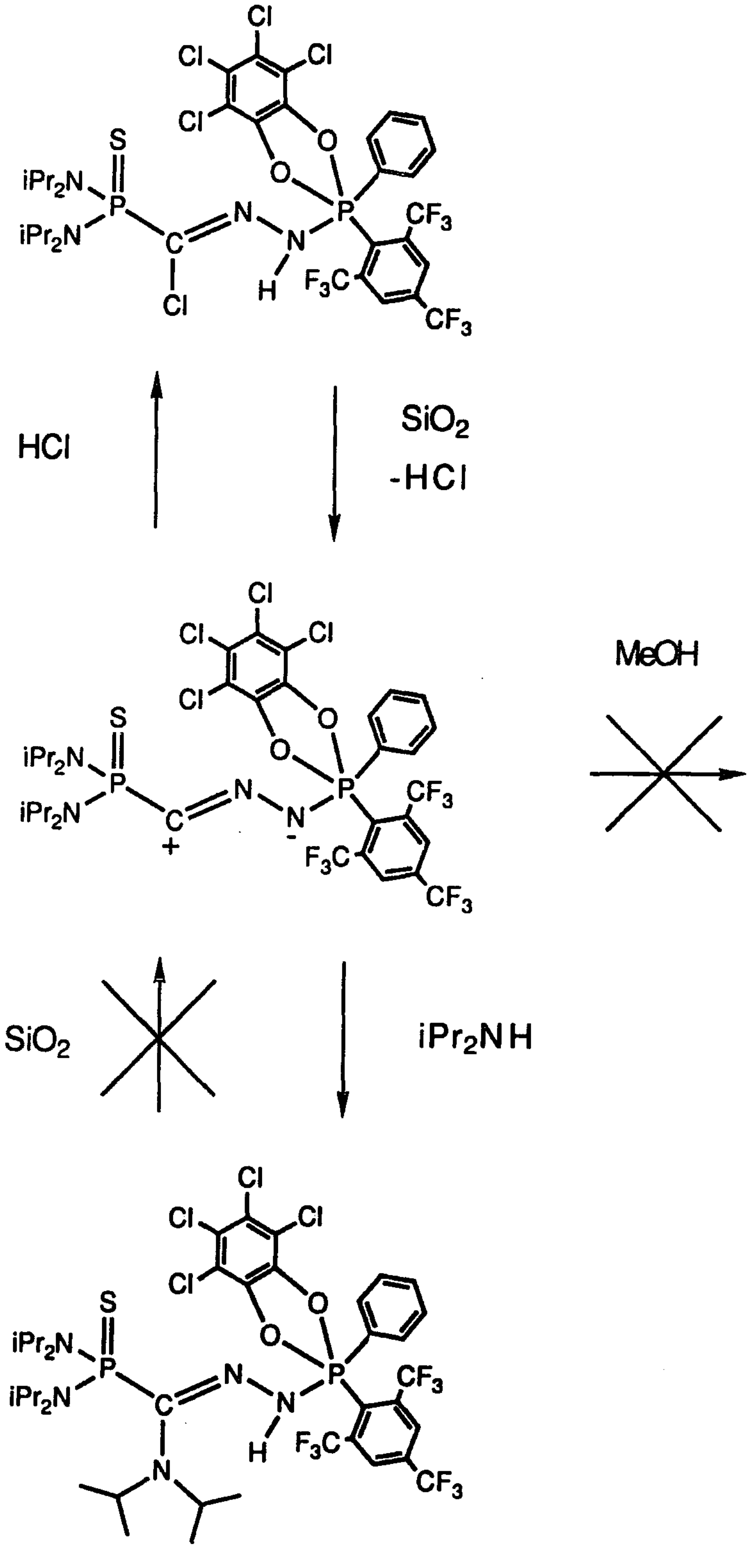
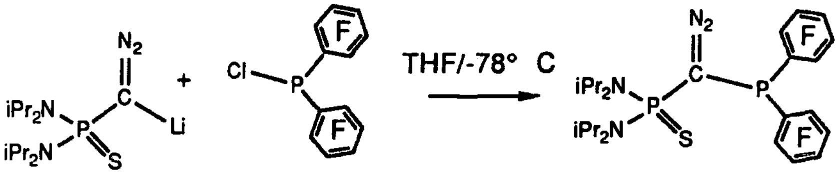


Figure 7.3 — The Chemistry of the P(V) - P(V) nitrile imine.

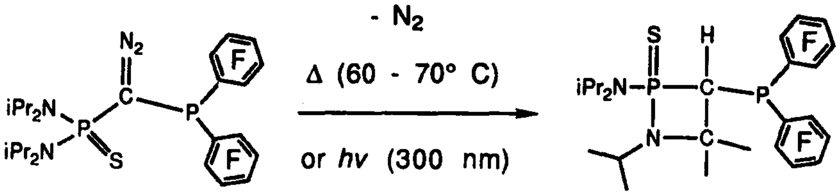
$C_6H_2(C_6F_5)PCl$, the initial product was the nitrile imine. However, replacement of the phenyl group with a pentafluorophenyl group resulted in a relatively less stable nitrile imine being formed, and after a few hours at room temperature there was isomerisation to the diazophosphine. Also, by contrast, trapping of the nitrile imine with TCOQ formed exclusively the oxonium nitrene (see fig. 7.4).

### 7.3.3 $(C_6F_5)_2PCl$ + Li-$C(N_2)$-P(S)$(NPr^i_2)_2$

When the lithium salt of H-$C(N_2)$-P(S)$(NPr^i_2)_2$, generated with LDA at -78°C, was reacted with an equimolar amount of the diarylchlorophosphine, $(C_6F_5)_2PCl$, the product was the diazophosphine, as follows:



When this product was heated or irradiated with ultra violet light there was elimination of nitrogen and insertion of the resultant carbene (attempts to trap this intermediate were unsuccessful) into the isopropyl C-H, bond forming the azathiophosphetane product[28]:



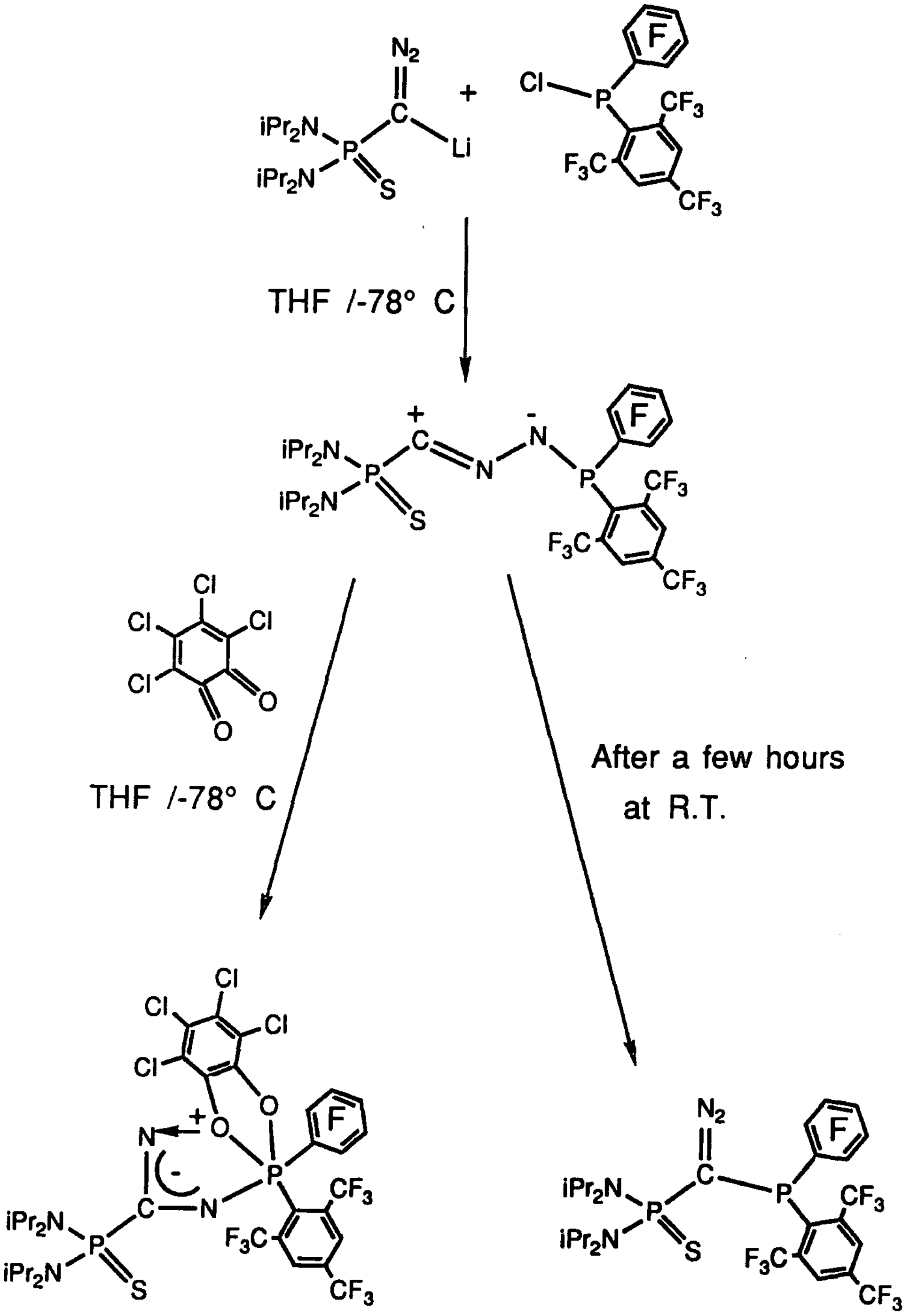


**Figure 7.4** — $(iPr_2N)_2P(S)\text{-}C(N_2)\text{-}Li$ + $2,4,6\text{-}(CF_3)_3C_6H_2(C_6F_5)PCl$

## 7.4 Conclusion

In the light of these results and other recent work in this area[29], one must conclude that, whereas it has been demonstrated that bulky substituents may stabilize phosphinocarbenes[25], electronic factors are also important. Thus the relatively electron-supplying diisopropylamino groups on phosphorus are more effective at helping to stabilize the carbene moiety than the more electronegative 2,4,6-$(CF_3)_3C_6H_2$ group.

With respect to nitrile imine stabilization, it has been shown that steric bulk of substituents is an important factor[18]. However, here again this alone is not the single over-riding influence. As has now been demonstrated for the $(iPr_2)_2P(S)$-CNN-P(R)R' system, R and R' must confer some degree of crowding for the nitrile imine to be stable to rearrangement to the corresponding diazophosphine. Thus, whereas when R = Ph and R' = 2,4,6-$(CF_3)_3C_6H_2$ the nitrile imine is stable, when R = R' = $C_6F_5$ there is no evidence for the nitrile imine and the diazophosphine isomer is formed immediately on preparation of the compound. However, in the case R = $C_6F_5$ and R' = 2,4,6-$(CF_3)_3C_6H_2$, the nitrile imine, although observable, is unstable with respect to its diazo isomer. Hence in the latter case, although the phosphino group has the most bulky overall combination of substituents, a less stable nitrile imine than the R = Ph analogue is formed, due probably to the overall more electro-negative nature of substituents in the phosphino group. This would add weight to the proposal that nitrile imines are best stabilized by having an electron-supplying substituent at one end and a relatively electron-withdrawing group at the other terminus of the -CNN- moiety[18]. This could be further tested by changing the substituents at the carbon end of the nitrile imine, and by investigating the analagous P(III) - P(III) systems.

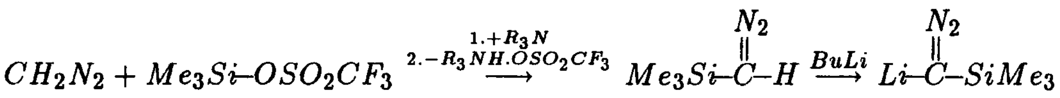
## 7.5 Experimental

### 7.5.1 General Strategy

The diazo systems studied were derived by substitution of diazomethane itself. As $CH_2N_2$ is highly toxic and explosively unstable, the diazal preparation of Hudlicky[30] is the method of choice. By this route diazomethane is never isolated but obtained in ether solution.

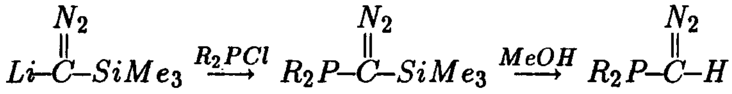
$$p\text{-}tolyl\text{-}SO_2\text{-}N(Me)NO + ROH \xrightarrow{\overset{KOH}{Et_2O}} CH_2N_2 + H_2O + p\text{-}tolyl\text{-}SO_2OR$$

Addition of trimethylsilyltriflate to $CH_2N_2$ in the presence of base then produces trimethylsilyldiazomethane[31], which can then be lithiated by BuLi or LDA at -78°C[32]



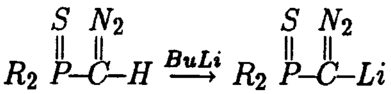
$$CH_2N_2 + Me_3Si\text{-}OSO_2CF_3 \xrightarrow{\overset{1.+R_3N}{2.-R_3NH.OSO_2CF_3}} Me_3Si\text{-}\overset{\overset{N_2}{\|}}{C}\text{-}H \xrightarrow{BuLi} Li\text{-}\overset{\overset{N_2}{\|}}{C}\text{-}SiMe_3$$

When this lithium salt is added to a suitable chlorophosphine the respective trimethylsilyldiazophosphine can be formed[33] and the carbon-silicon bond can be cleaved by methanolysis[18].



$$Li\text{-}\overset{\overset{N_2}{\|}}{C}\text{-}SiMe_3 \xrightarrow{R_2PCl} R_2P\text{-}\overset{\overset{N_2}{\|}}{C}\text{-}SiMe_3 \xrightarrow{MeOH} R_2P\text{-}\overset{\overset{N_2}{\|}}{C}\text{-}H$$

It may then be possible to lithiate the resultant diazophosphine or its thiophosphoranyl derivative (produced by the addition of elemental sulphur), and thereby achieve further substitution of the diazo species[18].



$$R_2\overset{\overset{S}{\|}}{P}-\overset{\overset{N_2}{\|}}{C}-H \xrightarrow{BuLi} R_2\overset{\overset{S}{\|}}{P}-\overset{\overset{N_2}{\|}}{C}-Li$$

Since it is generally known that diazolithium salts react with electrophiles affording substituted diazo derivatives[34], it is of primary interest to have a quick spectroscopic method to differentiate nitrile imines from diazo derivatives. $^{31}$P n.m.r. is a powerful tool when both substituents are phosphorus groups, as P-P coupling constants in diazo compounds ($^2$J) are generally much larger than for nitrile imines ($^4$J). In the infra-red both nitrile imine and diazo groups give strong absorptions in the region 2000 to 2200 cm$^{-1}$. However, the nitrile imine band is generally much broader (see fig. 7.5).

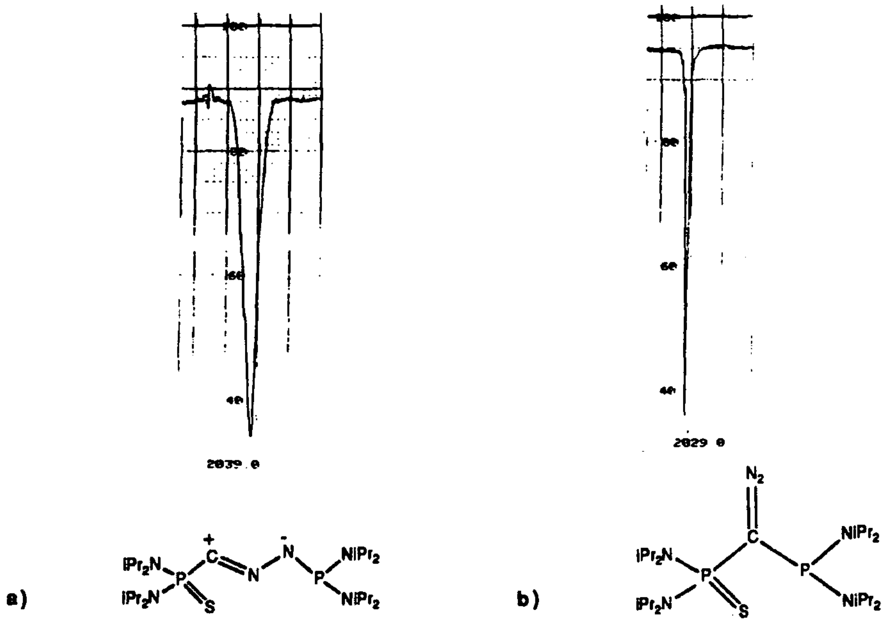
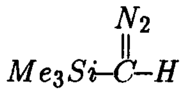


Figure 7.5 — Examples of I.R. Stretching Bands for (a) Nitrile Imine and (b) Diazo.

### 7.5.2 Preparation of Trimethylsilyldiazomethane



$$Me_3Si\text{–}\overset{\overset{N_2}{\|}}{C}\text{–}H$$

To a 250 ml round-bottom flask, mounted with a cold finger, was added 9 g (0.16 mol) of KOH dissolved in 15 ml of water, 52 ml of carbitol and 15 ml of diethyl ether. Whilst stirring the solution at 40°C, diazal, 32 g (0.15 mol) in 200 ml of diethyl ether was added dropwise. The diazomethane formed was condensed in ether solution on the cold finger and collected in a flask containing a few pellets of KOH as a drying agent. This ethereal solution of diazomethane was then transferred via canule and under argon into a 500 ml two-necked flask containing 16 g (0.12 mol) of diisopropylamine. Maintaining the inert atmosphere, the flask was then cooled to -78°C, following which 25 g (0.12 mol) of trimethylsilyl triflate was added, dropwise with stirring. A large amount of white precipitate was formed. The mixture was then allowed to warm to room temperature, upon which the salts were filtered off . The ether was removed by distillation at atmospheric pressure using a 30 cm long Vigreux column. The product was then purified by distillation (Bpt. 70°C, 760 mmHg). Yield 6 g (40 %); I.R. / ($C_6D_6$) 2040 $cm^{-1}$; $\delta$ $^1$H / ($C_6D_6$) = -0.2 ppm ($CH_3$-Si, s, 9 H), 2.1 ppm (CH, s, 1H).

### 7.5.3 Preparation of Bis(diisopropylamino)chlorophosphine

$$(iPr_2N)_2PCl$$

To a two-necked 500 ml round-bottom flask, fitted with reflux condenser, dropping funnel and maintained under argon, was added phosphorus trichloride 9.6 g

(0.062 mol) in toluene (60 ml). Diisopropylamine 39.9 g (0.39 mol) in toluene (20 ml) was then added dropwise, with stirring, via the dropping funnel. The mixture was then allowed to stir for a further 48 hours at 40°C. The reaction was followed by $^{31}P$ n.m.r. , and once finished the $iPr_2NH_2Cl$ salts were filtered off and the solvent removed by evaporation. The residue was recrystallised from acetonitrile, yielding the white solid - Bis(diisopropyl- amino)chlorophosphine. Yield 14.4 g (90 %); Mpt. = 84°C; $\delta$ $^{31}P$ / ($C_6D_6$) = 134 ppm; $\delta$ $^1H$ / ($C_6D_6$) = 1.15 ppm ($CH_3$-C, d 7 Hz, 12 H), 1.18 ppm ($CH_3$-C, d, 7 Hz, 12 H), 3.5 ppm (CH-N, sept., 7 Hz, 4 H).

### 7.5.4 Preperation of $(iPr_2N)_2P$-$C(N_2)$-$SiMe_3$

To a solution of the lithium salt of trimethylsilyldiazomethane (26 mmol) in THF (20 ml) maintained at -78°C was added a solution of bis(diisopropyl- amino)-chlorophosphine (26 mmol) in THF (90 ml). The solution was maintained at -78°C with stirring for 2 hours. After warming to room temperature, the solvents were removed under vacuum. The residue was taken up in pentane and the lithium salts were removed by filtration. The pentane was removed *in vacuo* and the 1'-$\alpha$diazophosphine was obtained in the form of a red oil. Yield 85 %; Bpt. 80 - 90°C, 0.01 mmHg; I.R. / ($C_6D_6$) 2010 $cm^{-1}$; $\delta$ $^{31}P$ / ($C_6D_6$) = 56 ppm; $\delta$ $^1H$ / ($C_6H_6$) = 0.2 ppm ($CH_3$-Si, s, 9 H), 1.1 ppm ($CH_3$-C, d, 7 Hz, 12 H), 1.15 ppm ($CH_3$-C, d, 7 Hz, 12 H), 3.3 ppm (CH-N, sept, 7 Hz, 4 H); m/e 344 ($M^+$).

### 7.5.5 Preparation of $(iPr_2N)_2P$-$C(N_2)$-H

To a THF solution of $(iPr_2N)_2P$-$C(N_2)$-$SiMe_3$ was added a ten-fold molar excess of methanol. The reaction mixture was allowed to stir for approximately 20 minutes at room temperature. The reaction was followed by $^{31}P$ n.m.r. , and as soon as methanolysis of the trimethylsilyl starting material was complete the solvent and excess methanol were removed under vacuum. In this way the product diazophosphine is produced in almost quantitative yield, in the form of a red oil. I.R. / ($C_6D_6$) 2050 $cm^{-1}$; $\delta$ $^{31}P$ / ($C_6D_6$) = 48 ppm; $\delta$ $^1H$ / ($C_6H_6$) 0.95 ppm ($CH_3$-C, d, 7 Hz, 12 H), 1.05 ppm ($CH_3$-C, d, 7 Hz, 12 H), 2.7 ppm ($C(N)_2$-H, d, 20 Hz, 1 H), 3.2 ppm (CH-N, sept, 7 Hz, 4 H); m/e 272 ($M^+$).

### 7.5.6 Preparation of $(iPr_2N)_2P(S)$-$C(N_2)$-H

To a pentane solution (30 ml) of $(iPr_2N)_2P$-$C(N_2)$-H 2.7 g (10 mmol) was added a slight molar excess of elemental sulphur. After standing overnight at room temperature, the mixture was filtered and the product was isolated by column chromatography (pentane / ether 90/10 $R_f$ = 0.5), as yellow crystals, 2.89 g (95 % yield); Mpt. 80 - 82°C; $\delta$ $^{31}P$ / ($CDCl_3$) = 57.6 ppm; $\delta$ $^1H$ / ($CDCl_3$) = 1.20 ppm ($CH_3$-C, d, 6.9 Hz, 12 H), 1.31 ppm ($CH_3$-C, d, 6.9 Hz, 12 H), 3.62 ppm (CH-N, sept d, 6.9 Hz, 19 Hz, 4 H), 3.86 ppm ($C(N)_2$-H, d, 10.6 Hz, 1 H); m/e 304 ($M^+$).

### 7.5.7 Preparation of TMP-$PCl_2$

(TMP = 2,2,6,6-tetramethylpiperidyl)

To a 50 ml three-necked flask fitted with reflux condenser, stirrer and dropping funnel was added a freshly prepared solution of lithium 2,2,6,6-tetramethylpiperidine 6.26 g (0.043 mol), in hexane (20 ml) and under an atmosphere of dry nitrogen. Phosphorus trichloride (0.043 mol) in hexane (10 ml) was then added dropwise with stirring over one hour. The mixture was allowed to stir for a further two hours before filtering to remove lithium salts. The solvent was then removed under vacuum and the product, a pale yellow solid, purified by sublimation (78°C, 2 mmHg). yield 6 g (58 %); Mpt. 62°C; $\delta$ $^{31}P$ / ($CDCl_3$) = 164 ppm; $\delta$ $^{1}H$ / ($CDCl_3$) = 1.48 ppm (d, 3.3 Hz, 12 H), 1.25 (m, 6 H).

### 7.5.8 Preparation of $2,4,6\text{-}(CF_3)_3C_6H_2\text{-}P(NMe_2)Cl$

To a solution of dimethylaminodichlorophosphine 2.6 g (17.8 mmol) in ether (20 ml), stirred in a 100 ml two-necked flask under nitrogen and at room temperature, was added (via canule) an ether/hexane solution containing 17.7 mmol of 2,4,6-tris(trifluoromethyl)phenyllithium. The reaction mixture was then allowed to stir for a further 1 hour at room temperature before being filtered to remove lithium salts. The solvents were then removed under reduced pressure and the product was purified by vacuum distillation, giving a yellow oil, 2.3 g (33 %); Bpt. 80°C 0.06 mmHg; $\delta$ $^{31}P$ / ($CDCl_3$) = 134.7 ppm (sept., $J_{PF}$ = 36 Hz).

### 7.5.9 Preparation of $2,4,6\text{-}(CF_3)_3C_6H_2\text{-}P(NPr^i_2)Cl$

To a solution of diisopropylaminodichlorophosphine 2.35 g (11.6 mmol) in ether (20 ml), stirred in a 100 ml two-necked flask under nitrogen and at room temperature, was added (via canule) an ether/hexane solution containing 11.6 mmol of 2,4,6-tris(trifluoromethyl)phenyllithium. The reaction mixture was then allowed to stir for a further 1 hour at room temperature before being filtered to remove lithium salts. The solvents were then removed under reduced pressure and the product was purified by vacuum distillation, giving a yellow oil, 1.6 g (31 %); Bpt. 90°C 0.1 mmHg; $\delta$ $^{31}P$ / ($CDCl_3$) = 121.0 ppm (sept., $J_{PF}$ = 44 Hz).

### 7.5.10 Preparation of 2,4,6-$(CF_3)_3C_6H_2P(NMe_2)$-$C(N_2)$-$SiMe_3$

To a 100 ml Schlenk containing trimethylsilyldiazomethane 0.3 g (2.6 mmol) in THF (20 ml), and maintained under nitrogen at -78°C, was added 2.6 ml of a 1 M solution of LDA in THF. The mixture was allowed to stir for a further 30 minutes before the dropwise addition of 2,4,6-$(CF_3)_3C_6H_2P(NMe_2)Cl$ 1.0 g (2.6 mmol) in THF (5 ml). The reaction mixture was then allowed to warm slowly to room temperature. The THF was removed under vacuum and toluene (20 ml) was added. The mixture was then filtered under nitrogen to remove lithium salts and the toluene taken off *in vacuo* , leaving a brown oil 0.9 g (74 %). $\delta$ $^{31}$P / (toluene) = 63.8 ppm ($J_{PF}$ = 35 Hz); I.R. 2060 cm$^{-1}$. Attempts to purify further the diazophosphine by distillation led to its decomposition and the formation of complex polymeric material.

### 7.5.11 Preparation of Ar(Ph)P-N(H)-N=C($Pr^i_2$N)-P(S)($NPr^i_2$)$_2$

(Ar = 2,4,6-$(CF_3)_3C_6H_2$)

To a solution containing 3.29 mmol of the lithium salt of [Bis(diisopropylamino)thiophosphino]diazomethane, prepared with LDA in THF (10 ml) at -78°C and maintained under an atmosphere of dry nitrogen, was added 2,4,6-$(CF_3)_3C_6H_2$-(Ph)PCl 1.4 g (3.3 mmol) in THF (10 ml). The mixture was allowed to stir at -78°C for 30 minutes before gradually warming to room temperature. The mixture was then stirred at room temperature for a further 2 days, (during which time the nitrile imine initially formed reacted with the liberated diisopropylamine), after which the THF was removed under vacuum and pentane (30 ml) was added. The mixture was then filtered to remove lithium salts and the pentane was removed *in vacuo* , leaving a brown residue. The product was purified by column chromatography over silica gel (hexane/ether 90/10, $R_f$ = 0.75) to yield a viscous yellow oil (0.3 g, 11.5 %). $\delta$ $^{31}P$ / (THF) = 67.8 ppm (s, >P(S)-), 39.9 ppm (sept, $J_{PF}$ =45 Hz, >P-); $\delta$ $^{1}H$ / ($CDCl_3$) = 1.06 ppm ($CH_3$-C, d, 7.0 Hz, 6 H), 1.21 ppm ($CH_3$-C, d, 7.0 Hz, 6 H), 1.34 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 1.38 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 1.40 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 1.41 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 3.66 ppm (CH-N, d, 6.8 Hz, 2 H), 4.05 ppm (CH-N, sept d, 6.8 Hz, 13.8 Hz, 2 H), 4.12 ppm (CH-N, sept d, 7.0 Hz, 13.8 Hz, 2 H), 7.12 - 7.32 ppm (aromatic C-H, m, 5 H), 7.97 ppm (NH, d, 11.8 Hz, 1 H), 8.19 ppm ($(CF_3)_3C_6H_2$, s, 2 H); $\delta$ $^{13}C$ /($CDCl_3$) = 21.56, 21.62, 22.68, 22.73, 23.54, 23.63, 23.73, 23.79, 24.15, 24.12 ppm ($CH_3$-C, s, 12 C), 46.90 ppm (CH-N, d, $J_{CP}$ =5.9 Hz, 2 C), 47.02 ppm (CH-N, d, $J_{CP}$ =6.0 Hz, 2 C), 49.45 ppm (CH-N, s, 2 C), 119.54 - 145.91 ppm (overlapping $CF_3$ / aromatic C signals), 149.59 ppm (>C=N-, d d, $J_{CP}$ = 167.0 Hz, 20.8 Hz).

### 7.5.12 TCOQ + 2,4,6-$(CF_3)_3C_6H_2$(Ph)P-NNC-P(S)$(NPr^i_2)_2$

*Isolation and characterisation of the products from this reaction were carried out by F. Castan, L.C.C., C.N.R.S., Toulouse.*

To a solution containing 3.29 mmol of the lithium salt of [bis(diisopropylamino)thiophosphino]diazomethane, prepared with butyllithium hexane / THF (10 ml) at -78°C and maintained under an atmosphere of dry nitrogen, was added 2,4,6-$(CF_3)_3C_6H_2$(Ph)PCl 1.4 g (3.3 mmol) in THF (10 ml). The mixture was allowed to stir at -78°C for 30 minutes before gradually warming to room temperature. The mixture was then cooled to 0°C before adding tetrachloroorthoquinone 1.08 g (4.4 mmol) in THF (10 ml). The solvents were then removed *in vacuo* and pentane (30 ml) added. The mixture was slowly filtered through silica gel to remove lithium salts and convert any hydrazonoyl chloride back to the nitrile imine. The nitrile imine and oxonium nitrene were then separated by column chromatography over silica gel (hexane / ether 95 / 5). The hydrazonoyl chloride was prepared by treating a small quantity of the nitrile imine with HCl in ether at room temperature. A small quantity of each product was then recrystallised from pentane / acetonitrile and characterised as follows: Nitrile imine (80 % of overall yield) white solid (Mpt. = 166.8°C); $R_f$ = 0.34 (hexane / ether 95 / 5); $\delta$ $^{31}$P /(THF) = 27.8 ppm (>P(S)-, d, $J_{PP}$ = 8.6 Hz), -24.4 ppm (P(V), d, $J_{PP}$ = 8.6 Hz); $\delta$ $^{1}$H /($CDCl_3$) = 1.26 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 1.38 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 1.40 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 1.41 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 3.74 ppm (CH-N, sept d, 20.7 Hz, 6.8 Hz, 2 H), 3.75 ppm (CH-N, sept d, 20.7 Hz, 6.8 Hz, 2 H), 7.37 - 7.80 ppm (aromatic H, m, 5 H), 8.07 ppm ($(CF_3)_3C_6H_2$, d, 3.7 Hz, 2 H); $\delta$ $^{13}$C /($CDCl_3$) = 22.11, 22.15, 22.39, 22.45, 22.75, ($CH_3$-C, s, 8 C), 46.88 ppm (CH-N, d, $J_{CP}$ =5.8 Hz, 2 C), 47.28 ppm (CH-N, d, $J_{CP}$ =5.6 Hz, 2 C), 65.53 ppm (-CNN-, d, $J_{CP}$ = 133.7 Hz, 1 C), 112.33 - 154.10 ppm (overlapping $CF_3$ / aromatic C signals); m/e = 939 (major peak of $M^+$ isotope envelope); I.R. (KBr disc) 2162 $cm^{-1}$.

Oxonium nitrene (20 % of overall yield) white crystals (Mpt. = 268.5°C); $R_f$ = 0.60 (hexane / ether 95 / 5); $\delta$ $^{31}$P /(THF) = 48.4 ppm (>P(S)-, d, $J_{PP}$ = 5.1 Hz), -32.1 ppm (P(V), d, $J_{PP}$ = 5.1 Hz); $\delta$ $^{1}$H /($CDCl_3$) = 1.04 ppm ($CH_3$-C, d, 6.7 Hz, 6 H), 1.33 ppm ($CH_3$-C, d, 6.7 Hz, 6 H), 1.42 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 1.48 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 3.56 ppm (CH-N, sept d, 17.5 Hz, 6.7 Hz, 2 H), 3.79 ppm (CH-N, sept d, 19.0 Hz, 6.8 Hz, 2 H), 7.37 - 8.55 ppm (aromatic H, m, 7 H), m/e = 939 (major peak of $M^+$ isotope envelope); I.R. (KBr disc) no characteristic band.

Hydrazonoyl chloride: white crystals (see above for X-ray structure); Mpt. = 169.1°C; $\delta$ $^{31}$P /(THF) = 61.0 ppm (>P(S)-, d, $J_{PP}$ = 4.7 Hz), -22.9 ppm (P(V), d, $J_{PP}$ = 4.7 Hz); $\delta$ $^{1}$H /($CDCl_3$) = 1.22 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 1.30 ppm ($CH_3$-C, d, 6.9 Hz, 6 H), 1.31 ppm ($CH_3$-C, d, 6.8 Hz, 6 H), 1.32 ppm ($CH_3$-C, d, 6.9 Hz, 6 H), 3.72 ppm (CH-N, sept d, 16.6 Hz, 6.8 Hz, 2 H), 3.75 ppm (CH-N, sept d, 13.4 Hz, 6.9 Hz, 2 H), 7.40 - 7.78 ppm (aromatic H, m, 5 H), 7.71 (NH, d, 28.9 Hz, 1 H), 8.10 ppm ($(CF_3)_3C_6H_2$, s, 2 H); $\delta$ $^{13}$C /($CDCl_3$) = 23.15, 23.19, 23.41, 23.46, 23.75, 23.81, 23.98, 24.06 ($CH_3$-C, s), 47.65 ppm (CH-N, d, $J_{CP}$ =5.3 Hz), 113.82 - 140.78 ppm (overlapping $CF_3$ / aromatic C signals), 147.19 ppm (>C=N-, d, $J_{CP}$ = 137.1 Hz); m/e = 939 (major peak of [$M^+$ - Cl] isotope envelope); I.R. (KBr disc) 3305.0 cm$^{-1}$ (NH).

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# Appendix A

# Lectures, Seminars & Colloquia

## A.1 Lectures by Invited Speakers

### A.1.1 1st August 1987 to 31st July 1988

**Birchall,** Prof. D. (I. C. I. Advanced Materials)

Environmental Chemistry of Aluminium 25th April 1988

**Borer,** Dr. K. (University of Durham Industrial Research Labs.)

The Brighton Bomb - A Forensic Science View 18th February 1988

***Butler,** Dr. A. R. (University of St. Andrews)

Chinese Alchemy 5th November 1987

**Cairns-Smith,** Dr. A. (Glasgow University)

Clay Minerals and the Origin of Life 28th January 1988

**Davidson,** Dr. J. (Herriot-Watt University)

Metal Promoted Oligomerisation Reactions of Alkynes November 1987

***Graduate Chemists,** (Northeast Polytechnics and Universities)

R. S. C. Graduate Symposium 19th April 1988

**Graham,** Prof. W. A. G. (University of Alberta, Canada)

Rhodium and Iridium Complexes in the Activation of Carbon-Hydrogen Bonds 3rd March 1988

**Gray,** Prof. G. W. (University of Hull)

Liquid Crystals and their Applications 22nd October 1987

**Hartshorn,** Prof. M. P. (University of Canterbury, New Zealand)

Aspects of Ipso-Nitration 7th April 1988

**Howard,** Dr. J. (I. C. I. Wilton)

Chemistry of Non-Equilibrium Processes 3rd December 1987

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|---|---|
| **Koch,** Prof. H. F. (Ithaca College, U. S. A.) | |
| Does the E2 Mechanism Occur in Solution? | 7th March 1988 |
| ***Ludman,** Dr. C. J. (Durham University) | |
| Explosives | 10th December 1987 |
| **McDonald,** Dr. W. A. (I. C. I. Wilton) | |
| Liquid Crystal Polymers | 11th May 1988 |
| ***Majoral,** J.-P. (Université Paul Sabatier) | |
| Stabilisation by Complexation of Short-Lived Phosphorus Species | 8th June 1988 |
| **Nieto de Castro,** Prof. C. A. (University of Lisbon and Imperial College) | |
| Transport Properties of Non-Polar Fluids | 18th April 1988 |
| **Olah,** Prof. G. A. (University of Southern California) | |
| New Aspects of Hydrocarbon Chemistry | 29th June 1988 |
| ***Palmer,** Dr. F. (University of Nottingham) | |
| Luminescence (Demonstration Lecture) | 21st January 1988 |
| **Pines,** Prof. A. (University of California, Berkeley, U. S. A.) | |
| Some Magnetic Moments | 28th April 1988 |
| **Richardson,** Dr. R. (University of Bristol) | |
| X-Ray Diffraction from Spread Monolayers | 27th April 1988 |
| **Robinson,** Dr. J. A. (University of Southampton) | |
| Aspects of Antibiotic Biosynthesis | 27th April 1988 |
| ***Rose,** van Mrs. S. (Geological Museum) | |
| Chemistry of Volcanoes | 29th October 1987 |
| **Sammes,** Prof. P. G. (Smith, Kline and French) | |
| Chemical Aspects of Drug Development | 19th December 1987 |
| **Seebach,** Prof. D. (E. T. H. Zurich) | |
| From Synthetic Methods to Mechanistic Insight | 12th November 1987 |
| **Swart,** Mr. R. M. (I. C. I) | |
| The Interaction of Chemicals with Lipid Bilayers | 16th December 1987 |

**Turner,** Prof. J. J. (University of Nottingham)

Catching Organometallic Intermediates 11th February 1988

**Underhill,** Prof. A. (University of Bangor)

Molecular Electronics 25th February 1988

**Williams,** Dr. D. H. (University of Cambridge)

Molecular Recognition 26th November 1987

***Winter,** Dr. M. J. (University of Sheffield)

Pyrotechnics (Demonstration Lecture) 15th October 1987

### A.1.2 1st August 1988 to 31st July 1989

**Aveyard,** Dr. R. (University of Hull)

Surfactants at your Surface 15th March 1989

**Aylett,** Prof. B. J. (Queen Mary College, London)

Silicon-Based Chips: The Chemist's Contribution 16th February 1989

***Baldwin,** Prof. J. E. (Oxford University)

Recent Advances in the Bioorganic Chemistry of
Penicillin Biosynthesis 9th February 1989

**Baldwin & Walker,** Drs. R. R. & R.W. (Hull University)

Combustion: Some Burning Problems 24th November 1988

**Butler,** Dr. A. R. (St. Andrews University)

Cancer in Linxiam: The Chemical Dimension 15th February 1989

***Cadogan,** Prof. J. I. G. (British Petroleum)

From Pure Science to Profit 10th November1988

**Casey,** Dr. M. (University of Salford)

Sulphoxides in Stereoselective Synthesis 20th April 1989

**Crich,** Dr. D. (University College London)

Some Novel Uses of Free Radicals in Organic Synthesis 27th April 1989

**Dingwall,** Dr. J. (Ciba Geigy)

Phosphorus-Containing Amono Acids: Biologically
Active Natural and Unnatural Products 18 October 1988

**Errington,** Dr. R. J. (University of Newcastle-upon-Tyne)
Polymetalate Assembly in Organic Solvents 1st March 1989

**Frey,** Dr. J. (Southampton University)
Spectroscopy of the Reaction Path:
Photodissociation Raman Spectra of NOCl 11th May 1989

***Graduate Chemists,** (Polytechs and Universities in North East England)
R. S. C. Symposium for the presentation of papers
by postgraduate students 12th April 1989

***Hall,** Prof. L. D. (Addenbrooke's Hospital, Cambridge)
NMR - Window to the Human Body 2nd February 1989

**Hardgrove,** Dr. G. (St. Olaf Collage, U. S. A.)
Polymers in the Physical Chemistry Laboratory December 1988

**Harwood,** Dr. L. (Oxford University)
Synthetic Approaches to Phorbols Via Intramolecular
Furan Diels-Alder Reactions: Chemistry under Pressure 25th January 1989

**Jäger,** Dr. C. (Friedrich-Schiller University GDR)
NMR Investigations of Fast Ion Conductors of the
NASICON Type 9th December 1988

***Jennings,** Prof. R. R. (Warwick University)
Chemistry of the Masses 26th January 1989

**Johnson,** Dr. B. F. G. (Cambridge University)
The Binary Carbonyls 23rd February 1989

**Ludman,** Dr. C. J. (Durham University)
The Energetics of Explosives 18th October 1988

**MacDougal,** Dr. G. (Edinburgh University)
Vibrational Spectroscopy of Model Catalytic Systems 22nd February 1989

**Marko,** Dr. I. (Sheffield University)

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|---|---|
| Catalytic Asymmetric Osmylation of Olefins | 9th March 1989 |
| **McLauchlan,** Dr. K. A. (University of Oxford) | |
| The Effect of Magnetic Fields on Chemical Reactions | 16th November 1988 |
| **Moody,** Dr. C. J. (Imperial College) | |
| Reactive Intermediates in Heterocyclic Systems | 17th May 1989 |
| **Paetzold,** Prof. P. (Aachen) | |
| Iminoboranes XB≡NR - Inorganic Acetylenes? | 23rd May 1989 |
| **Page,** Dr. P. C. B. (University of Liverpool) | |
| Stereocontrol of Organic Reactions Using 1,3-dithiane-1-oxides | 3rd May 1989 |
| **Pola,** Prof. J. (Czechoslovak Academy of Sciences) | |
| Carbon Dioxide Laser Induced Chemical Reactions - New Pathways in Gas-Phase Chemistry | 15th June 1989 |
| **Rees,** Prof. C. W. (Imperial College London) | |
| Some Very Heterocyclic Compounds | 27th October 1988 |
| ***Schmutzler,** Prof. R. (Technische Universitat Braunschweig) | |
| Fluorophosphines Revisited - New Contributions to an Old Theme | 6th October 1988 |
| **Schrock,** Prof. R. R. (M. I. T.) | |
| Recent Advances in Living Metathesis | 13th February 1989 |
| **Singh,** Dr. G. (Teeside Polytechnic) | |
| Towards Third Generation Anti-Leukaemics | 9th November 1988 |
| **Snaith,** Dr. R. (Cambridge University) | |
| Egyptian Mummies: What, Where, Why and How? | 1st December 1988 |
| **Stibr,** Dr. R. (Czechoslovak Academy of Sciences) | |
| Recent Developments in the Chemistry of Intermediate Sited Carboranes | 16th May 1989 |
| **Von Rague Schleyer,** Prof. P. (Universitat Erlangen Nurnberg) | |
| The Fruitful Interplay Between Calculational and Experimental Chemistry | 21st October 1988 |

**Wells,** Prof. P. B. (Hull University)

Catalyst Characterisation and Activity 10th May 1989

### A.1.3 1st August 1989 to 31st July 1990

**Badyal,** Dr. J. P. S. (Durham University)

Breakthroughs in Heterogeneous Catalysis 1st November 1989

**Becher,** Dr. J. (Odense University)

Synthesis of New Macrocyclic Systems using Heterocyclic Building Blocks 13th November 1989

**Bercaw,** Prof. J. E. (California Institute of Technology)

Synthetic and Mechanistic Approaches to Ziegler-natta Polymerization of Olefins 10th December 1989

**Bleasdale,** Dr. C. (Newcastle University)

The Mode of Action of Some Anti-tumor Agents 21st february 1989

**Bowman,** Prof. J. M. (Emory University)

Fitting Experiment with Theory in Ar-OH 23rd March 1990

**Butler,** Dr. A. (St. Andrews University)

The Discovery of Penicillin: Facts and Fancies 7th December 1989

**Cheetham,** Dr. A. K. (Oxford University)

Chemistry of Zeolite Cages 8th March 1990

**Clark,** Prof. D. T, (I. C. I. Wilton)

Spatially Resolved Chemistry (using Nature's Paradigm in the Advanced Materials Arena) 22nd February 1990

**Cole-Hamilton,** Prof. D. J. (St. Andrews University)

New Polymers from Homogeneous Catalysts 29th November 1989

**Crombie,** Prof. L. (Nottingham University)

The Chemistry of Cannabis and Khat 15th February 1990

**Dyer,** Dr. U. (Glaxo)

Synthesis and Conformation of C-Glycosides 31st January

**Floriani,** Prof. C. (University of Lausanne, Switzerland)

Molecular Aggregates - A Bridge between
Homogeneous and Heterogeneous Systems 25th October 1989

**German,** Prof. L. S. (USSR Academy of Sciences, Moscow)

New Syntheses in Fluoroaliphatic Chemistry:
Recent Advances in the Chemistry of Fluorinated Oxiranes 9th July 1990

**Graham,** Dr. D. (B. P. Research Centre)

How Proteins Absorb to Interfaces 4th December 1989

**Greenwood,** Prof. N. N. (University of Leeds)

Novel Cluster Geometries in Metalloborane Chemistry 9th December

**Holloway,** Prof. J. H. (University of Leicester)

Noble Gas Chemistry 1st February 1990

**Hughes,** Dr. M. N. (King's College, London)

A Bug's Eye View of the Periodic Table 30th November 1989

**Huisgen,** Prof. R. (Universität München)

Recent Mechanistic Studies of [2+2] Additions 15th December 1989

**Klinowski,** Dr. J. (Cambridge University)

Solid State NMR Studies of Zeolite Catalysts 13th December 1989

**Lancaster,** Rev. R. (Kimbolton Fireworks)

Fireworks - Principles and Practice 8th February 1990

**Lunazzi,** Prof. L. (University of Bologna)

Application of Dynamic NMR to the Study of
Coformational Enantiomerism 12th February 1990

**Palmer,** Dr. F. (Nottingham University)

Thunder and Lightning 17th October 1989

***Parker,** Dr. D. (Durham University)

Macrocycles, Drugs and Rock 'n' Roll 16th November 1989

**Perutz,** Dr. R. N. (York University)

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|---|---|
| Plotting the Course of C-H Activations with Organometallics | 24th January 1990 |
| **Platonov,** Prof. V. E. (USSR Academy of Sciences - Novosibirsk) | |
| Polyfluoroindanes: Synthesis and Transformation | 9th July 1990 |
| **Powell,** Dr. R. L. (I. C. I.) | |
| The Development of CFC Replacements | 6th December 1989 |
| **Powis,** Dr. I. (Nottingham University) | |
| Spinning off in a huff: Photodissociation of Methyl Iodide | 21st March 1990 |
| **Rozhkov,** Prof. I. N. (USSR Academy of Sciences, Moscow) | |
| Reactivity of Perfluoroalkyl Bromides | 9th July 1990 |
| **Stoddart,** Dr. J. F. (Sheffield University) | |
| Molecular Lego | 1st March 1990 |
| **Sutton,** Prof. D. (Simon Fraser University, Vancouver BC) | |
| Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium | 14th February 1990 |
| **Thomas,** Dr. R. K. (Oxford University) | |
| Neutron Reflectometry from Surfaces | 28th February 1990 |
| **Thompson,** Dr. D. P. (Newcastle University) | |
| The role of Nitrogen in Extending Silicate Crystal Chemistry | 7th February 1990 |

(* Lecture attended by auther).

## A.2 First Year Induction Course - 1987

This course consisted of a series of one hour lectures on the services available in the department.

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|---|---|
| Departmental Organisation | Dr. E. F. J. Ross |
| Safety Matters | Dr. M. R. Crampton |
| Electrical Appliances | Mr. B. T. Barker |
| Chromatography and Microanalysis | Mr. T. F. Holmes |
| Atomic Absorption and Inorganic Analysis | Mr. R. Coult |
| Library Facilities | Mr. R. B. Woodward |
| Mass Spectrometry | Dr. M. R. Jones |
| Nuclear Magnetic Resonance Spectroscopy | Dr. R. S. Matthews |
| Glass Blowing Techniques | Mr. R. Hart & Mr G. Haswell |

## A.3 Publication of this Work

Aspects of the work in this thesis have been formally presented as follows:

- **Poster** - *"Polyfluoroaryl Ligands as Stabilisers for Low Coordinated States of Main Group Elements"*, K. B. Dillon*, H. P. Goodwin, T. A. Straw and R. D. Chambers. **PSIBLOCS Conference, Paris - Palaiseau** (August 1988).
- **Poster** - *"Structures of Aryl-chlorophosphoranes"*, R. D. Chambers, K. B. Dillon and T. A. Straw*, **ICI Poster Session** (December 1989).
- **Lecture Tour** - *"Effects of Bulky Ligands on the Stability of some Main Group Species"*, K. B. Dillon*, H. P. Goodwin, T. A. Straw and R. D. Chambers, (given by K. B. Dillon in the Universities of Bielefeld, Braunschweig, Göttingen, München and Kaiserslautern, 1989).
- **Communication** -*Synthesis and Structure of the Phosphorane* $P(CH_2Cl)Cl_4$" K. B. Dillon* and T. A. Straw, *J. Chem. Soc., Chem. Commun.* (1990) in press.
- **Communication** - *"Title to be arranged"*, R. D. Chambers*, K. B. Dillon*, I. Gosney and T. A. Straw, submitted to *J. Fluorine Chem.* (December 1991).