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NEW AND UNUSUAL CO-ORDINATION OF MAIN GROUP ELEMENTS

by

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University of Durham

A Thesis submitted in part fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Durham.

February 1990
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DECLARATION

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham between October 1986 and October 1989. All the work is my own, unless stated to the contrary, and it has not been submitted previously for a degree at this or any other University.

(The part of the work carried out in Toulouse was with official permission.)
To Mum and Dad.
ACKNOWLEDGEMENTS

I would like to thank Dr. K.B. Dillon, for his continual help and encouragement, and Professor R.D. Chambers for his ideas and interest in this work. I would also like to express my thanks to Dr. R. Matthews and J. Banks for NMR data and allowing my access to the NMR facilities. Thank you to Dr. M. Jones and V. McNeill for mass spectra, and B. Coul and M. Cox for elemental analyses.

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ABSTRACT

NEW AND UNUSUAL CO-ORDINATION OF MAIN GROUP ELEMENTS.

There is considerable current interest in the chemistry of low coordinate main group elements, the extensive development of which was highlighted at last year's Eucem Conference Psiblocs in Paris-Palaiseau (August 1988).

This area has been stimulated by the isolation of low coordination compounds stabilised by the use of bulky groups, for example, Supermes, mes (see Chapters 3 and 4).

Following the synthesis of 1,3,5 tris-trifluoromethyl benzene (ArH) by R.D. Chambers et al. (Chapter 1), and the facilities available to synthesise this material it seemed very worthwhile to study the influence of this substituent on low coordinate main group species.

As a result, this group has been incorporated into phosphines, diphosphenes, phosphaalkenes, antimony and boron derivatives. Its involvement in other systems, for example borinium and phosphoranide species, and its incorporation into the cation associated with halo and pseudohalo borate anions, have also been examined. In particular, the low coordination chemistry of phosphorus has involved the synthesis, isolation and full characterisation of the new diphosphene (19) [prepared independently by Edelmann et al.]† and the unsymmetrical diphosphene (20) (Figure C1). The 2,6-bis(trifluoromethylphenyl) substituent has been employed by Escudie et al.‡

![Figure C1](image)

**Figure C1:** The Ar-substituted symmetrical and unsymmetrical diphosphenes.


The formation of the species ArP=PMes (21) and ArP=PNiPr₂ (22) [where Ar = (CF₃)₃C₆H₂], in solution has been demonstrated by NMR.

The first phosphaalkene containing the Aryl group on phosphorus stable to vacuum distillation has been prepared i.e. ArP=C(Cl)₂ (31) and a synthetic route to other phosphaalkenes containing the Ar group has been elucidated (Chapter 4). Where appropriate, the structure, characteristics of stabilisation, spectroscopic parameters and transition-metal coordination have been critically examined.

The first nitrileimines containing boron with phosphorus and silicon respectively were synthesised (Chapter 11). Their reactivity was studied, including their use as synthons for heterocycles, and their rearrangement by photolysis to new carbodiimides.

In view of the wide range of studies included it was decided to present the various aspects as separate chapters. The references are given at the end of each chapter. Experimental details and suggestions for further work are also provided within the appropriate chapters.

Helen Goodwin (February 1990)
ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>Ar</td>
<td>2,4,6-Tris(trifluoromethyl)phenyl</td>
</tr>
<tr>
<td>Ar'</td>
<td>2,6-Bis(trifluoromethyl)phenyl</td>
</tr>
<tr>
<td>Ar&quot;</td>
<td>2-Trifluoromethylphenyl</td>
</tr>
<tr>
<td>Mes</td>
<td>2,4,6-Tri-(methyl)phenyl</td>
</tr>
<tr>
<td>Supermes</td>
<td>2,4,6-Tri-(t-butyl)phenyl</td>
</tr>
<tr>
<td>tmp</td>
<td>Tetramethyipiperidine</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TCOQ</td>
<td>Tetrachloroorthoquinone</td>
</tr>
<tr>
<td>DBU</td>
<td>![DBU structure]</td>
</tr>
<tr>
<td>DABCO</td>
<td>![DABCO structure]</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>MNDO</td>
<td>Modified Neglect of Diatomic Overlap</td>
</tr>
<tr>
<td>AM1</td>
<td>Austin Model 1</td>
</tr>
<tr>
<td>LDA</td>
<td>Lithium diisopropylamide</td>
</tr>
<tr>
<td>UHF</td>
<td>Unrestricted Hartree-Fock</td>
</tr>
<tr>
<td>RHF</td>
<td>Restricted Hartree-Fock</td>
</tr>
<tr>
<td>NI</td>
<td>Nitrileimine</td>
</tr>
<tr>
<td>CD</td>
<td>Carbodiimide</td>
</tr>
<tr>
<td>CA</td>
<td>Cycloadduct</td>
</tr>
<tr>
<td>DCD</td>
<td>Dewar-Chatt-Duncanson</td>
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12.1 CONCLUSION

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CHAPTER ONE

ORGANOLITHIUM STARTING MATERIALS
1,3,5-Tris(trifluoromethyl)benzene (ArH) (1) was prepared using high pressure techniques by R.D. Chambers et al.\cite{1} (Figure 1.1). Some aspects of the chemistry of this species have been investigated\cite{1}. It was shown to lithiate directly when treated with butyl or methyl lithium forming 2,4,6-tris(trifluoromethyl)phenyllithium (ArLi) (2)\cite{1}. The lithium compound could then be used to prepare organometallic derivatives for example with Sn(IV) and Cu(I).

\[
\begin{align*}
\begin{array}{c}
\text{HO}_2\text{C} \\
\text{CO}_2\text{H} \\
\text{CO}_2\text{H}
\end{array}
\end{align*}
\xrightarrow{\text{SF}_4} \begin{array}{c}
\text{CF}_3 \\
\text{CF}_3 \\
\text{CF}_3
\end{array}
\]

\text{150}^\circ\text{C}
\begin{align*}
\text{12 hr}
\end{align*}

\text{(1)}

\text{Figure 1.1: The synthesis of ArH (1).}

For the first time it was hoped to study the influence of this substituent on the possible stabilisation of low coordinate complexes, and its introduction into phosphorus, antimony and boron compounds. Some of the work on phosphorus was independently carried out by Edelmann et al.\cite{2}. Some of the selective reactions carried out in this work illustrate the behaviour of Ar as an electron withdrawing group (A), and its behaviour as a sterically hindering moiety (B).

(A) No normal oxidative fluorination of chlorophosphines occurs with strongly electronegative groups attached to phosphorus.\cite{3}. ArPF\textsubscript{2} (3) was prepared as shown (Figure 1.2) and details are given in Section 2.3.1.
Figure 1.2: The synthetic route to ArPF₂.

(B) No formation of Ar₃P was observed (Equation 1.1), attributed to steric crowding around the phosphorus atom. The ¹⁹F NMR data for Ar₂BCl (4) (Equation 1.2) shows an inequivalence of the ortho-trifluoromethyl groups, similarly ascribed to steric crowding around the trigonal boron, also observed in the MNDO calculation (Section 8.7).

\[
\begin{align*}
3 \text{ArLi} (2) + \text{PCl}_3 & \xrightarrow{X} \text{Ar}_3\text{P} \\
2 \text{ArLi} (2) + \text{BCl}_3 & \xrightarrow{} \text{Ar}_2\text{BCl} (4)
\end{align*}
\]

1.2 INTRODUCTION TO ORGANOLITHIUM COMPOUNDS

An excellent up-to-date review on the preparation of organolithium species is available [4]. The methods may be summarised as follows:

1) (a) Preparation from organo halides (Equation 1.3);
   (b) Metal/halogen exchange (Equation 1.4). Early work has been comprehensively reviewed in this area by G. Köbrich [5].

\[
\begin{align*}
\text{RX} + 2\text{Li} & \xrightarrow{} \text{RLi} + \text{LiX} \\
\text{RLi} + \text{R'X} & \xrightarrow{} \text{R'Li} + \text{RX} \\
\text{RLi} + \text{R'H} & \xrightarrow{} \text{RH} + \text{R'Li}
\end{align*}
\]

2) Preparation by metallation (Equation 1.5) [6]. A reaction occurs with a relatively strongly acidic hydrocarbon and when a proton is activated by an α- or β-heteroatom, thus increasing the kinetic or
thermodynamic acidity of a particular hydrogen atom [4]. Lithiation takes place with alkyl-lithium, eg. BuLi. However, when nucleophilic character is incompatible, for example in the presence of a carbonyl functionality, reagents with high basicity but relatively low nucleophilicity are employed, for example lithium diisopropyl amide (LDA).

3) Three less widely used methods are:

(a) Preparation from other organometallic compounds (Equation 1.6).
(b) From ethers and thioethers (Equation 1.7) and
(c) From sulphonylhydrazone (Equation 1.8)[4]

\[
\text{(CH}_2\text{=CH)}_4\text{Sn} + 4 \text{BuLi} \rightarrow 4\text{CH}_2\text{=CHLi} + \text{Bu}_4\text{Sn} \quad (1.6)
\]

\[
\text{CH}_2\text{CHCH}_2\text{OPh} + 2\text{Li} \rightarrow \text{CH}_2\text{=CHCH}_2\text{Li} + \text{LiOPh} \quad (1.7)
\]

\[
\text{ArSO}_2\text{HNHNH}_2 + \text{NNHSO}_2\text{Ar} + 2\text{R''Li} \rightarrow \text{Li} + \text{N}_2 + \text{ArSO}_2\text{Li}^+ + 2\text{R''H} \quad (1.8)
\]

1.3 ArLi SYNTHESIS AND STRUCTURE

ArLi (2) was generated via route 2 (Equation 1.5) [1]. The species is ideally set up for this reaction because of the ortho-trifluoromethyl groups which significantly increase the acidity of the proton. In THF, ArH would not lithiate on the addition of BuLi. It is unclear why this should be so. In order to attempt isolation of ArLi in a crystalline form, TMEDA was added to the ArLi solution in ether. No crystals were formed even on cooling. In comparison, 2,4,6-tri(t-butyl)phenyllithium·TMEDA, is soluble in ether down to -100 °C [7]. Lower temperatures may allow isolation of the ArLi·TMEDA complex and hence its structural elucidation.
To compare the ArLi (2) with other lithium compounds: 2,4,6-tri-(t-butyl)phenyllithium (5) is monomeric in THF, and 2,4,6-(trimethyl)phenyl lithium (6), due to its solubility problems, could only be recorded by NMR in the presence of TMEDA, so it was not surprising that a monomeric structure was found \[7\] (Figure 1.3).

![Figure 1.3: MesLi Compound (6).](image)

For ArLi (2), because of the electron density which must exist around the ortho-trifluoromethyl groups, a monomeric structure is postulated with the association of ether.

Attempts to remove the bulk diethylether at 40 °C from ArLi (2) \textit{in vacuo} led to an explosion, attributed to the removal of the stabilising coordinated ether molecules. However, the prevalence of ether explosions due to peroxides may provide an alternative explanation. Isolation of a crystalline solid from ether failed due to its long term decomposition over 2 months in this solvent system, even with cooling (see Section 1.8.5). Numerous attempts have been made to identify the products of decomposition, primarily by NMR analysis. Unfortunately this gave no information on the mechanism of decomposition, or indeed on the species formed. A mixture of products was evident, interestingly in the "fluoride" region of the $^{19}$F NMR spectrum (Figure 1.13).

After a prolonged time in solution attack of 2,4,6-tris(trifluoromethyl)phenyllithium (2) on a second molecule [or indeed on the small amount of 1,3,5-tris(trifluoromethyl)benzene (1) present] may be postulated [Figure 1.4(a)] or a possible intramolecular decomposition \textit{via} LiF elimination [Figure 1.4(b)].
The stability of ArLi (2), however, is in marked contrast to pentafluorophenyllithium which readily loses lithium fluoride, a decomposition mode which is common in compounds containing lithium and fluorine in a vicinal position. Pentafluorophenyllithium is usually prepared at -78°C, since even at -10°C 25% decomposition occurs within forty minutes [8].

1.4 NMR STUDIES

1.4.1 $^7$Li NMR

The $^7$Li NMR of ArLi showed a single peak indicative of a symmetrical aggregate environment of the lithium, or a monomeric structure. Considerable broadening attributed to interactions with the fluorine was observed.

1.4.2 $^{19}$F NMR

The $^{19}$F NMR gave two signals in a 2:1 intensity ratio, characteristic of equivalent ortho trifluoromethyls (integral 2) and a non-equivalent para-trifluoromethyl (integral 1) (see Section 1.8.2). The
spectrum (Figure 1.5) illustrates a conversion of *ca.* 50%. In general the percentage conversion to ArLi was calculated from the $^{19}$F integration. Average values of ~85% conversion were achieved. It is interesting to compare these data with those for the 2,4,6-tri(t-buty)phenyl lithio derivative. The ortho-protons in this case resonate down field, postulated as being a result of their close proximity to the more positively charged lithium (Li$^+$) [7]. An exactly similar downfield shift of the ortho fluorines is observed in ArLi (2) which may be ascribed in a similar way to reduced $\pi$-electron density and increased $\sigma$-electron density at the metallated carbon. The $\pi$-electron density is polarised away from the ipso-carbon - illustrated in the MNDO calculation (Section 1.7).

![19F NMR spectrum of ArLi (2) in diethylether.](image)

**Figure 1.5:** $^{19}$F NMR spectrum of ArLi (2) in diethylether.
1.4.3 A Predicted 2D-NMR Spectrum

By using two-dimensional Heteronuclear Overhauser Spectroscopy the interaction between lithium and fluorine may be determined, \textit{i.e.} \( ^{6}\text{Li} \) \textit{via} \( ^{19}\text{F} \). A two channel NMR would be required for this which was not available in Durham. The predicted features of the 2D-NMR are presented in Figure 1.6, reflecting the close contact between the two groups \cite{9,7}.

![Figure 1.6: Predicted 2D Heteronuclear Overhauser Spectrum of ArLi (2), \( ^{6}\text{Li} \) versus \( ^{19}\text{F} \).](image)

The structure and possible aggregation of the ArLi species is of particular interest. Ideally the isolation of a crystalline solid was sought. This failed and hence other methods were tried.

1.4.4 \( ^{13}\text{C} \) NMR

Using \( ^{13}\text{C} \) NMR it should be possible by looking directly at the coupling of the quaternary carbon with lithium to determine the number of lithiums to which it is coupled, and hence the number of molecules in the aggregate. Work on the more reactive organolithium species (\textit{e.g.} \( \text{R} = \text{Bu} \)) has to be carried out at very low temperatures. In this case in diethylether, the quaternary carbon is split into seven lines as a
Figure 1.7: $^{13}C$ NMR spectrum of $ArLi$ (2) in deuterobenzene.
result of its coupling to two $^{7}$Li isotopes. Hence a dimeric structure can be assigned[7].

As discussed earlier, attempts to isolate 2,4,6-tris(trifluoromethyl)phenyllithium (2) by removal of Et$_2$O resulted in an explosion. However, with a small quantity of material (20 mmol) and by exercising great caution it was maintained in vacuo for 12 hours without incident. The $^{13}$C NMR of the resulting pale brown powdery solid is presented in Figure 1.7. It is evident that Et$_2$O remains coordinated. No $^{13}$C-$^{7}$Li or $^{13}$C-$^{6}$Li coupling is clearly resolved.

1.5 OTHER TRIFLUOROMETHYL SUBSTITUTED BENZENES

It is interesting to compare the electronic properties of the compounds (7), (1) and (8) (Table 1.1).

![Chemical structures](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>NMR Data</th>
<th>Physical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7)†</td>
<td>Liquid Bpt 116 °C</td>
<td>White solid Mpt: 92-94°C.</td>
</tr>
<tr>
<td>(1)*</td>
<td>Liquid Bpt 119 °C (ref.1).</td>
<td>Both positions equally favoured and disfavoured for lithiation.</td>
</tr>
<tr>
<td>(8)*</td>
<td>All 3 positions equally activated.</td>
<td>(Even by increasing the base strength it is not possible to see any lithiation). This solid was difficult to purify.</td>
</tr>
</tbody>
</table>

Proton A: most kinetically favourable proton, least hindered most accessible.

TMEDA promotes the removal of the most thermodynamically favourable proton B.

Table 1.1: Electronic properties of compounds (1), (7) and (8); †Commercially available from Aldrich; *Synthesised via high pressure techniques (ref.10).
1.6 PREPARATION OF FURTHER ORGANOLITHIUM DERIVATIVES

A great deal of work was directed toward the preparation of organolithium species in view of the synthesis of many secondary phosphines, as precursors to phosphaalkenes (Chapter 4). Some of the species prepared and the general routes by which they were synthesised are given in Table 1.2. For experimental details see Section 4.12.1 and 4.12.2.

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>PREPARATIVE ROUTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCHCl₂ (9)</td>
<td>1 (Section 4.12.2)</td>
</tr>
<tr>
<td>PhCH₂Li·TMEDA (10)</td>
<td>2 (Section 4.12.1)</td>
</tr>
<tr>
<td>Ph₂CHLi·TMEDA (11)</td>
<td>3 (Section 4.12.1)</td>
</tr>
</tbody>
</table>

Table 1.2

The importance of controlling temperature, concentration and solvent to reduce unwanted side reactions and increase yields was realised [11-13]. For example, there is the possibility of THF cleavage with prolonged reaction of organolithium species at 65 °C [13]. Concentrations exceeding 0.3 M may cause loss of yield due to the Wurtz reaction, and result in the formation of a gelatinous precipitate [11,12].

1.7 MNDO CALCULATIONS ON ArLi

MNDO studies on the ArLi (2) species are presented below. AM1 calculations on ArLi (2) did not give a great deal of information. In this calculation type, the Li⁺ is treated as a point charge so that any lithium-fluorine interaction is entirely electrostatic. In MNDO, however, the lithium is assigned with 2s and 2p orbitals and therefore it has orbital coefficient values. The molecular geometry is shown in
Figure 1.8: \textit{ArLi (2) geometry from MNDO calculations.}

The HOMO and HOMO-1 are shown in Figure 1.9. The HOMO is $\pi$-bonding around the ring system with a small amount of $p_z$ lithium coefficient. There is more lithium involvement in the HOMO-1 and it is possible to see direct lithium-fluorine bond interaction and a lithium-carbon bond.

\textbf{Figure 1.9: Predicted HOMO's for ArLi (2).}

Charges and Bond Order are shown in Figure 1.10. Note the alternating charges around the ring (\textit{cf.} benzene). The calculation assigns negative charge $\alpha$ to a -CF$_3$ group. The para fluorines all have a charge of -0.23 [F(18), F(19) and F(10)]. This is the same for the ortho CF$_3$ groups [F(16), F(17), F(13), F(14)]. F(15) and F(12) donate negative charge toward the lithium and hence have a reduced value of -0.16, this correlates well with the $^{19}$F NMR data (Figure 1.5).
Figure 1.10: Predicted charge separation and bond orders for ArLi (2).

1.8 EXPERIMENTAL

1.8.1 Preparation of 1,3,5-Tris(trifluoromethyl)benzene (ArH)

(High Pressure Technique)

\[
\text{HO}_2\text{C} \quad \text{CO}_2\text{H} \quad + \quad 3\text{SF}_4 \quad \rightarrow \quad \text{F}_3\text{C} \quad \text{CO}_2\text{H} \quad + \quad 3\text{SO}_2 \quad 3\text{HF}
\]

A steel vacuum line was designed specifically for work involving sulphur tetrafluoride. Its constitution is outlined below (Figure 1.11). The upper reservoir has a known capacity (425 cm\(^3\)) and holds ca. 150 g of SF\(_4\). After evacuation this cylinder was allowed to fill completely with SF\(_4\) over a period of 30 minutes. Subsequently its contents were condensed into a small sample bottle. From its tare the accurate weight of SF\(_4\) collected could be determined. This process was repeated until the required quantity of SF\(_4\) [550 g (3.9 mole) - 3 sample bottles] had been obtained.
Figure 1.11: The apparatus used for the manipulation of $SF_4$.

A 1 litre steel bomb was charged with 150 g (0.71 mole) trimesic acid (benzene-1,3,5-tricarboxylic acid). This vessel was evacuated and cooled to $-190 \, ^\circ C$ by liquid air. The bomb design used is shown in Figure 1.12.

Figure 1.12: The 1-litre steel bomb.

An aspect of particular interest is the recent safety introduction of the bursting valve (A).
The contents of the four weighed small cylinders were condensed into the bomb. After completion the bomb was transferred at -190 °C in a large Dewar of liquid air to the high pressure reaction chamber. Within the high pressure cell the bomb was allowed to equilibrate to ambient temperature, before thermocouples enabled a temperature of 150 °C to be maintained for a maximum period of 12 hours. The bomb was vented in an efficient hood to release any unreacted sulphur tetrafluoride, sulphur dioxide and hydrogen fluoride, before the liquid contents of the bomb were poured onto crushed ice (to remove any unreacted trimesic acid and HF). This mixture was filtered to discard any solid impurities. The filtrate was treated with 4 aliquots of 150 ml NaOH (2M) and washed well with water. The oily product was subsequently dried with anhydrous magnesium sulphate. Distillation yielded pure product (1) 159.5g (80%); Bpt 119 °C (760 mm Hg); $^{19}$F (CDCl$_3$) δ: -65.3 ppm (s, CF$_3$); $^1$H (CDCl$_3$) δ: +8.1 ppm (s, CH ring) [1].

This technique was modified to maximise the yields obtained. This is of particular significance (as in all preparative chemistry) because of the high cost of these materials. A few selective reactions illustrating the effect of variation in reaction conditions are presented in Table 1.3. Reaction yields were maximised (increasing the viability of this technique) with prolonged reaction times, and slightly larger quantities of SF$_4$ relative to the trimesic acid starting material. The effect of increase in reaction time with yield was also recognised by Edelmann et al. [2] (reaction time 24 hours). In our hands it was found that no significant increase in yield was achieved by extending the reaction period beyond 12 hours.
<table>
<thead>
<tr>
<th>REACTION NUMBER</th>
<th>TEMP</th>
<th>MASS OF SF₄ /g</th>
<th>REACTION TIME</th>
<th>YIELD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>480</td>
<td>6 hours</td>
<td>55%</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>500</td>
<td>6 hours</td>
<td>65%</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>550</td>
<td>6 hours</td>
<td>67%</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>550</td>
<td>6 hours</td>
<td>70%</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>450</td>
<td>10 hours</td>
<td>72%</td>
</tr>
<tr>
<td>6</td>
<td>150</td>
<td>550</td>
<td>12 hours</td>
<td>80%</td>
</tr>
<tr>
<td>7</td>
<td>150</td>
<td>550</td>
<td>18 hours</td>
<td>80%</td>
</tr>
</tbody>
</table>

Table 1.3: Conditions used for the preparation of ArH (1): These may be compared to yields of 35% (ref.1).

1.8.2 Preparation of 2,4,6-Tris(trifluoromethyl)phenyllithium (2)

\[
\text{ArH} + \text{BuLi} \xrightarrow{\text{Et}_2\text{O}} \text{ArLi} + \text{BuH}
\]

BuLi (2.5M in hexane, 31.2 ml, 78.0 mmol) was added dropwise over 5 minutes to a stirred solution of ArH (20.0g, 71.0 mmol) in Et₂O (100 ml) at -10 °C. The solution was allowed to reach room temperature and stirred for 5 hours, yielding a deep brown gelatinous solution (with a larger volume of ether it remains free-flowing). The percentage conversion was determined by \(^{19}\text{F NMR}\). The ArLi (2) was not isolated, but used from this stage \textit{in situ} (0.54 M). Consistent yields of the order 85%-90% were achieved, calculated from the distinctive \(^{19}\text{F NMR}\). \(^{19}\text{F NMR} \text{(Et}_2\text{O)} \delta: -62.6 \text{ (s,6F,o-CF}_3\text{)}, -62.8 \text{ (s,3F,p-CF}_3\text{)} \text{ppm}; \text{^7Li NMR (Et}_2\text{O)} \delta: +0.2 \text{ ppm.}

1.8.3 Attempted Reaction of ArH with BuLi in THF

BuLi (2.5M in hexane, 15.6 ml, 39.0 mmol) was added dropwise over 5 minutes to a stirred solution of ArH (10.0g, 35.5 mmol) in THF (100 ml) at -10 °C. This reaction mixture was stirred at room temperature for 5
hours. The solution became deep brown, but no reaction of ArH had occurred. $^{19}$F NMR (THF) δ: -65.0 (s) ppm. This mixture was brought to reflux for 2 hours and no change in the $^{19}$F NMR was observed.

1.8.4 Addition of TMEDA to ArLi/Et$_2$O (2) Solution

TMEDA (6.9 ml, 45.7 mmol) in Et$_2$O (25 ml) was added dropwise over 5 minutes to a stirred solution of ArLi/Et$_2$O (0.45 M, 102.0 ml, 45.9 mmol) at -10 °C. Copious amounts of solid appeared to form. This mixture was cooled to -50 °C and filtered. The separation process was not successful, and only a brown oil collected on the frit, which appeared to contain ArLi. It was not proven whether TMEDA was coordinated. Attempts to recrystallise the oil from Et$_2$O (ca. 10 ml) at -40 °C failed.

1.8.5 Attempted Isolation of ArLi (2)

ArLi was prepared as described in Section 1.8.2. Attempts to concentrate this solution [initially 20 ml (0.54 M) which was reduced to half-volume by the removal of ether in vacuo] and cooling gave no precipitate (a viscous brown oil was produced). $^{19}$F (Et$_2$O) δ: -62.6 (s, 6F, o-CF$_3$), -62.8 (s, 3F, p-CF$_3$) ppm.

An ArLi sample (approximately 1 M) was allowed to stand at room temperature (inert atmosphere) for 8 weeks. Clear transparent crystals (ca. 50 mg) were isolated from below a supernatant liquid. Mpt. 110-111 °C; Analysis found: C, 15.60; H, 3.74; (No lithium detected); Required for C$_9$H$_2$F$_9$Li: C, 37.53; H, 0.70%. The $^{19}$F spectrum of the supernatant liquid is shown in Figure 1.13. It is clear that many products are present. The large crystals were cut and mounted for X-ray analysis. (The crystals showed a unit cell smaller than that expected
Figure 1.13: Illustrating the $^{19}$F NMR spectrum of the supernatant liquid obtained from the decomposition mixture.
for ArLi, but larger than for LiOH and Li₂O). The crystal structure remained incomplete. It was assumed to be a decomposition product and was not further investigated by crystallography. (The peak at -111 ppm ($^{19}\text{F}$) may represent a fluoride ion).

Refluxing the ArLi (2) (0.7 M, 25 ml, 17.5 mmol) over a period of 2 days gave no evidence of LiF elimination. The ArLi (2) remained intact apart from a small amount of hydrolysis (approximately 7%) to ArH (1). This was observed by $^{19}\text{F}$ NMR. $^{19}\text{F}$ (Et₂O) ArLi δ: -62.6 (s,6F,o-CF₃), -62.8 (s,3F,p-CF₃) ppm; ArH δ: -65.3 (s,CF₃) ppm.

1.8.6 ArLi/Et₂O Standing at Room Temperature

A solution of ArLi in Et₂O (0.7 M, 50 ml, 35 mmol) remained standing in a glove box for a period of two months. Its $^{19}\text{F}$ NMR was recorded every few days. The solution darkened on standing and a sticky black solid precipitated which was redissolved in Et₂O for analysis by NMR. The decomposition process postulated (Section 1.3) was not repeated. Gradual hydrolysis of ArLi to ArH (a single peak in the $^{19}\text{F}$ NMR) was observed. $^{19}\text{F}$ NMR (Et₂O) δ: -65.3 (s,CF₃) ppm. ArH (1).

1.8.7 $^{13}\text{C}$ Studies on ArLi (2)

An ArLi/ArH Et₂O solution (0.7 M, 100 ml, 70 mmol) was placed in vacuo in order to remove the diethyl ether. The resultant oily residue was warmed gradually to 40 °C with an oil bath to remove any remaining solvent and inherent ArH. This resulted in an explosion. With a small quantity of the lithium species (2) (1 M) in diethylether (20 ml, 20 mmol) and executing great caution the mixture was allowed to pump in vacuo for a period of 12 hours at room temperature to yield a powdery
pale brown solid. 25 mg of this material was redissolved in deuterobenzene, C_{6}D_{6} (2 ml) and its \textsuperscript{13}C NMR was recorded (Figure 1.7).

1.9 REFERENCES


10. R.D. Chambers, T.F. Holmes and T. Straw, unpublished work, University of Durham, South Road, Chemistry Department (1988).


2.1 INTRODUCTION

There are many preparative routes available for organohalo-phosphorus compounds [1] and many species are known [2]. This work has concentrated on their synthesis using:

(A) The action of organocadmium or organozinc reagents on PCl₃ (Equation 2.1) [3,4].

(B) Cleavage of phosphinous/phosphonous amides with anhydrous HX and an inert solvent (Equation 2.2) [5].

(C) Exchange methods (Equation 2.3).

\[
\begin{align*}
R_2Cd + 2PCl_3 & \quad \rightarrow \quad 2RPCl_2 + CdCl_2 \quad (2.1) \\
R_2PNR_2 + 2HCl & \quad \rightarrow \quad R_2PCl + R_2NH.HCl \quad (2.2) \\
RPCl_2 + 2AgCN & \quad \rightarrow \quad RP(CN)_2 + 2AgCl \quad (2.3)
\end{align*}
\]

Many phosphines have been prepared throughout this work as:

1) Synthons to observe their acceptor properties (Chapter 6), eg. ArPCl₂ (12), CF₃PCl₂ (13), i-Pr₂NPCl₂, (i-Pr₂N)₂PCl, (Et₂N)PCl₂, (Et₂N)₂PCl and their respective cyano derivatives.

2) Synthons for attempts at unsymmetrical diphosphene preparation (Chapter 3), eg. t-BuPCl₂, C₆F₅PCl₂, MesPCl₂, t-BuPH₂, Ar'PCl₂, Ar'PH₂ [where Ar' = 2,6-bis(trifluoromethyl)phenyl].

3) Synthons for phosphaalkene preparation, eg. Me₃SiCH₂PCl₂, PhCH₂PCl₂, CH₃PCl₂ and many secondary phosphines were prepared from these starting materials (Chapter 4).

Other phosphines were precursors for the synthesis of the P(V) derivatives as counterions in halo and pseudohalo borate chemistry (Chapter 10). Of particular interest are the new phosphines containing the aryl group, 2,4,6-tris(trifluoromethyl)phenyl: ie. ArPCl₂ (12), Ar₂PCl (14), ArPF₂ (3), ArPH₂ (15) and ArP(CN)₂ (16). These are
discussed in more detail in the next section.

2.2 Ar SUBSTITUTED PHOSPHINES

2.2.1 ArPF$_2$ (3)

ArPF$_2$ (3) was prepared by the action of SbF$_3$ on ArPCl$_2$ (12). No oxidative fluorination to yield the fluorophosphorane, ArPF$_4$ was observed (see Section 2.3.1).

This represents an example of a stable fluorophosphine attributed to the increase in Lewis acidity of the P(III) compound bearing an electron-withdrawing substituent, Ar$^{[6,7]}$. An alternative synthetic route could be via the organo lithium reagent with ClPF$_2$$^6$.

This is a particularly interesting compound since difluorophosphines have become known only relatively recently, due not so much to the synthetic problems but to their inherent instability, as indicated by a recent scheme by R. Schmutzler$^6$. Such difficulties were not experienced here and ArPF$_2$ (3) was comparatively stable.

2.2.2 ArPH$_2$ (15)

This was prepared in high yield via one of two routes from ArPCl$_2$ (12) (Equations 2.4 and 2.5)$^{[8,9]}$ (Section 2.3.2). The structure of ArPH$_2$ and its $^{31}$P NMR parameters are shown in Figure 2.1.

\[
\begin{align*}
\text{ArPCl}_2 + 2\text{Bu}_3\text{SnH} & \rightarrow \text{ArPH}_2 (15) + 2\text{Bu}_3\text{SnCl} \\
\text{ArPCl}_2 + 1/2\text{LiAlH}_4 & \rightarrow \text{ArPH}_2 (15) + 1/2\text{LiAlCl}_4
\end{align*}
\]
Figure 2.1: The structure and $^{31}P$ NMR spectrum of ArPH$_2$ (15); $^{31}P$ $\delta$: -139.8 ppm (triplet of septets), $^4J$(PF) 28.9 Hz, $^1J$(PH) 217.9 Hz.

The second route (Equation 2.5) was employed with anticipation of CF$_3$ cleavage, since it was reported [8] that in the 2,6-bis(trifluoromethyl)Ph derivative there was attack at the CF$_3$ group. This was not observed here. A clear liquid with a very pungent smell was obtained. Compare this with 2,4,6-tri(tert-butyl)phenylphosphine (17) which is an odourless white solid (Mpt. 150-152°C) [10].

2.2.3 ArPCl$_2$ (12)

Representatives of this class of dichlorophosphines (Equation 2.6) have been in the literature since the 19th Century [11]. This new dichlorophosphine was obtained as a clear oil (Figure 2.2) (Section 2.3.3).

$$\text{ArLi (2) + PCl}_3 \rightarrow \text{ArPCl}_2 (12) \quad (2.6)$$
A variable temperature NMR experiment to low temperature (-60 °C) was carried out. The aim of this experiment was to attempt to "freeze" ring rotation to cause inequivalence in the ortho-CF$_3$ groups. The $^{31}$P NMR was observed (Table 2.1). No change was detected - inequivalence of the CF$_3$ groups would have been expected to increase the complexity of this spectrum.

<table>
<thead>
<tr>
<th>TEMPERATURE</th>
<th>$^{31}$P /ppm</th>
<th>$^4J$(PF) /Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>294</td>
<td>144.4 (septet)</td>
<td>61.4</td>
</tr>
<tr>
<td>273</td>
<td>144.4 (septet)</td>
<td>61.4</td>
</tr>
<tr>
<td>253</td>
<td>144.4 (septet)</td>
<td>61.4</td>
</tr>
<tr>
<td>233</td>
<td>144.4 (septet)</td>
<td>61.4</td>
</tr>
<tr>
<td>213</td>
<td>144.4 (septet)</td>
<td>61.4</td>
</tr>
</tbody>
</table>

Table 2.1 A variable temperature NMR study on ArPCl$_2$

The results indicate either continuation of ring rotation, or the "freezing" of the ring with a symmetrical geometry. It would be interesting to carry out this experiment on Ar$_2$PCl (14) (Section 2.2.4) where the greater steric limitations may cause ring "freezing" at a higher temperature.
2.2.4 Ar$_2$PCl (14)

The use of ArLi in slight excess of two-fold stoichiometry gave high yields of Ar$_2$PCl as a pure white crystalline solid (Equation 2.7).  $^{31}$P NMR spectral data is presented in Figure 2.3.

$$2\text{ArLi (2)} + \text{PCl}_3 \longrightarrow \text{Ar}_2\text{PCL (14)} \quad (2.7)$$

![31P NMR spectrum of Ar$_2$PCL (14); $^{31}$P δ: -74.2 ppm (19 line multiplet), $^4$J(PF) 42.0 Hz.]

Figure 2.3: $^{31}$P NMR spectrum of Ar$_2$PCL (14); $^{31}$P δ: -74.2 ppm (19 line multiplet), $^4$J(PF) 42.0 Hz.

The attachment of two such bulky groups geminal on one phosphorus is unusual [12-14]. The first successful preparation of a compound carrying two very bulky geminal 2,4,6-$^{t}$butylphenyl groups on one element was achieved for the synthesis of bis(2,4,6-$^{t}$butylphenyl)phosphinic chloride [12]. Ar$_3$P does not appear to form even by the use of a large excess of ArLi and refluxing the reaction mixture in ether. This may be attributed to the steric requirement of the aryl group in the tetrahedral environment. Trimesitylphosphine is the largest tertiary phosphine known and was synthesised as early as 1901 [13].

2.2.5 ArP(CN)$_2$ (16)

This was prepared via chlorine substitution in ArPCl$_2$ by cyanide (Equation 2.8).
The $^{31}\text{P}$ shift of -87 ppm is indicative of the higher degree of shielding in the cyanide species. However, the increase in electrophilicity of the phosphorus and apparent increase in its susceptibility to hydrolysis can be attributed to the electronegativity of cyanide.

2.2.6 'ArP(H)Cl'

To complete this series of phosphines it would be interesting to consider the chemistry of ArP(H)Cl. In general RP(H)A, where R is a hydrocarbon group and A an electronegative group, are normally unstable as they tend to lose AH to give the corresponding cyclopolyphosphine \((\text{RP})_n\) \[^{[15]}\]. Significant exceptions exist with R as a highly electronegative group, e.g. \(R = \text{CF}_3\); \(A = \text{Cl}, \text{Br}\) \[^{[16]}\], or when RP(H)Hal is coordinated to a transition metal \[^{[15]}\]. A third consideration is the stability of SupermesP(H)Cl \[^{[15b]}\] which may be explained in terms of a possible bimolecular decomposition process with HCl elimination to form cyclopolyphosphines, and therefore with very bulky R groups formation of the transition state is precluded. The steric and electron-withdrawing nature of Ar = 1,3,5-tris(trifluoromethyl)benzene should allow its isolation and indeed a facile route to its preparation has been suggested \[^{[17]}\], involving the refluxing of ArPH$_2$ in the presence of an excess of CC1$_4$ and a catalytic quantity of the radical initiator AIBN possibly by the route shown in Figure 2.4. This, however, was not successful, and irradiation with gamma rays gave very low yields (Section 7.3).
2.3 EXPERIMENTAL PROCEDURES

2.3.1 Preparation of ArPF2 (3)

\[
\text{ArPCl}_2 + \text{SbF}_3 \rightarrow \text{ArPF}_2
\]

(12) (3)

SbF3 (2.3g, 13.0 mmol) was added to a stirred solution of ArPCl2 (3.8g, 10.0 mmol) in CH2Cl2 (50 ml) at room temperature. The SbF3 was only sparingly soluble in CH2Cl2. The mixture was refluxed overnight for a period of 12 hours to ensure complete conversion to ArPF2. The solution was filtered to remove the excess SbF3, and the CH2Cl2 removed by distillation at atmospheric pressure. The product was obtained by distillation at reduced pressure and collected as a clear pure oil at 54 °C (8 mm Hg). Yield was 2.2g (63%). Analysis found: C, 30.97; H, 0.37; Required for C9H2F9PF2: C, 30.88; H, 0.58%; IR (Film) \( \nu_{\text{max}} \): 1400-1150 (s,CF3), 900 (s,P-F) cm\(^{-1}\); UV-Vis (CCl4) \( \lambda_{\text{max}} \): 262 (39877) nm; MS (Intensity%) EI: 331 (100,ArPF+) 262 (40,Ar-F+); \( ^{31}\text{P} \) (CDCl3) \( \delta \): +184.6 ppm (doublet of septets), \( ^{1}\text{JP} \) 1179.6, \( ^{4}\text{JP} \) 50.6 Hz; \( ^{19}\text{F} \) \( \delta \): -55.5 ppm (6F, doublet of triplets), \( ^{4}\text{JF} \) 50.6, \( ^{5}\text{JFF} \) 18.6 Hz, -64.5 ppm (s,3F), -90.9 (2F, doublet of septets), \( ^{1}\text{JP} \) 1179.6, \( ^{5}\text{JFF} \) 18.6 Hz; \( ^{1}\text{H} \) (CDCl3) \( \delta \): 8.13 (s) ppm.
The preparation was also attempted by the reaction of ArP\textsubscript{Cl\textsubscript{2}} with LiF:

\[ \text{ArPCL}_2 + 4\text{LiF} \rightarrow \text{ArPF}_2 \]

Lithium fluoride (0.55g, 21.2 mmol) was added to a stirred solution of ArP\textsubscript{Cl\textsubscript{2}} (1.8g, 4.7 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (50 ml). This mixture was refluxed overnight. There was no evidence of fluorination and unchanged ArP\textsubscript{Cl\textsubscript{2}} was recovered.

### 2.3.2 Preparations of ArPH\textsubscript{2} (15)

#### 2.3.2.1

\[ \text{ArPCL}_2 + \frac{1}{2}\text{LiAlH}_4 \rightarrow \text{ArPH}_2 + \frac{1}{2}\text{LiAlCl}_4 \]  

LiAlH\textsubscript{4} (2.6 ml, 1M solution in Et\textsubscript{2}O, 2.6 mmol) was added dropwise over 5 minutes, to a stirred solution of ArP\textsubscript{Cl\textsubscript{2}} (2.0g, 5.2 mmol) in Et\textsubscript{2}O (50 ml) at 0 °C. A white precipitate (LiAlCl\textsubscript{4}) was seen to form almost instantaneously. This was filtered with a fine sinter yielding a yellowish filtrate, which gave a signal in the \textsuperscript{31}P{\textsuperscript{1}H} NMR at -139.8 ppm (septet). The Et\textsubscript{2}O was removed by distillation at atmospheric pressure and ArPH\textsubscript{2} was distilled, as a clear oil, at 56 °C (12 mm Hg). Yield was ca. 1.0g (61%). (As is clear from these results, and the \textsuperscript{19}F NMR of the filtrate there was no inherent attack at CF\textsubscript{3} by LiAlH\textsubscript{4}) \[9\].

#### 2.3.2.2

\[ \text{ArPCL}_2 + 2\text{Bu}_3\text{SnH} \rightarrow \text{ArPH}_2 + 2\text{Bu}_3\text{SnCl} \]  

Bu\textsubscript{3}SnH (1.62 ml, 6.0 mmol) in Et\textsubscript{2}O (10 ml) was added dropwise over 5 minutes to a stirred solution of ArP\textsubscript{Cl\textsubscript{2}} (1.15g, 3.0 mmol) in Et\textsubscript{2}O (15 ml) at 0 °C. The mixture was stirred at 0 °C for 30 minutes and then allowed to reach room temperature. The solution turned from colourless
to yellow. The clear solution was attributed to the solubility of Bu₃SnCl in Et₂O. The ether was removed by distillation at atmospheric pressure. ArPH₂ was distilled directly from the crude ArPH₂/Bu₃SnCl residue. Yield of clear oil was 0.61g (65%). Bpt. 48 °C (5 mm Hg); Analysis found: C, 34.48; H, 1.00; Required for C₉H₂F₉PH₂: C, 34.42; H, 1.28%; IR (Film) νmax: 3100 (w,ArCH), 2360 (s,P-H), 1630 and 1570 (m,ArC=C), 1400-1000 (m,C-F), ca. 900 (m,ArCH) cm⁻¹; UV-Vis (CCl₄) λmax (ε): 340 (13688), 262 (54753) nm; MS (Intensity%) EI: 314 (90,ArPH₂⁺), 295 (26.9,ArPH₂⁻F⁺), 263 (98.0,Ar⁻F⁺); CI⁺: 314 (100,ArPH₂⁺), 371 (20.0), 357 (47.0); ³¹P (CDCl₃) δ: -139.8 (triplet of septets), ⁴JPF 28.9 Hz, ¹JPH 217.9 Hz; ¹⁹F δ: -61.4 ppm (6F, doublet of triplets), -63.8 ppm (s,3F), ⁴JPF 28.9 Hz, ⁵JFH 5.5 Hz; ¹H (CDCl₃) δ: 7.95 (s) ppm.

2.3.3 Preparation of ArPCl₂ (12)

2.3.3.1 ArLi + PCl₃ → LiCl, ArPCl₂

ArLi (0.72 M, 100 ml, 72.0 mmol) solution in Et₂O was added dropwise over 10 minutes to a stirred solution of PCl₃ (12.6 ml, 19.8g, 0.14 mole) in Et₂O (150 ml) at -78 °C. On allowing the reaction mixture to warm gradually to room temperature a precipitate was formed. The reaction mixture was stirred for 2 hours, filtered through a fine sinter to remove LiCl, and the volatile material, Et₂O excess PCl₃ and the small amount of residual ArH were removed from the filtrate in vacuo. A yellowish oil: crude ArPCl₂ remained. This was purified by vacuum distillation. Yield was 19.8g (72%); Bpt 62 °C (0.5 mm Hg); IR (Film): νmax: 3100 (w,ArCH), 1630 and 1570 (m,ArC=C), 580 and 440 (m,P-Cl) cm⁻¹; UV-Vis (CCl₄) λmax (ε): 295 (10802), 280 (13904), 273
(13262) nm; MS (Intensity%) EI: 382 (13.5, ArPCL$_2^+$), 262 (100, Ar-F$^+$);
$^{31}$P (CDCl$_3$) $\delta$: +144.4 ppm (septet), $^4$J$_{PF}$ 61.4 Hz; $^{19}$F $\delta$: -53.3 ppm
(6F, doublet, o-CF$_3$), $^4$J$_{PF}$ 61.4, -64.5 ppm (s, 3F, p-CF$_3$); $^1$H (CDCl$_3$) $\delta$: 8.25 (s) ppm.

2.3.3.2 Variable Temperature studies on ArPCL$_2$ (12)

CDCl$_3$ (1 ml) was added to a small volume of ArPCL$_2$ (0.5g, 1.3 mmol), making it possible to lock on in the NMR and cool to a lower temperature without freezing. Results are described in Section 2.2.3.

2.3.4 Preparation of Ar$_2$PCl (14)

$$2\text{ArLi} + \text{PCl}_3 \rightarrow \text{Ar}_2\text{PCl}$$

(2) (14)

ArLi (0.52 M, 150 ml, 78 mmol) as a solution in Et$_2$O was added dropwise over 10 minutes to a stirred solution of PCl$_3$ (5.3g, 38.5 mmol) at 0°C. A visible precipitate of LiCl was observed. The mixture was stirred at room temperature for a period of six hours. The insoluble LiCl was removed by filtration through a fine sinter, and the resulting yellowish filtrate concentrated by the removal of Et$_2$O in vacuo, yielding a yellowish sticky solid of crude Ar$_2$PCl. This was most effectively purified by distillation (as often an inherent small amount of ArPCL$_2$ remained which complicated sublimation attempts). By the use of an air condenser in the standard distillation apparatus Ar$_2$PCl was obtained as a pure colourless oil with a boiling point of 110-112°C (0.1 mm Hg) which solidified in the receiver flask as a white crystalline solid. Yield was 17.2g (71%). Crystallisation of this product at low
temperature (-40 °C) from a small volume of CH₂Cl₂ (10 ml) yielded crystals suitable for X-ray analysis. These were subsequently mounted in 0.3 μm Lindemann capillaries and submitted for crystallographic analysis. Bpt. 110-112 °C (0.1 mm Hg); MPt. 91-92 °C; Analysis found: C, 34.87; H, 0.67; Cl, 5.23; Required for C₁₈H₄F₁₉PCl: C, 34.39; H, 0.64; Cl, 5.63%; IR (Nujol) νₘₐₓ: 3100 (w,ArCH), 1630 and 1580 (s,ArC=C), 1400-1000 (s,C-F), 540 (m,PCl) cm⁻¹; UV-Vis (CCl₄) λₘₐₓ (ε): 282 (34685) nm; MS (Intensity%) EI: 628 (32.7,Ar₂PCl⁺), 593 (12.3,Ar₂P⁺), 347 (12,ArPCl⁺); Cl⁺: 628 (10.7, Ar₂PCl⁺), 377 (100); ³¹P (CDCl₃) δ: +73.3 (13 line multiplet), ⁴JₚF 42.0 Hz; ¹⁹F δ: -54.9 ppm (d,12F), ⁴JₚF 42.0 Hz, -64.8 (s,6F) ppm; Solid state ³¹P NMR δ: +73.2 (13 line multiplet), ⁴JₚF 42.0 Hz.

See Chapter 6 for the preparation of ArP(CN)₂ (16).

2.4 REFERENCES


3.1 INTRODUCTION

A brief historical perspective of diphosphenes is first presented:

1877 C₆H₅PH₂ and C₆H₅PCl₂ were coupled to form a "phosphabenzene" formulated as C₆H₅P=PC₆H₅ [1].

1957 The oligomeric structure of phosphabenzene was elucidated (C₆H₅P)₄, (C₆H₅P)₅ [2].

1964 X-ray studies showed that "phosphabenzene" had pentameric or hexameric structure [3].

1966-67 Compounds of composition P₂H₂ were detected in mass spectrometry from the thermolysis of P₂H₄ [4, 5].

1968 P₂H₄ gave P₂H₂ by photolysis at room temperature [6].

1981 The first stable diphosphenes were prepared (Supermes P)₂ [7].

1983 The first heteroatom substituted diphosphenes was prepared (R₁R₂NP)₂ where R₁R₂ = SiMe₃ [8].

3.2 DIPHOSPHENE SYNTHESIS

There are many synthetic routes to diphosphenes. These are considered here in three major parts (Table 3.1):

1) The formation of symmetrical diphosphenes.

2) The formation of unsymmetrical diphosphenes.

3) The use of a diphosphene as the preparative starting material for further derivatives.

A considerable overlap exists between these classifications, for example (2a) allows the selective synthesis of both symmetrical and unsymmetrical diphosphenes [9-20], (see Sections 3.10.2.2, 3.10.5.1/2). Side reactions have been indicated where they are known to occur.
Table 3.1: Synthetic routes to diphosphenes; in Table 3.1, Ar', Ar'' refer to aryl species generally.
SupermesPCl₂ + GeI₂ → (Supermes)₂P₂ + SupermesPH₂ + GeI₂Cl₂ \[17\] (1h)

\((\text{SiMe}_3)_2\text{NPH-PCl}((\text{SiMe}_3)_2)\text{LiN(SiMe}_3)\text{Bu}_x((\text{Me}_3\text{Si})_2\text{NP})_2 \xrightarrow{x^2} \text{Dimer}\] \[12\] (1i)

\(\text{PCl}_3 + 2\text{Li(Supermes)} \xrightarrow{\Delta} \text{[Supermes}^2\text{]} \xrightarrow{x^2} \text{Supermes}_2\text{P}_2 \] \[18\] (1j)

\[2\text{PARCl}_2 \xrightarrow{\frac{1}{2}P} 2\text{ArPClPClAr} \xrightarrow{\text{ArP=PAR}} \] \[19\] (1k)

where: \(P = \begin{bmatrix} \text{Et} & \text{Et} \\ \text{Et} & \text{Et} \end{bmatrix}\); \(Q = \begin{bmatrix} \text{Et} \\ \text{Et} & \text{Cl} \end{bmatrix}\)

\(\text{ArPH}_2 + \text{Ar'}\text{PCl}_2 \xrightarrow{\text{DBU}} \text{ArP=PAR'} \) \[20\] (2a)

\(\text{SupermesP(H)GeCl}_3 + \text{Ar'}\text{P(H)GeCl}_3 \rightarrow \text{AA, BB, AB} \) \[10\] (2b)

(2b) is unselective, generating both symmetrical and unsymmetrical species.

\(\text{SupermesPCl}_2 + (\text{Me}_3\text{Si})_2\text{PMes} \xrightarrow{2\text{Me}_3\text{SiCl}} \text{SupermesP=PMes} \) \[11\] (2c)

\(\xrightarrow{} \text{Supermes-P(Cl)SiMe}_3 \xrightarrow{x^2} (\text{Supermes})_2\text{P}_2 \)

\(\text{(Me}_3\text{Si})_3\text{CPCl}_2 + \text{SupermesPCl}_2 \xrightarrow{\text{sodium naphthalenide}} \text{AA, BB, AB} \) \[21\] (2d)

(2d) A phosphaalkene formed using the lithium reagent \((\text{Me}_3\text{Si})_3\text{CLi}\)

**Table 3.1:** *Synthetic routes to diphosphenes (cont’d).*
\[ C_{5}Me_{5}PCL_{2} + \text{SupermesPHLi} \rightarrow C_{5}Me_{5}PCL-\text{PHSupermes} \quad [22] \]
\[ \downarrow -\text{HCl} \]
\[ C_{5}Me_{5}P=\text{PSupermes} \quad (2e) \]
\[ \uparrow -\text{Me}_{3}\text{SiCl} \]
\[ C_{5}Me_{5}PCL_{2} + \text{SupermesP(SiMe}_{3}\text{)Li} \rightarrow C_{5}Me_{5}PCL-P(SiMe}_{3}\text{)Supermes} \]

\[ \text{RNH-PCl}_{2} + \text{SupermesPH(SiMe}_{3}\text{)} \rightarrow \text{RNH-PClP(H)Supermes} \quad [23] \quad (2f) \]
\[ \rightarrow \text{Et}_{3}\text{N} \rightarrow \text{Et}_{3}\text{NHCl} \]
\[ \text{RNH-P=Phosphene} \]

(2f) The first synthetic route to a diphosphene with a cis conformation. The conformation is substituent dependent.

\[ \text{Me}_{3}\text{Si}-\text{C}=\text{PCL} + \text{P-Supermes} \rightarrow \text{LiCl} \quad [24] \quad (2g) \]
\[ \text{Me}_{3}\text{Si} \quad \text{X} \quad \text{Me}_{3}\text{Si} \quad \text{X} \quad \text{Me}_{3}\text{Si} \quad \text{X} \quad \text{C}=\text{P'-Supermes} \]
\[ \downarrow 1,3-\text{migration} \]
\[ (\text{Me}_{3}\text{Si})_{2}\text{CX}=\text{PSupermes} \]

(2g) An interesting isomerisation to a diphosphene, based on 1,3 "X" migration, for example \( X = \text{SiMe}_{3}\). If the group on phosphorus is small (e.g. butyl), no migration occurs.

\[ \text{i-P}_{2}\text{NP=PSupermes} \xrightarrow{2\text{HCl.THF}} \text{ClP=PSupermes} \xrightarrow{\text{RLi}} \text{RP=PSupermes} [25, 26] \quad (3a) \]
\[ \text{R} = (\text{Me}_{3}\text{Si})_{2}\text{C}, \text{tBu}_{2}\text{P}, \text{tBuS} \]

\[ \text{SupermesP=PN(SiMe}_{3}\text{)}_{2} \rightarrow \text{BuLi} \rightarrow \Theta \rightarrow \text{SupermesP-P(tBu)}\text{N(SiMe}_{3}\text{)}_{2} \quad [27] \quad (3b) \]
\[ \rightarrow \text{-tBu(Me}_{3}\text{Si})_{2}\text{NPLi} \rightarrow (\text{Me}_{3}\text{Si})_{2}\text{NLi} \]
\[ \text{SupermesP=PSupermes} \rightarrow \text{SupermesP:} \rightarrow \text{SupermesP=PtBu} \]

Table 3.1: Synthetic routes to diphosphenes (cont'd).
The classical Double-bond rule states that "elements having a principal quantum number greater than two should not be able to form a $P\pi-P\pi$ bond with themselves or other elements" [28]. This is essentially correct for simple unprotected molecules, e.g. $HP=PH$ and $HP=CH_2$. However, the $P\pi$ hybrid state can be stabilised by one (or a combination) of the following approaches:

1. Incorporation into a delocalised system
2. Incorporation into a charged system
3. Coordination to a metal centre
4. Steric protection by bulky groups.

Points 1-3 relate to stabilisation of a thermodynamic nature, and point 4 to kinetically derived stabilisation. For non-coordinated moieties points 1 and 4 are applicable.

The new diphosphanes synthesised in this work include $ArP=PAr$ (19), $ArP=PAr'$ (20), $ArP=PMes$ (21) and $ArP=PN'Pr_2$ (22). Their stabilisation is attributed to the large steric demand of the Ar substituent. In (20), (21) and (22) the large size of Ar', mesityl, and $iPr_2N$ respectively, may contribute to stabilise the system. The electron-withdrawing nature of the aryl ring may also offer a degree of electronic, (thermodynamic) stabilisation by decreasing the availability of the lone pairs, and hence their susceptibility to attack. In the diphosphenes (22), stabilisation by delocalisation may be possible as a result of the nitrogen directly attached to phosphorus. Predominantly, stabilisation in systems (19-22) is kinetic, however another factor to be considered is that some thermodynamic stabilisation may originate from the lesser steric interaction in diphosphanes than in the cyclic species.
The chemistry of these diphosphenes has been developed and will be considered here in four major parts:

1. Synthetic routes (Section 3.4)
2. Characterisation and structure (MNDO) (Section 3.5/6)
3. Reactivity (Section 3.9)
4. Coordination chemistry with transition metal fragments (Chapter 5).

### 3.4 Synthetic Routes to New Diphosphenes

The diphoslene (19) was synthesised by the three major routes outlined below:

1. Dechlorination with bisimidazolidine (an electron rich olefin) [Table 3.1, reaction (1k)] [19]. It was thought that the mechanism of this reaction was unlikely to proceed through a phosphinidene intermediate [19]. The proposed route is shown in Equation 3.1.

   \[
   2\text{PArCl}_2 \rightarrow 2\text{ArP}^\bullet\text{Cl} \rightarrow \text{ArPCl-P}\text{ClAr} \rightarrow \text{Ar}_2\text{P}_2
   \]  

(3.1)

2. Coupling of ArPH\textsubscript{2} and ArPCl\textsubscript{2} by dehydrochlorination with DBU (Equation 3.2) [Table 3.1, reaction (2a)] [9,20].

   \[
   \text{ArPCl}_2 + \text{ArPH}_2 \xrightarrow{2\text{DBU}} \text{ArP} = \text{PAr}
   \]  

(3.2)

3. Dechlorination by magnesium (Equation 3.3) [Table 3.1, reaction (1a)] [7,11]

   \[
   2\text{ArPCl}_2 \xrightarrow{\text{Mg}} \text{ArP} = \text{PAr}
   \]  

(3.3)

This reaction gave a brown inhomogeneous mixture showing predominantly the characteristic diphoslene signal in the $^{31}$P NMR (+473 ppm), and a small peak at -139 ppm corresponding to the reduction
product ArPH$_2$. The highest yields were obtained from method (1) of the order of 72%. Method (2) is arguably the most convenient route to the diphosphene since the precursors have been synthesised (Section 2.3.2/3) and DBU is commercially available (yield 68-70%), whereas the bisimidazolidine is not.

The diphosphene (19) has also been synthesised and isolated via the following indirect routes:

(4) ArPH$_2$ + C$_6$Cl$_5$PCl$_2$ $\xrightarrow{\text{DBU}}$ ArP=Par [conversion 38% wrt ArPH$_2$ (15)]

(15) (23) (19)

(5) ArPH$_2$ + Ph$_2$CCl$_2$ $\xrightarrow{\text{DBU}}$ ArP=Par (Section 4.3.4)

(15) (19)

(6) Following the distillation of Ar$_2$PCl (14) the residual solid was analysed as Ar$_2$P$_2$ (19). This was attributed to a possible concentration effect, with the coupling to form the diphosphene preceded by phosphinidene formation [Table 3.1, reaction (1j)] [18] (for example, see Figure 3.1)

\[
\begin{align*}
\text{Ar}_2\text{PCl} & \longrightarrow \text{Ar}_2\text{P}^\bullet + \text{Cl}^\bullet \\
\text{ArCl} & \stackrel{(a)}{\longrightarrow} \text{Ar}^\bullet + \text{ArP}^\bullet: \longrightarrow \text{ArP}=\text{Par}
\end{align*}
\]

Figure 3.1

No mechanistic studies were carried out on the formation of the diphosphene. However, on the basis of previous results an intramolecular dehydrochlorination or dechlorination [Figure 3.2(a)] (as suggested in Equation 3.1), or an intermolecular process via the phosphinidene intermediate [Figure 3.2(c)] may be postulated. A proposed rationalisation for the diphosphene formation in (4) and (5)
Figure 3.3: (a) $^{31}P$ NMR and (b) $^{19}F$ NMR parameters of the diphosphene (19) in CDCl$_3$. 
(and further examples) has been given in Section 7.3

![diagram](https://example.com/diagram.jpg)

**Figure 3.2:** Intramolecular dehydrochlorination (a) or dechlorination (b) and the phosphinidene intermediate (c); (refs.9,11,20).

### 3.5 SPECTROSCOPIC DATA FOR THE SYMMETRICAL DIPHOSPHENE

#### 3.5.1 $^{19}F$ and $^{31}P$ NMR

A significantly deshielded thirteen line multiplet was observed in the $^{31}P$ NMR at +473 ppm. This characteristic $^{31}P$ chemical shift is due to a significant increase in the paramagnetic shielding term caused by the existence of low-lying excited states. This is a dominant effect in multiply bonded compounds [29].

A pseudo-triplet was observed in the $^{19}F$ NMR with a through-space coupling from fluorine to phosphorus $^4J_{PF} + ^5J_{PF} = 45$Hz. This phenomenon exists in many systems, for example, the Escudie diphosphene $Ar_2P_2$ [10], $(CH_3)_2P-P(CH_3)_2$ [30a], and is observed in the $^{13}C\{1H\}$ NMR spectrum of (Supermes)$_2P_2$ [7]. The NMR parameters ($^{31}P$ and $^{19}F$) for the diphosphene (19) are shown in Figure 3.3(a) and 3.3(b) respectively.

#### 3.5.2 Solid state $^{31}P$ NMR

The solid state NMR of the diphosphene (19) is presented in Figure 3.4. The static solid state NMR of this species would be extremely broad and of a characteristic shape. By the technique of magic angle spinning this is split into a set of lines consisting of a centre band
Figure 3.4: The $^{31}P$ solid state NMR spectrum of diphosphene (19).
and spinning side bands \cite{30b}. [The centre band has been denoted by \( \sigma \)
and the spinning side-bands at distances \( n f_R \) from the centre bands by \( n \)
and \( n' \), \( f_R \) is the sample rotation frequency].

The isotopic shift has been obtained from a comparison of the spectra measured at slightly different sample rotation rates, and its value is \(+466.7 \text{ ppm}\). The total width of the spinning side-band pattern indicates that the chemical shift anisotropy is large spanning \(1320 \text{ ppm} \) (from \(-100 \) to \(+1220 \text{ ppm}\)) \cite{31}. (The smaller the anisotropy the smaller the number of side bands observed). It would be of interest to calculate the principal elements of the chemical shielding tensor for the diphosphene (19). Procedures exist to derive these elements from the intensities of the spinning side-bands \cite{32a,b}. Problems, however, may be anticipated due to the simultaneous effect of dipolar coupling (P-P and P-F) and the chemical shift anisotropy. The simultaneous presence of the dipolar interaction and the anisotropic chemical shielding is known to considerably distort the NMR line shapes. This results in a poor agreement between theory and experiment: as the theoretical calculation considers only the chemical shift anisotropy \cite{32}.

3.5.3 Electronic Spectra and Molecular Orbitals of Diphosphenes

\textit{Ab initio} calculations (MO) on the model diphosphene, \textit{trans}-
P_2H_2 \cite{33-37}, reveal the LUMO possesses appreciable \( \rho-\rho^{*} \) character \cite{38}.

\[ \begin{array}{c}
+ \\
- \\
- \\
+ \\
\end{array} \]

2\( \beta \)

The two \textit{HOMO}s are closely spaced, with their order dependent on the calculation method.
Figure 3.5: **Visible and ultraviolet absorption for the diphosphenes ArP=PAR (19) and ArP=PAR' (20).**
The electronic spectral data show that the longer wavelength is much less intense. (The lone pair combination as the HOMO can therefore be deduced, since the corresponding n-π* transition is symmetry forbidden (g → g the Laporte selection rule) π-π* is symmetry allowed and therefore of a greater intensity. The red, orange and yellow colours of the diphosphenes are therefore a direct result of these n-π* and π-π* "P=P" transitions, (as the wavelengths are greater than 300 nm they lie outside the π-π* aromatic region). Some values of UV λ\(_{\text{max}}\) for known diphosphenes are given in Table 3.2.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>λ(max)/nm</th>
<th>ε</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supermes-P=P-Supermes</td>
<td>460</td>
<td>1360</td>
<td>[7,38]</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>7690</td>
<td></td>
</tr>
<tr>
<td>(Me(_3)Si)(_3)C-P=P-C(SiMe(_3))(_3)</td>
<td>484</td>
<td>63</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>9474</td>
<td></td>
</tr>
<tr>
<td>Supermes-P=P-C(H)(SiMe(_3))(_2)</td>
<td>427</td>
<td>370</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>325</td>
<td>13000</td>
<td></td>
</tr>
<tr>
<td>Supermes-P=P-Mes</td>
<td>456</td>
<td>220</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td>326</td>
<td>2500</td>
<td></td>
</tr>
<tr>
<td>Me(_5)C(_5)P=PC(_5)Me(_5)</td>
<td>407</td>
<td>1995</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>12589</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2: UV λ\(_{\text{max}}\) values for known diphosphenes.

Data obtained from this study are shown in Table 3.3 and the UV/Visible spectra are presented in Figure 3.5.

The UV spectral absorption for n-π* and π-π* transitions is about 70 nm less than for most other diphosphenes. The shift observed is hypsochromic (to shorter wavelength).
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>COLOUR</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\epsilon$</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArP=PAr (19)</td>
<td>pale yellow</td>
<td>389.6</td>
<td>5694</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>crystals</td>
<td>283.5</td>
<td>6763</td>
<td></td>
</tr>
<tr>
<td>ArP=PAr' (20)</td>
<td>white</td>
<td>264.2</td>
<td>40451</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>crystals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar'P=PAr' (24)</td>
<td>pale yellow</td>
<td>394 NM</td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>277 NM</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.3: UV data on diphosphenes (19),(20) and (24); †No n-\pi* transition was observed; NM=not measured.**

Another interesting feature of the UV-Visible data is that $\lambda_{\text{max}}$ for arylated and alkylated diphosphenes (Tables 3.2 and 3.3) are similar. This suggests that there is little conjugation between aryl groups and the "P=P" double bond. This is further supported by MNDO studies on the species Ar$_2$P$_2$ (19), ArAr'P$_2$ (20) and Ar'P$_2$ (24) in this study (Section 3.6).

### 3.5.4 Vibrational Spectroscopy

A resonance Raman study of (Supermes)$_2$P$_2$ has attributed a 610 cm$^{-1}$ band to the P=P stretch [40]. This vibration is symmetric with respect to the C-P=P-C linkage, consequently this band does not appear strongly in the infrared. This situation appears analogous for Ar$_2$P$_2$ and ArAr'P$_2$ (Experimental, Section 3.10). The nature of the P=P in (Supermes)$_2$P$_2$ has been studied using ESCA [41] (low 2p binding energy).

### 3.6 STRUCTURE

The structure of the three diphosphenes Ar$_2$P$_2$ (19), ArAr'P$_2$ (20) and Ar'P$_2$ (24) have been elucidated by MNDO calculations. The MNDO
structure of the symmetrical diphosphene (19) and the unsymmetrical diphosphene ArAr'P₂ (20) [illustrated in Figure 3.6(a) and 3.6(b) respectively] shows, in each case, the two rings to be parallel and not conjugated with the double bond.

![Figure 3.6(a): The MNDO structure of diphosphene (19).](image)

3.6.1 Ar₂P₂ (19)

The geometry as calculated by MNDO is illustrated in Figure 3.6(a). The HOMO in this species appears to lie much lower in energy than for the diphosphene (24), hence the compound is more difficult to ionise.

**HOMO:** the phosphorus lone pair  
**Energy:** -10.92 eV

**HOMO-1:** The π-system  
**Energy:** -11.74 eV
Figure 3.6(b): The predicted geometry of the unsymmetrical diphosphene $\text{Ar}^3\text{ArP}_2$ (20) by MNDO calculation.
Charge: The phosphorus atoms are positively charged

```
+0.15
P —— P
+0.15
```

Geometry: The Ar groups are orthogonal to the plane of the P=P.

```
107°
P1 —— P2
```

The potential surface at minimum energy (90°) is relatively flat, suggesting that the rings can twist slightly from this conformation.

\[ \pi \text{-bond order} \]

The total calculated \( \pi \)-electron density on \( P_1 \) is 1.09 of which 0.98 originates from \( P_2 \). There is therefore only a very small \( \pi \)-electron contribution from the ring.

The d-orbital on phosphorus is empty and available for electron donation from a metal (d-orbitals however are not considered in the MNDO calculation).

3.6.2 \( \text{Ar}^1\text{ArP}_2 \) (20)

The geometry as calculated by **MNDO** is illustrated in Figure 3.6(b).

```
P —— P
106.3°
```

\( \text{P=P bond length} \)
\( \text{calculated 1.8 Å} \)

Delocalised **HOMO**: The phosphorus lone pair

Energy -10.14 eV
(Ionisation potential)
HOMO-1: The $\pi$-orbital ($p_\pi-p_\pi$ overlap)

![Image of HOMO-1 orbital]

Energy $-11.06$ eV

Charge

3.6.3 Ar$_2^+$P$_2$ (24)

The two rings are orthogonal to the plane of the P=P bond (compare this with the X-ray structure) [42].

![Image of P=P bond]

P=P bond length calculated $1.86\text{Å}$

Delocalised HOMO: The phosphorus lone pair

Energy $-10.14$ eV

(Ionisation potential)

HOMO-1: The $\pi$-orbital ($p_\pi-p_\pi$ overlap)

Energy $-11.16$ eV

(p-$p_\sigma$ $-16.85$ eV)

Charge

It has been suggested that due to the close proximity between the phosphorus and the fluorines, the Ar$_2^+$P$_2$ (24) appears the most crowded of the known diphosphenes [42]. Nevertheless, the exceptional lack of reactivity (Section 3.9) observed for both (19) and (24) indicates that
Figure 3.7(a): (i) $^{31}$P NMR and (ii) $^{19}$F NMR spectra for the unsymmetrical diposphene, $ArAr'P_2$ (20) in CDCl$_3$. 
Figure 3.7(b): The $^{31}$P NMR data of (i) $ArP=PNes$ (21) and (ii) $i-Pr_2NP=PAR$ (22) in CDCl$_3$. 
Figure 3.8: Mixing Ar'PCl₂ and ArPH₂ in THF at ambient temperature. The 31P NMR spectrum of the solution.
the electronic effects give an important contribution to the stability.

The interactions of the fluorines in Ar$_2$P$_2$ (19) and Ar$_2$P$_2$ (24) may be anticipated to cause a longer bond, however, Escudié et al. \cite{42} suggested that the electronic effects could cause a shortening of the normal "$P=P"$ length. This may be a result of reduced electron density around the phosphorus atom with electron-withdrawing substituents attached. The X-ray structure shows the "$P=P"$ bond length to be 2.019 Å in Ar$_2$P$_2$ (24) and within the normal range (see Table 3.4).

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>P-P (Å)</th>
<th>P-P-C (°)</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Supermes)$_2$P$_2$</td>
<td>2.034</td>
<td>102.8</td>
<td>[7]</td>
</tr>
<tr>
<td>[(Me$_3$Si)$_3$C]$_2$P$_2$</td>
<td>2.014 *</td>
<td>108.1</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>2.004</td>
<td>108.9</td>
<td></td>
</tr>
<tr>
<td>Ar'Ar'P$_2$</td>
<td>2.019</td>
<td>98.0</td>
<td>[42]</td>
</tr>
</tbody>
</table>

Table 3.4: Bond lengths and angles of some selected diphosphenes; *two crystallographically independent molecules per unit cell.

This is also clearly illustrated for ArAr'P$_2$ (20) and Ar$_2$P$_2$ (19). The normal bond length—a probable result of the two competing effects.

3.7 UNSYMMETRICAL DIPHOSPHENES

As mentioned in Section 3.3, three unsymmetrical diphosphenes were synthesised: ArP=PAr' (20), ArP=PMes (21) and ArP=PN'Pr$_2$ (22). The latter two species were characterised by spectroscopic data only (Figure 3.7, Table 3.5). The coupling reactions (Equations 3.4 and 3.5) allowed the successful isolation of the unsymmetrical diphosphene, ArP=PAr' (20). As illustrated in Figure 3.8, this was somewhat surprisingly observed by simply mixing the two phosphorus components. Similarly the
derivative bearing the mesityl group (21) was prepared as shown in
Equation 3.6 [Figure 3.7b(i)].

\[
\begin{align*}
&\text{Ar'PH}_2 + \text{ArPCl}_2 \xrightarrow{\text{DBU}} \text{Ar'P=PAr} \quad (20) \quad (3.4) \\
&\text{Ar'PCl}_2 + \text{ArPH}_2 \xrightarrow{\text{DBU}} \text{Ar'P=PAr} \quad (20) \quad (3.5) \\
&\text{MesPCl}_2 + \text{ArPH}_2 \xrightarrow{\text{DBU}} \text{ArP=PMes} \quad (21) \quad (3.6)
\end{align*}
\]

Diphosphene (21) appeared less stable than (19). Its lifetime in
solution appeared to be only of the order of a few days. Ar'ArP \_2 \quad (20)
appeared stable in air over a few days, and indefinitely when stored in
an inert atmosphere at ambient temperature.

Diphosphene \_2^{iPr} \_2NP=PAr \quad (22) was obtained by dehydrochlorination
between \_2^{iPr} \_2NPCl \_2 and ArPH \_2 \quad (15). (22) is a particularly interesting
species since it is stabilised both by delocalisation attributed to the
attached nitrogen, giving interesting spectral parameters i.e. one phos-
phorus is significantly more shielded \[23\] [see Figure 3.7b(ii)], and by
the kinetic stabilisation of the large Ar group. The stability of this
compound (22) appeared to be analogous to that of species (21). It
would be interesting to vary the nature of R on the nitrogen, to study
its effect on diphosphene conformation. This has been investigated in
similar systems. \[43\]. The large \_J_{pp} coupling constant observed in
the species (20), (21) and (22) is evidence for the special bonding
situation i.e. \( \sigma \) between the 2 \_sp^2 hybridised phosphorus atoms, the high
s-character and rather short "P-P" bond length due to the additional
\( \pi \)-bond. A similar correlation exists between s-character and \_J_{cc}
coupling constants \[11\]. The diphosphene NMR data has been presented in
Table 3.5.
### Table 3.5: $^{31}P$ NMR parameters of new diphosphenes

(See Figure 3.7).

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>$^{31}P$</th>
<th>$^1J_{PP}$</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(19) Ar</td>
<td>Ar</td>
<td>+473.9</td>
<td>---</td>
<td>This work</td>
</tr>
<tr>
<td>(20) Ar</td>
<td>Ar'</td>
<td>+489.0</td>
<td>552</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+478.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(21) Ar</td>
<td>Mes</td>
<td>+524.7</td>
<td>566.8</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+484.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(24) Ar</td>
<td>Ar'</td>
<td>+477.1</td>
<td>---</td>
<td>Escudie [10,42]</td>
</tr>
<tr>
<td>(22) Ar</td>
<td>NR$_2$</td>
<td>+468.5</td>
<td>542.1</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+234.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 3.8 OTHER DIPHOSPHENES

An attempt was made at the synthesis of unsymmetrical diphosphenes with smaller groups forming direct phosphorus-carbon bonds, in general via the coupling reaction $\text{ArPH}_2 + \text{RPCl}_2 \rightarrow \text{ArP=PR}$ \[\text{where } R = \text{tBu (25), 2,(CF}_3\text{)C}_6\text{H}_4(\text{Ar"}) (26), C}_6\text{Cl}_5 (27) \text{ and } C}_6\text{F}_5 (28)\]. The requirement of two ortho substituents for diphosphene stabilisation with direct substitution by an aromatic species is well known \[7,9-11\]. It has been shown that two ortho t-butyl groups plus two ortho methyl groups can stabilise the diaryldiphosphene, whereas two ortho isopropyl groups at each aryl ring are insufficient \[11\]. It was of interest to study the possible stabilising effect by ortho chlorines (27) and ortho fluorines (28). Due to the stability of $\text{Ar}_2\text{P}_2$ (24) and $\text{Ar'}\text{ArP}_2$ (20), the reaction of $\text{Ar"P_CL}_2$ (26) with $\text{ArPH}_2$ (15) was also investigated.

In the t-butyl case no diphosphene was isolated, only upfield shifts were observed. The t-butyl group (25) was considered too small to offer a significant degree of stabilisation with its geometry offering very
little shielding of the attached phosphorus (Figure 3.9) (compare with the substituents C(SiMe$_3$)$_3$ and Supermes, used in the formation of the very first unsymmetrical diphosphene) [21].

![Geometry of a proposed t-butyl substituted diphosphene.](image)

Figure 3.9: Geometry of a proposed t-butyl substituted diphosphene.

For the coupling tBuP$_1$Cl$_2$ and ArP$_2$H$_2$, the mechanism would be expected to proceed via the initial attack of P$_2$ on P$_1$. The effectiveness of P$_2$ as a nucleophile is reduced by the presence of Ar (an electron-withdrawing substituent). Hence the coupling reaction tBuP$_1$H$_2$ and ArP$_2$Cl$_2$ was attempted. Nucleophilic attack at P$_2$ is now favoured by the presence of three electron-withdrawing substituents. Even with the application of a stronger base, eg. DABCO, similar results were obtained. No unsymmetrical diphosphene was obtained by similar coupling reactions (Equations 3.7 and 3.8).

\[
\text{ArPH}_2 \quad (15) + C_6\text{Cl}_5\text{PCl}_2 \quad (27) \xrightarrow{\text{DBU}} \quad \text{ArPH}_2 \quad (15) + C_6\text{F}_5\text{PCl}_2 \quad (28) \xrightarrow{\text{DBU}}
\]

(3.7)  (3.8)

The reaction with C$_6$Cl$_5$PCl$_2$ (27) again gave no evidence of the unsymmetrical diphosphene even at low temperature (213 K). Only peaks at -84 and -89 ppm were observed. As this reaction mixture reached room temperature, the symmetrical diphosphene (19) was isolated. It appears that Ar" (a single ortho CF$_3$ substituent), and both chlorine and fluorine do not give the unsymmetrical diphosphene, instead other
reactions intervene. The presence of the upfield peaks (-84, -89 ppm) observed here, has been seen in many other cases on reaction of a chlorine species with ArPH₂ and DBU. An attempted rationalisation of this is made in Section 7.3.

3.9 DIPHOSPHENE REACTIVITY.

Despite the requisite steric hindrance, many diphosphenes exhibit a varied and interesting reaction chemistry [44]. The reactivity patterns can be divided into three main areas: electrophilic attack, eg. with sulphur [45], selenium [46] or Au[PEt₃]⁺ (isolobal with H⁺) [47], oxygen [48]; nucleophilic attack, eg. H⁻ [49], BuLi, MeLi [50]; and coordination chemistry (see Chapter 5). There is a vast amount of reactivity exhibited by the first kinetically stabilised diphosphene, (Supermes)₂P₂ [7,50] containing a localised P=P bond.

It was therefore somewhat surprising when the diphosphene Ar₂P₂ (19) was treated with either strong acids, for example CF₃COOH and HBF₄·Et₂O, or with S₈ under mild conditions, that no reaction occurred. This was further supported by Edelmann et al. [9] who similarly observed no protonation with HBF₄·Et₂O and no reaction with Vanadocene. Further investigation into the reactivity of the diphosphene should involve the addition of methoxide (MeO⁻Na⁺), or methyllithium, i.e. small nucleophiles which may be expected to react with Ar₂P₂ (19) (LOW-LYING LUMO). The reaction of the diphosphene (19) with a carbene in an attempt to generate a cyclic diphosphirane was carried out [51]. A general scheme is shown in Figure 3.10.
Figure 3.10: General scheme for the formation of a diphosphirane by the reaction of a carbene with a diphosphene; \( R = \text{Cl, Br, Ph and Ar} \equiv \text{Supermes} \).

The absence of \([2+3]\) cycloadducts in this reaction, and the fact that cyclopropanation reactions only take place under conditions in which carbenes are formed, \( \Delta \) and \( hv \) indicate a direct carbene attack at a \( \text{P}=\text{P} \) double bond. In this work \((\text{^1Pr}_2\text{N})_2\text{PC(N}_2\text{)}\text{SiMe}_3\) was synthesised as the starting material (Section 11.4.2).

This was irradiated at 300 nm in pentane, in the presence of the diphosphene for 8 hours \([\text{ie.} \text{the nucleophilic Me}_3\text{SiC-}\text{P(NR}_2\text{)}_2\text{carbene was generated in situ}]\). (Carbenes have a vacant orbital and lone pair of electrons and hence can be nucleophilic or electrophilic: \( \text{Moss carbene scale} \)). The resulting solution showed the characteristic signal due to the carbene at -42 ppm \((^{31}\text{P NMR})\) \([52]\) and the presence of the unreacted diphosphene. The use of toluene to increase the solubility of the diphosphene showed a similar lack of reactivity. The specific diazo compound was used primarily because of its synthetic availability. It must not be overlooked that this lack of reactivity may be due to the nature of the carbene. It would be interesting to parallel the experiment, using the same diazo species as those in which the diphosphirane was observed \([51]\) with the starting material, \((\text{Supermes})_2\text{P}_2\).

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3.10 EXPERIMENTAL

3.10.1 1,3,1',3'-Tetraethyl-2,2'-bis(imidazolidine) [19]

\[
\text{Me}_2\text{NCH(OMe)}_2 + \text{EtNHCH}_2\text{CH}_2\text{NHEt} \rightarrow
\]

N,N-dimethylformamide dimethylacetal (17.9g, 20 cm\(^3\), 151 mmol) was added in one portion to a stirred solution of N,N'-diethylethylene diamine (15.1g, 18.3 ml, 130 mmol) in dry benzene (35 ml). This reaction mixture was heated in a distillation vessel to 110 °C for three hours, and the methanol/benzene azeotrope that was produced was collected. The vessel was cooled and the remaining benzene was removed \textit{in vacuo}. The residue was distilled under vacuum to give 1,3,1',3'-tetraethyl-2,2'-bis(imidazolidine). Yield was 11.7g (71%); Bpt. 87-88 °C (3 mm Hg). This was a low melting point, moisture and air sensitive solid, Mpt. 48 °C [19].

3.10.2 Preparation of Diphosphene, ArP=PAr (19)

\[
\begin{align*}
\text{Et} & \quad \text{Et} \\
\text{N} & \quad \text{N} \\
\text{Et} & \quad \text{Et} \\
\text{N} & \quad \text{N}
\end{align*}
\]

3.10.2.1 2ArPCl\(_2\) (12) \rightarrow ArP=PAr (19)

Bisimidazolidine (0.41g, 1.6 mmol) in toluene (10 ml) was added dropwise over 5 minutes to a stirred solution of ArPCl\(_2\) (1.22g, 3.2 mmol) in toluene (20 ml) at ambient temperature. On addition of the
base the solution turned yellow/orange immediately with a visible white precipitate. It was warmed to reflux by the use of an oil bath.

All the solid dissolved and the solution became a clear dark red. After refluxing for 1 hour the stirred solution was allowed to cool to ambient temperature. Quantitative conversion was observed by $^{31}$P NMR (+473.9 ppm). The solid was removed by filtration, and the toluene removed from the filtrate in vacuo. To the resulting yellowish/orange oil (crude yield 76%) a small volume of toluene (7 ml) was added. On cooling the solution to -40 °C crystals (pale yellow needles) of the diphosphene, ArP=PAr were obtained (0.65g, 65%). This yield could be increased by obtaining a second batch of crystals from the supernatant liquid. Total yield 72% (an additional 0.07g collected). It was very difficult to form crystals suitable for X-ray analysis. A solution of diphosphene (from several batches) (1.7g) in toluene (16 ml) was placed in a ripple tank oscillating between +10 and -20 °C. The crystals obtained were submitted for X-ray analysis. The diphosphene is a pale yellow needle-like crystalline solid, which is stable in air.

$\text{Ar}_2\text{P}_2$: Mpt. 185 °C; Analysis Found: C, 34.97; H, 0.87. Required for C$_{18}$H$_4$F$_{18}$P$_2$: C, 34.64; H, 0.65%; IR (KBr) $\nu_{\text{max}}$: 3100 (w,ArCH), 1630 and 1570 (m,ArC=C), 1400-1000 (s,CF$_3$), 780 and 680 (w,"P=P") cm$^{-1}$; UV-Vis (CHCl$_3$) $\lambda_{\text{max}}$ ($\varepsilon$): 283.5 (6763), 389.6 (5696) nm; MS EI (Intensity%): 343 (36,ArP$_2^+$); $^{31}$P (CDCl$_3$) $\delta$: +473.9 (13 line multiplet), $^4$J$_{PF} + ^5$J$_{PF}$ 45.0 Hz; $^{31}$P (solid state) $\delta$: +466.7 ppm, shielding anisotropy +1240 to -100 ppm; $^{19}$F (CDCl$_3$) $\delta$: -56.5 (triplet,12F), -63.8 (s,6F); $^1$H (CDCl$_3$) $\delta$: +8.3 (s).

---

$^1$It was possible to obtain exactly similar yields without refluxing the solution. The reaction mixture was stirred at ambient temperature for 1.5 hours.
3.10.2.2  \[ \text{ArPH}_2 + \text{ArPCl}_2 \xrightarrow{2\text{DBU}} \text{ArP=PAR} \]

DBU (1.44 g, 1.41 ml, 9.46 mmol) in THF (50 ml) was added dropwise over 10 minutes to a stirred solution of ArPH\textsubscript{2} (1.49 g, 4.75 mmol) and ArP\textsubscript{2}Cl\textsubscript{2} (1.82 g, 4.75 mmol) in THF (50 ml) at 0 °C. The solution became yellow and a white precipitate was formed. The reaction mixture was stirred at room temperature for 1 hour. The precipitate was removed by filtration and the solvent removed \textit{in vacuo} to give a yellow viscous oil which was redissolved in toluene (7 ml) and recrystallised at -40 °C to yield 2.01 g (68.0%). \text{Ar}_{2}P_{2} data as previously detailed.

3.10.2.3  \[ 2\text{ArPCl}_2 \xrightarrow{2\text{Mg}} \text{ArP=PAR (19)} \]

Magnesium (0.71 g, 29.2 mmol) was added to a stirred solution of ArP\textsubscript{2}Cl\textsubscript{2} (11.2 g, 29.2 mmol) in THF (150 ml) at 0 °C and the mixture was allowed to warm to room temperature over 30 minutes. The mixture became dark brown and was stirred for a further 10 minutes. The solution was concentrated to half volume and the $^{31}$P NMR recorded. This showed almost quantitative conversion to the diphosphene ($\delta = +473.8$ ppm) with a very small peak at -138 ppm which may be attributed to ArPH\textsubscript{2} (coupling with hydrogen yielded a triplet $^{1}J_{PH}$ 217.9 Hz). The product (19) was not isolated.
3.10.3 2,6-Bis(trifluoromethyl)phenyl dichlorophosphine, \( \text{Ar'}\text{PCl}_2 \)

\[
\text{Ar'}\text{H} + \text{BuLi} \cdot \text{TMEDA} \rightarrow \text{Ar'}\text{Li} \cdot \text{TMEDA} \quad \text{PCl}_3 \rightarrow \text{Ar'}\text{PCl}_2
\]

TMEDA (7.74 ml, 5.96g, 51.3 mmol) was added to a stirred solution of BuLi (1.6 M in hexane, 32.0 ml, 51.3 mmol) in diethylether (50 ml) to generate the BuLi-TMEDA complex. This solution was added dropwise over 10 minutes to a stirred solution of 1,5-bis(trifluoromethyl)benzene (Ar'H) (7.97 ml, 10.98g, 51.3 mmol) in diethylether (50 ml) at 0 °C. This mixture was stirred at room temperature for 8 hours (and became deep brown). It was then added dropwise over 10 minutes to a stirred solution of phosphorus trichloride (9.4 ml, 14.79g, 0.107 mole) in diethyl ether (50 ml) at -78 °C. The reaction mixture was allowed to warm to room temperature. All the volatiles were removed in vacuo and the product (a clear oil) was distilled from the brown oil/solid residue. Yield 5.2g (32%); Bpt 80 °C (10⁻¹ mm Hg); \(^1\text{H} \) NMR (CDCl₃) \( \delta \): 7.3-7.9 (m,aromatic H); \(^{31}\text{P} \) \( \{^1\text{H}\} \) \( \delta \): 146.6 (sept), \( ^{4}\text{J}_{\text{PF}} \) 61.0 Hz; \(^{19}\text{F} \) \( \delta \): -53.14 ppm (d, o-CF₃) \( ^{4}\text{J}_{\text{PF}} \) 61.0 Hz.

3.10.4 Preparation 2,6-Bis(trifluoromethyl)phenyl-phosphine, \( \text{Ar'}\text{PH}_2 \)

\( \text{Ar'}\text{PCl}_2 \xrightarrow{\text{2Bu}_3\text{SnH}} \text{Ar'}\text{PH}_2 \)

Tributyltinhydride (5.11 ml, 5.53g, 19.0 mmol) was added dropwise over 5 minutes to a stirred solution of \( \text{Ar'}\text{PCl}_2 \) (3.0 g, 9.5 mmol) in diethylether (30 ml) at 0 °C. This reaction mixture was then stirred for 2 hours at room temperature and distilled to yield 1.9g \( \text{Ar'}\text{PH}_2 \) (81.3%). Bpt 70 °C (20 mm Hg); IR (Film) \( \nu_{\max} \): 2370 (P-H) cm⁻¹; \(^1\text{H} \) (CDCl₃) \( \delta \): 3.9 (sept d,PH) \( ^1\text{J}_{\text{PH}} \) 214.0 Hz \( ^5\text{J}_{\text{PF}} \) 5.1 Hz, 6.9-7.6 (m,arom...
$^3$P $^1P \delta: -142.7$ ppm (sept) $^4J_{PF} 29.4$ Hz; $^{19}$P $\delta: -61.5$ (doublet of triplets) $^4J_{PF} 29.4$, $^5J_{PH}$ 5.0 Hz.

3.10.5 Preparation of Unsymmetrical Diphosphene, Ar'$\text{ArP}_2$ (20)

3.10.5.1 $\text{Ar'}\text{PH}_2 + \text{ArPCl}_2 \xrightarrow{2\text{DBU}} \text{ArP}'\text{PAr'}$ (20)

DBU (1.44 ml, 9.63 mmol) in THF (15 ml) was added dropwise over 5 minutes to a stirred solution of Ar'$\text{PH}_2$ (1.18 g, 4.80 mmol) and ArPCl$_2$ (1.84 g, 4.80 mmol) in THF (45 ml) at 0 °C. The solution turned a brown/yellow colour, with the formation of a precipitate. This mixture was stirred for 30 minutes at room temperature. The solid was removed by filtration and the filtrate concentrated to yield a pale yellow powder, (1.9 g, 3.4 mmol) - crude yield of (20) was 70%. This solid was washed with several aliquots of diethylether (10 ml), (it had a very limited solubility in this solvent), to yield a pure white solid 1.2 g (44%). Recrystallisation of this powder from CH$_2$Cl$_2$ (10 ml) gave a crystalline material, but only very small crystals were obtained.

The reverse coupling, i.e.

3.10.5.2 $\text{ArPH}_2 + \text{ArP}'\text{Cl}_2 \xrightarrow{2\text{DBU}} \text{ArP}=\text{PAr}'$

gave identical results and a similar yield. Quantities used were: ArPCl$_2$ (1.98 g, 6.3 mmol), ArPH$_2$ (1.97 g, 6.3 mmol), DBU (1.90 ml, 12.7 mmol), THF (100 ml) and the yield was 1.64 g (46%).

Employing the ripple tank oscillation technique between +10 and -30 °C for several days for the diphosphene (0.9 g) in toluene (7 ml) again yielded only small crystals.
ArAr'P₂: Mpt. 131 °C; Analysis Found: C, 36.33; H, 0.60. Required for C₁₇H₅F₁₅P₂: C, 36.72; H, 0.91%. IR (Nujol) vₘₐₓ: 3100 (w, ArCH), 1400-1000 (s, CF₃), 915 (m, CH ring), 710 and 685 (w, C-F "P−P") cm⁻¹; UV-Vis (CHCl₃) λₘₐₓ (ε): 264.2 (40451) nm; MS EI (Intensity%): 343 (10.5, ArP⁺), 324 (20, ArP⁺−F), (Ar ring fragmentation); ³¹P (CDCl₃) δ: +489.0 (P₁), 478.2 (P₂) ppm. ¹J_P₃₃ 552 Hz; ¹⁹F (CDCl₃) δ: ca. -53 (o-CF₃, 12F)², -64.1 (p-CF₃, 3F). No ⁴_J_P₃₃ coupling was resolved.

3.10.6 Preparation of Mesityl Dihalophosphine

\[
3\text{MesMgBr} + 3\text{PCl}_3 \longrightarrow \text{MesPBr}_2 + \text{MesPClBr} + \text{MesPCl}_2
\]

Mesityl magnesium bromide (45 ml, 4.5 mmol, 1 M solution in THF) was added dropwise over 5 minutes to a stirred solution of phosphorus trichloride (6.2 g, 3.9 ml, 45 mmol) in diethylether (150 ml) at -78 °C. This mixture was stirred for one hour. It was allowed to reach room temperature. A yellow solution with a precipitate formed. The latter was removed by filtration, and the solvent removed from the resultant filtrate in vacuo, to yield a crude yellow oil. ³¹P NMR indicated the presence of MesPBr₂ (168.4 ppm) MesPClBr (162.5 ppm) and MesPCl₂ (154.2 ppm) in the ratio 3:2:1 respectively. Yield ca. 8.8 g (70%).

The following stage of the reaction to form the unsymmetrical diphosphene Mes=P=PAr, involved dehydrohalogenation, and the ease of abstraction of HBr made it unnecessary to convert the MesPBr₂/MesPBrCl and MesPCl₂ mixture entirely to the dichloro-derivative.

²Complex o-CF₃ region consisting of two superimposed doublet of doublets, see Figure 3.8(a).

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3.10.7 Preparation of MesP=PAr (21)

\[
\text{MesPX}_2 + \text{ArPH}_2 \xrightarrow{2\text{DBU}} \frac{\text{MesP=PAr} (21)}{-2\text{DBU.HCl}}
\]

\(X=\text{Br, Cl}\)

DBU (0.96 ml, 0.98 g, 6.4 mmol) in THF (20 ml) was added dropwise to a stirred solution of MesPX\(_2\) (\(X=\text{Br, Cl}\)) (ca. 0.9 g, 3.2 mmol) and ArPH\(_2\) (1.0 g, 3.2 mmol) in THF (50 ml). A bright orange solution was formed with a white precipitate. The solid was removed by filtration. The solvent was removed from the resulting filtrate in vacuo to yield a yellowish oil. Yield of crude product ca. 0.62 g (42%); IR (Film) \(\nu_{\text{max}}\): 3100 (w, CH Ar ring), 2910 (m, CH alkyl, CH\(_3\)), 1600-1620 (m, C=C Ar), 1400-1000 (s, C-F), 700 (s, sharp), 680 (s, sharp), 550 (mbr, "P=P") cm\(^{-1}\); UV-Vis (CCl\(_4\)) \(\lambda_{\text{max}}\): 400, 260 nm; \(^{31}\text{P} (\text{CDCl}_3)\) \(\delta\): +524.7 (\(P_1\)), 484.4 (\(P_2\)) ppm; \(^{1}{J}_{\text{pp}}\) 566.8 Hz; \(^{19}\text{F} (\text{CDCl}_3)\) \(\delta\): -53.5 (d of d poorly resolved, 6F, o-CF\(_3\)), -64.0 (s, 3F, p-CF\(_3\)) ppm; \(^1\text{H} (\text{CDCl}_3)\) \(\delta\): 8.9 (2H, CH Ar ring), 8.8 (2H, CH Mes ring), 2.8 (9H, CH\(_3\)-groups).

3.10.8 Preparation of Unsymmetrical Diphosphene, \(^{1}\text{Pr}_2\text{N}-\text{P=P-Ar}\) (22)

Diisopropyl dichlorophosphine, \(^{1}\text{Pr}_2\text{NPCl}_2\), was prepared as described in Section 6.4.9. DBU (0.96 ml, 6.4 mmol) in THF (15 ml) was added dropwise over 5 minutes to a stirred solution of \(^{1}\text{Pr}_2\text{NPCl}_2\) (0.64 g, 3.2 mmol) and ArPH\(_2\) (1.0 g, 3.2 mmol) at room temperature. An orange solution was formed with a white precipitate. The solid was removed by filtration and the solvent removed in vacuo, to yield a yellowish oil. Yield of crude product was ca. 0.77 g (54%). IR (Film) \(\nu_{\text{max}}\): 3100 (vw, CH Ar), 2960 (m, CH alkyl), 1600 and 1620 (w, C=C Ar), 1260 (s), 1260-1000 (s, br, Ar-CF\(_3\)), 800 (s), 700 (w, "P=P") cm\(^{-1}\); \(^{31}\text{P} (\text{THF})\) \(\delta\): +468.5
$\delta (P_1), 234.7 \text{ (P}_2 \text{)} \text{ ppm } ^1J_{pp} 542.1; ^{19}F \text{ (CDC}_1\text{)} \delta: -54.9 \text{ (not resolved, 6F, o-CF}_3), -63.0 \text{ (s, 3F, p-CF}_3) \text{ ppm.}$

3.10.9 Preparation of $t^\text{BuPH}_2$

$$t^\text{BuPCl}_2 + 2\text{Bu}_3\text{SnH} \xrightarrow{\text{THF}} t^\text{-BuPH}_2 + 2\text{Bu}_3\text{SnCl}$$

$t^\text{BuPCl}_2$ was prepared according to S.H. Metzger et al. [53] [Bpt. 145-150 °C (760 mm Hg), $^{31}P \delta: +190.0 \text{ ppm}$.] $\text{Bu}_3\text{SnH}$ (7.02 ml, 7.6g, 26.1 mmol) in THF (20 ml) was added dropwise over 5 minutes to a stirred solution of $t^\text{BuPCl}_2$ (2.1g, 13.2 mmol) in THF (50 ml) at -10 °C. The solution was allowed to reach room temperature and stirred for 1 hour. A THF solution of $t^\text{BuPH}_2$ was collected by vacuum transfer (ca. 1g) and used in situ. $^{31}P\{^1\text{H}\} \delta: -90.23 \text{ ppm (s)} \ ^1J_{PH} 195 \text{ Hz.}$

3.10.10 Attempted Preparations of Other Unsymmetrical Diphosphenes

3.10.10.1

$$t^\text{BuPCl}_2 + \text{ArPH}_2 \xrightarrow{\text{2DBU}} 0\degree\text{C}$$

DBU (1.47 ml, 9.83 mmol) in THF (10 ml) was added dropwise over 5 minutes, to a stirred solution of ArPH$_2$ (1.54g, 4.91 mmol) and $t^\text{BuPCl}_2$ (0.78g, 4.91 mmol) in THF (50 ml) at 0 °C. The solution became deep red with the formation of a precipitate. As the mixture warmed to room temperature, it became clear pale yellow and the solid redissolved. $^{31}P\{^1\text{H}\} \delta: -74.9 \text{ (triplet) J 138.9 Hz, major signal +473.4 ppm [symmetrical diphosphene (19)]; } ^{31}P \delta: +190 \text{ ppm (unreacted } t^\text{BuPCl}_2).$
3.10.10.2 $^{t}\text{BuPH}_2 + \text{ArPCL}_2 \xrightarrow{2\text{DBU}}$

DBU (3.9 ml, 26.1 mmol) in THF (15 ml) was added dropwise over 5 minutes to a stirred solution of $^{t}\text{BuPH}_2$ (ca. 1 g, 12 mmol) in THF (70 ml) and ArPCL$_2$ (4.9g, 12.8 mmol) in THF (50 ml) at -10 $^\circ$C. A precipitate formed, but on warming to room temperature it redissolved to yield a clear yellow liquid. $^{31}\text{P}\{^1\text{H}\}$ $\delta$: +206.5 (s) -31(s), -89(s, unreacted $^{t}\text{BuPH}_2$) $^1J_{PH}$ 193.6 Hz. [Product(s) unassigned].

3.10.10.3 $\text{ArPH}_2 + \text{Ar''PCL}_2 \xrightarrow{2\text{DBU}}$

DBU (1.56 ml, 10.4 mmol) in THF (15 ml) was added dropwise over 5 minutes to a stirred solution of ArPH$_2$ (1.6g, 5.1 mmol) and Ar''PCL$_2$ (1.61g, 5.1 mmol) in THF (50 ml) at 0 $^\circ$C. The solution became dark orange with a solid formed. The solution became yellow on warming to room temperature. The $^{31}\text{P}$ spectrum indicated the presence of the symmetrical diphosphene Ar$_2$P$_2$ (19). $^{31}\text{P}\{^1\text{H}\}$ $\delta$: +473.8 ppm $^4J_{PF}$ + $^5J_{PF}$ 45.0 Hz (major signal). Other minor species $\delta$: +61.2, +30 (s), unassigned), +157.1 (q) $^4J_{PF}$ 86.6 Hz (unreacted Ar''PCL$_2$).

3.10.10.4 $\text{C}_6\text{F}_5\text{PCL}_2 + \text{ArPH}_2 \xrightarrow{2\text{DBU}}$

DBU (1.23 ml, 8.2 mmol) in THF (15 ml) was added dropwise over 5 minutes to a stirred solution of ArPH$_2$ (1.3g, 4.1 mmol) and C$_6$F$_5$PCL$_2$ (1.1g, 4.1 mmol) in THF (50 ml) at 0 $^\circ$C. A solid was precipitated and the solution became orange. On allowing to warm to room temperature it became clear and yellow. $^{31}\text{P}$ $\delta$: +473 (small signal), -83.8, -89.2 ppm (approximate intensity ratio 3:1) observed as singlets, no $^4J_{PF}$ resolved.
3.10.11 Variable Temperature Study of $C_6Cl_5PCl_2 + ArPH_2$ (DBU)

DBU (1.5 ml, 10.0 mmol) in THF (15 ml) was added dropwise over 5 minutes to a stirred solution of $C_6Cl_5PCl_2$ (1.76g, 5.0 mmol) and ArPH$_2$ (1.57g, 5.0 mmol) in THF (50 ml) cooled to -40 °C. A yellow solution was formed (it was difficult to assess whether the solid present was formed in the course of the reaction, or as a result of the insolubility of $C_6Cl_5PCl_2$ in THF). The $^3$P NMR at -40 °C showed only two signals at -83.8 (3P) and -89.2 (1P) ppm. The mixture was allowed to reach room temperature and the $^3$P NMR was re-recorded: 473.8 ppm (major product); 2.3, 0.3, -12.3, -27.8, -83.8 ppm (smaller peaks). It was then filtered, and all the volatile material removed in vacuo. The symmetrical diphosphene was extracted into CH$_2$Cl$_2$ (10 ml) and isolated by crystallisation at -40 °C. Yield was 1.2g (38% based on ArPH$_2$). Characterisation data as detailed in Section 3.10.2.1.

3.10.12 Reactions of Diphosphene Ar$_2$P$_2$ (19)

3.10.12.1 $\text{ArP=PAR} + \frac{1}{8} S_8$ ———

A five-fold excess of elemental sulphur (0.16g, 5.0 mmol) was added to a stirred solution of ArP=PAR (19) (0.64g, 1.0 mmol). This was stirred at room temperature for 6 hours. The $^3$P NMR showed no evidence of reaction (unreacted starting material, δ: +473.8 ppm).

---

$^3$singlets are only possible for *symmetrical* cyclic polyphosphines. A peak at ca. -83 ppm would indicate a hydrogen atom still attached to phosphorus (see Section 7.4).
3.10.12.2 \[ \text{ArP=PAr} + \text{CF}_3\text{COOH} \longrightarrow \]

A large excess of liquid trifluoromethylacetic acid, \(\text{CF}_3\text{COOH}\) (2.2 g, 1.5 ml, 19.3 mmol) was added, with stirring, to \(\text{ArP=PAr}\) (19) (0.82 g, 1.3 mmol) in THF (15 ml) at room temperature. No reaction was detected by \(\text{^31P NMR}\) (unreacted starting material, \(\delta: +473 \text{ ppm}\)).

3.10.12.3 \[ \text{ArP=PAr} + \text{HBF}_4\cdot\text{Et}_2\text{O} \longrightarrow \]

An approximate six-fold excess of tetrafluoroboric acid-diethyl ether complex, \(\text{HBF}_4\cdot\text{Et}_2\text{O}\) (0.92 g, 5.7 mmol) was added to a stirred solution of \(\text{ArP=PAr}\) (0.62 g, 1 mmol) in \(\text{Et}_2\text{O}\) (20 ml) at -10 °C. An orange solution was formed. The reaction mixture was allowed to reach room temperature and stirred for 4 hours. \(\text{^31P NMR}\) showed uniquely unreacted diphosphene \((\delta: +473 \text{ ppm})\).

3.10.12.4 \[ \text{Me}_3\text{SiC(NiPr}_2\text{)}_2 + \text{ArP=PAr} \xrightarrow{\text{h}\nu} \text{ArP-P-P-Ar} \]

\(\text{Me}_3\text{SiC(NiPr}_2\text{)}_2\) (0.55 g, 1.6 mmol) in pentane (7 ml) was added in one portion to a stirred solution of \(\text{Ar}_2\text{P}_2\) (1.0 g, 1.6 mmol) in pentane (50 ml). The mixture was irradiated at 300 nm for 6 hours. \(\text{^31P}\) \(\delta: -42 \text{ ppm (Me}_3\text{Si)}_5\text{CP(NiPr}_2\text{)}_2\) (carbene) [52], \(\text{ArP=PAr}\) 473.8 ppm. These two species remained in situ without reaction. (The same procedure was repeated in toluene and analogous results were obtained).
3.11 REFERENCES


30. a) R.K. Harris personnel communication - Durham University (September 1989).


    

    


CHAPTER FOUR

PHOSPHAALKENES
The most important highlights within the development of phosphaalkene chemistry \([1]\) are now outlined.

1964
Delocalised \(C_{2p}^{-} P_{3p}\) \(\pi\)-bond in phosphamethine cyanine cations. The first \(P=C\) containing compound stable at room temperature [Figure 4.1(a)] \([2]\). The structure was determined by X-ray analysis \([3]\).

1966 and 1971
The synthesis of 2,4,6-trisubstituted phosphabenzenes [Figure 4.1(b)]. The \((p-p) \pi\)-bonds are stabilised by forming part of an aromatic ring \([4,5]\).

![Figure 4.1: Early phosphaalkenes; (a) \(X = S, NR, -CH=CH-\) and \(R = CH_3, C_2H_5\); (b) \(R = Ar\) (ref.4), \(H\) (ref.5).](image)

1976
Becker initiated the breakthrough to isolable acyclic compounds with a localised \(P=C\) bond, by observation of the migration from phosphorus to oxygen in \(P\)-silylated acylphosphanes, and obtained the first example of the structural type: PhP=C(OSiMe\(_3\))\(^{t}\)Bu \([6]\).

A vast amount of work and development has taken place in this area by J.F. Nixon, F. Bickelhaupt, R. Appel, M. Yoshifuji and many others (see References, Section 4.13). This work concentrates on the synthesis of the first phosphaalkene compound containing the \(Ar\) group.
4.2 SYNTHESIS OF PHOSPHAALKENES: LITERATURE SURVEY

The aim of the detailed literature survey of the synthetic routes to phosphaalkenes is to illustrate the vast number of these compound types available. Tables 4.1-4.7 summarise the major developments in phosphaalkene synthesis and provide a fairly comprehensive list of the range of compounds previously described. Ar on phosphorus has been studied (Section 4.4). It would be interesting to study the effect on structure and reactivity of the trifluoromethyl aryl group on the carbon end of the molecule. Preliminary studies in this area have begun (Section 4.11).

\[
\begin{align*}
R_1 - P(X) - C - Y \xrightarrow{\text{Base}} & R_1 - P - C - Y
\end{align*}
\]

<table>
<thead>
<tr>
<th>R(_1)</th>
<th>R(_2)</th>
<th>R(_3)</th>
<th>Y</th>
<th>REF</th>
<th>BASE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supermes</td>
<td>Ph</td>
<td>Ph</td>
<td>H</td>
<td>7,8</td>
<td>DBU</td>
</tr>
<tr>
<td>t- Bu</td>
<td>SAlkyl</td>
<td>SAlkyl</td>
<td>H</td>
<td>7</td>
<td>DBU</td>
</tr>
<tr>
<td>Cl</td>
<td>SAlkyl</td>
<td>SAlkyl</td>
<td>H</td>
<td>9</td>
<td>Et(_3)N</td>
</tr>
<tr>
<td>Mes</td>
<td>fluorenyl</td>
<td>H</td>
<td>10</td>
<td>DBU</td>
<td></td>
</tr>
<tr>
<td>Supermes</td>
<td>Cl</td>
<td>Cl</td>
<td>H</td>
<td>11</td>
<td>DBU</td>
</tr>
<tr>
<td>Cl</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>12</td>
<td>2(Me(_3)Si)(_2)NNa</td>
</tr>
<tr>
<td>Mes</td>
<td>Mes</td>
<td>Mes</td>
<td>H</td>
<td>13</td>
<td>[X] DBU no HCl elimination</td>
</tr>
<tr>
<td>(Me(_3)Si)(_2)N</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>12</td>
<td>(Me(_3)Si)(_2)NNa - NaX, -(Me(_3)Si)(_2)NH</td>
</tr>
<tr>
<td>Ph</td>
<td>SiMe(_3)</td>
<td>SiMe(_3)</td>
<td>Cl</td>
<td>7</td>
<td>Li (THF)</td>
</tr>
<tr>
<td>Cl</td>
<td>SiMe(_3)</td>
<td>SiMe(_3)</td>
<td>SiMe(_3)</td>
<td>14</td>
<td>T&gt;100°C, -Me(_3)SiCl</td>
</tr>
<tr>
<td>Ar</td>
<td>R</td>
<td>NMe(_2)</td>
<td>OR</td>
<td>15,32</td>
<td>ROH ‡</td>
</tr>
</tbody>
</table>

Table 4.1: 1,2-Elimination reactions (-HX); X = Cl [†X = H]; Ar and Ar' refer to aryl species generally.
$$\text{CF}_3\text{PH}_2 \xrightarrow{\text{KOH/-HF}} \text{CF}_2=\text{PH} \xrightarrow{\text{KOH/-HF}} \text{F} \equiv \text{P} \quad (\text{ref. 16})$$

$$\text{(CF}_3\text{)}_2\text{PH} \xrightarrow{-\text{HF}} \text{F}_3\text{CP}=\text{CF}_2 \quad (\text{refs. 17, 18})$$

$$\text{(CF}_3\text{)}_2\text{PH} \xrightarrow{\text{MeOH}\Theta} \text{(CF}_3\text{)}_2\text{P}^- \xrightarrow{-\text{F}} [\text{CF}_3\text{P}=\text{CF}_2] \xrightarrow{\text{MeOH}^-} \text{CF}_3\text{P(0Me)CHF}_2$$

$$\text{OR} \xrightarrow{\text{MeOH}^\ominus} \text{CF}_3\text{P(H)=CF}_2^- \xrightarrow{\text{MeOH/F}^\ominus}$$

(\text{refs. 18, 19})

$$\begin{align*}
\text{Me}_3\text{SnP(CF}_3\text{)}_2 \xrightarrow{320^\circ\text{C}/10^{-3}T} & \text{Me}_3\text{SnF} + \text{F}_3\text{CP}=\text{CF}_2 \quad (\text{refs. 18, 21}) \\
\text{Me}_3\text{SnP(C}_2\text{F}_5\text{)}_2 \xrightarrow{320^\circ\text{C}/10^{-3}T} & \text{Me}_3\text{SnF} + \text{F}_3\text{C}_2\text{P}=\text{C(F)CF}_3 \quad (\text{ref. 18, 22, 23})
\end{align*}$$

\textbf{Table 4.2:} 1,2-\textit{Elimination} to reactive phosphaalkenes; $^\dagger$Careful observation of thermolysis of Me$_3$SnP(CF$_3$)CF$_2$H, Me$_3$SnP(CF$_3$)C$_2$F$_5$ and Me$_3$SnP(CF$_3$)(CF$_3$)$_2$ illustrates a preference for CF$_3$ preservation and attack of CF$_2$X or CF(CF$_3$)$_2$ (the perfluoro effect); $^*$nucleophilic initiated $^\text{H}$ shift from phosphorus to an $\alpha$-carbon atom.
\[
R_1-P \overset{R_2}{\underset{R_3}{\longrightarrow}} \overset{O=C}{\underset{R_5}{\rightarrow}} R_1-P=O \overset{R_4}{\underset{R_5}{\longrightarrow}} R_1-P=C \overset{R_4}{\underset{R_5}{\rightarrow}} R_2 R_4 O
\]

<table>
<thead>
<tr>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>( R_3 )</th>
<th>( R_4 )</th>
<th>( R_5 )</th>
<th>( \text{REF} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph, Mes</td>
<td>SiMe₃</td>
<td>SiMe₃</td>
<td>Ph, Mes</td>
<td>Ph, Mes</td>
<td>7, 25 (^{a} )</td>
</tr>
<tr>
<td>Ph</td>
<td>SiMe₃</td>
<td>SiMe₃</td>
<td>Me₂N</td>
<td>H</td>
<td>24 (^{a} )</td>
</tr>
<tr>
<td>tBu, Mes</td>
<td>SiMe₃</td>
<td>SiMe₃</td>
<td>Me₂N</td>
<td>H</td>
<td>24, 25 (^{a} )</td>
</tr>
<tr>
<td>C₆H₄NH₂</td>
<td>H</td>
<td>H</td>
<td>R (^{b} )</td>
<td>Cl ((\text{ref}))</td>
<td>15, 32</td>
</tr>
<tr>
<td>Supermes</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>C₆H₄Y (^{c} )</td>
<td>26</td>
</tr>
<tr>
<td>Supermes</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>Ar (^{f} )</td>
<td>27</td>
</tr>
<tr>
<td>Supermes</td>
<td>H</td>
<td>H</td>
<td>— fluorenyl —</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Mes</td>
<td>SiMe₃</td>
<td>Li</td>
<td>H</td>
<td>NMe₂</td>
<td>25</td>
</tr>
<tr>
<td>Supermes</td>
<td>SiMe₂Bu (^{t} )</td>
<td>Li</td>
<td>H</td>
<td>Ph</td>
<td>29</td>
</tr>
<tr>
<td>Supermes, Mes</td>
<td>SiMe₃</td>
<td>Li</td>
<td>C₆H₅Y</td>
<td>C₆H₅X</td>
<td>28</td>
</tr>
</tbody>
</table>

\[
R_1-P \overset{R_2}{\underset{R_3}{\longrightarrow}} C \overset{R_5}{\underset{R_6}{\longrightarrow}} R_1-P=C \overset{R_7}{\underset{R_6}{\rightarrow}} R_2 R_5 \overset{R_3 R_4}{\underset{R_7}{\rightarrow}}
\]

<table>
<thead>
<tr>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>( R_3 )</th>
<th>( R_4 )</th>
<th>( R_5 )</th>
<th>( R_6 )</th>
<th>( R_7 )</th>
<th>( \text{REF} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supermes</td>
<td>H</td>
<td>H</td>
<td>Cl</td>
<td>Cl</td>
<td>Cl</td>
<td>H (^{d} )</td>
<td>30, 31</td>
</tr>
<tr>
<td>Supermes</td>
<td>H</td>
<td>H</td>
<td>Cl</td>
<td>Cl</td>
<td>H</td>
<td>H (^{d} )</td>
<td>30, 31</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>H</td>
<td>OMe</td>
<td>OMe</td>
<td>—</td>
<td>—</td>
<td>32</td>
</tr>
<tr>
<td>Ph, Mes</td>
<td>H</td>
<td>H</td>
<td>OMe</td>
<td>OMe</td>
<td>NMe₂</td>
<td>H</td>
<td>32</td>
</tr>
<tr>
<td>Ph, Mes</td>
<td>H</td>
<td>H</td>
<td>OMe</td>
<td>OMe</td>
<td>NMe₂</td>
<td>Me</td>
<td>15, 32</td>
</tr>
<tr>
<td>( R_1 ) (^{e} )</td>
<td>SiMe₃</td>
<td>SiMe₃</td>
<td>F</td>
<td>F</td>
<td>NR₂</td>
<td>NR₂</td>
<td>7</td>
</tr>
</tbody>
</table>

**Table 4.3:** Addition and Condensation; a) with the elimination of hexamethyldisiloxane; b) \( R=H, CH₃, Ph, Me₂N \); c) \( Y=H, OCH₃, NMe₂ \); d) analogous to the isocyanate reaction; e) \( R_1=Me₃Si, tBu, Ph \); f) \( Ar=2,4(\text{MeO})₂C₆H₃ \).
**Table 4.4:** Condensation and 1,3-migration of the Me₃Si group; *the second chlorine atom may be further substituted.*
Table 4.5: Rearrangement and isomerisation to yield phosphaalkenes; (a) via Cope rearrangement (ref. 42); (b) Isomerisation $R_1$-$R_3 = Me_3Si$ (refs. 7, 43); (c) Keto-Enol isomerisation ($P=C$ stabilised by intramolecular H-bonding) (ref. 7).

Table 4.6: Altering group at carbon; $^\dagger R = Ph, SiMe_3, Br$; $^* R = Et, \text{iPr}$. 

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_4$</th>
<th>CONDITIONS</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supermes</td>
<td>SiMe$_3$</td>
<td>R</td>
<td>H</td>
<td>KF (DMF, H$_2$O), -1/2TMS$_2$O</td>
<td>53</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>F</td>
<td>F</td>
<td>NR$_2$</td>
<td>+2R$_2$NH, -R$_2$NH$_2$F</td>
<td>54</td>
</tr>
<tr>
<td>Supermes</td>
<td>Br/Cl</td>
<td>Br/Cl</td>
<td>SiMe$_3$</td>
<td>+BuLi, +TMSCl, -LiCl</td>
<td>11</td>
</tr>
<tr>
<td>Supermes</td>
<td>Br/Cl</td>
<td>Br/Cl</td>
<td>CH$_3$</td>
<td>+BuLi, +CH$_3$I, -LiCl</td>
<td>11</td>
</tr>
</tbody>
</table>
\[
R_1 - P = C \xrightarrow{R_2 \ R_3} \ \frac{R_2 \ R_1}{R_4 - P = C \ \frac{R_2 \ R_3}{R_4}}
\]

<table>
<thead>
<tr>
<th>(R_1)</th>
<th>(R_2)</th>
<th>(R_3)</th>
<th>(R_4)</th>
<th>CONDITIONS</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiMe₃</td>
<td>(R_2 \ N)</td>
<td>(R_2 \ N)</td>
<td>P((t)Bu)₂</td>
<td>+ClP((t)Bu)₂ - Me₃SiCl</td>
<td>46</td>
</tr>
<tr>
<td>SiMe₃</td>
<td>(R_2 \ N)</td>
<td>(R_2 \ N)</td>
<td>H</td>
<td>triethanolsilanol</td>
<td>46</td>
</tr>
<tr>
<td>Cl</td>
<td>Ph</td>
<td>SiMe₃</td>
<td>(-C_6H_4) (t)Bu</td>
<td>- MgBrCl</td>
<td>45</td>
</tr>
<tr>
<td>Cl</td>
<td>Ph</td>
<td>SiMe₃</td>
<td>RR'N (\dagger)</td>
<td>RR'NH/Et₃N</td>
<td>46-48</td>
</tr>
<tr>
<td>Cl</td>
<td>Ph</td>
<td>SiMe₃</td>
<td>OR</td>
<td>ROH/Et₃N</td>
<td>46,48</td>
</tr>
<tr>
<td>Cl</td>
<td>Ph</td>
<td>SiMe₃</td>
<td>(-N(R)-P=C-Ph) (\frac{1}{2}) RH₂/Et₃N</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>Ph</td>
<td>SiMe₃</td>
<td>PR₂ or PRR'</td>
<td>HPR₂/Et₃N or LiPR₂(-LiCl) or Me₃SiPR(R') (-Me₃SiCl)</td>
<td>48</td>
</tr>
<tr>
<td>Cl</td>
<td>Ph</td>
<td>SiMe₃</td>
<td>Supermes</td>
<td>-LiCl</td>
<td>48</td>
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<tr>
<td>Cl</td>
<td>Ph</td>
<td>SiMe₃</td>
<td>R*</td>
<td>(RmgBr)</td>
<td>48,49</td>
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<td>SiMe₃</td>
<td>(-C≡C-SiMe₃)</td>
<td>-LiCl</td>
<td>49</td>
</tr>
<tr>
<td>Cl</td>
<td>Ph</td>
<td>Me₃Si</td>
<td>RN(H)-N- R</td>
<td>NEt₃, -NEt₃·HCl</td>
<td>50</td>
</tr>
<tr>
<td>Me₃Si</td>
<td>OSiMe₃</td>
<td>CMe₃</td>
<td>Cl</td>
<td>+C₂Cl₆, -Me₃SiCl</td>
<td>46</td>
</tr>
<tr>
<td>(Me₃Si)₂N</td>
<td>H</td>
<td>SiMe₃</td>
<td>Supermes</td>
<td>+ArLi - (Me₃Si)₂NLi</td>
<td>51</td>
</tr>
<tr>
<td>(Me₃Si)₂N</td>
<td>H</td>
<td>SiMe₃</td>
<td>(i)Pr₂N</td>
<td>+(i)Pr₂NLi - (Me₃Si)₂NLi</td>
<td>51</td>
</tr>
<tr>
<td>Cl</td>
<td>SR</td>
<td>SR</td>
<td>(t)Bu₂P</td>
<td>-(t)Bu₂PH (Et₃N), -Et₃N·HCl</td>
<td>9, 52a,b</td>
</tr>
<tr>
<td>Cl</td>
<td>SR</td>
<td>SR</td>
<td>(t)Bu₂As</td>
<td>(t)Bu₂AsLi</td>
<td>9, 52b</td>
</tr>
<tr>
<td>Cl</td>
<td>SR</td>
<td>SR</td>
<td>(Me₃Si)₂N</td>
<td>(Me₃Si)₂NLi, -LiCl</td>
<td>52a</td>
</tr>
</tbody>
</table>

Table 4.7: Altering group at phosphorus; \(\dagger R = R' = iPr\) or \(R = H, R' = tBu; * R = Et, nBu, Ph.\)
Figure 4.1: $^{31}P$ NMR spectrum of ArPF$_2$ (3) generated by the addition of PhCH$_2$Li·TMEDA to ArCl$_2$ (12) in Et$_2$O.
4.3 SYNTHETIC PROCEDURES USED FOR PHOSPHAALKENES

The following methods (1-4) were used in the attempted synthesis of phosphaalkenes with Ar attached to phosphorus.

4.3.1 Method 1: Attempted Formation of a P-C Bond by Reaction of RLi with ArPCL₂

The first method employed for phosphaalkene synthesis is shown in Equation 4.1(a). Overall two major synthetic problems were encountered: (i) the inherent preference for tertiary phosphine formation [55] [Equation 4.1(b)] and (ii) attack at fluorine atoms on the ring system thought to be due to attack by the lithium species.

\[
\begin{align*}
RR_{1}CHLi + ArPCL_{2} & \rightarrow RR_{1}CH-PAr(Cl) \xrightarrow{DBU} R_{1}RC=PAr & (4.1a) \\
(R=Ph, R_{1}=Ph,H).
\end{align*}
\]

\[
2RR_{1}CHLi + ArPCL_{2} \rightarrow ArP(RR_{1}CH)_{2} + 2LiCl & (4.1b)
\]

Ph₂CHLi (11) and PhCH₂Li (10) were generated in the presence of TMEDA [56] and used in situ by dropwise addition to excess ArPCL₂ (12) dissolved in diethylether. ArPF₂ (3) was present in the \(^{31}\text{P}\) and \(^{19}\text{F}\) NMR spectra, and by concentrating the mixture it could be isolated, and its identify confirmed by measuring its boiling point and NMR parameters (Figure 4.1). On addition of PhCH₂Li·TMEDA (10) to ArPCL₂ some diphosphene (19) with its characteristic \(^{31}\text{P}\) shift (473.8 ppm) was observed in the NMR (Figure 4.2).
Figure 4.2: Possible routes for PhCH₂Li attack on ArPCl₂.

With Ph₂CHLi·TMEDA (11) a similar reaction was apparent, with the ¹⁹F NMR possessing a very complex "CF₃" region and a doublet of septets $[\delta=-90.9 \text{ ppm, } ^{1}J_{PF} 179.6, ^{5}J_{PF} 18.6 \text{ Hz, cf. } \text{ArPF}_2 (3)]$ corresponding to a possible "P-F" species. This problem, (aside from loss of yield due to tertiary phosphine formation)[55] was not seen with Cl₂CHLi addition to ArPCl₂. It is also interesting to note that no attack at the ring fluorines occurs on addition of butyllithium and methyllithium.

Attack on the ring was seen with lithium species in the presence of TMEDA. In general organolithium compounds (4 orbitals, 2 electrons) form aggregates. TMEDA is a good electron source and partially due to its steric demands will cause Ph₂CHLi (11) and PhCH₂Li (10) to be monomeric. (It must be noted that BuLi·TMEDA does not attack CF₃[57]). This may be attributed to an increase in the reactivity of the monomeric organolithium species. However, to develop this argument, information on the mechanism of attack for aggregates would be required. For example, do they break up before attacking as nucleophiles?
There are many other variables which may account for these results. The order of decreasing basicity in the lithio compounds used in this study is: Me > Bu > CHCl₂ > PhCH₂ > Ph₂CH. [CHCl₂Li (9) is generated by BuLi reaction with CH₂Cl₂, and hence butyllithium is the more basic]. ArPCl₂ has two distinctive electrophilic sites for nucleophilic attack, ie. P-Cl and C-F (Figure 4.3)

![Figure 4.3: Two possible sites for nucleophilic attack in ArPCl₂.](image)

It is not clear if steric effects do play a part, since Ph₂CHLi and PhCH₂Li are certainly the larger of the lithio species used, especially with TMEDA coordinated. However, it is assumed that the attack takes place at the ortho-CF₃ groups since peaks in the ¹⁹F NMR corresponding to the para-CF₃ groups appear to remain intact.

4.3.2 Method 2: Attempted Formation of a P-C Bond by the Reaction of a Geminal Dichlorocarbon Species with an Ar-Substituted Phosphide

One standard route to phosphaalkenes involves the action of the phosphide (29) on the geminal dichlorocarbon species (30). The process (Equation 4.2) is followed by treatment with base to eliminate HCl (Table 4.1) [7-15].

\[
\text{ArP(H)Li} + \text{Cl}_2\text{CR}_1\text{R}_2 \rightarrow \text{ArP(H)C(Cl)R}_1\text{R}_2 \quad (4.2)
\]

(29) (30)
Cooling ArPH$_2$ (15) to -78 °C in THF, and addition of 1 equivalent of butyllithium dropwise, resulted in an immediate black colouration. On addition of the carbon species (30) ($R_1 R_2 = \text{Ph}$), and allowing it gradually to reach room temperature only a very broad signal indicative of decomposition was observed in the $^{19}$F NMR. This was attributed to the attack of phosphide (29) on a second molecule at the CF$_3$. The inherent instability of the phosphide even at very low temperature was also apparent with 2,6-bis(trifluoromethylphenyl) as the substituent. This has since been verified by J Escudie [58].

4.3.3 Method 3: Reaction of ArPCl$_2$ with Dichlorocarbon Species

In view of the apparent attack by lithio species on the CF$_3$ groups, the following coupling reactions were attempted:

1. Ph$_2$CCl$_2$ + ArPCl$_2$ $\underset{\text{Mg}}{\text{\rightarrow}}$ symmetrical diphosphene.
   
   The copious amount of solid formed was attributed to possible Ph$_2$CCl$_2$ coupling with itself.

2. CCl$_4$ + ArPCl$_2$ $\underset{\text{Mg}}{\text{\rightarrow}}$
   
   Some diphosphene was formed and a signal was observed in the $^{31}$P NMR possibly corresponding to ArP=Cl(Cl)$_2$ (conversion to the phosphaalkene was ~ 50% w.r.t $^{31}$P NMR spectrum).

3. CH$_2$Cl$_2$ + ArPCl$_2$ $\underset{\text{Mg}}{\text{\rightarrow}}$ symmetrical diphosphene + small peak possibly due to Ar-P=C-(H)$_2$

   Attempts to isolate products from (2) and (3) were not successful.

The inherent competing symmetrical diphosphene (19) reaction (Equation 3.3, Section 3.4) illustrates the unsuitability of this reaction for phosphaalkene synthesis. In all cases preference for the initial formation of a P-C bond would be anticipated (Table 4.1).
The route to the phosphaalkene where it appeared to have formed may proceed via an initial carbon or even a "phosphorus based" Grignard, or via carbene generation, for example the greater stability \([59]\) of \(\text{Ph}_2\text{C}\) over \(\text{Cl}_2\text{C}\): in (1) may induce its more selective coupling to give \(\text{Ph}_2\text{C}\equiv\text{CPh}_2\) instead of forming a phosphaalkene.

### 4.3.4 Method 4 Reaction of ArPH\(_2\) with Dichlorocarbon species

More selective coupling was attempted by intermolecular dehydrohalogenation, i.e. by the following routes:

1. \(\text{HCCl}_3 + \text{ArPH}_2 \xrightarrow{\text{DBU}} \)  
   Signals upfield ca. -84 and -89 ppm (intensity ratio 3:1) were obtained (see Section 7.3).

2. \(\text{Ph}_2\text{CCl}_2 + \text{ArPH}_2 \xrightarrow{\text{DBU}} \text{ArP}=\text{P}-\text{Ar} (19) \) symmetrical diphosphene.  
   The upfield signals in (1), and the symmetrical diphosphene (19) formation in (2) are interesting observations. \(\text{ArPH}_2 (15)\) in the presence of DBU gives only a signal in the \(^{31}\text{P}\) NMR corresponding to unchanged \(\text{ArPH}_2\), no diphosphene is formed. In (2), therefore, a chlorine exchange process may be postulated (see Section 7.3).

### 4.3.5 Method 5: Reaction of ArPH\(_2\) with KOH and CHCl\(_3\)

The failure of the phosphaalkene synthetic route \([30,31]\) (Equation 4.3) was attributed to the strong nucleophilic base character of KOH.

\[
\text{ArPH}_2 (15) + \text{CHCl}_3 \xrightarrow{\text{KOH}} \text{ArP}≡\text{C(H)}\text{Cl} \quad (4.3)
\]

The complex \(^{19}\text{F}\) NMR is possibly indicative of OH\(^-\) attack at the fluorine site, causing decomposition (Figure 4.4).
Synthesis of Phospha-alkene

The dichloro-substituted phospha-alkene was synthesised by initial P-C bond formation followed by dehydrohalogenation.

\[ \text{b) } \text{CF}_3 - \text{C}_2 \text{H}_2 \text{Cl}_2 + \text{LiCHCl}_2 \rightarrow \text{LiCFC} \text{Cl}_2 \]

\[ \text{F}_3 \text{C} \]

\[ \text{F}_3 \text{C} \]

\[ \text{F}_3 \text{C} \]

\[ \text{F}_3 \text{C} \]

Figure 4.5: The synthesis and $^{31}$P NMR data of the new phospha-alkene, $\text{Ar-}P=\text{C(Cl)}_2$ (31).
4.3.6 Method 6: Acid Catalysed Reaction Between ArPH₂ and Carbonyls

A further route to phosphaalkenes is shown in Equation 4.4 (see also Table 4.3) [15, 24-27].

$$\text{Ph}_2\text{C}=\text{O} + \text{ArPH}_2 \xrightarrow{\text{H}^+ / \text{catalyst}} \text{ArP=C(Cl)2}$$ (4.4)

This reaction was not successful, even using benzaldehyde (greater $\delta^+$ carbon and smaller steric demand). This may be attributed to the reduced nucleophilic character of the phosphorus bearing an electron withdrawing group (Ar).

4.4 SYNTHESIS OF THE PHOSPHAALKENE ArP=C(Cl)₂ (31)

4.4.1 Characterisation

The first phosphaalkene containing the Ar group was synthesised according to the scheme depicted in Figure 4.5 (see Table 4.1). Its $^{31}$P NMR data and mass spectrum are illustrated in Figures 4.5 and 4.6 respectively. Phosphaalkene (31) was stable to vacuum distillation and fully characterised (see Section 4.12.3).
Figure 4.6: Mass spectra of the new phosphaalkene, Ar-P=C(Cl)₂ (31); (i) electron impact (EI); (ii) positive ion chemical ionisation (CI⁺).
4.4.2 MNDO Calculation

The molecular geometry resulting from an MNDO calculation on this new compound is now presented [Figure 4.7(a)]. The stability of Ar-P=C(Cl)$_2$ [where Ar = 2,4,6-tris(trifluoromethyl)phenyl] may be attributed to the resonance form shown in Figure 4.7(b).

![Figure 4.7: MNDO calculations on ArP=C(Cl)$_2$ (31); (a) molecular geometry and (b) resonance stabilisation.](image)

High stability is associated with $\pi$-acceptance at phosphorus and $\pi$-donation at carbon, and vice versa. Characteristically carbon attached to another atom Y [Y(R)C=PAr, eg. Y = Cl, N, O] leads to an increase in shielding of the phosphorus nuclei attributed to conjugation of the atom Y with the $\pi$-bond. This is most pronounced when the substituent at phosphorus is electron-withdrawing, eg. Ar. [This effect is illustrated by the shift sequence obtained in this work, ie. ArPCCl$_2$ (31) +202 ppm, ArP=C(Ph)H (32) +218 ppm, ArP=C(SiMe$_3$)H (33) +283 ppm].

4.5 ATTEMPTS TO SUBSTITUTE CHLORINE AT CARBON ON ArP=C(Cl)$_2$

In many similar systems of formula ArP=CCl$_2$, direct chlorine substitution for other organo groups, for example Me$_3$Si, Bu (see Table 4.5) provides a useful facile route to other phosphaalkene derivatives.
4.5.1 Substitution By $\text{Me}_3\text{Si}$

BuLi was added to the new species $\text{ArP} = \text{C(Cl)}_2$ [$\text{Ar} = 2,4,6$-tris-(trifluoromethyl)phenyl] at $-78$ °C. The solution blackened immediately even with maintenance of the low temperature. Dropwise addition of $\text{Me}_3\text{SiCl}$ and allowing to warm to room temperature showed no reaction proceeding as shown (Equation 4.5).

\[
\begin{align*}
\text{Ar-P=C(Cl)}_2 & \xrightarrow{\text{BuLi}} \text{Ar-P=C(Cl)Li} \xrightarrow{\text{Me}_3\text{SiCl}} \text{Ar-P=C(Cl)SiMe}_3 \\
(31) & \quad (34) & \quad (35)
\end{align*}
\]

Decomposition was indicated by a broad absorption in the $^{19}\text{F NMR}$, attributed to the inherent instability of the lithio derivative (34). This was possibly a result of LiCl elimination from (34) generating a reactive carbene, or an intermolecular reaction resulting in fluorine attack by the lithium species on a second molecule.

4.5.2 Substitution by Ar

The reaction $\text{ArP} = \text{C(Cl)}_2 + \text{ArLi}$ did not generate the required product i.e. $\text{Ar-P} = \text{C(Cl)}\text{Ar}$. This was as expected because of the low basicity of $\text{ArLi}$, illustrated by the reaction $\text{ArLi} + \text{CCl}_4 \rightarrow \text{ArCl}$ and by the reaction of $\text{ArLi}$ (2) with $\text{Cl}_2$ or $\text{C}_2\text{Cl}_6$ respectively [60e]. Indeed in this case $\text{ArP} = \text{C(Cl)}_2$ was the only phosphorus containing species observed in the $^{31}\text{P NMR}$. The $^{19}\text{F NMR}$ also showed the presence of $\text{ArCl}$ [61].
To avoid the presence of lithium species \textit{in situ} with the aryl group, or strong bases, or the requirement of a nucleophilic phosphorus, several possibilities were considered.

1) The preparation of a secondary chlorophosphine with an R group bearing on $\alpha$-H, and subsequent HCl elimination with DBU: (a) the R group could be introduced primarily onto PCl$_3$ followed by subsequent addition of ArLi (2) (ArLi is selective enough to allow mono substitution into a primary phosphine) or, (b) via a less reactive organometallic species, for example a Grignard, organocadmium or organozinc reagent substituting directly into ArPCl$_2$ (12).

2) Preparation of the halomethylene-phosphine, Cl-P=C(R)R' with the aim to substitute chlorine for aryl in the final stage.

The first route (1) was chosen since it allowed purification of the secondary phosphine before phosphaalkene generation. The species formed in (2) may be unstable and therefore require the maintenance of low temperature, for example Cl$_2$C=PCl. (However, halomethylene phosphines with two Me$_3$Si groups or a Me$_3$Si and a Ph group on carbon, are thermally stable and can be vacuum distilled without decomposition) [7].

4.7 PHOSPHAALKENE PREPARATIONS FROM SECONDARY PHOSPHINES

4.7.1 Synthetic Routes

Preparations were attempted of RAIPC1 [R = Me$_3$SiCH$_2$ (36), PhCH$_2$ (37), vinyl (38) and CHCl$_2$ (39)]. The R group may be introduced \textit{via} many routes (Chapter 2). The two employed in this case (Equations 4.6
and Equations 4.7) are now discussed. Slightly higher yields were obtained (from Equation 4.6) by the use of the lithio derivative.

\[
\begin{align*}
\text{(Et}_2\text{N)}_2\text{PCl} & \xrightarrow{\text{LiR or RMeBr}} \text{(Et}_2\text{N)}_2\text{PR} \quad \frac{4\text{HCl}}{2\text{Et}_2\text{NH}_2\text{Cl}^-} \\
\text{RPCl}_2 & \xrightarrow{-\text{LiCl}} \text{RP}(-\text{Ar})\text{Cl} \\
\text{(a) R}_2\text{Cd} + 2\text{PCl}_3 & \rightarrow 2\text{RPCl}_3 \xrightarrow{-\text{ArLi}} 2\text{RP}(-\text{Ar})\text{Cl} \\
\text{(b) R}_2\text{Cd} + 2\text{ArPCl}_2 & \rightarrow 2\text{ArP}(-\text{R})\text{Cl}
\end{align*}
\]

(4.6)

4.7.2 Specific Synthetic Problems

A disadvantage of the first method was that removal of all the amine salt, i.e. \(\text{Et}_2\text{NH}_2\text{Cl}^-\) proved difficult, and subsequent reaction with \(\text{ArLi}\) resulted in a loss of yield (Experimental, Section 4.12.5.1). This was overcome by the use of \(\text{ArLi}\) in a slight excess. Specific examples in which a particular preparative route is not applicable include the following: Equation 4.6 should not be used for the trimethylsilylmethyl substituent (36) since reaction with hydrogen chloride to remove the amine groups may cleave the carbon silicon bond. Equations 4.6 and 4.7(a) could not be used in the presence of vinyl (38) since this group must be introduced last [Equation 4.7(b)], as \(\text{ArLi}\) (2) may add across the unsaturated "C=C" functionality. Equations 4.6 and 4.7(a) are also not suitable for the synthesis of \(\text{ArP}(-\text{CHCl}_2)\text{Cl}\) (39), since \(\text{ArLi}\) (2) reacts with \(\text{CHCl}_2\text{PCl}_2\) causing \(\text{ArCl}\) formation, and [in Equation 4.6] would possibly induce rearrangement associated with a nucleophilic three-coordinated phosphorus atom, with an electrophilic atom in an \(\alpha\)-position \([12]\). The possible rearrangement is illustrated in Figure 4.8 and is known for \(X = \text{SiMe}_3\) \([12]\), although it may not occur for \(X = \text{Et}\).
Figure 4.11: $^{31}$P NMR spectra of compounds shown in Table 4.8; (i) $\text{ArP} = \text{C(SiMe$_3$)}(\text{H})$ (33); (ii) $\text{ArP} = \text{C(Ph)}(\text{H})$ (32) recorded as solutions in THF.
4.7.3 Products Obtained

The secondary phosphines shown in Table 4.8 were isolated. Dehydrochlorination with DBU did not appear to be problematic. Preliminary studies and attempts at the isolation of these compounds have begun (Figure 4.11). Limited coordination data is available on species (32) and (33). The vinyl derivative is a special case and is discussed separately (Section 4.10). In each case only one isomeric form was observed with respect to the $^{31}$P and $^{13}$C NMR parameters. This was assigned to the E-conformation (minimising non-bonding repulsions).

![Figure 4.8: Possible rearrangement for (Et$_2$N)$_2$P(CHCl$_2$).](image)

### Secondary phosphines

<table>
<thead>
<tr>
<th>Secondary phosphines</th>
<th>Phosphaalkenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCH$_2$P(Ar)Cl (37)</td>
<td>PhCH=PAr (32)</td>
</tr>
<tr>
<td>Me$_3$SiCH$_2$P(Cl)Ar (36)</td>
<td>Me$_3$SiCH=PAr (33)</td>
</tr>
<tr>
<td>VinylP(Cl)Ar (38)</td>
<td>(Section 4.10)</td>
</tr>
</tbody>
</table>

Table 4.8

Secondary phosphine (36) is a particularly interesting moiety, since there also exists the possibility of Me$_3$SiCl elimination [7-12] with the
4.8 THE EFFECT OF THE Ar GROUP ON CARBON POLARITY

Within phosphaalkene synthetic chemistry, the requirement of at least one substituent other than H β-displaced to phosphorus to allow HCl elimination, is well-known [1,7].

In view of the electron-withdrawing nature of the Ar group, it was considered valuable to study its influence on the acidity of the hydrogen atom at the carbon, from an increase in the P-C bond polarity (Figure 4.9).

![Figure 4.9](image)

Ar group effect on P-C bond polarity.

The secondary phosphine MeP(Cl)Ar (40), was prepared by the addition of ArLi to MePCl₂. No apparent HCl abstraction was observed even by increasing the base strength i.e. using DBU, DABCO and LDA. Signals in the upfield region of the ³¹P NMR were observed. This may be attributed to the nucleophilic displacement of the chlorine on phosphorus, particularly in the case of LDA (Figure 4.10).

![Figure 4.10](image)

Nucleophilic displacement of Cl

The phosphaalkene ClP=CH₂ has been obtained from the starting material Cl₂PCH₃ by thermolysis [62]. This technique may have a possible application here.
An interesting area to develop would involve a study of the reactivity of the phosphaalkene species. Many reactions of other phosphaalkenes are known. The presence of a weakly bonded \( \pi \)-system is responsible for their pronounced tendency to form new \( \sigma \)-bonds \cite{46}. Figure 4.12 illustrates five types of reactions of phosphaalkenes distinguished here in terms of the change in the coordination number (\( \sigma \)) and valence (\( \lambda \)) of the phosphorus atom in the course of the chemical conversion. Each class of these reactions has been extensively reviewed.

(a) 1,2-Addition at the \( P=C \) bond: \( \sigma^2 \lambda^3 \rightarrow \sigma^3 \lambda^3 \)

\[
\begin{align*}
-\quad P=\overset{\lambda^3}{\underset{\sigma^3}{\overset{\sigma}{C}}} + XY & \rightarrow \quad \overset{\lambda^3}{\underset{\sigma^3}{\overset{\sigma}{P}}}-\overset{\lambda^3}{\underset{\sigma^3}{\overset{\sigma}{C}}} \\
& \quad X \quad Y
\end{align*}
\]

(b) Formation of tri-coordinated pentavalent phosphorus: \( \sigma^2 \lambda^3 \rightarrow \sigma^3 \lambda^5 \)

\[
\begin{align*}
-\quad P=\overset{\lambda^3}{\underset{\sigma^3}{\overset{\sigma}{C}}} + X & \rightarrow \quad \overset{\lambda^3}{\underset{\sigma^3}{\overset{\sigma}{P}}}-\overset{\lambda^3}{\underset{\sigma^3}{\overset{\sigma}{C}}} \\
& \quad \overset{\lambda}{\underset{\lambda^3}{\overset{\lambda}{X}}} \\
& \quad \overset{\lambda}{\underset{\lambda^3}{\overset{\lambda}{X}}}
\end{align*}
\]

(c) Formation of tetra-coordinated pentavalent phosphorus: \( \sigma^2 \lambda^3 \rightarrow \sigma^4 \lambda^5 \)

\[
\begin{align*}
-\quad P=\overset{\lambda^3}{\underset{\sigma^3}{\overset{\sigma}{C}}} + XY & \rightarrow \quad \overset{\lambda^3}{\underset{\sigma^3}{\overset{\sigma}{P}}}-\overset{\lambda^3}{\underset{\sigma^3}{\overset{\sigma}{C}}} \\
& \quad X \quad Y
\end{align*}
\]

(d) Functionalisation occurring without a change in valence or coordination of phosphorus: \( \sigma^2 \lambda^3 \rightarrow \sigma^2 \lambda^2 \)

(e) 1,2-Elimination leading to compounds of mono-coordinated phosphorus: \( \sigma^2 \lambda^3 \rightarrow \sigma^1 \lambda^3 \)

\[
\begin{align*}
X-P=\overset{\lambda^3}{\underset{\sigma^3}{\overset{\sigma}{C}}} & \quad \overset{R}{\underset{\lambda^3}{\sigma^1}} \rightarrow \quad P=\overset{\lambda^3}{\underset{\sigma^3}{\overset{\sigma}{C}}} - Y + XY
\end{align*}
\]

Figure 4.12
This work has involved a study of the coordination chemistry of ArP=CCl₂ (31), ArP=CH(Ph) (32) and ArP=CH(SiMe₃) (33) with the Pt(II) dimer, (PEt₃)₂Pt₂Cl₄ (Chapter 5).

It is obvious that more work is required to purify ArP=CH(Ph) and ArP=CH(SiMe₃) to enable their full characterisation. However, it was considered appropriate to present the data and properties of these materials obtained so far, for completeness of this section of work.

4.10 PHOSPHAALLENES

4.10.1 Introduction

Many stable 1-phosphaallenes are known [63-67] and synthetic routes to these species are shown in Equation 4.8 [63, 64] and (via a phospha-ketene) Equation 4.9 [64, 65] and 4.10 [67].

\[
\begin{align*}
\text{ArPH}_2 + \text{BuLi} & \rightarrow \text{ArP(H)Li} + \text{BuMe}_2\text{SiCl} \\
\text{ArP-H} & \rightarrow \text{ArP(H)SiMe}_2\text{Bu}^t \\
\text{ArP}=\text{C}=\text{CPh}_2 & \rightarrow \text{BuMe}_2\text{SiO}^- \\
\text{ArP}=\text{C}=\text{CPh}_2 & \rightarrow \text{ArP}=\text{C}=\text{CPh}_2 \\
\end{align*}
\]

Equation 4.8

\[
\begin{align*}
\text{ArP}=\text{C}=\text{CPh}_2 + \text{BuMe}_2\text{SiO}^- & \rightarrow \text{ArP}=\text{C}=\text{CPh}_2 \\
\text{ArP}=\text{C}=\text{CH}(\text{Ph}) & \rightarrow \text{ArP}=\text{C}=\text{CH}(\text{Ph}) \\
\text{ArP}=\text{C}=\text{CPh}_2 & \rightarrow \text{ArP}=\text{C}=\text{CPh}_2 \\
\end{align*}
\]

Equation 4.9

\[
\begin{align*}
\text{ArP}=\text{C}=\text{CPh}_2 + \text{Ph}_3\text{PO} & \rightarrow \text{ArP}=\text{C}=\text{CPh}_2 \\
\text{ArP}=\text{C}=\text{CPh}_2 & \rightarrow \text{ArP}=\text{C}=\text{CPh}_2 \\
\end{align*}
\]

Equation 4.10
4.10.2 Attempted Preparation of 1-Phosphaallenes from a Secondary Vinyl Phosphine

The secondary chlorovinyl phosphine, ArP(Cl)CH=CH\textsubscript{2} (38) was isolated and fully characterised. This species was stable to vacuum distillation.

A possible route to the formation of a phosphaallene was postulated by the elimination of HCl from this molecule. This is a standard route used for the preparation of phosphaalkenes \[7-15\], from the phosphorus bearing an organo-group with an \(\alpha\)-H (and a substituent other than H increasing its acidity), together with a bond directly to chlorine. A similar method was used in the synthesis of a 1-phosphadiene \[68\].

4.10.3 Results

Following the addition of DBU in THF at 0 °C to (38), no phosphaallene with a characteristic \(^{31}\text{P}\) shift in the range \(-75\text{--}80\) ppm was observed \[63-67\]. Shielding with respect to the initial secondary phosphine would be expected, attributed to the resonance structure:

\[
\text{Ar-P=CCR}_2 \quad \rightarrow \quad \Theta \quad \Theta \\
\text{Ar-P=CCR}_2
\]

Instead, a clean reaction yielding a septet downfield at +221 ppm in the \(^{31}\text{P}\) NMR was observed. Unfortunately time did not allow isolation of the compound, although it appeared stable in solution for a few days. It may be postulated that a phosphaalkene has been formed, possibly by the initial formation of the allene \textit{via} HCl abstraction followed by either addition of further HCl, [Figure 4.13(a)] or by dimerisation [Figure 4.13(b)]. Other points of consideration include a possible Michael addition [Figure 4.13(c,d)].
A very recent publication [69] reports the observation of an unprecedented thermal isomerisation of a secondary vinylphosphine into a phosphaalkene via a radical mechanism (Figure 4.14). It is obvious here that further work must be carried out to isolate the postulated 'phosphaalkene' species.

Figure 4.14: Thermal isomerisation of a secondary vinylphosphine into a phosphaalkene; $^{31}\text{P NMR }$ δ: 210.5 ppm.

4.11 THE AR GROUP ON CARBON

4.11.1 Aryl Substituted Methyl Groups

In the hope of preparing phosphaalkenes with the carbon end bearing the new Ar substituent, the following substituted methyl derivatives
were prepared: ArCH$_3$ (41), ArCH$_2$OH (42), ArCH(CH$_3$)$_2$OH (43), ArCHPhOH (44) and ArCH$_2$Br (45).

Very recently the preparation of the phenol derivative (Equations 4.11 and 4.12) has been reported [70].

\[
\text{Me}_3\text{SiO-SiMe}_3 + \text{C}_6\text{H}_2(\text{CF}_3)_3\text{Li} \rightarrow \text{C}_6\text{H}_2(\text{CF}_3)_3\text{OSiMe}_3 + \text{Me}_3\text{SiOLi} \quad (4.11)
\]

\[
\text{C}_6\text{H}_2(\text{CF}_3)_3\text{OSiMe}_3 + \text{HCl} \rightarrow \text{C}_6\text{H}_2(\text{CF}_3)_3\text{OH} \quad (4.12)
\]

**4.11.2 Potential Synthons for Phosphaalkenes**

These should allow the formation of organometallic substituted methyl derivatives, and hence via secondary phosphines to phosphaalkenes, utilising the well-established phosphaalkene synthesis via HCl elimination (Figure 4.15).

\[
\text{ArC(R)H(OH)} \rightarrow \text{ArC(R)H(Br)} \rightarrow \text{ArC(R)H(MgBr)} + \text{PCl}_3
\]

\[
\text{ArCH}_3 \rightarrow \text{ArCH}_2\text{Li} \rightarrow \text{ArC(R)H(PCl}_2) \rightarrow \text{ArC(R)H(PCl}_3)
\]

\[
\text{Ar}(\text{R})\text{C}=\text{P}-\text{Cl} \rightarrow \text{DBU} \rightarrow \text{DBU-HCl}
\]

**Figure 4.15:** Proposed route to phosphaalkenes with the carbon end bearing the Ar substituent; R=H, CH$_3$, Ph; †possibly via a less reactive organometallic reagent.

The advantage of this approach would be the ability to substitute the chlorine on the phosphorus for other groups [7,44-52].

**4.11.3 Potential Synthons for Phosphaalkynes**

With 2 α-hydrogen atoms on the carbon, it may be possible to eliminate two moles of HCl to generate the respective phosphaalkyne.
Figure 4.16: IR film spectra of the alcohols (42), (43) and (44).
Phosphaalkyne preparation (Equations 4.13) and reactivity has attracted much attention, for example their synthesis [71-73] and reactivity (3 + 2 cycloaddition) [74].

4.11.4 The Alcohols

With the alcohols, ArC(OH)HR it was interesting to consider the interaction between the hydroxyl group and the fluorine atoms on the ortho-trifluoromethyl groups, to determine the extent of the intra- or inter-molecular hydrogen-bonding by infrared spectroscopy [75]. Figure 4.16 illustrates the decreasing effect of hydrogen-bonding in the series of compounds: ArCH₂(OH) (42) (νOH 3200 cm⁻¹), ArCH(CH₃)(OH) (43) (νOH 3400 cm⁻¹) and ArCH(Ph)(OH) (44) (νOH 3420 cm⁻¹).

Crystals of ArCH₂OH and ArCH(CH₃)(OH) have been obtained. By X-ray structure elucidation it may be possible to determine quantitative data on the HO⋯F distance.

With these systems and ArCH₃ the broad lines in the ¹⁹F NMR were attributed to a significant interaction between the hydrogen and the fluorine, illustrated for ArCH₃ (Figure 4.17), and presumably slowing down the equivalencing of the CF₃ groups by rotation. These systems merit further investigation by temperature-dependence ¹⁹F NMR studies.
4.12 EXPERIMENTAL PROCEDURES

4.12.1 Preparation of ArPF$_2$ from Ph$_2$CHLi·TMEDA and ArPCl$_2$

Ph$_2$CHLi·TMEDA was synthesised as described in the literature [56]. Ph$_2$CHLi·TMEDA (100 ml, 10 mmol, 0.1 M in THF) was added dropwise over 10 minutes to a stirred solution of ArPCl$_2$ (3.28 g, 10 mmol) in THF (150 ml) at -78°C. The solution became deep brown with addition of the first drop of the lithio derivative. The mixture was allowed to warm to room temperature. NMR data on the solution gave: $^{31}$P $\delta$: +473 [Ar$_2$P$_2$ (19)], +184.6 ppm [t of sept, ArPF$_2$ (3)] $^1$JP 1179.5 Hz, $^4$JP 50.8 Hz; $^{19}$F $\delta$: -56.3 (t, o-CF$_3$) $^4$FP 45 Hz, -63.8 ppm (p-CF$_3$) [Ar$_2$P$_2$ (19)]; -55.5 (d of t,6F) $^4$FP 50.6 Hz $^5$FP 18.6 Hz, -64.5 (s,3F), -90.9 ppm (d of sept,2F) $^1$FP 1179 Hz $^5$FP 18.6 Hz [ArPF$_2$ (3)]. The $^{31}$P NMR spectrum indicated a conversion to ArPF$_2$ of approximately 65% (w.r.t. ArPCl$_2$). The Et$_2$O (35.5°C), THF (67°C) and TMEDA (120°C) were removed at atmospheric pressure, and the ArPF$_2$ was collected by distillation at reduced pressure, bpt. 54°C (8 mm Hg). Yield was 1.92 g (55%). Exactly similar results were obtained with PhCH$_2$Li·TMEDA (0.1 M solution).
4.12.2 Preparation of ArP(CHCl₂)Cl

4.12.2.1 Via the Lithio Species, CHLiCl₂

\[
\text{CH}_2\text{Cl}_2 \xrightarrow{\text{BuLi}} \text{CHLiCl}_2 \xrightarrow{\text{ArPCl}_2} \text{ArP(CHCl}_2\text{)Cl}
\]

CHLiCl₂ was prepared as described in the literature [76,77]. BuLi (5.2 ml, 13.0 mmol, 2.5 M solution in hexane) was added dropwise over 5 minutes to a stirred solution of CH₂Cl₂ (1.0g, 0.75 ml, 11.8 mmol) in THF:Et₂O:petroleum ether (4:1:1 v/v, 150 ml) at -130 °C (pentane/liquid nitrogen slush). This lithio reagent was added to a stirred solution of ArPCl₂ (5.0g, 13.0 mmol) in Et₂O (50 ml) at -140 °C. The reaction mixture turned red and was allowed to warm to room temperature. A white precipitate was formed and filtered off. The solvent was removed \textit{in vacuo} yielding a crude yellow oil.

The $^{31}$P NMR showed three peaks corresponding to ArPCl₂ (12) (+145.4 ppm), the required ArP(CHCl₂)Cl (39) (+63.6 ppm) and ArP(CHCl₂)₂ (+6.5 ppm). The tertiary phoshine ArP(CHCl₂)₂ was removed as a solid by crystallisation from diethylether at -40 °C. The product ArP(CHCl₂)Cl was distilled at 68 °C (0.1 mm Hg) as a clear oil. Yield was 2.1g (41%); Analysis found: C, 27.32; H, 1.08. Required for C₁₀H₉Cl₃F₃P: C, 27.80; H, 0.70%; $^{31}$P (CDCl₃) δ: 63.6 ppm (septet) $^{4}$JPF 49.8 Hz; $^{19}$F δ: -54.7 (d,6F), -64.8 (s,3F) ppm.
4.12.2 Via the Organocadmium Reagent

\[2\text{CH}_2\text{Cl}_2 \xrightarrow{\text{BuLi}} 2\text{CHLiCl}_2 \xrightarrow{\text{CdCl}_2} (\text{CHCl}_2)_2\text{Cd} \xrightarrow{2\text{ArPCl}_2} 2\text{ArP(CHCl}_2\text{)}\text{Cl}\]

\(\text{CHLiCl}_2\) (ca. 11.8 mmol in 150 ml \(\text{Et}_2\text{O}\)) was prepared as described in Section 4.12.2.1. \(\text{CdCl}_2\) (1.08g, 5.9 mmol) was added directly to the stirred solution of \(\text{CHLiCl}_2\) (\(\text{Et}_2\text{O}\)) at -130 °C. The reaction mixture was allowed to reach 0°C and stirred for 1 hour, followed by the addition in one portion of \(\text{ArPCl}_2\) (4.60g, 12.0 mmol) in \(\text{Et}_2\text{O}\) (50 ml). The solution was refluxed for 1 hour, allowed to cool to room temperature, filtered and concentrated in vacuo. A single signal (septet) was observed in the \(^{31}\text{P}\) NMR at 63.6 ppm. The compound was distilled as a clear oil, bpt.68 °C (0.1 mm Hg). Yield was 1.49g (65%). Characterisation data were as presented in Section 4.12.2.1.

4.12.3 Preparation of \(\text{ArP=C(Cl)}_2\) (31)

\[\text{ArP(CHCl}_2\text{)}\text{Cl} (39) \xrightarrow{\text{DBU}} -\text{DBU.HCl} \xrightarrow{\text{DBU}} \text{Ar-P=C(Cl)}_2 (31)\]

\(\text{DBU}\) (0.58 ml, 3.74 mmol) in THF (10 ml) was added dropwise over 5 minutes to a stirred solution of \(\text{ArP(CHCl}_2\text{)}\text{Cl} (39)\) (1.61g, 3.74 mmol) in THF (25 ml) at 0 °C. The solution was allowed to warm to room temperature. It became yellow with a white insoluble precipitate (\(\text{DBU.HCl}\)), which was removed by filtration. THF was removed by distillation at atmospheric pressure, and the product collected as a clear oil at 76 °C (0.7 mm Hg). Yield was 0.88g (59.6%). Analysis found: C, 30.55; H, 0.92. Required for \(\text{C}_{10}\text{H}_2\text{Cl}_2\text{F}_9\text{P}\): C, 30.41; H, 0.51%; UV-Vis (\(\text{CCl}_4\)) \(\lambda_{max}\): 327, 227 nm; MS (Intensity%) EI: 394 [13.1, \(\text{ArP=C(Cl)}_2^+\)], 359 [100,\(\text{Ar-P=C}^+\)]; \(^{31}\text{P}\) (CDCl\(_3\)) \(\delta\): +202.9 ppm (septet)
\( ^{4}\text{J}_{PF} \) 21.4 Hz; \( ^{19}\text{F} \) (CDCl\(_3\)) \( \delta \): -61.0 (d, 6F) \( ^{4}\text{J}_{PF} \) 21.4 Hz, -65.1 (s, 3F) ppm; \( ^{13}\text{C} \) (CDCl\(_3\)) \( \delta \): 164.4 (d) \( ^{1}\text{J}_{PC} \) 45.4 Hz, 140.0 (q, CF\(_3\)) \( ^{1}\text{J}_{CF} \) 30.3 Hz, 150.0 (q, CF\(_3\)), 127.1 (s, ArCH ring), 125.0 (q, CF\(_3\)), 121.0 (q, CF\(_3\)) ppm. 
\( ^{1}\text{J}_{CF} \) not resolved.

4.12.4 Preparation of PhCH\(_2\)PCl\(_2\)

4.12.4.1 Via (Et\(_2\)N)\(_2\)PCl

\[
\begin{align*}
\text{PhCH}_2\text{MgBr} & \quad \xrightarrow{(\text{Et}_2\text{N})_2\text{PCl}} \quad (\text{Et}_2\text{N})_2\text{P(CH}_2\text{Ph)} & \quad \xrightarrow{2\text{HCl}} & \quad \text{Cl}_2\text{P(CH}_2\text{Ph)} \\
-2 \quad \text{Et}_2\text{NH}_2\text{Cl}^- & \quad \\
\end{align*}
\]

PhCH\(_2\)MgBr (12.8 ml, 1 M solution in Et\(_2\)O, 12.8 mmol) was added dropwise to a stirred solution of (Et\(_2\)N)\(_2\)PCl (2.7g, 12.8 mmol) in Et\(_2\)O (40 ml) at 0 °C. The mixture was allowed to reach room temperature, and the LiCl removed by filtration. The \( ^{31}\text{P} \) NMR of the filtrate showed the presence of \([(\text{Et}_2\text{N})_2\text{P(CH}_2\text{Ph)}]\) at +90.9 ppm. The mixture was cooled to -10 °C, while HCl gas was slowly bubbled through it. Copious amounts of white amine salt were formed (an average rate of 2 bubbles per second for 10 minutes allowed quantitative conversion with respect to the \( ^{31}\text{P} \) NMR of PhCH\(_2\)PCl\(_2\)), \( ^{31}\text{P} \) \( \delta \): 175.2 ppm. Pentane (100 ml) was added to precipitate the amine salt, which was subsequently removed by filtration. The pentane and ether were removed by distillation, and PhCH\(_2\)PCl\(_2\) was collected at 118 °C (12 mm Hg). Yield was 1.5g (61%). Results agree well with Weil \textit{et al.} [78].
4.12.4.2 Via the Organocadmium Reagent

\[ \text{R}_2\text{Cd} + 2\text{PCl}_3 \rightarrow 2\text{RPCl}_2 + \text{CdCl}_2 \ (R = \text{PhCH}_2) \]

CdCl₂ (4.58g, 25 mmol) in Et₂O (25 ml) as a slurry was added in one portion to a stirred solution of PhCH₂MgBr (50 ml, 1 M solution, 50 mmol) in Et₂O at 0 °C. This solution was stirred at 0 °C for 2 hours, followed by the addition of PCl₃ (6.9g, 4.4 ml, 50 mmol) in Et₂O (40 ml). The mixture was refluxed for 1 hour before cooling to ambient temperature, filtering and removing Et₂O and excess PCl₃ by distillation at atmospheric pressure. PhCH₂PCl₂ was distilled as a pure oil at 118 °C (12 mm Hg) [78]. Yield was 4.0g (41%). ³¹P NMR δ: +175.2 (s) ppm.

4.12.5 Preparation of ArP(CH₂Ph)Cl (37)

4.12.5.1 From ArLi on PhCH₂PCl₂

\[ \text{PhCH}_2\text{PCl}_2 + \text{ArLi} \rightarrow \text{ArP(CH}_2\text{Ph)Cl} \ (37) \]

ArLi (0.25 M, 46 ml, 11.5 mmol) in Et₂O was added dropwise over 5 minutes to a stirred solution of PhCH₂PCl₂ (2.2g, 11.3 mmol) in Et₂O (50 ml) at -78 °C. The reaction mixture was allowed to warm to room temperature. LiCl was removed by filtration and the filtrate concentrated \textit{in vacuo} to yield a crude yellow oil (4.2g, 85%). This was purified by vacuum distillation. A colourless oil was collected at 122 °C (0.3 mm Hg). Yield 3.7g (75%). Analysis found: C, 43.82; H, 2.00; Required for C₁₆H₉ClF₉P: C, 43.81; H, 2.07%; IR (Film): 3100 (w, ArCH), 3000-2030 (m, CH), 1630 and 1570 (m, ArPh, C=C), 1380 (m, P-CH), 900 (m, C-H), 540 (m, P-Cl) cm⁻¹; ³¹P (CDCl₃) δ: 86.4 ppm (septet) ⁴JPF 52.3 Hz; ¹⁹F (CDCl₃)
\( \delta: -54.2 \text{ (d, 6F)}, -64.6 \text{ (s, 3F)} \) ppm. A slight excess of ArLi was added to compensate for a small amount of amine salt remaining in solution.

### 4.12.5.2 Via \((\text{PhCH}_2)_2\text{Cd on ArPCl}_2\)

\[
2\text{PhCH}_2\text{MgBr} \xrightarrow{\text{CdCl}_2} (\text{PhCH}_2)_2\text{Cd} \xrightarrow{2\text{ArPCl}_2} 2\text{ArP(PhCH}_2)\text{Cl (37)}
\]

\(\text{PhCH}_2\text{MgBr (11.0 ml, 1 M Et}_2\text{O solution, 11.0 mmol)}\) was added dropwise over 5 minutes to a stirred suspension of \(\text{CdCl}_2\) (1g, 5.5 mmol) in \(\text{Et}_2\text{O (50 ml)}\) at 0 °C. The solution was stirred at 0°C for 1 hour, followed by the addition in one portion of \(\text{ArPCl}_2\) (4.25g, 11.1 mmol) in \(\text{Et}_2\text{O (40 ml)}\). The mixture was brought to reflux for a period of 4 hours, and then cooled to room temperature, filtered and the filtrate concentrated in vacuo. The residual yellow oil was purified by vacuum distillation, bpt. 122 °C (0.3 mm Hg). Yield was 3.1g (64%). Characterisation data were as presented in Section 4.12.5.1.

### 4.12.6 Preparation of \(\text{ArP=CH(Ph) (32)}\)

\[
\text{ArP(PhCH}_2\text{Ph)Cl (37)} \xrightarrow{\text{DBU}} \text{ArP=CH(Ph) (32)}
\]

\(\text{DBU (0.33 ml, 2.2 mmol)}\) in THF (10 ml) was added over 5 minutes to a stirred solution of \(\text{ArP(PhCH}_2\text{Ph)Cl (965 mg, 2.2 mmol)}\) in THF (20 ml) at 0 °C. The solution became green. It was allowed to warm to room temperature and the insoluble DBU.HCl salt was removed by filtration. The \(^{31}\text{P NMR}\) of the filtrate showed a downfield signal at \(\delta 218.1 \text{ ppm (septet)}\) \(^4J_{PP} 23.7 \text{ Hz}\), attributed to the presence of \(\text{ArP=CH(Ph)}\) (a quantitative conversion with respect to the \(^{31}\text{P NMR}\)); UV-Visible (THF) \(\lambda_{\text{max}} 327, 225 \text{ nm}\). The THF was removed in vacuo to yield a brown
decomposition product. $^{31}\text{P NMR } \delta: 0.9$ (intense singlet), 10.8, 19.2 and 24.4 ppm. The phosphaalkene, Ar-P-CH(Ph) (32) did not appear to be stable to isolation. The coordination chemistry of this species in solution has been investigated (Chapter 5).

4.12.7 Preparation of ArP(Me$_3$SiCH$_2$)Cl (36)

\[
2\text{Me}_3\text{SiCH}_2\text{MgBr} \xrightarrow{\text{CdCl}_2} (\text{Me}_3\text{SiCH}_2)_2\text{Cd} \xrightarrow{2\text{ArPCl}_2} 2\text{ArP(Cl)(CH}_2\text{SiMe}_3)
\]

Me$_3$SiCH$_2$MgBr (40 ml, 1 M Et$_2$O solution, 40 mmol) was added dropwise over 5 minutes to a stirred solution of CdCl$_2$ (3.7g, 20.1 mmol) in Et$_2$O (50 ml) at 0 °C. The reaction mixture was stirred at this temperature for 1 hour. The resultant pale yellow solution containing (Me$_3$SiCH$_2$)$_2$Cd was added in one portion to a stirred solution of ArPCl$_2$ (16.8g, 43.8 mmol) in Et$_2$O (40 ml) at room temperature. The mixture was brought gradually to reflux for a period of 4 hours. The precipitate was removed by filtration and the resulting filtrate concentrated by the removal of the solvent in vacuo to yield 15.2g crude yellow oil. This was purified by vacuum distillation. The first fraction was unreacted ArPCl$_2$, bpt. 62 °C (0.5 mm Hg); $^{31}\text{P } \delta: +145$ ppm (septet) $^4\text{J}_{PF}$ 61 Hz; and the product was isolated as the second fraction, a very pale yellow oil, bpt. 84 °C (0.5 mm Hg). Yield was 9.2g (53%). Higher yields may have been obtainable via the direct use of the Grignard on ArPCl$_2$. It seems possible that the relative bulk of the trimethylsilylmethyl group could allow mono-substitution, cf. the synthesis of Me$_3$SiCH$_2$PCL$_2$ via the direct action of Grignard on PCl$_3$ [79]. Analysis found: C, 36.50; H, 3.30; Required for C$_{13}$H$_{13}$Cl$_9$PSi: C, 36.00; H, 2.78%; MS (Intensity%) EI: 434 [24.5, ArP(Cl(CH$_2$SiMe$_3$))$^+$]; $^{31}\text{P (CDC}_3$) $\delta: +92.1$ ppm (septet) $^4\text{J}_{PF}$ 51.8 Hz; $^{19}\text{F } \delta: -54.7$ (d,6F) $^4\text{J}_{PF}$ 51.8 Hz, -64.0 (s,3F) ppm.
4.12.8 Preparation of ArP=C(SiMe₃)H (33)

\[
\text{ArP(CH₂SiMe₃)Cl (36) → } \text{DBU} \quad \text{ArP=C(SiMe₃)H (33)} \quad \text{DBU.HCl}
\]

DBU (0.52 ml, 3.5 mmol) in THF (10 ml) was added dropwise over 5 minutes to a stirred solution of ArP(CH₂SiMe₃)Cl (1.52g, 3.5 mmol) in THF (25 ml) at 0 °C. A brown solution and a precipitate formed. The solid was removed by filtration. The solvent was removed in vacuo to yield a yellow oil. Crude yield was 1.1g (77%). IR (Film) \( \nu_{\text{max}} = 3100 (w, \text{ArCH}), 2960 (w, \text{Me/C-H alkyl}), 1650 \) and \(1625 (m, \text{Ar/C=C}), 1380 (w, P=C), 1280-1000 (s, CF₃), 850-800 (m, SiCH₃)\) cm⁻¹; UV-Vis (CCl₄) \( \lambda_{\text{max}} = 325, 260 \) nm; \( \text{¹³P} (\text{CDCl₃}) \delta: +287.9 \) ppm (septet) \( 4J_{PF} 26.5 \) Hz; \( \text{¹⁹F} (\text{CDCl₃}) \delta: -56.7 (d, 6F) 4J_{PF} 26.5 \) Hz, -64.1 (s, 3F) ppm; \( \text{¹³C} (\text{CDCl₃}) \delta: 157.5 1J_{PC} 118.6, 137.6 \) Hz (quaternary C on ring), 130.2 (ArCH ring), 124.6 (quaternary C-Ar ring), 2.2 (SiMe₃) ppm.

4.12.9 Preparation of ArP(CH=CH₂)Cl (38)

\[
2\text{CH₂=CHMgBr} + \text{CdCl₂} \rightarrow (\text{CH₂=CH})₂\text{Cd} \quad \text{ArPCl₂} \rightarrow \text{ArP(CH=CH₂)Cl (38)}
\]

CH₂=CHMgBr (60 ml, 1 M solution in Et₂O, 60 mmol) was added dropwise over 5 minutes to a stirred suspension of CdCl₂ (5.5g, 30 mmol) in Et₂O (50 ml) at 0 °C. A dark brown solution was formed which was stirred at 0 °C for 1 hour, followed by the addition of ArPCl₂ (23.0g, 60 mmol) in Et₂O (40 ml) in one portion. The mixture was refluxed for 4 hours. The solid was filtered off, and the filtrate concentrated in vacuo.

¹The \(\text{¹³C} \text{ NMR was recorded in deuterated THF. The signals ascribed to ring-CH and the CF₃ and CH₃ groups, were evident. This doublet, (attributed to the P=C) however, could not be assigned unambiguously.}
The residual brown oil was purified by vacuum distillation. It is important to heat uniformly. Any excessive heat caused decomposition and the formation of white fumes. First fraction [ArPCl₂]: bpt. 62 °C (0.1 mm Hg). Second fraction [product ArP(CH=CH₂)Cl]: bpt. 68-70 °C (0.1 mm Hg). Yield 11.4g (51%). Analysis found: C, 35.44; H, 1.52; Required for C₁₁H₅ClF₉P: C, 35.27; H, 1.34%; ³¹P (CDCl₃) δ: +68.7 ppm (septet) ¹⁴Jₚₚ 51.4 Hz; ¹⁹F δ: -54.2 (d,6F) ¹⁴Jₚₚ 51.4 Hz, -64.2 (s,3F) ppm.

4.12.10 Attempted Reaction of ArP(CH=CH₂)Cl (38) with DBU

\[
\text{ArP(CH=CH₂)Cl (38) } \xrightarrow{\text{DBU}} \text{?}
\]

DBU (1.4 ml, 9.4 mmol) in THF (10 ml) was added dropwise over 5 minutes to a stirred solution of ArP(CH=CH₂)Cl (3.5g, 9.3 mmol) in THF (50 ml) at 0 °C. A green solution was formed, and a solid which was filtered off. The ³¹P NMR of the filtrate gave a clean spectrum ³¹P{¹H} δ: +221.3 ppm (septet) ¹⁴Jₚₚ 20.0 Hz; ¹⁹F δ: -55.2 (d,6F), -64.1 (s,3F) ppm. The filtrate was concentrated in vacuo. The residual brown oil showed ³¹P δ: ca. 26 and 33 ppm, attributed to decomposition.

4.12.11 Attempted Reaction of Phosphide on Ph₂CCl₂

\[
\text{ArPH₂ (15) } \xrightarrow{-78^\circ \text{C}} \text{ArPHLi} \xrightarrow{\text{Ph₂CCl₂}} \text{X} \rightarrow \text{ArP(H)CCl(Ph)₂}
\]

BuLi (2.7 ml, 6.8 mmol, 2.5 M in hexane) was added dropwise over 5 minutes to a stirred solution of ArPH₂ (2.1g, 6.7 mmol) in THF (40 ml) at -78 °C. The solution turned black immediately. The solution was stirred at -78 °C for 20 minutes, followed by the dropwise addition over
5 minutes of dichlorodiphenylmethane, Ph₂CCl₂ (1.6g, 1.3 ml, 6.7 mmol) in THF (20 ml). The reaction mixture was allowed to reach room temperature. This yielded a deep brown/black solution with the presence of a fine white precipitate. The ³¹P NMR showed no reaction with Ph₂CCl₂ - attributed to ArPH(Li) decomposition before coupling with Ph₂CCl₂. ³¹P NMR showed a very poor broad signal at δ +32 ppm.

4.12.12 Preparation of ArP(CH₃)Cl (40)

\[
\text{CH}_3\text{PCl}_2 + \text{ArLi (2)} \longrightarrow \text{ArP(CH}_3\text{)Cl (40)}
\]

ArLi (30 ml, 26 mmol, 0.86 M in Et₂O) was added dropwise over 5 minutes to a stirred solution of CH₃PCl₂ (3.0g, 26 mmol) in Et₂O (120 ml) at -78 °C. The solution was allowed to warm to room temperature. A yellow solution was formed with a white insoluble precipitate. This was removed by filtration and the filtrate concentrated \textit{in vacuo} to yield a crude yellow oil. This was purified by vacuum distillation, bpt. 66-67 °C (0.1 mm Hg), yield of clear oil was 5.6g (59%); Analysis found: C, 33.57; H, 1.57; Required for C₁₀H₅ClF₉P: C, 33.13; H, 1.39%; ³¹P (CDCl₃) δ: +83.5 ppm (septet) \(^4J_{PF} 54.1\) Hz; \(^{19}F\) δ: -54.4 (d,6F), -64.4 (s,3F) ppm.
4.12.13 Attempted Abstraction of HCl from ArP(CH₃)Cl

4.12.13.1 Reaction with DBU

ArP(CH₃)Cl (40) + DBU → ?

DBU (0.28 ml, 1.9 mmol) in THF (10 ml) was added dropwise over 2 minutes to a stirred solution of (CH₃)PArCl (0.65g, 1.8 mmol) in THF (20 ml) at room temperature. A dark brown solution was formed. $^{31}$P{¹H} δ: 46.2 (doublet of septets) J 294.6 (d), 15.6 (septet), -22.4 (septet) J 32.4, -39 ppm, species unassigned.

4.12.13.2 Reaction with DABCO

ArP(CH₃)Cl (40) + DABCO → ?

DABCO (0.21g, 1.9 mmol) in THF (10 ml) was added dropwise over 2 minutes to a stirred solution of ArP(CH₃)Cl (0.65g, 1.8 mmol) in THF (20 ml) at room temperature. A brown solution was obtained. $^{31}$P{¹H} δ: +12.2 (s), +19.2 (s), 45.4 (s), species unassigned.

4.12.13.3 Reaction with LDA

ArP(CH₃)Cl (40) + LDA → ?

LDA was prepared as follows: BuLi (10 ml, 25 mmol, 2.5 M in hexane) was added dropwise to a stirred solution of ¹Pr₂NH (3.5 ml, 2.5g, 25 mmol) in Et₂O (30 ml) at 0 °C. This was stirred at room temperature for 1 hour.
The as-prepared LDA solution (25 mmol) was added dropwise over 5 minutes to a stirred solution of ArP(CH₃)Cl (9.1g, 25 mmol) in THF (25 ml) at 0 °C. The reaction mixture was allowed to reach room temperature and stirred for 1 hour. A white precipitate and a black solution was formed. The solid was removed by filtration. The ³¹P{¹H} NMR of the filtrate showed a complex set of signals. The major product occurred at δ -82.3 ppm (an apparent triplet) J 183.5 Hz.

4.12.14 Coupling Reactions of ArPCl₂

4.12.14.1 With Mg/CCl₄

ArPCl₂ (12) + 2Mg/CCl₄ →

Magnesium turnings (0.40g, 16.5 mmol) were added to a stirred solution of ArPCl₂ (3.1g, 8.0 mmol) and CCl₄ (1.2g, 0.77 ml, 8.0 mmol) in THF (20 ml) at room temperature. ³¹P NMR of the brown solution:
+201.6 ppm ⁴Jₚₚ 21.8 Hz [Ar-PC(Cl)₂]; 145 ppm ⁴Jₚₚ 61.4 Hz [ArPCl₂].

4.12.14.2 With Mg/CH₂Cl₂

ArPCl₂ (12) + 2Mg/CH₂Cl₂ →

Magnesium turnings (0.2g, 8.2 mmol) were added to a stirred solution of ArPCl₂ (1.5g, 3.9 mmol) and CH₂Cl₂ (0.33g, 0.25 ml, 3.9 mmol) in THF (25 ml) at room temperature. A dark brown solution was formed. ³¹P{¹H} δ: +473 ppm [Ar₂P₂]; +255.3 ppm (septet) ⁴Jₚₚ 44.1 Hz ["Ar-P=CH₂"].
4.12.14.3 With Mg/Ph₂CCl₂

\[
\text{ArPCl₂ (12) + 2Mg/Ph₂CCl₂} \rightarrow
\]

Magnesium turnings (0.23g, 9.46 mmol) were added to a stirred solution of ArPCl₂ (1.72g, 4.5 mmol) and Ph₂CCl₂ (1.1g, 0.86 ml, 4.5 mmol) in THF (25 ml) at room temperature. A deep brown solution and copious amounts of solid were produced. \(^{31}\text{P} \{^{1}\text{H}\} \delta: +473 \text{ ppm} \ [\text{Ar}_2\text{P}_2]; +145 \text{ ppm} \ ^4J_{\text{PF}} 61.4 \text{ Hz} \ [\text{ArPCl}_2].

4.12.15 Coupling Reactions of ArPH₂

4.12.15.1 With DBU/CHCl₃

\[
\text{ArPH₂ (15) + 2DBU/CHCl₃} \rightarrow
\]

DBU (0.69 ml, 4.61 mmol) in THF (15 ml) was added dropwise over 5 minutes to a stirred solution of ArPH₂ (15) (0.72g, 2.3 mmol) and HCl (0.27g, 0.18 ml, 2.3 mmol) in THF (25 ml) at 0 °C. A yellow solution and a solid was formed which turned deep brown at room temperature. \(^{31}\text{P} \text{ NMR} \delta: -83.3 \text{ and } -88.9 \text{ ppm} \ (\text{singlets, intensity ratio 3:1}). \ ^4J_{\text{PF}} \text{ unresolved.}

4.12.15.2 With DBU/Ph₂CCl₂

\[
\text{ArPH₂ (15) + 2DBU/Ph₂CCl₂} \rightarrow
\]

DBU (0.78 ml, 5.2 mmol) in THF (15 ml) was added dropwise over 5 minutes to a stirred solution of ArPH₂ (15) (0.81g, 2.6 mmol) and Ph₂CCl₂ (0.62g, 0.50 ml, 2.6 mmol) in THF (25 ml) at 0 °C. A dark brown
solution and a solid was formed. $^{31}$P NMR $\delta$: 200.6 $^4J_{PF}$ 23Hz (small signal), -0.4 (s), -83.3 and -88.9 (singlets) $^4J_{PF}$ unresolved. The latter two were the major signals and had intensities in the ratio 3:1. Further addition of DBU (0.1 ml, 0.6 mmol) resulted in the replacement of the peaks at -83.3 and -88.9 ppm by a signal due to the symmetrical diphosphene, $\text{Ar}_2\text{P}_2$ (19) ($\delta$: +473 ppm $^4J_{PF}$ + $^5J_{PF}$ 45.0 Hz).

### 4.12.16 Attempted Substitution of Chlorine in ArP=C(Cl)$_2$

#### 4.12.16.1 By Me$_3$Si

$$\text{ArP=C(Cl)}_2 \ (31) \xrightarrow{\text{BuLi}} \left[ \text{ArP=C(Li)(Cl)} \right] \xrightarrow{\text{Me}_3\text{SiCl}} \text{ArP=C(SiMe}_3\text{)Cl}$$

BuLi (0.52 ml, 1.3 mmol, 2.5 M in hexane) was added dropwise over 1 minute to a stirred solution of ArP=C(Cl)$_2$ (0.5g, 1.3 mmol) in THF (20 ml) at -78 °C. The solution immediately turned black. The mixture was stirred for 20 minutes at -78 °C followed by the dropwise addition over 2 minutes of Me$_3$SiCl (0.16 ml, 1.3 mmol) in THF (10 ml). The black solution was allowed to warm to room temperature. A fine white precipitate was observed. $^{31}$P NMR $\delta$: 37.1 ppm, line width (half height) = 10 ppm (decomposition)!

#### 4.12.16.2 By Ar

$$\text{ArP=C(Cl)}_2 + \text{ArLi} \xrightarrow{\text{X}} \text{ArP=C(Cl)Ar}$$

ArLi (2.4 ml, 1.3 mmol, 0.54 M solution in Et$_2$O) was added dropwise to a stirred solution of ArP=C(Cl)$_2$ (0.5g, 1.3 mmol) in THF (10 ml) at -10 °C. The deep brown solution formed was stirred at room temperature
for 30 minutes. \(^{31}\)P NMR showed a peak corresponding to \(\text{ArP} = \text{C(Cl)}_2\) only 
\[\delta: 202 \text{ ppm } ^4J_{PF} 23 \text{ Hz}\] whilst the \(^{19}\)F spectrum also showed the presence of 
\(\text{ArCl} [\delta: -65.0 (s, 6F, o-\text{CF}_3), -65.4 (s, 3F, p-\text{CF}_3)]\) [61].

4.12.17 Reaction of \(\text{ArPH}_2\) with \(\text{PhCHO}\)

\[
\begin{align*}
\text{ArPH}_2 + \text{PhCHO} & \quad \longrightarrow \quad \text{ArP=CH}_2 + \text{H}_2\text{O} \\
\end{align*}
\]

A catalytic quantity of toluene sulphonate was added to a 
stirred mixture of \(\text{ArPH}_2\) (15) (1.21g, 3.8 mmol) and \(\text{PhCHO}\) (0.40g, 0.38
ml, 3.8 mmol) in THF (25 ml). This mixture was refluxed for 8 hours.
The \(^{31}\)P NMR indicated that no reaction had occurred 
\[\delta: -139.8 \text{ ppm (t of sept) } ^1J_{PH} 217.9 \text{ Hz } ^4J_{PF} 28.9 \text{ Hz}\].

4.12.18 Reaction of \(\text{ArPH}_2\) with \(\text{CHCl}_3\)

\[
\text{ArPH}_2 + \text{HCCl}_3 \xrightarrow{2\text{KOH}} ?
\]

Powdered semi-conductor grade KOH (0.71g, 12.6 mmol) was added to a 
stirred solution of \(\text{ArPH}_2\) (1.97g, 6.3 mmol) and spectroscopic grade 
chloroform (0.75g, 0.50 ml, 6.3 mmol) in THF (30 ml) at room 
temperature. The reaction was exothermic and the solution became jet 
black. The \(^{31}\)P and \(^{19}\)F NMR were recorded, each indicative of ring 
decomposition: \(^{31}\)P \(\delta: 1.8 \text{ (s) ppm; } ^{19}\)F \(\delta: -55 \text{ to } -58 \text{ ppm (very broad).}

- 100 -
4.12.19 Preparation of ArCH$_3$ (41)

\[ \text{ArLi} + \text{CH}_3\text{I} \rightarrow \text{ArCH}_3\text{(41)} + \text{LiI} \]

A solution of ArLi (100 ml, 40 mmol, 0.4 M in Et$_2$O) was added dropwise over 5 minutes to a stirred solution of methyl iodide (6.24g, 44 mmol) in ether (50 ml) at room temperature. No apparent precipitate was formed, attributed to the solubility of LiI in Et$_2$O. (The slight purple colour of the solution was probably due to the liberation of iodine). The ether and the excess methyl iodide were separated by distillation at atmospheric pressure and the product distilled as a colourless oil, bpt. 123$^\circ$C (760 mm Hg); Analysis found: C, 40.53; H, 1.07; Required for c$_{10}$H$_5$F$_9$: C, 40.56; H, 1.70%; IR (Film) $\nu_{\text{max}}$: 3100 (w,ArCH), 1390 (m,CH$_3$ alkyl), 1400-1000 (s,C-F) cm$^{-1}$; $^{19}$F (CDCl$_3$) $\delta$: -62.21 (s,6F), -64.12 (s,3F) ppm; $^1$H (CDCl$_3$) $\delta$: 7.84 (s,2H,Ar ring), 2.40 (s,3H,CH$_3$) ppm.

4.12.20 Preparation of ArCH$_2$OH (42)

\[ \text{ArLi} + \text{H}_2\text{CO} \rightarrow \text{ArCH}_2\text{O}^-\text{Li}^+ \xrightarrow{\text{HCl}} \text{ArCH}_2\text{OH} + \text{LiCl} \]

Paraformaldehyde (6g, 0.2 mole) was heated to 120$^\circ$C (decomposition temperature) under reduced pressure (0.1 mm Hg). The formaldehyde monomer was passed through a glass wool filter cooled to -48$^\circ$C in CaCl$_2$/ice mixture to remove particles of polymer, then dried by passage over P$_2$O$_5$ and condensed into Et$_2$O (250 ml). The formaldehyde is only sparingly soluble in ether, and on cooling to room temperature some re-polymerises. ArLi (0.02M) in Et$_2$O (50 ml) was added dropwise to a stirred solution of the formaldehyde in Et$_2$O (250 ml) over 10 minutes at
0°C (ice bath). Sufficient formaldehyde remained in solution to react quantitatively, according to the $^{19}$F NMR recorded. The reaction mixture was stirred at room temperature for one hour. HCl (50 ml, 2 M) was then added in one portion and the mixture shaken vigorously for 30 minutes, after which it was poured onto crushed ice (35 g) and the product extracted into ether (100 ml). The ether layer was separated, dried (MgSO$_4$) and evaporated at reduced pressure to yield a viscous oil, which distilled under reduced pressure at 60°C (0.2 mm Hg). The oil, when redissolved in Et$_2$O (5 ml) and allowing the ether to evaporate slowly over a period of 24 hours, gave rhombic crystals. Yield was 2.6g (41%). Analysis found: C, 38.22; H, 1.39; Required for C$_{10}$H$_5$F$_9$O: C, 38.48; H, 1.61%; MS EI: 291 [ArC$^+$], 273, 263, 244 [ring fragmentation]; CI$^+$: 312 [ArC(OH)H$_2$$^+$], 291, 273, 263, 244 [ring fragmentation]; CI$^-$: 292, 272; $^{19}$F (CDCl$_3$) $\delta$: -55.5 (s,6F), -60.4 (s,3F) ppm; $^1$H (CDCl$_3$) $\delta$: 7.8 (s,2H,Ar ring), 4.6 (s,2H,CH$_2$-alkyl), 2.0 (s,broad,1H,OH) ppm.

IR figure 4.16

Initially the formaldehyde (0.6g, 1 equivalent) was condensed directly into the ArLi solution (0.02 mole in 50 ml Et$_2$O) at -78°C. However, as this solution warmed to room temperature it exploded. This was possibly due to the basic nature of the ArLi inducing rapid polymerisation of the formaldehyde. In all cases extreme care must be taken.

4.12.21 Preparation of ArC(CH$_3$)H(OH) (43)

ArLi + CH$_3$(H)C=O $\xrightarrow{\text{HCl}}$ ArCHO$^-$ (CH$_3$)Li$^+$ + HCl $\rightarrow$ Ar(CH$_3$)H(OH)

A solution of ArLi (150 ml, 40 mmol, 0.4 M in Et$_2$O) was added dropwise over 5 minutes to a stirred solution of ethanal (3.1g, 0.07 mole) cooled to -78°C. The reaction mixture was stirred vigorously at room temperature for two hours. HCl (50 ml, 2 M) was then added in one
portion and the mixture shaken vigorously for 30 minutes, after which it was poured onto crushed ice (30 g) and the product extracted into Et₂O (50 ml). The ether layer was separated, dried (MgSO₄) and evaporated at reduced pressure to yield a viscous oil. This was distilled, bpt. 75°C (0.4 mm Hg). The oil was dissolved in Et₂O (5 ml) and the solvent allowed to evaporate slowly, giving a pure white solid. Yield was 7.8 g (40%). Analysis found: C, 40.53; H, 2.07; Required for C₁₁H₇F₉O: C, 40.51; H, 2.16%; IR (Nujol) ν_max: 3400 (s,broad,OH), 3100 (w,ArCH), 3000-2900 (m,CH alkyl), 1730, 1640, 1560 (m, C=CAr), 1400-1300 (s, C-F), 1060 (m, ν_C-O) cm⁻¹; ¹⁹F (CDCl₃) δ: -56.83 (s, 6F, o-CF₃), -63.77 (s, 3F, p-CF₃) ppm; ¹H (CDCl₃) δ: 8.19 (s, 2H, Ar ring), 5.61 (q, 1H, CH) 3J_HH 6.61 Hz, 2.65 (s, broad, OH), 1.67 ppm (d, 3H, CH₃) 3J_HH 6.61 Hz. IR figure 4.16

4.12.22 Preparation of ArC(Ph)H(OH) (44)

A solution of ArLi (65 ml, 26 mmol, 0.4 M in Et₂O) was added dropwise over 5 minutes to a stirred solution of benzaldehyde (3.5 g, 33 mmol) in Et₂O (100 ml) at -78°C. The reaction mixture was stirred at room temperature for one hour. HCl (50 ml, 2 M) was then added in one portion and the mixture shaken vigorously for 30 minutes, after which it was poured onto crushed ice (20 g) and the product extracted with Et₂O (50 ml). The ether layer was separated, dried (MgSO₄) and evaporated at reduced pressure to yield a viscous oil. This was purified by crystallisation by the addition of Et₂O (10 ml) and allowing its slow evaporation over 8 hours. A powdery white solid was obtained. Yield was 6.41 g (63%). MS (Intensity%) EI: 388 [100, ArC(Ph)H(OH)+], 371 [ArC(Ph)H]+, 374, 309 [ArCH(OH)+]; CI+: 388 [ArC(Ph)H(OH)+], 371 [ArC(Ph)H]+, 262 [(Ar-F)+]; ¹⁹F (CDCl₃) δ: -58.40 (s, 6F), -61.25 (s, 3F) ppm; ¹H (CDCl₃) δ: 8.27 (2H, Ar ring), 7.32 (3H, PhCH), 7.12 (2H, PhCH),
6.61 (s, 1H, CH)², 1.95 (s, broad, 1H, OH); ¹³C (CDCl₃) δ: 141 (ArCF₃), 132 (ArCF₃), 126 (ArCH arom), 125 (ArCH ring), 65 (CH) ppm. IR figure 4.16

4.12.23 Preparation of ArCH₂Br (45)

4.12.23.1 Via Ph₃PBr⁺Br⁻ salt

\[
\text{Ph}_3\text{P} (\text{CCl}_4) \xrightarrow{\text{Br}^2-} \text{Ph}_3\text{PBr}^+\text{Br}^- \ (\text{xs}) + \text{ArCH}_2\text{OH} \longrightarrow \text{ArCH}_2\text{Br}
\]

The Ph₃PBr⁺Br⁻ salt was precipitated and washed with carbon tetrachloride. A three-fold excess of Ph₃PBr⁺Br⁻ (3.3 g, 7.8 mmol) was added to a stirred solution of ArCH₂OH (0.82 g, 2.6 mmol) in acetonitrile (20 ml). The mixture was refluxed for a period of two hours. The ¹⁹F and ¹H NMR spectra showed the conversion to be very low (ca. 20%).

4.12.23.2 Via C₂(Cl₂Br)₂

\[
\text{ArCH}_2\text{OH} + \text{C}_2(\text{Cl}_2\text{Br})_2 + \text{PPh}_3 \longrightarrow \text{ArCH}_2\text{Br} + \text{Ph}_3\text{PO} + \text{Cl}_2\text{C} = \text{CCl}_2 + \text{HBr}
\]

Ph₃P (0.92 g, 3.5 mmol) was added as a solid to a stirred solution of ArCH₂OH (1 g, 3.2 mmol) at 0°C. 1,2-dibromo-tetrachloroethane (1.15 g, 3.53 mmol) in Et₂O (15 ml) was added dropwise over 5 minutes. A white solid precipitated immediately. The reaction mixture was stirred at room temperature for 1 hour. The solution was filtered and the solvent removed in vacuo. The bromo compound was distilled from the remaining solid/product mixture to give a clear oil, bpt. 40°C (0.1 mm Hg). Yield was 0.5 g (41.5%). Analysis found: C, 32.45; H, 0.73; Required for C₁₀H₄BrF₉: C, 32.03; H, 1.07%. IR (Film) ν_max: 3100 (w, ArCH), 3000 (m, correct shielding for the surrounding substituents.

- 104 -
CH\(_2\) 1480 (m, C-H), 1400-1000 (s, C-F) cm\(^{-1}\); MS (Intensity%) 1480 (ar CH\(_2\)Br\(^+\)), 1467 [(ArCH\(_2\)Br-F)\(^+\)], 295 [100, ArCH\(_2\)Br\(^+\)]; Cl\(^+\): 312 (100), 272; Cl\(^-\): 374 [ArCH\(_2\)Br\(^-\)], 310, 292, 272, 79 [Br\(^-\)]; \(^{19}\)F (CDCl\(_3\)) \(\delta\): -55.94 (s, 6F), -60.18 (s, 3F) ppm; \(^1\)H (CDCl\(_3\)) \(\delta\): 7.66 (s, 2H, Ar ring), 4.20 (s, 2H, CH\(_2\) alkyl) ppm.

4.12.24 Preparation of ArCH\(_2\)MgBr (48)

\[
\text{ArCH}_2\text{Br} \xrightarrow{\text{THF}} \xrightarrow{\text{Mg}} \text{ArCH}_2\text{MgBr}
\]

Magnesium (0.32g, 13 mmol) was added to a stirred solution of ArCH\(_2\)Br (0.5g, 1.3 mmol) in THF (10 ml). This mixture was refluxed for five minutes, during which time it became deep brown. This reagent was used \textit{in situ} for the preparation of ArCH\(_2\)PCI\(_2\) (49), via the organocadmium derivative.

4.12.25 Preparation of 'ArCH\(_2\)PCI\(_2\)' (49)

ArCH\(_2\)MgBr (ca. 0.5 g, 1.3 mmol) in THF (15 ml) (prepared as described in Section 4.12.24), was added dropwise to a stirred solution of CdCl\(_2\) (0.12g, 0.65 mmol) in THF (35 ml) at 0 °C. The solution was stirred for 1 hour at 0 °C, followed by the addition of excess PCI\(_3\) (0.26g, 0.17 ml, 1.9 mmol) in THF (15 ml). The yellow solution was refluxed for 2 hours, filtered and the solvent and PCI\(_3\) (excess) removed \textit{in vacuo}, yielding a crude yellow oil. Yield was 0.25g (48%); \(^{31}\)P \(\delta\): +178 ppm (singlet). Further data are required for assignment.
4.12.26 Reaction of 'ArCH₂PCl₂' with DBU

\[
\text{ArCH₂PCl₂} \rightarrow \text{ArC≡P (?)}
\]

DBU (0.18 ml, 1.2 mmol) in THF (10 ml) was added dropwise over 2 minutes to a stirred solution of the crude phosphine 'ArCH₂PCl₂' (0.48g, 1.2 mmol) in THF (15 ml) at 0 °C. A bright green solution and white precipitate was formed. \(^{31}\text{P} \text{NMR}\ \delta: \ -15.2, \ -10.8, \ -5.6, \ -1.7 \text{ ppm.}\) These signals could not be assigned.

4.13 REFERENCES


CHAPTER FIVE

THE COORDINATION CHEMISTRY OF NEW PHOSPHINES,
DIPHOSPHENES AND PHOSPHAALKENES
The great majority of the elements are known to form at least a few complexes with phosphorus donors \[1\] (Figure 5.1). In particular the platinum complexes of some of these species may have exciting applications as anti-tumour agents. The anti-tumour properties of platinum(II), for example, cisplatin\(^{\text{TM}}\) \([\text{cis-Cl}_2(\text{NH}_3)_2\text{Pt}]\) and related compounds are well known \[2\]. The lack of success in attempting to replace nitrogen-containing ligands by phosphorus donors in complexes of this type, has been attributed to the strong trans effect exerted in dichloro-Pt(II) compounds. It has been suggested \[3\] that the subtle \(\sigma\)-donor and \(\pi\)-acceptor properties of fluorophosphines within these systems may give rise to improved anti-tumour properties.

Aspects of the coordination chemistry of phosphines, phosphaalkenes and diphosphenes, all bearing the 2,4,6-tris(trifluoromethyl)phenyl substituent are presented here, together with a very preliminary investigation of the ligative behaviour of the phosphorus/boron containing nitrileimine (Section 5.4).

Figure 5.1: Elements known to form complexes with phosphorus donors.

\* N.B. Correct format for metal complex formulae is \([M\times_x(L)_y\times_z]\) etc.
5.1.1 Diphosphenes

The coordination chemistry of the new diphosphene \([(\text{CF}_3)_3\text{C}_6\text{H}_2\text{P})_2\] (19) is of considerable interest because of the presence of the strongly electron withdrawing substituents as compared with the well established supermesityl group \([4]\) (see Chapter 3).

The coordination chemistry of the diphosphene is complicated by the fact that it can utilise more than one type of bonding mode. Table 5.1 illustrates the possible bonding types, with reference to specific examples under each classification. A brief discussion of the energy levels in diphosphenes involved in coordination is now presented.

*Ab initio* calculations on the parent system HP=PH \([23]\) show the HOMO as being representative of the lone pair of electrons on the phosphorus. The three diphosphenes \(\text{Ar}_2\text{P}_2\) (19), \(\text{ArAr}'\text{P}_2\) (20) and \(\text{Ar}_2\text{P}_2\) (24) were considered. \(\text{Ar}_2\text{P}_2\) (24) appeared very unreactive toward coordination \([24a]\). In contrast, coordination complexes of \(\text{Ar}_2\text{P}_2\) (19) and \(\text{ArAr}'\text{P}_2\) (21) have been obtained in this work. The MNDO calculations (Section 3.7) were carried out in an attempt to rationalise these differences. However, each showed the HOMO to be the lone pair of electrons, and the HOMO-1 the \(\pi \text{"P-P"} \) as expected. The geometry from the MNDO calculation on \(\text{Ar}_2\text{P}_2\) (24) was verified by comparison with its known X-ray structure \([24b]\). There appear to be no significant orbital differences between the three species. It may therefore be valuable to reinvestigate the coordination potential of \(\text{Ar}_2\text{P}_2\). (It must not be overlooked that the apparent difference in observed reactivity may be attributed to d-orbital involvement, the concept of which is not incorporated into the MNDO approximation).
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**Table 5.1:** The modes of coordination of diphosphines; \( \dagger R=\text{Et}, C_6H_{11} \).
The coordination types for phosphaalkenes so far recognized together with some selective examples are given in Table 5.2. This chemistry has been extensively reviewed by J.F. Nixon [34].

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Table 5.2: The modes of coordination of phosphaalkenes; †page 1344.
Energy Levels

The phosphorus lone pair \( \sigma \)-orbital and the \( \pi \)-orbital of the P=C bond are the highest occupied molecular orbitals of nearly equal energy [36-38]. The level of the lowest \( \pi^* \) is relatively low. This enables high versatility, whereby coordination may occur in a DCD synergic \( \sigma \)-donating \( \pi \)-backbonding side on \( \eta^2 \) mode, or via a lone pair with the formation of a \( \sigma \)-coordinate bond. A very interesting illustration of these two bonding modes is the establishment of the following equilibrium [36-39]:

\[
\begin{align*}
\text{Mes} & \quad \text{P} \equiv \text{CH(Ph)} \\
\text{Ph}_3 & \quad \text{P} \equiv \text{CH(Ph)}
\end{align*}
\]

\( \eta^1 \) (solid) \( \rightleftharpoons \) \( \eta^2 \) (solution)

5.1.3 Phosphaalkynes

It is worth offering a comparison here with the phosphaalkyne system. The HOMO is of the \( \pi \)-type with the phosphorus lone pair a lot lower in energy. Phosphaalkynes characteristically give the \( \eta^2 \)-mode of coordination [34,40,41], although following \( \eta^2 \)-coordination the \( \pi \)-orbital energy may be sufficiently lowered to allow \( \eta^1 \)-coordination, indeed some examples of this are known [42].

5.2 Coordination with the CIS Pt(II) Dimer

5.2.1 Results

Complexes were prepared of the Pt(II) derivative \([(\text{Et}_3\text{P})\text{PtCl}_2]_2\) [43] with the following phosphorus containing species: \( \text{ArP=PAr} \) (19), \( \text{ArP=PAr}^1 \) (20), \( \text{ArPF}_2 \) (3), \( \text{ArPH}_2 \) (15), \( \text{ArPCl}_2 \) (12), \( \text{ArP=CH(Ph)} \) (32), \( \text{ArP=CH(SiMe}_3 \) (33) and \( \text{ArP=C(Cl)}_2 \) (31) and results are presented in Table 5.3.
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<td></td>
<td>†534.3</td>
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<td></td>
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Table 5.3: Square-planar complexes obtained; $^2J(PP)$ coupling; *it is not possible to distinguish whether $Pt$ is attached to $P_1$ or $P_2$; $^1J(P_1P_2)$ coupling.
Their facile synthesis involved the addition at ambient temperature of 0.5 equivalents of the cisplatinum (II) dimer Cl₄Pt₂(PEt₃)₂ to 1 equivalent of the phosphorus compound in CH₂Cl₂, with stirring. The formation of the diphosphene complex was interesting, since with Cl₂Pt-(PhCN)₂ at ambient temperature there was no evidence of coordination. The complexes (51)-(54),(56), (57) and (59) (Table 5.3) were obtained as crystalline white solids, and according to their ³¹P NMR spectral data (¹JPₚ large) have η¹-commodation and are all of cis configuration, deduced from their small ²JPₚₛₜₜ coupling [44]. In general the crystals were soluble in CDCl₃. ³¹P NMR data for some of these complexes is presented in Figure 5.2 (where the following abbreviations are used: T/C = trans/cis isomers, S = starting material, I = impurity). Figure 5.3 illustrates selected mass spectra for these platinum complexes. The high melting point before decomposition may be the reason for the observation of the important fragmentation ions including the molecular ion. The crystal structure of ArPCl₂[PtCl₂(PEt₃)] (58) has been obtained (Figure 5.4).

The magnitude of ¹JPₚt in phosphine complexes has been shown to be proportional to the s-character of the phosphorus lone pair [26]. A further effect is that within complexes where the second phosphorus ligand is cis to PEt₃, the ¹JPₚt value is larger than when the two phosphorus ligands are trans to each other. In the latter case the ligands compete for electrons giving a strong trans influence [45] and hence reducing the ¹JPₚt coupling.

The sequence of phosphorus ligands in terms of increasing ¹JPₚt values (~2000 to ~7000) is as follows, for the cis square planar complexes:

ArP=PAr⁻¹ < ArP=PAr < ArPH₂ < ArP=CH(Ph) < ArP=CCl₂ < ArPCl₂ < ArPF₂
(52) (51) (54) (59) (57) (56) (53)
Figure 5.2a: $^{31}P$ NMR spectrum of cis-ArP=PAr[PtCl$_2$(PEt$_3$)] (51) in CDCl$_3$; an expansion of the downfield region of the spectrum, nb. some diphosphene remains uncoordinated.
Figure 5.2b: $^{19}$F NMR spectrum of ArP-PAr$[[\text{PtCl}_2(\text{PEt}_3)]$ (51) in CDCl$_3$; an expansion of the signals due to the $o$-$\text{CF}_3$ groups.
Figure 5.2c: $^{31}$P NMR spectrum of cis-ArPF$_2$[PtCl$_2$(PEt$_3$)] (53) in CH$_2$Cl$_2$. 
Figure 5.2d: $^{31}$P NMR spectrum of cis-$ArPH_2\{PtCl_2(PEt_3)\}$ (54) in CDCl$_3$; coupled to hydrogen.
Figure 5.2e: $^{31}P$ NMR spectrum of $\text{ArPCl}_2[\text{PtCl}_2(\text{PEt}_3)]$ (55) and (56) in CDCl$_3$; illustrates the presence of the trans isomer (55) and the cis isomer (56).
Figure 5.2f: $^{19}F$ NMR spectrum of cis-$\text{ArPCl}_2[\text{PtCl}_2(\text{PEt}_3)]$ (56) in $\text{CDCl}_3$. 
Figure 5.2g: $^{31}P$ NMR spectrum of cis-ArP=C(Cl)$_2$[PtCl$_2$(PEt$_3$)] (57) in CDCl$_3$. 
Figure 5.2h: $^{19}$F NMR spectrum of cis-ArP=C(Cl)$_2$[PtCl$_2$(P$_3$Et)] (57) in CDCl$_3$. 
Figure 5.2i: $^{31}P$ NMR spectrum of $\text{ArP}=\text{C}(\text{Ph})(\text{H})\text{[PtCl}_2(\text{PET}_3)]}$ (58) and (59) in THF; both the trans isomer (58) and the cis isomer (59) are present.
Figure 5.3a: The mass spectrum of $'ArP=C(Ph)(H)[PtCl_2(PEt_3)]'$ (59)
Figure 5.3b: The mass spectrum of ArPF₂[PtCl₂(PEt₃)] (53)
Figure 5.4a: The crystal structure of ArPCl2[PtCl2(PEt3)] (58); the cis conformation is evident; Bond lengths: Pt-Cl(1) = 2.349Å, slightly longer than Pt-Cl(2) (2.322Å); Pt-P(1) = 2.162Å, slightly shorter than Pt-P(2) (2.263Å) and characteristic of $\eta^1$-coordination.
### Tabella Verbindung
### Kristallsystem
### Raumgruppe
### a
### b
### c
### alpha
### beta
### gamma
### Volumen
### Z
### F(000)
### M
### D(ber)
### Kristallgroesse (mm)
### Messtemperatur (C)
### Strahlung
### Wellenlänge
### Absorptionskoeffizient
### Absorptionskorrektur
### Maximale Transmission (%)
### Minimale Transmission (%)
### Scan-Methode
### 2Theta-Messbereich
### [sin(theta)/lamda]max
### hkl-Messbereich
### Reflexbreite
### gemessene Reflexe
### beobachtete Reflexe
### Ablehnungskriterium
### R(int)
### Parameterzahl
### R
### Rw
### Instabilitätsfaktor p
### Letzter Shift/asd
### Restelektronendichte

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Figure 5.4b: Crystal packing data for ArPCl2[PtCl2(PEt3)] (58)
Figure 5.4c: (i) Bond lengths and (ii) bond angles for 
ArPbCl₂[PtCl₂(Pb₃)] (58).
As has been discussed above all the compounds which have been isolated here appear to be square planar and of cis $\eta^1$-conformation. With the phosphines ArPH$_2$ (15), ArPF$_2$ (3) and ArPCl$_2$ (12), it is only in the latter case that an initial observation of the trans isomer [Figure 5.2(e)] was observed in the $^{31}$P NMR, possibly attributed to the increased crowding around phosphorus in this species, with non-bonded repulsions being reduced in the trans configuration. It would be of interest to extend this investigation to the coordination of Ar$_2$PCl (14). A similar behaviour is observed for ArP=CH(Ph) and ArP=CH(SiMe$_3$) [see Figure 5.2(i)] and has been shown in other examples [26,46]. The $^{31}$P NMR data on the trans complex of ArP=CH(SiMe$_3$) (60) was obtained after a period of 6 hours in solution. It would have been interesting to record the data following a longer time period. In these examples [Figures 5.2(e,i)] the initial magnitude of $^1J_{PPt}$ and $^2J_{P(Pt)}$ lie-in the expected range for mutually trans PR$_3$ ligands attached to Pt(II)[26,46].

With the diphosphenes Ar$_2$P$_2$ (19) and ArAr'P$_2$ (20) only the $\eta^1$ cis isomers are observed, similarly with the phosphaalkene ArP=CCl$_2$ (31).

It is possible that the trans isomer is favoured kinetically in all these reaction but is not observed where a possible rapid rate of conversion to the cis form occurs. It has been well established that the cis isomer is the thermodynamically more stable [26,47]. This is attributed to the more effective overlap of the d-orbital at the metal centre in the cis configuration than in the trans. An interesting example where no isomerisation to the cis form occurs, thought to be due to the steric demand of the substituents, is illustrated in Figure 5.5 [48].

---

1Spectroscopic characteristics: $\eta^1$: $^1J$(PtP) large, small change in the $^{31}$P chemical shift; $\eta^2$: large coordination shift, small $^1J$(P(Pt)). The greater shielding attributed to a rise in electron concentration at the phosphorus resulting from the r-back donation from metal to phosphorus, decreasing the s-contribution to the bonding between Pt and P.
5.2.2 The Pt(II) Complex of the Symmetrical Diphosphene

The $^{19}$F NMR of the $^1\eta$ square planar complex of the symmetrical diphosphene is particularly interesting. Figures 5.2(a,b) illustrate the $^{19}$F and $^{31}$P expansion at P(122)(51). An apparent $^9J_{FP}$ coupling may be observed between the fluorine atoms on $C_A$ and $C_B$ (Figure 5.6) (a through-space effect), with the fine coupling observed in Figure 5.2(b). This observation may be interpreted as inferring a "Z" configuration in the complex (Figure 5.6). However, it may also be the result of a secondary spectrum caused by fluorine coupling with platinum.

The isomerisation to the Z form postulated may be a result of the lowering of the barrier to isomerisation on coordination\[49\]. Beautiful crystals could be grown, a sample of which has been submitted for X-ray crystal structure determination. From the $^{19}$F and $^{31}$P NMR data on the unsymmetrical species $\text{ArP=PAr'}$ it was not possible to determine which phosphorus was coordinated. Crystals were obtained but unfortunately these proved to be unsuitable for X-ray analysis.
In previous examples [10] the reaction of a metal fragment, for example \( \text{M(CO)}_5 \), with an unsymmetrical diphosphene has resulted in coordination to the less hindered site (eg. Equation 5.1).

\[
\text{SupermesP} = \text{PMes} \quad \quad \text{SupermesP} = \text{PMes} \quad \quad \downarrow \\
\text{Cr(CO)}_5
\]

However the MNDO calculation on the species \( \text{ArP=PAr'} \) (20) suggests the more positive charge resides on the phosphorus with the smaller group attached. It may therefore be anticipated that in this situation coordination to the more sterically hindered phosphorus may be observed.

**5.3 PHOSPHORUS LIGAND COMPLEXES OF Pt(0) COMPOUNDS**

**5.3.1 Introduction**

The aim of this part of the work was to investigate a possible \( \eta^2 \) mode of coordination for the symmetrical diphosphene (19). This involved the reaction of the diphosphene \( \text{Ar}_2\text{P}_2 \) (19) with a Pt(0) complex [cf. Section 5.2, \( \eta^1 \) diphosphene coordination with Pt(II)].

A broad overview of some examples where specific conditions have influenced a particular coordination mode is presented here. Calculations on the theoretical model compound \( (\text{H}_3\text{P})_2\text{PtH}_2 \) \([50]\) showed that it is the \( d_{xz} \) orbital on platinum which is responsible for electron transfer from the metal via \( \pi \) back-bonding to the \( \pi^* \)-orbital of "the ligand" \( \text{PH}_3 \) in both the \( \eta^1 \) and \( \eta^2 \) bonding modes.

(1) Changing ligands on the coordinating metal to decrease the L-M-L interligand bond angle activates effectively and selectively the \( d_{xz} \) metal orbital. This transfers electrons to the reactant \( \text{H}_2 \) with the effect that the Pt-H bonds are strengthened \([50]\). It can
be deduced that the larger interligand bond angle, imposed by a change from PPh₃ in Pt(PPh₃)₂MesP=CPh₂ to the more sterically demanding PCy₃ ligand, stabilises the dₓz orbital of the PtL₂ fragment to the effect of decreasing the π-back donation component in Ptₓ₋₋₋P=C hence η¹ predominates (Figure 5.7) [50].

![Figure 5.7: A phosphaalkene in η¹-coordination mode.](image)

Alternatively, reducing the L-M-L angle results in extensive electron transfer from the destabilised Pt dₓz orbital to the π* orbital of P=C in a square planar complex. This can be achieved by the use of a chelating ligand with a suitable bite angle. For example bipy N-Ni-N (Figure 5.8) [31, 50].

![Figure 5.8: A phosphaalkene in η²-coordination mode; COD = 1,5-cyclooctadiene; Xyl = 2,6-dimethylphenyl; Bipy = 2,2'-bipyridine.](image)

This example combines the smallest L-M-L interligand bond angle with the largest P=C bond lengthening, indicating an extensive π-backbonding component.

(2) Ligands with π-acceptor properties on the metal, for example CO, reduce the ability of the metal to interact datively with the π*LUMO of the phosphaalkene destabilising η², eg. Ni(CO)₃[η¹-XylP=C(Ph)₂]. Weakly π-accepting ligands eg bipy, promote η² (Figure 5.8) [50].
(3) **Metal oxidation state.** The lower the oxidation state of the metal (electron rich) the greater the electron donation from the metal \(d_{xz}\) orbital to the \(\pi^*\) orbital of the "ligand" (e.g. \(P=C, P=P\)) favouring \(\eta^2\).

(4) **Changing the nature of the ligand on the phosphaalkene.** When the \((PPh_3)_2Pt\) unit is kept constant, but the relative accessibility of \(\sigma(P)\) and \(\pi(P=C)\) is influenced by a change in the phosphaalkene stereochemistry, the \(\eta^1/\eta^2\) balance is disturbed \([39,50]\). Example (A) illustrates \(\eta^2\) bonding (Figure 5.9.), the \(\eta^1\) bonding mode is less favourable than in (B) because of repulsion between the fluorene \(H(1)\) or \(H(8)\) and \(Pt(PPh_3)_2\).

![Figure 5.9: Examples of \(\eta^1\) (A) and \(\eta^2\) (B) coordination modes in phosphaalkenes; in the solid state.](image)

An example whereby the ligands on the metal were designed specifically to promote \(\eta^1\)-coordination of a phosphaalkyne is in the displacement of dinitrogen by \(BuGP\) from \(trans-[M(N_2)_2\cdot(R_1PCH_2CH_2PR_2)_2]\) \((M = Mo, R = Bu, R' = p-CIC_6H_4)\) \([51]\).

5.3.2 **The Reaction of Pt(O)-Complex (61) with \(Ar_2P_2\) (19)**

The Pt(0) species (61) used in the reaction with the symmetrical diphosphene \(Ar_2P_2\) (19) is shown in Figure 5.10. This zero-valent Pt-ethene complex of 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolan has recently been applied as a chiral derivatising agent for the \(^{31}\)P NMR assay of the enantiomeric purity of certain alkenes and allenes \([52]\).
This complex was used primarily because of its availability. The presence of a chelating ligand and the metal oxidation state of zero, act to favour $\eta^2$-coordination [discussed in Section 5.3.1, (1) and (3)]. The mixture of the Pt(0) complex and the diphosphene was stirred at ambient temperature in THF. To obtain any evidence of coordination gentle heating to $35^\circ$C was necessary. The results obtained were not conclusive, however, as an unresolved peak was obtained at +251 ppm in the $^{31}$P NMR. This was attributed to $\eta^2$-coordination, giving a characteristic upfield shift, and a corresponding decrease in the $^{1}J_{P-Pt}$ coupling. In this instance since the expected value of $^{1}J_{P-Pt}$ was ~60 Hz, resolution would not be observed with a sweep width of 500 ppm (23.50 ppm cm$^{-1}$). This compound did not appear to be stable in solution. Decomposition to ArPH$_2$ and other reduction products was evident, with the probable formation of metallic Pt(0), since a grey solid was seen to precipitate in the reaction vessel. The preliminary stages of this area of work show some promise and could be developed with the aim of isolating the product, and varying the nature of the Pt(0) species used.

5.4 COORDINATION CHEMISTRY OF THE BORON/PHOSPHORUS CONTAINING NITRILEIMINE

The reaction of the boron-phosphorus containing nitrileimine (62) (Chapter 11) with the Pt(II) complex (PEt$_{3}$)$_{2}$Pt$_{2}$Cl$_{4}$ was carried out with
Figure 5.13: NMR spectra of nitriileimine (62), with [PtCl₂(PEt₃)]₂ in THF recorded (a) after 1 hour; (b) after 12 hours; these two spectra are related by time dependence only.
the aim of providing structural information on the nitrileimine as a ligand and its behaviour in coordination chemistry. Possible modes of coordination are illustrated in Figure 5.11.

![Figure 5.11: Possible mode of coordination of nitrileimine (62).](image)

There is evidence for $\eta^1$-coordination by phosphorus in the nitrileimine from the magnitude of the $^1J_{PPt}$ value, which is ca. 3251.0 Hz. Another isomer may be possible by rearrangement of the nitrileimine around C (Figure 5.12), but presumably retaining the trans P-Pt-P arrangement as $^2J_{PP}$ coupling is observed of magnitude 635 Hz. The two possible conformations of the nitrileimine are shown in Figure 5.12.

![Figure 5.12: Proposed isomeric forms of (62) in Pt(II) complex.](image)

A shift downfield is observed on coordination (Figure 5.13) (cf. low field shift on coordination of the phosphorus species, Table 5.3).

$^2$Expected range for $\eta^1 \ ^1J(PPt)$ is 3000-4000 Hz (ref.44).
This preliminary study simply serves to promote work in this area. This is a new ligand type, and from the indication here would merit further investigation.

5.5 Octahedral Complexes of the Symmetrical Diphosphene with the Transition Metal in Zero Oxidation State

5.5.1 Synthesis

The diphosphene, Ar₂P₂ (19) was reacted with the following species: Mo(CO)₅·THF, Cr(CO)₅·THF and W(CO)₅·THF. The types of coordination by diphosphene displacement of THF were deduced primarily from the $^{31}$P and $^{19}$F NMR data the former of which is presented in Table 5.4.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>$\delta^{31}$P</th>
<th>$^1$Jpp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar$\text{Mo(CO)}_5$ (63)</td>
<td>412.7</td>
<td>510</td>
</tr>
<tr>
<td>Ar$\text{W(CO)}_5$ (64)</td>
<td>386.5</td>
<td>478</td>
</tr>
<tr>
<td>Ar$\text{Cr(CO)}_5$ (65)</td>
<td>428.4</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 5.4: $^{31}$P NMR data for $\eta^1$ coordination complexes; $^{1}J(^{183}$W-$^{31}$P).
Preparation of transition metal derivatives of \( \text{ArP} = \text{PAr} \)

\[
\begin{align*}
\text{a) } \quad \text{Mo(CO)}_6 & \xrightarrow{\text{h}u, \text{THF}} \text{Mo(CO)}_5 \cdot \text{THF} \\
\text{b) } \quad \text{Mo(CO)}_5 \cdot \text{THF} & \xrightarrow{\text{Mo(CO)}_5 \cdot \text{THF}} \text{Mo(CO)}_5 \cdot \text{THF}
\end{align*}
\]

\[\text{F}_3\text{C} \quad \text{CF}_3 \quad \text{CF}_3 \quad \text{P} = \text{P} \quad \text{CF}_3 \quad \text{F}_3\text{C} \]

\[\text{F}_3\text{C} \quad \text{CF}_3 \quad \text{CF}_3 \quad \text{Mo(CO)}_5 \quad \text{THF} \quad \text{F}_3\text{C} \quad \text{CF}_3 \quad \text{CF}_3 \]

\( ^{31} \text{P N.M.R.} \)

\[
\begin{align*}
\text{(Unreacted diposphene (XIII))} & \quad \text{(AB type spec. (XIV))} \\
\delta^{31} \text{P}_1 & = 412.7, \quad J_{\text{P-P}} = 510. \\
\delta^{31} \text{P}_2 & = 407.7. \\
& \quad \text{(P-F coupling unresolved.)}
\end{align*}
\]

\( ^{19} \text{F N.M.R.} \)

\[
\begin{align*}
\delta^{19} \text{F}_1 & = -54.6 \text{ (6F)}, \quad \delta^{19} \text{F}_2 = -65.1 \text{ (6F)} \\
\delta^{19} \text{F}_2 & = -58.9 \text{ (6F)}
\end{align*}
\]

Only one phosphorus coordinates to the molybdenum by its' lone pair in an \( \eta^1 \) fashion making the two rings inequivalent. This shows up distinctly in the \( ^{31} \text{P N.M.R.} \) as an AB pattern resulting from phosphorus-phosphorus' coupling. Some uncoordinated diposphene is present.

Figure 5.15: \( ^{31} \text{P NMR spectrum of ArP=PAR[Mo(CO)}_5 \text{]} \) (63) in THF.
5.5.2 Results

It appeared that the $\eta^1$ mode of coordination was observed exclusively. The molybdenum complex (63) was isolated pure as deep-red needle-like crystals which were characterised by $^{31}$P NMR (Figure 5.15), $^{19}$F NMR (Figure 5.16), IR and elemental analysis for carbon and hydrogen (Section 5.6.14). Mass spectrometry here however caused problems, as did that of the tungsten and chromium complexes. Accurate mass spectra were unobtainable because of contamination within the mass spectrometer.

The crystals of the molybdenum complex (63) have been submitted for an X-ray analysis, from which it will be possible to assign unambiguously the configuration as E or Z. The E form is proposed, as depicted in Table 5.4.

Complex (64) was characterised by its $^{31}$P NMR spectrum and its characteristic tungsten-phosphorus-coupling ($^{183}$W: 14% abundance), verifying the phosphorus as the donor atom [53].

The formation of the symmetrical complex (65) has been postulated to explain the singlet observed in the $^{31}$P NMR spectrum (Figure 5.17). This centrosymmetric complex with a phosphorus-phosphorus double bond is proposed in preference to the $\eta^2$-type complex. The basis for this assignment is discussed below. Deep brown/orange crystals of (65) were obtained, and have also been submitted for X-ray analysis, although separation difficulties may make this impossible. (The microanalysis was inaccurate due to the presence of Cr(CO)$_6$ which appeared to co-crystallise). The downfield $^{31}$P shift and UV spectrum support the bis-$\eta^1$ structure presented. The E conformation was assigned because of the expected steric demand of the Ar substituent. In the absence of a crystal structure, however, it was not possible to confirm this assignment unambiguously.
Figure 5.16: $^{19}$F NMR spectrum of $\text{ArP=PAr[Mo(CO)_{5}]}$ (63) in THF; some uncoordinated diphosphene is also present.
Interestingly, there was no evidence of the initial mono $\eta^1$ complex, even with a reaction stoichiometry of one Cr(CO)$_5$·THF to one diphosphene (19). This yielded unreacted diphosphene and complex (65) only (see Figure 5.17). A possible explanation may be the ability of the chromium pentacarbonyl moiety to line up in conjugation with the phosphorus-phosphorus double bond. Being Cr(0) and hence electron-rich, it can donate into the P=P bonding system, with concomitant increase in the reactivity of the second lone pair. Preferential reaction here would therefore explain why no mono-coordinated intermediate is observed. This difference in behaviour compared with the molybdenum and tungsten derivatives may be a result of their increase in size, disallowing such extensive overlap with the $\pi$-system. This is possibly also partially reflected in the shielding of the phosphorus (Table 5.4 and Figure 5.18).

![Figure 5.18: $^{31}P$ shift of complex; *values of similar complexes for the diphosphene ($\text{Me}_3\text{SiCH}_2$)$_2\text{P}_2$ have been included for comparative purposes.](image)

The assumption has been made that the most shielded phosphorus is directly coordinated to the metal. Similar complexes have been isolated with other diphosphenes [53-55]. It is worth considering a possible interpretation for the mode of coordination of complex (65) in terms of
Figure 5.17: $^{31}P$ NMR spectrum of $ArP-PAr[Cr(CO)_{5}]_{2}$ (65) in THF; some unreacted $Ar_{2}P_{2}$ (19).
an $\eta^6$ bonding mode to a Cr(CO)$_3$ fragment via the aromatic ring. This coordination type has been verified with the very sterically crowded diphosphene, (SupermesP)$_2$ [10,56]. The $\eta^1$ coordination of Cr(CO)$_5$ in (65) appears justified in terms of the reaction conditions employed. (For 'ring-coordination' there is an increase in the harshness of the conditions used [56], for example via refluxing in dioxane). The $\eta^6$-arene coordination complex would also be considered unlikely in this situation, due to the electron deficiency of the Ar ring system, when compared with that of the supermesityl derivative.

In general, the end-on $\eta^1$ coordination of the M(CO)$_5$ group (M = Cr, Mo, W) would not be expected to exert an influence on the bond order of "P=P", although it acts to shield slightly the phosphorus nuclei, as reflected by the shift of the resonances to lower frequency (Table 5.4 and Figure 5.18).

5.5.3 Complex Stability

The molybdenum complex, Ar$_2$P$_2$-Mo(CO)$_5$ (63) appeared relatively stable in air over a period of weeks. Exposure of the deep brown complex, Ar$_2$P$_2$[Cr(CO)$_5$]$_2$ (65) to the atmosphere over a few hours caused a green colouration, attributed to the oxidation of Cr(0) to Cr(III). Isolation of the tungsten derivative (64) was not successful (Section 5.6.16).

5.5.4 Relative Rates of Coordination of M(CO)$_5$ (M = W, Cr, Mo)

It was of interest to study the relative rates of coordination of the metal pentacarbonyl fragments, M(CO)$_5$ with the diphosphene, Ar$_2$P$_2$ (19) with respect to the gradual size increase Cr, Mo, W, as the group
is descended.

The procedure followed initial generation of the THF adduct by irradiation of the metal hexacarbonyl in THF [25] for a standard period of 8 hours. The adduct was formed as a preliminary stage to avoid any rate dependence on this. It was used in a two-fold excess with the diphosphene (19). The $^{31}\text{P NMR}$ of each sample was recorded in subsequent 5 hour intervals. For chromium only, there was evidence of reaction after the first time interval. A small singlet (+428.4 ppm), corresponding to ca. 5% conversion and indicative of $\eta^1$ bis coordination (65), was evident in the $^{31}\text{P NMR}$ (Table 5.5 and Figure 5.19). However, after 20 hours a 30% conversion to the $\eta^1\text{Mo(CO)}_5\text{Ar}_2\text{P}_2$ (63), 10% to $\text{W(CO)}_5\text{Ar}_2\text{P}_2$ (64) and 45% conversion to $\text{Ar}_2\text{P}_2[\text{Cr(CO)}_5]^2$ (65) was observed. A general observation of higher reactivity of the smaller Cr(CO)$_5$ fragment, with intermediate reactivity of Mo(CO)$_5$, and significantly reduced reactivity of W(CO)$_5$ is apparent. Improved yields of the order of 20% (see Sections 5.6.14-5.6.16) of complexes (63)-(65) were obtained by in situ irradiation of a mixture of the metal hexacarbonyl (2-fold excess) with the diphosphene in THF, and exactly analogous NMR data were obtained. It is worth mentioning here that irradiation of ArPH$_2$ in the presence of a two-fold excess of Mo(CO)$_6$ in THF, appeared to generate ArPH$_2[\text{Mo(CO)}_5]$ (66) (see Experimental, Section 5.6.13). It is likely that these reactions also proceed via the initial THF adduct, although direct displacement of carbon monoxide cannot be ruled out [50b].
Figure 5.19: Rate of reaction of $M(CO)_{5}$ ($M = Mo, Cr, W$) with $Ar_{2}P_{2}$ (19).

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>Cr (65)</th>
<th>Mo (63)</th>
<th>W (64)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>~5</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>10</td>
<td>~15</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>15</td>
<td>~35</td>
<td>17</td>
<td>8</td>
</tr>
<tr>
<td>20</td>
<td>45</td>
<td>30</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 5.5: Rate of reaction of $M(CO)_{5}$ ($M = Mo, Cr, W$) with $Ar_{2}P_{2}$ (19); †derived from $^{31}$P NMR.

5.6 EXPERIMENTAL DETAILS

5.6.1 Preparation of $ArPF_{2}[(PEt_{3})PtCl_{2}]$ (53)

$ArPF_{2}$ (3) + $1/2Cl_{4}Pt_{2}(PEt_{3})_{2} \rightarrow ArPF_{2}[(PEt_{3})PtCl_{2}]$ (53)

($PEt_{3})_{2}Pt_{2}Cl_{4}$ (768 mg, 1.0 mmol) was added to a stirred solution of $ArPF_{2}$ (0.7 g, 2.0 mmol) in $CH_{2}Cl_{2}$ (15 ml) at room temperature. A clear
pale yellow solution was formed. This was cooled to -40 °C to give white crystals. Yield was 800 mg (54%). This solid was recrystallised again from CH₂Cl₂ (5 ml) to obtain a sample suitable for X-ray analysis. The cis isomer was isolated. Mpt. 190 °C; ³¹P (CDCl₃) δ: +124.0 ppm ('pseudo triplet' of triplets), ¹Jₚₚₚ +6252.1, ¹JₚF 1146.1 Hz; (LIGAND PEt₃): +11.5 ppm ('pseudo triplet'), ¹Jₚₚₚ 2876.9 Hz; ¹⁹F δ: -55.3 to -55.6 ppm (o-CF₃,6F, very complex '2nd order'), -64.4 (p-CF₃,3F); MS [Intensity%] CI⁻: 733 [100, ArPF₂(Et₃PtCl₂)]⁻, 616 [49, ArPF₂(PtCl₂)]⁻.

5.6.2 Preparation of ArPH₂[(PEt₃)PtCl₂] (54)

ArPH₂ (15) + 1/2Cl₄Pt₂(PEt₃)₂ → ArPH₂[(PEt₃)PtCl₂] (54)

(PEt₃)₂Pt₂Cl₄ (500 mg, 0.65 mmol) was added to a stirred solution of ArPH₂ (0.41 g, 1.30 mmol) in CH₂Cl₂ (20 ml) at room temperature. This was stirred for 1 hour. The pale yellow solution was cooled to -40 °C with the precipitation of clear crystals. Yield of the cis isomer was 800 mg (88%). These have been submitted for X-ray analysis. Mpt. 310-312 °C; ³¹P (CDCl₃) δ: -74.2 ppm ('pseudo triplet' of triplets), ¹Jₚₚₚ +3809.1, ¹JₚH 412.9, ²Jₚₚ 20.6 Hz; (LIGAND PEt₃): +9.3 ppm ('pseudo triplet'), ¹Jₚₚₚ 3034.8, ²Jₚₚ 20.6 Hz; ¹⁹F δ: -50 to -60 ppm (o-CF₃,6F, very complex '2nd order' spectrum), -64.6 ppm (p-CF₃,3F); MS [Intensity%] CI⁻: 314 [100, ArPH₂].
5.6.3 Preparation of \( \text{ArPCl}_2[(\text{PET}_3)\text{PtCl}_2] \) (56)

\[
\text{ArPCl}_2 + \frac{1}{2}(\text{PET}_3)_2\text{PtCl}_4 \rightarrow \text{ArPCl}_2[(\text{PET}_3)\text{PtCl}_2]
\]

\( (\text{PET}_3)_2\text{PtCl}_4 \) (500 mg, 0.65 mmol) was added to a stirred solution of \( \text{ArPCl}_2 \) (500 mg, 1.3 mmol) in \( \text{CH}_2\text{Cl}_2 \) (20 ml) at room temperature. The mixture was stirred for 1.5 hours. The \( ^{31}\text{P} \) NMR showed no evidence of coordination. The solution was warmed to 35 °C for 2 hr. A low conversion (ca. 5%) to the \textit{trans} isomer of the desired complex was observed. After a further two hours complete conversion to the \textit{cis} isomer was detected. The pale yellow solution was cooled to -40 °C giving pale yellow crystals. Yield was 350 mg (35%). An X-ray analysis was obtained on these crystals (Figure 5.4). \textit{Trans} isomer: \( ^{31}\text{P} \) (CDCl\(_3\)) \( \delta: +135.8 \text{ ppm} \) ('pseudo triplet' of doublets), \( ^1\text{J}_{\text{PtP}} 2885.8, ^2\text{J}_{\text{PP}} 679.0 \text{ Hz} \); (LIGAND \text{PET}_3): 14.3 ppm ('pseudo triplet' of doublets), \( ^1\text{J}_{\text{PtP}} +2840.0, ^2\text{J}_{\text{PP}} +694.8 \text{ Hz} \). \textit{Cis} isomer: \( ^{31}\text{P} \) (CDCl\(_3\)) \( \delta: +90.3 \text{ ppm} \) ('pseudo triplet'), \( ^1\text{J}_{\text{PtP}} 5511.0 \text{ Hz} \); (LIGAND \text{PET}_3): 13.6 ppm ('pseudo triplet'), \( ^1\text{J}_{\text{PtP}} 2756.3 \text{ Hz} \); \( ^{19}\text{F} \) \( \delta: -49.0 \text{ ppm} \) (o-\text{CF}_3 , apparent AB, 4 lines unusually deshielded), -64.1 ppm (p-\text{CF}_3); \( ^1\text{H} \) \( \delta: 7.18 \) (2H, CH on Ar), 2.21 (6H, CH\(_2\)/Et), 1.17 (9H, CH\(_3\)/Et) ppm.

The apparent quartet observed in the \( ^{19}\text{F} \) NMR may be assigned to fluorine splitting by platinum [Figure 5.2(f)], and further splitting by phosphorus (Figure 5.20). If these were of similar magnitude this would offer an explanation for the pseudo quartet observed. If this explanation is valid the values are \( ^4\text{J}_{\text{PF}} 27.6 \text{ Hz} \) and \( ^5\text{J}_{\text{PtF}} \) ca. 24.2 Hz. This is supported by a very similar value of \( ^5\text{J}_{\text{PtF}} \) (32.5 Hz) for the phospha-alkene coordination \( \text{ArP}=\text{C(Cl)}_2[\text{PET}_3\text{PtCl}_2] \) (57) (Section 5.6.6). The crystal structure data for complex (56) is presented in Figure 5.4.
5.6.4 Preparation of $\text{Ar}_2\text{P}_2[(\text{PET}_3)\text{PtCl}_2]$ (51)

$\text{ArP}=\text{PAr} \ (19) + 1/2(\text{PET}_3)_2\text{Pt}_2\text{Cl}_4 \rightarrow \text{Ar}_2\text{P}_2[(\text{PET}_3)\text{PtCl}_2] \ (51)$

$(\text{PET}_3)_2\text{Pt}_2\text{Cl}_4 \ (461 \text{ mg}, \ 0.60 \text{ mmol})$ was added to a stirred solution of $\text{ArP}=\text{PAr} \ (0.81 \text{ g}, \ 1.3 \text{ mmol})$ in $\text{CH}_2\text{Cl}_2 \ (25 \text{ ml})$ at room temperature. The pale yellow solution was stirred for 1 hr, and then cooled to $-40 \ ^\circ\text{C}$ to give pale yellow crystals. Yield was $0.84 \text{ g} \ (64\%)$. These crystals were submitted for X-ray analysis. $^{31}\text{P} \ (\text{CDCl}_3) \ \delta: \ P_1 +346.6 \ \text{ppm} \ ('\text{pseudo triplet'} \ of \ doublets), \ 1J_{\text{PPt}} \ 2602.9, \ 2J_{\text{PP}} \ 534.3 \ \text{Hz}, \ P_2 \ 337.2 \ \text{ppm}$ (doublet), $^2J_{\text{PP}} \ 534.3 \ \text{Hz}; \ (\text{LIGAND PET}_3): \ +9.5 \ \text{ppm} \ ('\text{pseudo triplet'}), \ 1J_{\text{PPt}} \ 4024.3 \ \text{Hz}; \ 19\text{F} \ (\text{CDCl}_3) \ \delta: \ -55.9 \ (\text{d of t,o-CF}_3), \ -57.9 \ (\text{t of d, o-CF}_3), \ -63.7 \ (\text{s,p-CF}_3), \ -63.9 \ (\text{s,p-CF}_3) \ \text{ppm}, \ 1J_{\text{FF}} \ +5.2 \ \text{Hz},^3 \ (\text{between the o-CF}_3 \ \text{groups on opposite rings}), \ ['J_{\text{PF}} \ 18 \ \text{Hz}', \ \text{from} \ the \ 19\text{F NMR} \ (\text{Section} \ 5.2.2) \ \text{it appears that one set of the o-CF}_3 \ \text{groups on one ring is seeing two phosphorus atoms to split it into a real triplet, whilst the other is seeing one phosphorus atom resulting in a doublet}].$

\[\text{Figure 5.20: Predicted coupling pattern for ArPCl}_2[(\text{PET}_3)\text{PtCl}_2] \ (56)\]

\[\text{Figure 5.2(b)}\]

\[\text{Figure 5.20} \text{ Predicted coupling pattern for ArPCl}_2[(\text{PET}_3)\text{PtCl}_2] \ (56)\]

\[\text{Figure 5.2(b)}\]

\[^3\text{or this may be attributed to a second order fine coupling with platinum [Figure 5.2(b)].}\]
5.6.5 Preparation of $\text{ArP=PAr'}[(\text{PEt}_3)\text{PtCl}_2]$ (52)

\[
\text{ArP=PAr'} (20) + \frac{1}{2}(\text{PEt}_3)_2\text{Pt}_2\text{Cl}_4 \rightarrow \text{ArP=PAr'}[(\text{PEt}_3)\text{PtCl}_2] \quad (52)
\]

$(\text{PEt}_3)_2\text{Pt}_2\text{Cl}_4$ (0.58g, 0.76 mmol) was added to a stirred solution of $\text{ArP=PAr'}$ (0.85g, 1.5 mmol) at room temperature. This mixture was stirred for 1 hr. The solution was cooled to -40 °C, and the $\eta^1$ complex isolated as small transparent crystals which were submitted for X-ray analysis, but no suitable crystals were obtained. Yield was 0.62g (64%). From the $^{19}\text{F}$ and $^{31}\text{P}$ NMR it was not possible to determine which phosphorus the platinum was coordinated to, so an X-ray structure would have been of particular interest here. $^{31}\text{P} \delta: 386.4$ ppm, $^1\text{J}_{\text{PPt}} 2550.0$ Hz, $P_1 +343.7$ ppm, $^1\text{J}_{\text{PP}} 501.2$ Hz; $^{19}\text{F}$ (CDCl$_3$) $\delta$: very complex spectrum: -55 to -60 (o-CF$_3$, 12F), -64.0 (p-CF$_3$, 3F) ppm.

5.6.6 Preparation of $\text{ArP=Cl}_2[(\text{PEt}_3)\text{PtCl}_2]$ (57)

\[
\text{ArP=Cl}_2 (31) + \frac{1}{2}(\text{PEt}_3)_2\text{Pt}_2\text{Cl}_4 \rightarrow \text{ArP=Cl}_2[(\text{PEt}_3)\text{PtCl}_2] \quad (57)
\]

$(\text{PEt}_3)_2\text{Pt}_2\text{Cl}_4$ (461 mg, 0.60 mmol) was added to a stirred solution of $\text{ArP=Cl}_2$ (474 mg, 1.2 mmol) in CH$_2$Cl$_2$ (10 ml) at room temperature. The mixture was stirred for one hour. The pale yellow solution was cooled to -40 °C. Clear transparent plates were isolated and submitted for X-ray analysis. Yield was 390 mg (42%). Cis isomer: $^{31}\text{P} \delta: 152.1$ ('pseudo triplet'), $^1\text{J}_{\text{PPt}} 5006.4$ Hz, $^2\text{J}_{\text{PP}} +18$ Hz; (LIGAND P$\text{Et}_3$): +11.1, $^1\text{J}_{\text{PPt}} 3831.8$ Hz; $^{19}\text{F} \delta$: -56.8, $^5\text{J}_{\text{PtF}} 32.5$ Hz (pseudo triplet,o-CF$_3$), -63.0 (s,p-CF$_3$) ppm.
5.6.7 Preparation of trans- and cis-ArP=C(Ph)H[(PEt\(_3\))PtCl\(_2\)] (58,59)

ArP=CH(Ph) (32) + 1/2(PEt\(_3\))\(_2\)PtCl\(_4\) \(\rightarrow\) ArP=CH(Ph)[(PEt\(_3\))PtCl\(_2\)]

(58) trans
(59) cis

(PEt\(_3\))\(_2\)PtCl\(_4\) (400 mg, 0.52 mmol) was added to a stirred solution of ArP=CH(Ph) (ca. 440 mg, 1.1 mmol) in THF\(^4\) (15 ml) at room temperature. The solution was stirred for 0.5 hours. The \(^{31}\)P NMR showed the presence of two isomers. After the mixture was stirred for 2 hr. only the cis isomer was detected. The pale yellow solution was cooled to -40 °C and white crystals were precipitated. Yield was 0.41g (47%). Trans isomer: \(^{31}\)P (THF) \(\delta\): +178.6 ppm ('pseudo triplet' of doublets), \(^1\)J\(_{PPt}\) 2456.5, \(^2\)J\(_{PP}\) 569.5 Hz; (LIGAND PEt\(_3\)): 15.8 ppm ('pseudo triplet' of doublets), \(^1\)J\(_{PPt}\) +3253.4, \(^2\)J\(_{PP}\) 569 Hz. Cis isomer: \(^{31}\)P (THF) \(\delta\): +149.6 ppm ('pseudo triplet'), \(^1\)J\(_{PPt}\) 4599.6 Hz; (LIGAND PEt\(_3\)): 9.86 ppm, \(^1\)J\(_{PPt}\) 3219.1 Hz; MS (Intensity%) Cl\(^-\): 635 [26.8;ArP=CH(Ph)PtP\(_2\)], 593 [66], 381 [51;Et\(_3\)PPtCl\(_2\)], 312 [10.7,ArP\(^-\)], 331; \(^{19}\)F \(\delta\): The \(^{19}\)F NMR is complex, but as observed in the \(^{31}\)P NMR (Figure 5.2) there are some impurities, which appear to contain fluorine, however a pseudo triplet at -64.1 ppm is evident and a tentative value of \(^5\)J\(_{PF}\) 31.8 Hz may be derived. There is also a peak at -67.2 ppm corresponding to the p-CF\(_3\) groups. The \(^5\)J\(_{PF}\) value here is notably similar to the values obtained for compounds (56) and (57).

\(^4\)A THF solution of the phosphaalkene ArP=CH(Ph) had to be used since it was unstable to isolation.
5.6.8 Preparation of trans-ArP=CH(SiMe₃)[(PEt₃)PtCl₂] (60)

\[
\text{ArP=CH(SiMe₃)} \quad \text{(33) } + \quad (\text{PEt}_3)_2\text{Pt}_2\text{Cl}_4 \quad \rightarrow \quad \text{ArP=CH(SiMe₃)}[(\text{PEt}_3)\text{PtCl}_2] \quad \text{(60)}
\]

\[(\text{PEt}_3)_2\text{Pt}_2\text{Cl}_4 \quad \text{(400 mg, 0.52 mmol)} \text{ was added to a stirred solution of ArP=CH(SiMe₃) (ca. 0.1g, 0.25 mmol) in THF (10 ml). This was stirred at room temperature for 6 hrs. The ³¹P NMR showed the trans isomer. Conversion (w.r.t. ³¹P NMR) was 78\%. ³¹P (THF) δ: +245.1 ppm, ¹J_{PPt} 3714.0, ²J_{PP} 788.0 Hz; (LIGAND PEt₃): 15.4 ppm, ¹J_{PPt} 3000, ²J_{PP} 787 Hz.}
\]

5.6.9 Reaction of Ar₂P₂ (19) with the Pt(0) Complex (61)

\[
\begin{align*}
\text{ArP-PAr (19) + Ph₂P} & \quad \text{PPh₂ (61)} \\
& \quad \rightarrow \quad [\text{Pt(0)-diphosphene complex}]
\end{align*}
\]

The Pt(0) complex (61) (150 mg, 0.22 mmol) was added to a stirred solution of ArP=PAr (0.137g, 0.21 mmol) in THF (25 ml) at room temperature. No reaction was observed after stirring for 2hr. This solution was warmed gently with a hair-dryer. The ³¹P NMR showed a peak at 251 ppm : phosphorus ligand +6.3 ppm, ¹J_{PPt} 3189.9 Hz. There were small peaks at -189, -0.5 and -2.4 (s) possibly from a reduction product such as ArPH₂, since a small amount of grey metallic solid was observed, which could have been platinum metal. The ¹⁹F NMR spectrum showed unreacted diphosphene with an apparent triplet at -52.3 ppm. This may be attributed to the η² complex: a ⁴J_{PF} + ⁵J_{PF} value of 79 Hz may be tentatively assigned.
5.6.10 Preparation of bis-benzonitrile-Pt(II) chloride [57]

PtCl₂ (1.1g, 4.1 mmol) was dissolved in a minimum of hot benzonitrile (15 ml, 100 °C). After filtering, this solution was cooled to give a heavy precipitate of (PhCN)₂PtCl₂ (1.89g, 4.0 mmol) collected by filtration. A further crop of crystals was obtained by diluting the filtrate with low boiling point petroleum ether. Yield was 98%. The product was recrystallised from benzene.

5.6.11 Addition of (PhCN)₂PtCl₂ to Ar₂P₂ (19)

(PhCN)₂PtCl₂ (xs) + ArP=PAR (19) ——X—>

ArP=PAR (0.42g, 0.67 mmol) in CH₂Cl₂ (10 ml) was added to a stirred solution of (PhCN)₂PtCl₂ (0.51g, 1.1 mmol) in CH₂Cl₂ (20 ml) at room temperature. This was stirred for 4hr. ³¹P NMR showed no reaction (+473.8 ppm).

5.6.12 Reaction of nitrileimine (62) with [(PEt₃)PtCl₂]

(¹Pr₂N)₂P-C=N=N-B(N¹Pr₂) (62) Cl₄Pt₂(PEt₃)₂

Cl₂CH₂

(PEt₃)₂Pt₂Cl₄ (0.51g, 0.66 mmol) was added at room temperature to a solution of nitrileimine (¹Pr₂N)₂P-C=N=N-B(N¹Pr₂) (0.82g, 1.7 mmol) and stirring was continued for 1 hr. The resultant yellow solution gave a complex ³¹P NMR spectrum [Figure 5.13(a)] which simplified after 12 hours [Figure 5.13(b)]. The IR showed no nitrileimine absorption. On cooling the CH₂Cl₂ solution to -40 °C no crystals were obtained. ³¹P (THF) δ₁: 72.24 ppm, ¹Jpp 3247.6 Hz, ²Jpp 637.9 Hz; δ₂: +67.73 ppm,
$^{1}J_{PP}$ 3251.0 Hz. Figure 5.13(b) showed $\delta_1$ only.

5.6.13 Preparation of $\text{ArPH}_2[\text{Mo(CO)}_5]$ (66) in solution

$$\text{ArPH}_2 (15) + \text{Mo(CO)}_6 \xrightarrow{\text{THF}} h\nu \xrightarrow{\text{ArPH}_2[\text{Mo(CO)}_5]} (66)$$

Mo(CO)$_6$ (2.0 g, 7.6 mmol) was added to a stirred solution of ArPH$_2$ (1.2 g, 3.8 mmol) at room temperature in a quartz vessel. This mixture was irradiated for 1.5 hr. at 254 nm (Hg lamp). A deep-red solution was formed. The product was not isolated. The $^{31}$P NMR showed an approximate 55% conversion to the postulated $\eta^1$ coordination complex. $^{31}$P (THF) $\delta$: -78.2 ppm (d of t), $^{1}J_{PP}$ +354.0, $^{4}J_{PF}$ +17.0 Hz; $^{19}$F (THF) $\delta$: -58.6 (d of t, o-CF$_3$), $^{4}J_{PF}$ +17.0, $^{5}J_{FF}$ 3.1 Hz, -64.2 (p-CF$_3$) ppm.

5.6.14 Preparation of $\text{ArP}=\text{PAr}[\text{Mo(CO)}_5]$ (63)

$$\text{ArP}=\text{PAr} (19) + \text{Mo(CO)}_6 \xrightarrow{\text{THF}} h\nu \xrightarrow{\text{ArP}=\text{PAr}[\text{Mo(CO)}_5]} (63)$$

ArP=PAr (0.61 g, 1.0 mmol) in THF (10 ml) was added to a stirred suspension of Mo(CO)$_6$ (0.53 g, 2.0 mmol) in THF (15 ml) in a quartz tube at room temperature. This mixture was irradiated for 12 hr at 254 nm, giving a dark-red solution. All the volatile material was removed in vacuo and the reddish oil was extracted with pentane (20 ml). This was cooled to -40 °C and dark red crystals were obtained. Yield was 0.57 g (66%). Analysis found: C, 32.45; H, 0.73; Required for C$_{23}$H$_4$F$_{18}$O$_5$P$_2$Mo: C, 32.09; H, 0.47%; $^{31}$P (CDCl$_3$) $\delta$: +412.7 (d), +407.7 (d) ppm, $^{1}J_{PP}$ 510 Hz; $^{19}$F (CDCl$_3$) $\delta$: -54.9 (6F), -58.9 (6F) (apparent triplet, coupling 18.05 Hz, finer coupling 7 Hz), -65.1 (6F) ppm (see Figure 5.16); IR
(Nujol) $\nu_{\text{max}}$: 2000 (s), 1980 (s), 1960 (s), 1945 (s, $\nu_{\text{CO}}$), 1450 and 1370 (s, C-F), 590 (w, "P=P") cm$^{-1}$.

5.6.15 Preparation of $\text{ArP=PAR}[\text{Cr(CO)}_5]^2$

$$\text{ArP=PAR} (19) + 2\text{Cr(CO)}_6 \xrightarrow{\text{THF} \text{h} \nu} \text{ArP=PAR}[\text{Cr(CO)}_5]^2 (65)$$

$\text{ArP=PAR} (1.5\text{g}, 2.4 \text{mmol})$ in THF (10 ml) was added to a stirred suspension of $\text{Cr(CO)}_6 (1.06\text{g}, 4.8 \text{mmol})$ in a quartz vessel in THF (50 ml) at room temperature. This mixture was irradiated at 254 nm (Hg lamp) for 12 hr. All the volatiles were removed from the resulting deep-red solution in vacuo. Pentane (10 ml) was added, and the mixture was cooled to -40 $^\circ$C. A crystalline dark red solid was precipitated. Yield was 1.6g (66% assuming molecular formula as $\text{ArP=PAR}[\text{Cr(CO)}_5]^2$).

$^{31}\text{P}$ (THF) $\delta$: +428.4 (singlet); IR (Nujol) $\nu_{\text{max}}$: 3100 (w, CHAr), 2080 (w, sharp), 2000 (w), 1985 (w), 1950 (s, $\nu_{\text{CO}}$), 1460 (m, ArC=C), 1380 (w, ArC=C), 1260 (s), 1200-1000 (s, C-F), 800 (s), 700-650 (m, "P=P") cm$^{-1}$; UV-Vis $\lambda_{\text{max}}$ (Abs): 291 (0.39), 261 (0.69).

5.6.16 Preparation of $\text{ArP=PAR}[\text{W(CO)}_5]^1$ (64)

$$\text{ArP=PAR} (19) + \text{W(CO)}_6 \xrightarrow{\text{THF} \text{h} \nu} \text{ArP=PAR}[\text{W(CO)}_5]^1 (64)$$

$\text{ArP=PAR} (0.81\text{g}, 1.3 \text{mmol})$ in THF (10 ml) was added to a stirred suspension of $\text{W(CO)}_6 (0.91\text{g}, 2.6 \text{mmol})$ in THF (50 ml) in a quartz vessel at room temperature. The mixture was irradiated at 254 nm (Hg lamp) for 12 hr. The solution became deep-red. $^{31}\text{P}$ NMR showed a low yield (~30%) of the proposed $\eta^1$-coordination complex had formed. All the volatiles
were removed in vacuo to give a black oil. Pentane (5 ml) was added. The solution was cooled to -40 °C, and a colourless solid was isolated containing no fluorine or phosphorus, deduced to be unreacted W(CO)$_6$. $^{31}$P (THF) $\delta_1$: +386.5 ppm (doublet); $\delta_2$: +359.9 ppm (doublet), $J_{183^{31}P}$ 292.8 Hz, $^1J_{pp}$ +478 Hz; IR (Nujol) $\nu_{\text{max}}$: 2200 (w), 2080 (m), 1980 (m) and 1950 (s,br) (all $\nu_{\text{CO}}$ cm$^{-1}$; $^{19}$F $\delta$: ca. -58.7 (o-CF$_3$), ca. -65.0 (p-CF$_3$) ppm.

5.6.17 Preparation of ArP=PAr[Mo(CO)$_5$] (63)

$$\text{Mo(CO)}_6 \xrightarrow{\text{THF}} \text{Mo(CO)}_5 \cdot \text{THF} + \text{ArP=PAr} \rightarrow \text{ArP=PAr[Mo(CO)}_5\text{]} \quad (63)$$

Mo(CO)$_6$ (0.3g, 1.1 mmol) in THF (50 ml) was irradiated at 254 nm (Hg lamp) for 4 hr. ArP=PAr (0.62g, 1.0 mmol) in THF (10 ml) was added to this pale yellow solution, and the mixture stirred for 20 hr. at room temperature to give a deep-red solution. The solvent was removed in vacuo, and the resultant red oil was extracted with pentane (10 ml). This was cooled to -40 °C. A dark red solid was obtained. Yield was 0.26g (30%). Characterisation data appear in Section 5.6.14.

5.6.18 Preparation of ArP=PAr[Cr(CO)$_5$]$_2$ (65)

$$2\text{Cr(CO)}_6 \xrightarrow{\text{THF}} 2\text{Cr(CO)}_5 \cdot \text{THF} + \text{ArP=PAr} \rightarrow \text{ArP=PAr[Cr(CO)}_5\text{]}_2 \quad (65)$$

Cr(CO)$_6$ (0.48g, 2.2 mmol) in THF (50 ml) was irradiated at 254 nm (Hg lamp) for 4 hr. ArP=PAr (0.62g, 1.0 mmol) in THF (10 ml) was added to this clear yellow solution. The mixture was stirred for 20 hr. at room temperature to give a deep-red solution. Yield (from $^{31}$P NMR
measurement) was ca. 45%. All the volatile material was removed in vacuo, and the resulting red/orange oil was extracted into pentane (10 ml). This was cooled to -40 °C. Deep red needle-like crystals were obtained. Yield was 0.37g (37% w.r.t. 1 equivalent of diphosphene assuming the molecular formula to be ArP=PAr[Cr(CO)5]2). Characterisation data appear in Section 5.6.15.

5.6.19 Preparation of ArP=PAr[W(CO)5] (64)

\[ W(CO)_6 \overset{\text{THF}}{\text{hv}} W(CO)_5\cdot \text{THF} + \text{ArP}=\text{PAr} \rightarrow \text{ArP}=\text{PAr}[W(CO)_5] \] (64)

W(CO)6 (0.4g, 1.1 mmol) in THF (50 ml) was irradiated at 254 nm (Hg lamp) for 4 hr. ArP=PAr (0.62g, 1.0 mmol) was added. The mixture was stirred for 20 hr. to give a dark-red solution. The solvent was removed in vacuo. The residual brown oil was extracted into pentane (20 ml) and cooled to -40 °C. A dark-red solid was precipitated, however under magnification this appeared to contain a white solid attributed to unreacted W(CO)6 ∼10% recovery w.r.t. 31P NMR. Characterisation data appear in Section 5.6.16.

5.7 REFERENCES

   
   
   
   

   


   


43. This dimer was very kindly supplied by Professor J.F. Nixon of Sussex University.


CHAPTER SIX

ACCEPTOR PROPERTIES OF P(III) COMPOUNDS
6.1 INTRODUCTION

A large number of organohalophosphines have been prepared (see Chapter 2), and a large volume of data are available [1]. Many organophosphorus pseudohalides have been isolated [2-6], more recently by R. Ali (1986) and in this work. The acceptor properties of RP(CN)\textsubscript{2} have been investigated with R = Me, Ph, Et or C\textsubscript{6}F\textsubscript{5} and X = Cl, Br, I or NCS (Equation 6.1) [7,8]. Addition of CN\textsuperscript{-} to RP(CN)\textsubscript{2} (R = Ph, Me and Et), resulted in reductive elimination, yielding the cyanophosphide, RP(CN)\textsuperscript{-} and cyanogen (CN)\textsubscript{2} [9]. This phenomenon is also known in the addition of CN\textsuperscript{-} to P(CN)\textsubscript{3} giving P(CN)\textsubscript{2} and cyanogen [10].

It is interesting to note that some P(III) trihalides show acceptor properties, behaving as Lewis acids towards halides and pseudohalides, and several anionic derivatives, PX\textsubscript{4} (X = F, Cl or Br) have been obtained [11-15]. The first phosphoranide isolated (as its Pr\textsubscript{4}N\textsuperscript{+} salt) was PBr\textsubscript{4}\textsuperscript{-} [16a]. These can be compared with adduct formation (Equation 6.2) [17] and substitution (Equation 6.3) [2-6].

$$\text{RP(CN)\textsubscript{2} + X}^{-} \rightarrow \text{RP(CN)\textsubscript{2}X}^{-} \quad (6.1)$$

$$\text{MePCl\textsubscript{2} + NMe\textsubscript{3} \rightarrow MePCl\textsubscript{2}NMe\textsubscript{3} \quad (6.2)}$$

$$\text{X}^{-} + \text{MePCl\textsubscript{2} \rightarrow MePClX + Cl}^{-} \quad (6.3)$$

These substitution reactions only proceed if X forms stronger bonds to phosphorus in the normal way, cf. Equation 6.1 (eg. NCS, NCO, N\textsubscript{3}, CN). They will not go with Br or I unless some additional driving force is provided, for example with LiI as the reagent, where formation of LiCl in a suitable solvent make the reaction possible.

The acceptor properties of RPX\textsubscript{2} are of particular interest as the resulting phosphoranide may play an important role in nucleophilic substitution at the phosphorus(III) centre, and also in coordination.
chemistry \[8,13,15\]. By isolation of the "intermediate" (II) (Equation 6.4) it should be possible by structural determination to obtain an insight into the mechanism of the overall reaction.

\[
\text{RPX}_2 + Y^- \rightarrow \text{RPX}_2Y^- \rightarrow \text{RPXY} + X^- \quad \text{(6.4)}
\]

Previous work revealed the X-ray crystallographic structure of some phosphoranides. Some selected examples are given in Table 6.1, including the first structurally determined phosphoranide containing an organo-group \([\text{PhP(CN)}_2\text{Cl}]^-\).

\[
\begin{array}{ccc}
\text{Cl} & \text{Cl} & \text{Br} \\
\text{Br} & \text{P} & \text{Cl} \\
\end{array}
\quad (A)
\]

\[
\begin{array}{ccc}
\text{Br} & \text{Cl} & \text{Br} \\
\text{Br} & \text{P} & \text{Br} \\
\end{array}
\quad (B)
\]

<table>
<thead>
<tr>
<th>PHOSPHORANIDE</th>
<th>STRUCTURE</th>
<th>TYPE</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Et}_4\text{N}^+ \text{PCl}_4^-)</td>
<td>trigonal bipyramid</td>
<td>(A)</td>
<td>13,14</td>
</tr>
<tr>
<td>([\text{Ph}_3\text{P}=\text{CH}-\text{PPh}_3]^+ \text{P(CN)}_3\text{Cl}^-)</td>
<td>asymmetric dimer</td>
<td>(B)</td>
<td>13,14,16a</td>
</tr>
<tr>
<td>(\text{Pr}_4\text{N}^+ \text{PBr}_4^-)</td>
<td>symmetrical dimer</td>
<td>(B)</td>
<td>13,14</td>
</tr>
<tr>
<td>(\text{Na}^+ \text{P(CN)}_3\text{Br}^-)</td>
<td>with halogen bridges</td>
<td>(B)</td>
<td>13,14</td>
</tr>
<tr>
<td>(\text{Et}_4\text{N}^+ \text{PCl}_2\text{PhCl}^-)</td>
<td>trigonal bipyramid</td>
<td>†</td>
<td>18 *</td>
</tr>
</tbody>
</table>

Table 6.1: Shapes of some phosphoranides; †18C6=Na(C\(_12\)H\(_{24}\)O\(_6\))(THF)\(_2\); †similar to PCl\(_4^-\) with equatorial Ph group with long (281 pm) axial P-Cl bond; *see Figure 6.2.

The purpose of this study was aimed at the exploration of the effect of the organo group (R) on the acceptor properties of RPX\(_2\) and RP(CN)\(_2\).

\(^1\)A very recent publication (ref. 16b) with the cation Et\(_4\)N\(^+\) illustrates a monomeric structure for the PBr\(_4^-\). An extremely distorted \(\phi\)-trigonal bipyramidal structure with axial P-Br distances of 2.970 Å and 2.305 Å. In this case at least the crystal structure is apparently cation dependent.
This area was extensively developed by R. Deng and R. Ali [7,8,18,19]. A brief summary of these groups, alongside previous ones for clarity, is presented in Table 6.2.

\[
\text{RPX}_2 + Y^- \rightarrow \text{RPX}_2Y^-
\]

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>R</th>
<th>X</th>
<th>Y</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeP(CN)₂Cl⁻</td>
<td>Me</td>
<td>CN</td>
<td>Cl</td>
<td>18</td>
</tr>
<tr>
<td>MeP(CN)₂Br⁻</td>
<td>Me</td>
<td>CN</td>
<td>Br</td>
<td>18</td>
</tr>
<tr>
<td>MeP(CN)₂I⁻</td>
<td>Me</td>
<td>CN</td>
<td>I</td>
<td>18</td>
</tr>
<tr>
<td>PhP(CN)₂Cl⁻</td>
<td>Ph</td>
<td>CN</td>
<td>Cl</td>
<td>18</td>
</tr>
<tr>
<td>PhP(CN)₂Br⁻</td>
<td>Ph</td>
<td>CN</td>
<td>Br</td>
<td>18</td>
</tr>
<tr>
<td>PhP(CN)₂I⁻</td>
<td>Ph</td>
<td>CN</td>
<td>I</td>
<td>18</td>
</tr>
<tr>
<td>C₆F₅P(Cl)₃⁻</td>
<td>C₆F₅</td>
<td>Cl</td>
<td>Cl</td>
<td>19</td>
</tr>
<tr>
<td>C₆F₅P(NCS)₃⁻</td>
<td>C₆F₅</td>
<td>NCS</td>
<td>NCS</td>
<td>19</td>
</tr>
<tr>
<td>C₆F₅P(CN)₂Cl⁻</td>
<td>C₆F₅</td>
<td>CN</td>
<td>Cl</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 6.2

In these examples the use of cyanide increases the positive charge at phosphorus in the phosphine, and delocalises the negative charge at the phosphorus centre in the resulting phosphorane, e.g. \( R_2P==N^- \). It has been shown that the use of a sufficiently electron-withdrawing group on phosphorus, e.g. for \( C_6F_5PCl_2 \), allows the acceptor properties without the need for cyanide [19].

6.2 FURTHER ACCEPTOR PROPERTIES OF RPX₂ (X = Cl, CN)

This study involved the R groups Ar \([Ar = 2,4,6-(CF₃)₃C₆H₂]\) and CF₃ and the results are presented in Tables 6.3 and 6.5 respectively. Cl⁻ was used since it gives the greatest limiting shift.
6.2.1 Results for $R = \text{Ar}$

<table>
<thead>
<tr>
<th>REACTION</th>
<th>RESULT</th>
<th>$^{31}$P NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{ArPCl}_2$ (12) $\xrightarrow{\text{Cl}^-}$ no reaction</td>
<td>[145 ppm, $^4J(\text{PF})$ 61 Hz]</td>
<td></td>
</tr>
<tr>
<td>$\text{ArP(CN)}_2$ (16) $\xrightarrow{\text{Cl}^-}$ $\text{ArP(CN)}_2\text{Cl}^-$ (67)</td>
<td>[-137.4 ppm, $^4J(\text{PF})$ 34.5 Hz]</td>
<td></td>
</tr>
<tr>
<td>$\text{ArP(CN)}_2$ (16) $\xrightarrow{\text{CN}^-}$ no reaction</td>
<td>[-86.8 ppm, $^4J(\text{PF})$ 40.0 Hz]</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.3: Acceptor properties of $\text{ArPX}_2$ ($X = \text{CN, Cl}$).

The $^{31}$P NMR values obtained on successive addition of Cl$^-$ ($\text{Et}_4\text{NCl}$) to the dicyanophosphine (16) are presented in Table 6.4. The results were attributed to the setting up of the equilibrium shown in Equation 6.5.

$$\text{ArP(CN)}_2$ (16) + Cl$^- \rightleftharpoons \text{ArP(CN)}_2\text{Cl}^-$ (67) (6.5)

<table>
<thead>
<tr>
<th>MOLAR RATIO</th>
<th>$^{31}$P NMR ($\delta$/ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^- : \text{ArP(CN)}_2$ (16)</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>-103.5</td>
</tr>
<tr>
<td>1.0</td>
<td>-120.2</td>
</tr>
<tr>
<td>1.2</td>
<td>-129.2</td>
</tr>
<tr>
<td>1.5</td>
<td>-137.4</td>
</tr>
<tr>
<td>2.0</td>
<td>-137.4</td>
</tr>
</tbody>
</table>

Table 6.4: "Limiting Shift".

The limiting shift was achieved here only when the tetraethylammonium chloride was in excess ($\sim 1.5$ fold). This effect is illustrated graphically in Figure 6.1.

It has been shown that $\text{C}_6\text{F}_5$ is more strongly electron withdrawing in nature than the aryl substituent [21]. This may account for the non-acceptor properties of $\text{ArPCl}_2$ (12) compared with the phosphoranide formation by $\text{C}_6\text{F}_5\text{PCl}_2$. This may also be attributed to the greater steric demand of the aryl substituent. The predominance of this factor may account for the fact that no phosphoranide was observed on reaction of
ArP(CN)₂ (16) with cyanide (Table 6.3). Numerous attempts at low temperature crystallisation of [Et₄N][ArP(CN)₂Cl] (67) were made, but these were not successful.

![Figure 6.1: Successive addition of Cl⁻ to the dicyanophosphine ArP(CN)₂ (16).](image)

Structural details of (67) would be of particular interest because of the electron-withdrawing nature of the aryl group and its size - it may occupy the axial position in the trigonal bipyramid. The general rule of apicophilicity² places the most electronegative group axial. As discussed, the only other known structural parameters of a phosphoranide containing an organo-group are for PhP(CN)₂Cl⁻ [18]; here this balance of steric and electronic properties of R is not so pronounced. The very recent publication of the crystal structure of this species has been presented (Figure 6.2).

²The change in energy when two groups exchange apical and equatorial positions in a trigonal bipyramid.
The geometry of the anion [NEt₂][PPh(CN)₂Cl]

Figure 6.2: Recently published X-ray structure of PhP(CN)₂Cl⁻.

6.2.2 MNDO Calculation

The results of a MNDO calculation on the species ArP(CN)₂Cl⁻ (67) are presented in Figure 6.3. The aryl group is axial and as expected orientated slightly toward the equatorial lone pair. Poor results were obtained, as expected from this calculation on the phosphoranide (67) since the phosphorus is hypervalent, and the MNDO calculation fails to consider d-orbital involvement (calculated P-Cl length = 2.2A). The expected P-Cl bond length in phosphoranides is of the order of 2.85Å in PCl₄ and 2.81Å in PhP(CN)₂Cl⁻ [18].
Figures 6.2 and 6.3 illustrate the cyanide to be definitely less apicophilic than halogen (Cl, Br). In the specific case of $P(CN)_3X^-$, ($X$: Cl, Br) dimerisation prevents the CN group from being forced into an apical position [13].

6.2.3 Results for $R = \text{CF}_3$

Addition of $\text{Et}_4\text{NCN}$ to $\text{CF}_3P(CN)_2$ (68) expected to possess high acceptor properties does not show the phosphoranide $\text{CF}_3P(CN)_3$ (69). However, a downfield signal at +77 ppm was present with the concomitant disappearance of $\text{CF}_3P(CN)_2$ (68). Results are presented in Table 6.5 and illustrated in Figure 6.4. An extension of this work could involve the addition of $\text{Cl}^-$ to $\text{CF}_3P(CN)_2$ (68). This would be expected to accept to form the respective phosphoranide.

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>$31P \text{ NMR}$ (δ/ppm)</th>
<th>COUPLING $^{2}J(\text{PF})$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CF}_3\text{PCl}_2$ (13)</td>
<td>133.47</td>
<td>7.9</td>
</tr>
<tr>
<td>$\text{CF}_3P(CN)_2$ (68)</td>
<td>-80</td>
<td>89</td>
</tr>
<tr>
<td>$[\text{CF}_3\text{PCN}]^-$ (70)</td>
<td>+77</td>
<td>43.1</td>
</tr>
</tbody>
</table>

Table 6.5

The quartet at +77 ppm is assigned to the cyanophosphide, $[\text{CF}_3\text{PCN}]^-$ (70) (Equation 6.6). The overall reaction and the $31P \text{ NMR}$ parameters are shown in Equation 6.6 and Table 6.5 respectively, with the phosphoranide (69) proposed as the intermediate.

$$\text{CF}_3P(CN)_2$ (68) $\overset{\text{CN}^-}{\longrightarrow} \text{CF}_3P(CN)_3$ (69) $\longrightarrow [\text{CF}_3\text{PCN}]^-$ (70) + (CN)$_2$ (6.6)

The brown colouration of the solution was attributed to rapid cyanogen polymerisation providing the driving force for the reaction.
Figure 6.4: The addition of $Bu_4NCN$ to $CF_3P(CN)_2$ (68) with the apparent formation of the cyanophosphide, $[CF_3PCN]^-$ (70).
The species was not stable to isolation. This may be compared with other phosphides \[9\]. This was considered unusual since the presence of the electronegative CF\(_3\) groups would be expected to stabilise the anion.

The particular interest in the nature of the Ar group led us to explore the acceptor properties of the boron derivatives (4,73) (Chapter 8). No acceptance was observed in the case of either ArBCl\(_2\) or Ar\(_2\)BCl.

### 6.3 AN AMINO GROUP AS THE ORGANO SUBSTITUENT

The nature of R\(_2\)N in this context was considered for the first time. Reactions were carried out with R\(_2\)NPCl\(_2\) and (R\(_2\)N)\(_2\)PCl, and their cyanide derivatives, the analogous chloroboron systems were also considered. With the following systems no acceptance properties with Cl\(^-\) were observed even by decreasing the group size on nitrogen, indicating that the steric effects do not appear to be significant.

\[(\text{tPr}_2\text{N})_2\text{PCl} (\text{\(31\text{P}\) \(\delta\): 139.9 ppm})^{[22]}; (\text{tPr}_2\text{N})_2\text{PCN} (\text{\(31\text{P}\) \(\delta\): 30.0 ppm})^{[23]}, \]
\[\text{tPr}_2\text{NPCl}_2 (\text{\(31\text{P}\) \(\delta\): 167.7 ppm})^{[24]}, \text{tPr}_2\text{NP}(\text{CN})_2 (\text{\(31\text{P}\) \(\delta\): -19.3 ppm})^{[23]}, \]
\[(\text{Et}_2\text{N})_2\text{PCl} (\text{\(31\text{P}\) \(\delta\): 147.9 ppm})^{[24]}, (\text{Et}_2\text{N})_2\text{PCN} (\text{\(31\text{P}\) \(\delta\): 29.5 ppm})^{[22]}, \]
\[\text{Et}_2\text{NPCl}_2 (\text{\(31\text{P}\) \(\delta\): 160.8 ppm})^{[24]}, \text{Et}_2\text{NP}(\text{CN})_2 (\text{\(31\text{P}\) \(\delta\): -17.1 ppm})^{[22]}, \]
\[(\text{Et}_2\text{N})_2\text{BCl} (\text{\(11\text{B}\) \(\delta\): +28.4 ppm})^{[25]}, (\text{Et}_2\text{N})\text{BCl}_2 (\text{\(11\text{B}\) \(\delta\): +23.3 ppm})^{[25]}, \]
(see Section 6.4.11).

It had been expected that the boron derivatives would accept more readily because of their greater Lewis acidity. The fact that no acceptor properties were observed can possibly be attributed to lone pair back donation from nitrogen to boron, i.e.,

\[\text{idPr}_2\text{N}^\delta-\text{B}^\delta+X^\delta-\text{X}^\delta\]
\( R_2N \) is used universally in the stabilisation of 2 coordinate boron and phosphorus cations (borinium and phosphinium moieties) \([26]\).

6.4 EXPERIMENTAL DETAILS

6.4.1 Preparation of \( \text{ArP(CN)}_2 \) (16)

\[
\text{ArPCl}_2 (12) + 2\text{AgCN} \rightarrow \text{ArP(CN)}_2 (16) + 2\text{AgCl}
\]

\( \text{ArPCl}_2 \) was prepared as described in Section 2.3.3. \( \text{AgCN} \) (1.1g, 8.2 mmol) was added to a stirred solution of \( \text{ArPCl}_2 \) (1.51g, 3.96 mmol) in \( \text{CH}_3\text{CN} \) (20 ml) at room temperature. This mixture was gradually brought to reflux. After refluxing for 2 hours complete conversion to \( \text{ArP(CN)}_2 \) was verified by the \( ^{31}\text{P} \) NMR of -86.8 ppm, \( 4J_{PF} \) 40.0 Hz. \( \text{CH}_3\text{CN} \) was removed \textit{in vacuo}, and the product was extracted into \( \text{Et}_2\text{O} \). Extraction into pentane gave very poor yields due to the low solubility of \( \text{ArP(CN)}_2 \) in this solvent. The insoluble silver salts were removed by filtration, and the pentane removed \textit{in vacuo} to yield a white solid. Extreme care had to be taken on manipulation due to its extreme sensitivity to hydrolysis giving peaks in the \( ^{31}\text{P} \) NMR at approx 0 ppm. The initial \( \text{AgCN} \) added must be stored with rigorous exclusion of light and moisture, since a poor \( \text{AgCN} \) sample (grey Ag deposits) gave very poor results even when added in excess. Best yields were obtained from a fresh sample. From the above preparation, \( \text{ArP(CN)}_2 \) (16) (0.7g, 49%) was obtained as a white solid. Mpt. > 75 °C (dec); Analysis found: C, 36.33; H, 0.60; N, 7.39; Required for \( \text{C}_{11}\text{H}_2\text{F}_9\text{N}_2 \): C, 36.28; H, 0.55; N, 7.69%; IR (Nujol) 3120 (\text{m,C aromatic}), 2190 (\text{s,CN}), 1850 (\text{m}), 1630 (\text{m}), 1585 (\text{m}), 1480-800 (\text{s,CF}_3) \text{ cm}^{-1} \); MS (Intensity%) EI: 364 \([10.3,(\text{ArP(CN)}_2^+)\]), 83 \([100,(\text{P(CN)}_2^+)\]); CI+: 364 \([10.3,(\text{ArP(CN)}_2^+)\]), 83 \([100,(\text{P(CN)}_2^+)\]; \( ^{31}\text{P} \) δ:
- 87.2 ppm (septet) $^4J_{PF} = 40.6$ Hz; $^{19}F\;\delta: -54.9$ (d,6F) $^4J_{PF} = 40.6$ Hz, -64.1 (s,3F) ppm.

6.4.2 Attempted Preparation of ArP(CN)$_2$ (16) via ArPCl$_2$/LiCN

$$\text{ArPCl}_2(12) + \text{LiCN (xs)} \xrightarrow{\text{DMF}} \text{ArP(CN)}_2(16)$$

A solution of lithium cyanide (22 ml, 11 mmol, 0.5 M in DMF) was added dropwise over 5 minutes to a stirred solution of ArPCl$_2$ (2.1 g, 5.4 mmol) in CH$_3$CN (25 ml) at room temperature. This was refluxed for 2 hours. The recording of the $^{31}$P NMR showed a singlet species at 4.97 ppm, attributed to complete hydrolysis of material. LiCN·DMF solution was commercially available [Aldrich Cat.No. 24,660-3].

6.4.3 Preparation of ArP(CN)$_2$Cl$^-$ (67)

$$\text{ArP(CN)}_2(16) + \text{Cl}^- \rightarrow \text{ArP(CN)}_2\text{Cl}^- (67)$$

Et$_4$NCl$^-$ (0.27 g, 1.63 mmol) in CH$_3$CN (10 ml) was added dropwise to a stirred solution of ArP(CN)$_2$ (1.2 g, 3.3 mmol) in CH$_3$CN (25 ml) at room temperature. The reaction mixture was stirred for 1 hour. Successive 0.5 equivalents of Et$_4$N$^+Cl^-$ (0.27 g, 1.63 mmol) in CH$_3$CN (10 ml) were added, and the reaction mixture stirred for 1 hour after each addition. The $^{31}$P NMR was recorded after each stage. Results and graph are shown in Section 6.2.1. Removal of the CH$_3$CN in vacuo yielded a sticky oil, and addition of a minimum volume of CH$_2$Cl$_2$ (ca. 5 ml), and cooling to -40 °C over one week gave no precipitation (it was hoped that the greater solubility of Et$_4$N$^+Cl^-$ in CH$_2$Cl$_2$ would keep it in solution).
The C,H,N elemental analysis showed that the compound obtained was not pure (\%C \sim 7\% too low and similarly low value for \%N).

With respect to the $^{31}\text{P}$ NMR an almost quantitative yield of the phosphoranide was achieved: $^{31}\text{P} \delta: -137.4$ ppm (septet) $^{4}\text{J}_{\text{PF}}$ 34.5 Hz.

6.4.4 Attempted Preparation of $\text{Bu}_4\text{N}^+ \text{ArP(CN)}_3^-$

$$\text{ArP(CN)}_2 (16) + \text{Bu}_4\text{N}^+\text{CN}^- (xs) \longrightarrow \text{ArP(CN)}_3^-$$

$\text{Bu}_4\text{NCN} (1.1g, 4.1 \text{ mmol})$ in $\text{CH}_3\text{CN} (10 \text{ ml})$ was added dropwise over 5 minutes to a stirred solution of $\text{ArP(CN)}_2 (1.2g, 3.3 \text{ mmol})$ in $\text{CH}_3\text{CN} (25 \text{ ml})$. This mixture was stirred at ambient temperature for 6 hours. No reaction was detected in the $^{31}\text{P}$ NMR. $^{31}\text{P} (\text{CH}_3\text{CN}) \delta: -86.8$ ppm (septet) $^{4}\text{J}_{\text{PF}}$ 40 Hz (unchanged starting material).

6.4.5 Preparation of $\text{CF}_3\text{PCl}_2$ via $\text{CF}_3\text{P} (\text{Et}_2\text{N})_2$

$\text{CF}_3\text{PCl}_2$ was prepared by the method of Volbach and Ruppert [29] and also the method of Ruppert [30]. In this work the experiment was modified to involve $\text{CF}_3\text{I}$ in place of $\text{CF}_3\text{Br}$. Both gave satisfactory results, but the $\text{CF}_3\text{I}$ was superior, as expected from the weaker C-I bond strength. Yields of the latter were of the order of 70-75\%.

The two methods (Equations 6.7 and 6.8) differ only in that the first involves attack of $\text{PCl}_3$ on $(\text{Et}_2\text{N})_3\text{P}$ to form equimolar quantities of each starting material.

$$5(\text{Et}_2\text{N})_3\text{P} + \text{PCl}_3 \longrightarrow 3(\text{Et}_2\text{N})_3\text{P} + 3(\text{Et}_2\text{N})_2\text{PCl} \overset{3\text{CF}_3\text{X}}\longrightarrow 3[(\text{Et}_2\text{N})_3\text{PCl}]^+X^- + 3\text{CF}_3\text{P}(\text{NEt}_2)_2 (X = \text{I, Br}) \quad (6.7)$$

$$\overset{\text{CF}_3\text{X}}\rightarrow [(\text{Et}_2\text{N})_3\text{PCl}]^+X^- + \text{CF}_3\text{P}(\text{NEt}_2)_2 \quad (6.8)$$
The first method (Equation 6.7) stated the use of diethyl carbonate as the solvent, although some results were obtained in hexane using the other method (Equation 6.8). This gave lower yields and CH₂Cl₂ was superior. Some explanation for the lack of success of the non-polar solvent can be gained from the postulate of Volbach and Ruppert [29] concerning the formation of an ionic intermediate, \((\text{Et}_2\text{N})_3\text{PBr}^+\text{CF}_3\). This may be unfavourable in hexane which did not appear capable of keeping all the reactants in a single homogeneous phase. This effect is obviously dominant over the insolubility of \((\text{Et}_2\text{N})_3\text{PCl}^+\text{Br}^-\) driving the reaction to completion. In hexane, reactions were carried out at temperatures below the boiling points of the CF₃X (X = Br, I) species, which did not appear to be reactive at these temperatures. The more polar solvents allowed the CF₃I and CF₃Br to be introduced at higher temperatures without boiling off.

The product CF₃P(\text{Et}_2\text{N})₂ was separated from oxides and side products. The applicability of GLC was tested on a small sample - it showed a good peak separation, but proved to be an unsuitable technique for such an air-sensitive compound. Purification was best achieved by low temperature crystallisation, allowing the precipitation of unwanted oxides in a small volume of hexane. The filtrate was treated \textit{in situ} with gaseous HCl to yield CF₃PCl₂ (a one pot reaction sequence). The CF₃PCl₂ was then distilled from the hexane, bpt. 36 °C (760 mm Hg) [31]; $^{31}\text{P} \delta$: 133.5 ppm, $^2\text{J}_{\text{PF}}$ 79.9 Hz. 
6.4.6 Preparation of CF₃P(CN)₂ (68)

\[ \text{CF}_3\text{PCl}_2 + 2\text{AgCN} \rightarrow \text{CF}_3\text{P(CN)}_2 (68) \]

CF₃PCl₂ (1.5g, 8.8 mmol) in CH₃CN (25 ml) was added to a slight excess of AgCN (ca. 2.5g, 18.7 mmol, 2.4 equivalents). This mixture was stirred for at least 4 hours and the reaction was monitored by ³¹P NMR. It appeared that several exchange equilibria were established, e.g. signals were observed at ³¹P δ: -70 ppm, ⁴JₚF 40 Hz, -74 ppm, ⁴JₚF 46 Hz. After 4 hours a limiting NMR chemical shift was recorded (³¹P δ: -80.1 ppm, ²JₚF 89.0 Hz; ¹⁹F δ: -52.2 ppm). This agrees well with the previously recorded NMR parameters [32-33]. CH₃CN was removed in vacuo, and the product was extracted into pentane. The pentane was removed to give an oil in approximately 45% yield (0.6g).

6.4.7 Preparation of [Et₄N][CF₃PCN] (70)

\[ \text{CF}_3\text{P(CN)}_2 (68) + 3\text{CN}^- \rightarrow [\text{CF}_3\text{PCN}]^- (70) + (\text{CN})_2 + 2\text{Cl}^- \]

A solution of CF₃P(CN)₂ (0.7g, 4.6 mmol) in CH₃CN (20 ml) and 1.1 equivalents of Bu₄NCN (1.36g, 5.1 mmol), stirred at room temperature for 2 hours did not give the expected upfield shift corresponding to CF₃P(CN)₃. The solution turned brown. A peak downfield was seen in the ³¹P NMR (+77 ppm ²JₚF 43.1 Hz) with the disappearance of the peak at -80.1 ppm (corresponding to starting material) (see Figure 6.4). This peak was attributed to [Bu₄N⁺][CF₃PCN⁻] caused by loss of cyanogen - its rapid polymerisation causing colouring of the solution. Removal of the solvent, and redissolving the resulting sticky brown oil in a minimum volume of CH₃CN on cooling gave no precipitation, and neither did
dropwise addition of pentane. Re-observation of the $^{31}$P NMR spectrum indicated decomposition, possibly polymerisation or hydrolysis, giving a $^{31}$P shift of approximately 0 ppm.

6.4.8 Preparation of $(iPr_2N)_2PCl$ and $(Et_2N)_2PCl$

$$PCl_3 + 4R_2NH \rightarrow (R_2N)_2PCl + 2R_2NH_2^+Cl^- \quad (R = iPr, Et)$$

These were prepared according to N.D.A.H. Khabbass $^{[27]}$. A low boiling point petroleum was used for the solvent system, however, since this allows its facile removal in vacuo. $^{31}$P NMR data for $(iPr_2N)_2PCl$ and $(Et_2N)_2PCl$ agree well with previously published results $^{[1]}$, $\delta$: +147.9 and +139.9 ppm, respectively.

6.4.9 Preparation of $(iPr_2N)PCl_2$ and $(Et_2N)PCl_2$

$$PCl_3 + 2R_2NH \rightarrow R_2NPCL_2 + R_2NH_2^+Cl^-$$

These were prepared similarly, according to King and Sadanani (1985) $^{[24]}$. $iPr_2NPCl_2$ $^{[21,22]}$, bpt. 75-80 °C (3.5 mm Hg); $^{31}$P $\delta$: +167.7 ppm. $Et_2NPCl_2$ $^{[24,27]}$, bpt. 68-70 °C (3.5 mm Hg); $^{31}$P $\delta$: +160.8 ppm.

6.4.10 Preparation of $(Et_2N)_3P$

$$6Et_2NH + PCl_3 \xrightarrow{Et_2O} (Et_2N)_3P + 3Et_2NH_2^+Cl^-$$

Hexaethylphosphorus triamide was prepared according to A. Michaelis $^{[28]}$ and also commercially available from Aldrich [Cat. 25,318-9]. Bpt. 85-90 °C (10 mm Hg); $^{31}$P $\delta$: +117.4 ppm.
6.4.11 Preparation of \((\text{Et}_2\text{N})_2\text{BCl}\) and \((\text{Et}_2\text{N})\text{BCl}_2\)

\((\text{Et}_2\text{N})_2\text{BCl}\) was prepared according to W. Gerrard et al.\[25b\], and \((\text{Et}_2\text{N})\text{BCl}_2\) according to A.J. Banister \[25c\]. \(^{11}\text{B}\) NMR shifts were verified from known data \[25a\]. \((\text{Et}_2\text{N})_2\text{BCl}\), bpt. 83-85°C (16 mm Hg) \[25b\]; \(^{11}\text{B}\) \(\delta\): 28.4 ppm. \((\text{Et}_2\text{N})\text{BCl}_2\), bpt. 75-75.5°C (63-64 mm Hg) \[25c\]; \(^{11}\text{B}\) \(\delta\): +23.3 ppm \[25a\]. Preparation of the \(^{1}\text{Pr}_2\text{N}\) derivatives is described in Chapter 11 and the disubstituted derivative in Chapter 9.

6.4.12 Preparation of Cyanide Derivatives

The solvent used in the preparation of the cyanide derivative was CH\(_3\)CN since CH\(_2\)Cl\(_2\) may possibly exchange Cl\(^-\) with CN\(^-\), lowering the effective cyanide concentration. The general technique of extracting the cyanide derivative into pentane allows separation from hydrolysis products at this stage.

6.4.12.1 Preparation of \(^{1}\text{Pr}_2\text{NP}(\text{CN})_2\)

\[^{1}\text{Pr}_2\text{NPCL}_2 + 2 \text{AgCN} \xrightarrow{\text{MeCN}} ^{1}\text{Pr}_2\text{NP(CN)}_2\]

Silver cyanide (7.65g, 57 mmol) was added to a stirred solution of \(^{1}\text{Pr}_2\text{NPCL}_2\) (5.66g, 28 mmol) in CH\(_3\)CN (50 ml) at room temperature. This was refluxed for 16 hours until quantitative conversion to the dicyanide was verified by \(^{31}\text{P}\) NMR. The solvent was removed \textit{in vacuo} and the product extracted into pentane (25 ml). The insoluble silver salts were removed by filtration and the pentane \textit{in vacuo} to yield a thermally unstable whitish oil. Yield of crude product was 3.2g (63%). \(^{31}\text{P}\) \(\delta\): -19.29 ppm.
6.4.12.2 Preparation of $\text{Et}_2\text{NP(CN)}_2$

\[ \text{Et}_2\text{NP} \text{Cl}_2 + 2 \text{AgCN} \rightarrow \text{Et}_2\text{NP(CN)}_2 \]

The experimental procedure and molar quantities are exactly analogous to that described for $\text{^{1}Pr}_2\text{NP(CN)}_2$ (Section 6.4.12.1), however, for this stage it was purified by vacuum distillation. A clear oil was obtained in 60% yield. Bpt. 71 °C (0.5 mm Hg); $\delta^{31P} = -17.1$ ppm [22].

6.4.12.3 Preparation of $(\text{Et}_2\text{N})_2\text{PCN}$

$(\text{Et}_2\text{N})_2\text{PCl} + \text{AgCN} \rightarrow \text{AgCl} + (\text{Et}_2\text{N})_2\text{P(CN)}$

A similar preparation to the dicyanide analogues however a stoichiometry $\text{AgCN} : (\text{^1Pr}_2\text{N})_2\text{PCl} = 1:1$ is required. This was distilled as an oil, yield 50%. Bpt. 66-68 °C (1 mm Hg) [22]; $\delta^{31P} = 30.2$ ppm.

6.4.12.4 Preparation of $(\text{^1Pr}_2\text{N})_2\text{PCN}$

$(\text{^1Pr}_2\text{N})_2\text{PCl} + \text{AgCN} \rightarrow (\text{^1Pr}_2\text{N})_2\text{P(CN)} + \text{AgCl}$

Crude yield 55%, $\delta^{31P} = +30.0$ ppm. This was also obtained as a by-product from hydrolysis occurring in the nitrileimine species (62) (Chapter 11) [23], $\delta^{31P} = +29.5$ ppm.

6.4.13 Addition of $X^-$

In a typical experiment to investigate the acceptance of $X^-$ [where $X = \text{CN}^- (\text{Bu}_4\text{N}^+\text{CN}^-), \text{Cl}^- (\text{Et}_4\text{N}^+\text{Cl}^-)$, the cyanide or chlorophosphorus deriv-
ative (0.01 mol) was dissolved in CH$_3$CN. To this was added Et$_4$N$^+$Cl$^-$ or Bu$_4$N$^+CN^-$ (1 equivalent), and the mixture stirred for a period of 6 hours at room temperature. The NMR was recorded. No X$^-$ acceptance of species bearing R$_2$N groups was observed.

6.5 REFERENCES


CHAPTER SEVEN

HALO AND DIHALOSTIBINES AND THE ATTEMPTED FORMATION OF OTHER LOW COORDINATED, MULTIPLY-BONDED COMPOUNDS
7.1 ORGANOANTIMONY COMPOUNDS

7.1.1 Introduction

Halostibines, \( R_2\text{SbX} \) and dihalostibines, \( \text{RSbX}_2 \) (where \( R = \text{alkyl}, \text{aryl} \) and \( X = \text{halogen} \)), can be prepared by standard methods \([1]\). For example the stibine \((\text{Me}_3\text{Si})_2\text{CHSbCl}_2\) may be prepared by treatment of \( \text{SbCl}_3 \) with \((\text{Me}_3\text{Si})_2\text{CHMgCl}\) in \( \text{Et}_2\text{O} \) \([2]\), and the synthetic route to \( \text{Ph}_2\text{SbF} \) \([3]\) has been described. An interesting cyclisation yielding an antimony heterocycle resulted from the attempted synthesis of 2,4,6-(\(^{t}\text{Bu})_3\text{C}_6\text{H}_2\text{SbCl}_2\) by treatment of 2,4,6-(\(^{t}\text{Bu})_3\text{C}_6\text{H}_2\text{Li} \) with \( \text{SbCl}_3 \) \([4]\).

7.1.2 New Organoantimony Compounds

\( \text{ArSbCl}_2 \) and \( \text{Ar}_2\text{SbCl} \) were prepared \textit{via} the classical procedure (Equations 7.1 and 7.2) (see Figure 7.1).

\[
\text{ArLi (2) + SbCl}_3 \rightarrow \text{ArSbCl}_2 \quad (7.1)
\]

\[
2\text{ArLi (2) + SbCl}_3 \rightarrow \text{Ar}_2\text{SbCl} \quad (7.2)
\]

\( \text{Figure 7.1: ArSbCl}_2 \) (71) and \( \text{Ar}_2\text{SbCl} \) (72).
Figure 7.2: $^{13}C(1H)$ NMR spectrum of ArSbCl$_2$ (71) in CDCl$_3$. 
The reactions were carried out in diethyl ether. The fact that SbCl$_3$ is insoluble in non-polar solvents allowed the product to be extracted into pentane. High yields of these compounds were obtained. With slow controlled addition of ArLi to the required stoichiometric amount of SbCl$_3$ at low temperature, it was possible to substitute selectively chlorine for aryl, avoiding a loss of yield by tertiary stibine formation.

The high instability of ArSbCl$_2$ (71) caused a great many problems. It was possible by preparing, and immediately recording its spectral parameters, and elemental analysis (its sensitivity precluded a very accurate analysis), to characterise it. However, even in the inert atmosphere of the glove box, the powdery yellow solid visibly decomposed to a reddish viscous oil. This was also confirmed by L. Weber [5]. In contrast, Ar$_2$SbCl (72) was stable in storage indefinitely under an inert atmosphere at room temperature. The $^{13}$C NMR of ArSbCl$_2$ (71) in CDCl$_3$ (illustrating the presence of Et$_2$O) is shown in Figure 7.2 and the mass spectra of ArSbCl$_2$ (71) and Ar$_2$SbCl (72) in Figures 7.3 and 7.4 respectively.

7.2 ATTEMPTED FORMATION OF OTHER LOW-COORDINATE, MULTIPLY BONDED SPECIES

7.2.1 Introduction

The use of bulky aryl and alkyl substituents has allowed the isolation of low coordinate, multiply bonded Group (V) compounds with the general formula R'-X=Y=R" [2,6,7]. Some examples are presented in Table 7.1.
Figure 7.4: Mass spectrum of ArS(O)Cl (72).

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\[
\text{R}'XCl_2 + \text{R}''\text{YH}_2 \xrightarrow{\text{DBU}} \text{R}'X=\text{YR''}
\]

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<th>R''</th>
<th>X</th>
<th>Y</th>
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<td>(Me_3Si)_2CH</td>
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\[
\text{R}'\text{X}(\text{SiMe}_3)\text{Li} + \text{R}''_2\text{NCl}_2 \xrightarrow{-\text{LiCl}} \text{R}'\text{X}=\text{YNR}''_2
\]

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</tbody>
</table>

Table 7.1: Low coordinate, multiply bonded Group (V) compounds; ‡this phosphastibene decomposes to give the symmetrical diphosphenes, (Supermes)_2P₂ (a source of free phosphinidene! ref. 7); *crystal structure reported (ref. 7); †The dimer, diphosphadiboretane only. The boraphosphene is generated by thermolysis in the vapour phase.

It is known that the stability of X=Y decreases for lower groups and higher periods, i.e. towards the left and bottom of the periodic table. The potential of the Ar group as a steric shield has been illustrated by the formation of the stable diphosphenes (19) and the phosphaalkene (31).

Many possible precursors for the preparation of X=Y materials are now available, i.e. ArSbCl₂ (71), ArPH₂ (15), ArPCl₂ (12), ArAsF₂ (prepared by Edelmann et al.) [10], and from Group III ArBCl₂ (73), (see Chapter 8).

Although it is conceivable that boron may form a symmetrical double bonded species, i.e. RB=BR, so far no examples of this compound type are known. There are, however, many examples of boron possessing multiply bonded character, for example B=C (see Section 11.3).
7.2.2 Attempted Synthesis of RB=BR (R = Ar, tmp)

Symmetrical coupling of ArBCl\textsubscript{2} analogous to that used in the generation of the diphosphene (19) (Section 3.4) was attempted. On addition of bisimidazolidine or magnesium respectively, no B=B double bond was characterised. Since it was considered\textsuperscript{1} that the electron-withdrawing nature of the ring might destabilise this system, a parallel reaction was carried out with tmpBCl\textsubscript{2} and bisimidazolidine. [The lone pair of the nitrogen substituent is able to participate in bond formation resulting from \(\sigma\)-\(\pi\) overlap with the vacant \(p\)-orbital of boron (see Chapter 9)]. This yielded upfield signals in the \({}^{11}\text{B}\) NMR, attributed to coupling to form tmp(Cl)B-B(Cl)tmp, or a polymeric boron containing material, a possible result of the insufficient bulk of the tmp for the kinetic stabilisation of this species. This may be compared with the inherent instability of SupermesP=Btmp with respect to dimer formation \textsuperscript{[9]}.

7.2.3 Attempt to form Phosphastibene and Boraphosphene

The unsymmetrical coupling between ArPH\textsubscript{2} (15) and ArSbCl\textsubscript{2} (71) or ArBCl\textsubscript{2} (73) respectively was also attempted. For the antimony/phosphorus mixture, only the symmetrical diphosphene was characterised. In each case the required product did not appear to be formed. Since, (with both the boron and antimony systems) an apparent change in the appearance of the product occurred on warming the mixture to room temperature, it may be interesting to monitor initial product formation at low temperature. An attempted rationalisation of the observations made is presented in

\textsuperscript{1}The absence of Lewis acid/base behaviour may be attributed to the presence of too much steric hindrance.
Section 7.3.

The Ar substituent may prove effective in stabilising these species, and it may be possible to extend the work to give a route to the distibene and, using the arsenic derivative, to the diarsene. It might also prove to be a precursor to the first B=B double bond. This exciting new area is currently under investigation by P. Paetzold and many other research groups.

7.3 SOME GENERAL OBSERVATIONS ON ArPH₂ COUPLING REACTIONS

7.3.1 Introduction

Many varied coupling reactions between ArPH₂ (15) and chlorine species were carried out, with the aim of obtaining unsymmetrical diphosphenes (Section 3.8), phosphaalkenes (Section 4.3), phospha-stibenes (Section 7.2.3) and other low-coordinate species.

7.3.2 Results

A common observation in these reactions was the appearance of two peaks (septets) at -84 ppm and -89 ppm in the ³¹P NMR, or the presence of the symmetrical diphosphene, Ar₂P₂ (19) in place of the desired product. In the specific case of C₆Cl₅PCl₂ (23) the peaks at -84 and -89 ppm were discovered (by ³¹P NMR observation) to convert completely to the symmetrical diphosphene (19) on warming to room temperature. A similar observation with the system Ph₂CCl₂, ArPH₂ (15) and DBU, was the appearance of resonances at -84 and -89 ppm, and rapid conversion to the symmetrical diphosphene (³¹P δ: +473 ppm) on addition of a further 0.5 equivalents of DBU.
The two peaks around -87 ppm were also observed with the substituent Ar' [2,6-bis(trifluoromethyl)phenyl], but these were shifted slightly upfield. This observation was made in attempted Ar'PH₂ coupling reactions with Ar₂SnCl₂ and Ar'AsCl₂ to form the phosphastannene and phosphaarsene respectively [11]. Interestingly, these peaks were also observed in the gamma source irradiation of Ar'PH₂ in CCl₄ [11] [together with other products attributed to ArP(H)Cl and ArP(H)CCl₃].

Specific examples and the conditions in which these species predominate, are presented in the relevant experimental sections of this thesis, whilst a summary of this information appears in Table 7.2.

Each of the two observed peaks appeared to be split into a doublet by P-H coupling, and further split into septets by coupling with the fluorine atoms of the ortho-CF₃ groups (indicative of an Ar group and a hydrogen attached to phosphorus). The upfield chemical shift also indicates the presence of hydrogen.

The assignment of the species to the general formula, ArP(H)P(H)Ar was made. With this structure an asymmetry must be considered which may account for the two peaks seen close together in the ³¹P NMR. The shifts could possibly be attributed to the meso and racemic forms illustrated in Figure 7.5.

![Figure 7.5: The possible isomeric forms of ArP(H)P(H)Ar.](image)

Consistently the peak furthest upfield was lower in intensity, and there is no evidence as to which is the major and which is the minor product formed. The optical activity of similar compounds, for example
<table>
<thead>
<tr>
<th>CHLORINATED COMPOUND</th>
<th>MAJOR $^{31}$P δ/ppm</th>
<th>NMR PEAKS 4J(PF) °C</th>
<th>CONDITIONS</th>
<th>SECTION / REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-BuPCl₂</td>
<td>473</td>
<td>†</td>
<td>RT/4h</td>
<td>3.8</td>
</tr>
<tr>
<td>C₆F₅PCl₂</td>
<td>473</td>
<td>†</td>
<td>RT</td>
<td>3.8</td>
</tr>
<tr>
<td>C₆F₅PCl₂</td>
<td>-83.8 (3P)</td>
<td>22</td>
<td>-40°C</td>
<td>3.8</td>
</tr>
<tr>
<td>C₆Cl₅PCl₂</td>
<td>472</td>
<td>†</td>
<td>RT</td>
<td>3.8</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>-84.4 (4P)</td>
<td>NR</td>
<td>RT/1h</td>
<td>4.3</td>
</tr>
<tr>
<td>Ph₂CCl₂</td>
<td>-83.3 (3P)</td>
<td>25.4</td>
<td>RT/2DBU</td>
<td>4.3</td>
</tr>
<tr>
<td>Ph₂CBr₂</td>
<td>473</td>
<td>†</td>
<td>2.5DBU</td>
<td>4.3</td>
</tr>
<tr>
<td>ArSbCl₂</td>
<td>473</td>
<td>†</td>
<td>RT/4h</td>
<td>7.2</td>
</tr>
<tr>
<td>ArBCl₂</td>
<td>473</td>
<td>†</td>
<td>RT/4h</td>
<td>7.2</td>
</tr>
</tbody>
</table>

| Ar'AsCl₂ *            | -84.0               | 24.5            | RT/THF     | [11]         |
| Ph₂CBr₂               | -90.1               | 25.3            |             |              |
|                      | 192†                |                 |             |              |
|                      | 167†                |                 |             |              |
| Ar'AsCl₂ *            | 473                 |                | CDCl₃ extract |            |
| Ar₂SnCl₂               | -84.0 (3P)          | 24.5            | RT/THF     | [11]         |
| Ph₂CBr₂               | -90.0 (1P)          | 25.3            |             |              |
|                      | 192†                |                 |             |              |
|                      | 167†                |                 |             |              |
| CCl₄                  | -84.0               | 24.5            | γ irradiated | [11]         |
| Ph₂CBr₂               | -90.0               | 25.3            |             |              |
|                      | 192†                |                 |             |              |
|                      | 167†                |                 |             |              |

Table 7.2: Results of coupling ArPH₂ (top) and Ar'PH₂ (bottom) with various chlorinated compounds; †4J(PF) + 5J(PF) = 45 Hz; DBU in equivalents; *19F δ: -57.7 ppm (major); -57.4 (minor); ††J(PH) coupling.
with supermes substituents, does not appear to have been extensively studied [2]. However, the supermes derivative has been isolated [13,14] and shows interesting spectral parameters. This derivative was obtained by the reduction of the diphosphene Supermes₂P₂ [14], which indeed may be a route via Ar₂P₂ (19) to isolate and fully characterise the ArP(H)P(H)Ar species.

7.3.3 Mechanism

It is very difficult to write a mechanism for the formation of this product, and the formation of the symmetrical diphosphene. Only starting materials are observed with ArPH₂ and DBU in situ, hence a chlorine source is implicated in the mechanism. A radical process cannot be ruled out on the present evidence, however. Further mechanistic studies are certainly required to understand this system fully.

7.3.4 Reaction Rate

The phosphorus-phosphorus bond appears to form in each case much faster than the desired 'P-X' material. However derivatives, for example, SupermesP=SbCH(SiMe₃)₂ [2] and SupermesP=AsCH(SiMe₃)₂ [2], can be formed successfully via a similar route.

To form unsymmetrical species with the Ar or Ar' substituent on 'PH₂' it appears that it is necessary to promote coupling with the other component. One possibility would be via the phosphide, ArP(H)Li. However, this has already been shown to be inherently unstable with Ar or Ar' (Section 4.3). The formation of the 'P-P' species is a result of the presence of ArPH₂, hence it may be worthwhile reversing the coupling substituents, for example via ArXH₂ and ArPCl₂.
This predominant 'P-P' symmetrical coupling appears to interfere in many of these reactions. However, it is interesting to note that coupling between ArPH₂ and the iPr₂N-, Ar'- and Mes- derivatives of PCl₂ resulted in the formation of the unsymmetrical diphosphene.

7.4 EXPERIMENTAL

7.4.1 Preparation of ArSbCl₂ (71)

ArLi (2) + 1.3SbCl₃ \rightarrow ArSbCl₂ (71)

ArLi/ArH (100 ml, 45 mmol, 0.45 M solution in Et₂O) was added dropwise over 10 minutes to a stirred solution of antimony trichloride (10.8 g, 47.3 mmol) in Et₂O (50 ml) at -78 °C. An orange/brown solution was formed with no visible precipitation of LiCl. The reaction mixture was stirred for 2 hours at room temperature. Pentane (150 ml) was added to the reaction mixture and shaken vigorously. Two apparent layers formed. The lower dense brown oil gave no signal in the ¹⁹F NMR so this was attributed to excess SbCl₃ (and LiCl). The pentane was removed \textit{in vacuo} from the upper layer, yielding a yellow powdery solid which was recrystallised from CH₂Cl₂ (25 ml). Yield was ca. 12.2 g (57%). As an isolated solid this is extremely unstable. Any amount of exposure to the atmosphere in the glove box caused it to turn from a yellow solid to a red oil. This instability may have led to an inaccuracy in the elemental analysis. The ¹²¹Sb NMR spectrum was not useful, showing only a very broad absorption due to the low symmetry of ArSbCl₂.

However, from the ¹³C NMR, Et₂O appears to have remained coordinated. This would also partially account for the elemental analysis obtained (high %carbon). It seemed unlikely, however, that ether of
coordination would be retained after the extraction of the solid into pentane. Mpt. >62 °C (dec). Analysis found: C, 26.87; H, 0.98; Required for C₉H₂F₉SbCl₂: C, 22.82; H, 0.43%; Required for C₉H₂F₉SbCl₂·(1/2Et₂O): C, 25.86; H, 1.38%; Required for C₉H₂F₉SbCl₂·(Et₂O): C, 28.50; H, 2.21%; IR (Nujol) ν max: 3100 (w,ArCH), 2900(CH) 1630 and 1570 (m,C=C/Ar), 1400-1000 (s,C-F), ~900 (m,CH ring), 700 (s,CF₃) cm⁻¹; UV-Visible (CCl₄) λ max(ε): 273 (52093.0) nm; MS (Intensity%) EI: 439 [56.7,ArSbCl⁺], 402 [16.5, ArSb⁺], 262 [10,(Ar-F)⁺], 243 [100,(Ar-2F)⁺]; ¹⁹F δ: -55.6 (s,6F), -64.9 (s,3F) ppm; ¹³C δ: 151.3 (s, slightly broadened, possibly due to its attachment to Sb), 136.9 (q,CF₃) ¹JCF 33.7 Hz, 132.9 (q,CF₃) ¹JCF 35.0 Hz, 127.5 (d,CH) ¹JCH 284 Hz, 125.6 (s,quaternary C on Ar ring), 121.2 (s,quaternary C on Ar ring), 67.4 (Et₂O), 17.1 (Et₂O) ppm.

7.4.2 Preparation of Ar₂SbCl (72)

2ArLi + SbCl₃ ————> Ar₂SbCl (72) + 2LiCl.

ArLi (100 ml, 45 mmol, 0.45 M solution in Et₂O) was added dropwise over 10 minutes to a stirred solution of SbCl₃ (5.1g, 22.4 mmol) in Et₂O (50 ml) at -78 °C. The reaction mixture was allowed to reach room temperature, filtered and the solvent removed in vacuo to give a reddish amorphous solid, crude yield 10g (62%). This was recrystallised in a minimum volume of CH₂Cl₂ (15 ml) at low temperature (-40 °C) to yield pale yellow crystals. Filtration at low temperature gave maximum yields of ca. 7.6g (45-50%). The isolated solid was very sensitive even to the atmosphere of the glove box, but appeared more stable than the analogous ArSbCl₂. Crystals suitable for X-ray analysis were obtained and have been submitted, mounted in Lindemann (0.3 μm) capillaries. Mpt. 195-196 °C; Analysis found: C, 30.07; H, 0.48; Cl, 5.31; Required for
C_{18}H_{14}F_{18}SbCl: C, 30.05; H, 0.56; Cl, 4.93%; IR (Nujol) \nu_{\text{max}}: 3100 (w, ArCH), 1630 and 1570 (m, C=C/Ar), 1400-1000 (s, C-F), \sim 900 (m, CH/Ar) cm^{-1}; UV-Visible (CCl₄) \lambda_{\text{max}} (\epsilon): 273 (27368.4) nm; MS (Intensity\%) EI: 718 [0.16, Ar₂SbCl⁺], 682 [72.5, Ar₂Sb⁺], 438 [96.3, ArSbCl⁺], 401 [14.41, ArSb⁺], 262 [(Ar-F)⁺], 243 [100, (Ar-2F)⁺]; Cl⁺: 6992 [1.15, (Ar₂SbCl-F)⁺], 454 [100, (ArSbCl·NH₃⁺)]; ¹⁹F (CDCl₃) \delta: -55.4 (s, 12F), -64.0 (s, 6F) ppm.

7.4.3 Attempted Reactions of ArBCl₂ to form ArB=BAR

7.4.3.1 With Bisimidazolidine

\[ \text{Et} \quad \text{Et} \quad \text{Et} \quad \text{Et} \]

\[ 2\text{ArBCl}_2 \xrightarrow{X} \text{ArB=BAr} \]

A solution of bisimidazolidine (1.1g, 4.4 mmol) in toluene (10 ml) was added dropwise over 5 minutes to a stirred solution of ArBCl₂ (3.2g, 8.8 mmol) in toluene (25 ml) cooled to 0°C. No apparent reaction occurred, and the solution remained a clear yellow colour. ¹¹B (toluene) \delta: 26 ppm; ¹⁹F \delta: -56.6 (o-CF₃), -63.8 (p-CF₃). This is indicative of unchanged ArBCl₂. On warming to room temperature and refluxing for 6 hours, there was still no apparent reaction.

²Isotopic pattern as expected for one Sb and one Cl, i.e. intensities: 19.32, 3.96, 19.55, 4.17 and 4.96%
7.4.3.2  With Magnesium

\[
\begin{align*}
2\text{Mg} & \quad 2\text{ArBCl}_2 \rightarrow \text{X} \rightarrow \text{ArB=BAr}
\end{align*}
\]

Magnesium (0.08g, 3.3 mmol) was added in one portion to a stirred solution of ArBCl\(_2\) (1.21g, 3.3 mmol) in THF (40 ml) at ambient temperature. This mixture was refluxed for ten hours. No apparent reaction occurred. The change in colour of the solution from pale yellow to a pale grey suspension, was attributed to the presence of magnesium. \(^{11}\text{B} \text{NMR (THF)} \delta: +26 \text{ ppm}; \quad ^{19}\text{F} \delta: -56.4 \text{ (o-CF}_3), -63.6 \text{ (p-CF}_3) \text{ ppm. ArBCl}_2 \text{ appears to remain unchanged.}\)

7.4.4  Attempted Preparation of tmpB=Btmp

\[
\begin{align*}
\text{bisimidazolidine} & \quad 2\text{tmpBCl}_2 \rightarrow \text{tmpB=Btmp}
\end{align*}
\]

Bisimidazolidine (1.89g, 7.5 mmol) in toluene (15 ml) was added dropwise over 5 minutes to a stirred solution of tmpBCl\(_2\) (2.9g, 13.0 mmol) in toluene (25ml) at 0°C. The solution turned dark orange with no obvious precipitate. \(^{11}\text{B} \text{NMR (toluene)} \delta: +33.4 \text{ (small signal, unchanged tmpBCl}_2), +16.1 \text{ (major signal,tmp(Cl)B=B(Cl)tmp?), +2.0 \text{ (small signal). On warming to room temperature no change in the NMR spectrum was observed.}\)

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7.4.5 Attempted Preparation of \( \text{ArP=SbAr} \)

\[
\text{ArPH}_2 + \text{ArSbCl}_2 \xrightarrow{2 \text{DBU}} \text{ArP=SbAr}
\]

DBU (0.93g, 0.91 ml, 6.1 mmol) in THF (15 ml) was added dropwise over 5 minutes to a stirred solution of ArSbCl\(_2\) (1.42g, 3.0 mmol) and ArPH\(_2\) (0.94g, 3.0 mmol) in THF (50ml) at 0°C. The solution became deep brown and a precipitate formed. On warming to room temperature it became clear and pale yellow in colour. \( ^{31}\text{P} \{ ^{1}\text{H} \} \) (THF) \( \delta: +473.4 \text{ ppm} \quad ^{4}\text{J}_{\text{PF}} + ^{5}\text{J}_{\text{PF}} 45 \text{ Hz} \) [major signal, symmetrical diphosphene (19) (see Section 3.5 for data)], small peaks at +174 and +67.5 ppm were also observed.

7.4.6 Attempted Preparation of \( \text{ArP=BAr} \)

DBU (1.32g, 1.30 ml, 8.7 mmol) in THF (15 ml) was added dropwise over 5 minutes to a stirred solution of ArBCl\(_2\) (1.56g, 4.3 mmol) and ArPH\(_2\) (1.35g, 4.3 mmol) in THF (50ml) at -60°C. The reaction mixture became red after addition of the first drop of DBU solution, and some solid was evident. On warming the solution to room temperature it became clear and pale yellow in colour. \( ^{31}\text{P} \) (THF) \( \delta: +473.4 \text{ ppm} \quad ^{4}\text{J}_{\text{PF}} + ^{5}\text{J}_{\text{PF}} 45 \text{ Hz} \) [major signal, symmetrical diphosphene (19)], -0.45 ppm (small unassigned peak); \( ^{19}\text{F} \) \( \delta: -56.4 \text{ (s, o-CF}_3\text{)}, -63.4 \text{ (s, p-CF}_3\text{)}. \)
7.5 REFERENCES


CHAPTER EIGHT

ARYL BORON HALIDES
8.1 INTRODUCTION

The most important methods for the preparation of alkyl (and aryl) boron dihalides and dialkyl (and diaryl) boron halides have depended essentially on one of the following three procedures [1].

1. The interaction of organometallic compounds with boron halides or substituted boron halides (Equations 8.1-8.5) [1-3].

2. The reaction of trialkylborons or amino dialkyl borons with halogenating agents (Equation 8.6) [1].

3. The reaction of boronic or boronous acid with boron halides (Equation 8.7) [1].

\[
\begin{align*}
\text{Zn(C}_6\text{H}_5)_2 + \text{BF}_3 & \rightarrow \text{C}_6\text{H}_5\text{ZnF} + \text{C}_6\text{H}_5\text{BF}_2 \\
\text{Zn(Me)}_2 + \text{BF}_3 & \rightarrow \text{MeZnF} + \text{MeBF}_2 \\
\text{ArHgX} + \text{BX}_3 & \rightarrow \text{ArBX}_2 + \text{HgX}_2 \quad (X = \text{Cl, Br}) \\
\text{Al(Me)}_3 + 3\text{BBr}_3 & \rightarrow 3 \text{MeBBr}_2 + \text{AlBr}_3 \\
\text{Me}_3\text{SnC}_6\text{F}_5 + 2\text{BCl}_3 & \rightarrow \text{Me}_2\text{SnCl}_2 + \text{MeBCl}_2 + \text{C}_6\text{F}_5\text{BCl}_2 \\
\text{B(Bu)}_3 + \text{HBr} & \xrightarrow{\text{BuH}} \text{Bu}_2\text{BBr} \\
\text{(MeBO)}_3 + 2\text{BF}_3 & \rightarrow 3\text{MeBF}_2 + \text{B}_2\text{O}_3
\end{align*}
\]

8.2 Ar SUBSTITUTED ORGANOBORON

It was of particular interest, with respect to its electronic and steric effects to investigate the effect of attaching the Ar group to boron. Attempts to synthesise the Ar\(_2\)B\(^+\) borinium ion are described in Section 9.6.

Three species have been prepared: (i) ArBCl\(_2\) (73); (ii) Ar\(_2\)BCl (4) and (iii) Ar\(_3\)B (75). These compounds will now be considered in sequence.
Many attempts were made to synthesise \( \text{ArBCl}_2 \) (73). The general route involved the addition of ArLi to \( \text{BCl}_3 \). This gave interesting results with a distinctive competing decomposition reaction evident. The presence of direct B-F bonds was observed in the \(^{19}\text{F} \) and \(^{11}\text{B} \) NMR spectra, (the only source of fluorine being the CF\(_3\) groups on the ring). A possible mechanism for the formation of the B-F bonds is illustrated in Figure 8.1.

\[
\text{F}_3\text{C}\backslash\text{CF}_2\backslash\text{CF}_3\stackrel{\text{Li}}{\longrightarrow}\text{F}_3\text{C}\backslash\text{CF}_2\backslash\text{CF}_3
\]

\( \text{(2)} \) 

\[
\text{Cl} \cdot \text{BCl}_2
\]

\( \text{BFCl}_2 \cdot \text{Et}_2\text{O} \) (77)

\( \text{(76)} \)

Figure 8.1: The proposed effect of BCl\(_3\) on ArLi (2).

The existence of species (77) was verified by setting up an equilibrium between BF\(_3\)·Et\(_2\)O and BCl\(_3\)·Et\(_2\)O, generating species of identical chemical shift, splitting patterns and distinctive B-F couplings [4].

The MNDO calculation on ArLi (2) (Section 1.3) showed extensive interaction between the lithium and the fluorine, weakening the carbon-fluorine bond. The reaction proposed (Figure 8.1) must be a consequence of the presence of lithium, since no reaction was observed with ArH in the presence of an excess of BCl\(_3\).

This decomposition process (Figure 8.1) may be attributed to the interaction of the electrons on the fluorines in ArLi with the empty orbital on boron, and the thermodynamic favourability of forming a boron-fluorine bond.

The proximity of the fluorines to the boron centre in \( \text{ArBCl}_2 \) (73) may allow π\(\pi\) interaction, resulting in the partial occupation of the
Figure 8.2: Mass spectral data for APCI2 (79).
fourth covalency of boron. This reasoning may account for the anomaly of the more shielded nature of the $^{11}\text{B NMR}$ chemical shift for $\text{ArBCl}_2$ (73), and the unusual small variation in chemical shift with a directly coordinating solvent, *i.e.* $\text{ArBCl}_2$, $^{11}\text{B (Et}_2\text{O)}$ $\delta$: $+27$ ppm; $(\text{CH}_2\text{Cl}_2)$ $\delta$: $+32$ ppm ($\Delta\delta = +5$ ppm). This can be compared with $\text{BCl}_3$, $^{11}\text{B (Et}_2\text{O)}$ $\delta$: $+11$ ppm; $(\text{CH}_2\text{Cl}_2)$ $\delta$: $+47$ ppm ($\Delta\delta = +36$ ppm).

A dimeric structure may also be proposed, offering an explanation for the two points above, and possibly explaining the small peaks to higher mass in the mass spectrum (Figure 8.2). However, this would seem unlikely as further examples of symmetrically bridged halogeno organoboron compounds have not been reported in the literature. The steric demand of the aryl group would also be expected to disfavour the tetrahedral configuration demanded by a dimeric conformation (Figure 8.3).

It should be noted that once the species $\text{BFCl}_2$·$\text{Et}_2\text{O}$ (77), $\text{BF}_2\text{Cl}$·$\text{Et}_2\text{O}$ *etc.*, and $\text{ArBCl}_2$ (73) are present together in solution there is considerable scope for boron-halogen exchange (see Chapter 10). The result of this exchange is seen in the possible presence of "ArBF$_2$" in the reaction mixture (Figure 8.4). The reaction of $\text{ArBCl}_2$ and $\text{SbF}_3$ (Section 8.9.4.1) gave similar distinctive $^{19}\text{F NMR}$ parameters attributed to ArBF$_2$ which was not isolated (Figure 8.4).

The $^{19}\text{F NMR}$ (Figures 8.3 and 8.4) shows $\text{Et}_2\text{O}$·BFCl$_2$ (77), and the "CF$_3$", "CF$_2$" regions appear very complex. Other species may possibly be as shown in Figure 8.5.

Figure 8.5: Species possibly indicated by $^{19}\text{F NMR}$ from the reaction of $\text{ArLi}$ with $\text{BCl}_3$. 

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Figure 8.3: Possible dimeric configuration of $\text{ArBCl}_2$ (73).

Figure 8.4: $^{19}F$ NMR spectra: Addition of ArLi to $\text{BCl}_3$. 
This major side-reaction has been indicated. However, it was possible to isolate ArBCl$_2$ (73) pure from this reaction, presumably as shown in Equation 8.8 (possibly with a contribution from the reaction shown in Equation 8.9). Indeed lithium fluoride and chloride were found in the precipitate.

\[
\text{ArLi (2)} + \text{BCl}_3 \rightleftharpoons \text{ArBCl}_2 (73) + \text{LiCl} \quad (8.8)
\]

\[
\text{BFCl}_2 \cdot \text{Et}_2\text{O} (77) + \text{ArLi} \rightleftharpoons \text{ArBCl}_2 (73) + \text{LiF} \quad (8.9)
\]

8.2.2 \( \text{Ar}_2\text{BCl} \) (4)

The preparation of \( \text{Ar}_2\text{BCl} \) by the use of an excess of ArLi showed a similar side reaction, attributed to the same effect. Again "B-F" species and specifically "ArBF$_2$" were evident in the reaction. However, yields of \( \text{Ar}_2\text{BCl} \) were significantly higher than in the attempts at the synthesis of ArBCl$_2$ making a satisfactory preparative route to \( \text{Ar}_2\text{BCl} \).

Interestingly the action of ArBCl$_2$ with ArLi was found to act in a similar way to BCl$_3$ (Figure 8.6).

This reaction has a much lower significance, possibly due to the fluorine : boron intramolecular interaction reducing the electrophilic character of the boron. An MNDO calculation on Ar$_2$BCl together with its $^{11}$B and $^{19}$F NMR data is presented in Section 8.7, Figures 8.18 and 8.19.
To develop this chemistry further an attempt was made at the standard ArBF$_2$ preparation by the reaction of ArLi with BF$_3$·Et$_2$O \[^5\]. Since BF$_3$ is a weaker Lewis acid than BC$_1$$_3$, the breaking of a B-F bond is possibly unfavourable. (The products formed in this process must also be considered.)

If the side-reaction described earlier (Section 8.2) occurs in this system, as one fluorine leaves this boron another fluorine goes back on (Figure 8.7).

![Figure 8.7: The proposed interaction of BF$_3$ with ArLi.](image)

No ArBF$_2$ was observed. A brown inhomogeneous material was isolated which unfortunately could not be fully characterised. The $^{19}$F spectrum indicated a number of products present with a very complex "CF$_3$" region. No precipitate was visible from this reaction, possibly because the "LiF" generated is solubilised in an "active" form \[^6\].

It can be concluded that BF$_3$ seems to be acting to decompose catalytically the Ar ring system. Even with a 1:1 stoichiometric ratio of ArLi : Et$_2$O·BF$_3$, substantial amounts of BF$_3$ appeared to remain in the reaction mixture from the $^{19}$F NMR, adding further weight to this hypothesis (Figure 8.8). Further evidence can be found from earlier work \[^7\] illustrating the decomposition of CF$_3$BF$_2$ to give BF$_3$ (Figure 8.9). (Crystals of ArBCl$_2$ (73) and Ar$_2$BCl (74) were isolated from the methods described, and were submitted for X-ray analysis.)
An interesting area of research which may be further pursued in the light of this finding would be the possible synthetic use of BF$_3$ or BCl$_3$ in the catalytic elimination of LiF from other species, with CF$_3$ similarly displaced from Li, for example:
The low yield of ArBCl₂ led to the exploration of a different synthetic route (Section 8.4).

8.4 ORGANO Tin DERIVATIVES

8.4.1 Trimethyl Ar Tin (78)

ArSnMe₃ (78) was synthesised via the reaction of the ArLi precursor with Me₃SnCl, and distilled as a colourless oil. It was hoped to initiate exchange between the Ar group and chlorine on boron trichloride. In the compound PhSnMe₃, Ph would be expected to exchange before Me [9]. The ease of Sn-X cleavage by halogens, or other reagents varies with the nature of the organic group - generally increasing in the sequence [9] (Bu being the most stable):

Bu < Pr < Et < Me < vinyl < Ph < Bz < allyl < CH₂CN < CH₂CO₂R

Based on this hypothesis, ArSnMe₃ and BCl₃ were mixed. No exchange was observed in Et₂O [10]. A more polar solvent was required, such as CH₂Cl₂.

In CH₂Cl₂ a peak in the ¹¹B NMR indicative of MeBCl₂ [4] with a chemical shift of +62.3 ppm was clearly seen, with the ¹⁹F spectrum indicating the formation of a different Ar-containing species attributed to ArSnMe₂Cl (79). Very recent work on a similar exchange system between boron and tin (R = allyl) has been reported [11].
To indicate whether the new Ar species had the Ar group attached to tin or boron, a $^{119}$Sn NMR spectrum should have been recorded. However, the volatility of the boron species (removed in vacuo), giving a shift in the $^{11}$B NMR at +62 ppm suggested it was MeBCl$_2$, and therefore the Me group had been transferred first. The reaction appeared to proceed as shown in Figure 8.10.

$$\text{Me}_3\text{SnAr} (78) \xrightarrow{\text{BCl}_3, \text{CH}_2\text{Cl}_2} \text{MeBCl}_2 + \text{Me}_2\text{SnArCl} (79)$$

$$\downarrow \text{BCl}_3$$

$$\text{MeBCl}_2 + \text{ArBCl}_2 (73) + \text{Me}_2\text{SnCl}_2$$

Figure 8.10: Reaction of ArSnMe$_3$ (78) with BCl$_3$ in CH$_2$Cl$_2$.

The signal at +32 ppm in the $^{11}$B NMR was assigned to ArBCl$_2$ (73). The slight deshielding was attributed to CH$_2$Cl$_2$ being less coordinating than Et$_2$O (NB. No further Me exchange appears to occur from Me$_2$SnCl$_2$ - this species appeared to be stable in solution)\[9,10\]. Many tin compounds of the general formula R$_3$SnX or R$_2$SnX$_2$ are strongly associated with bridging X groups raising the coordination number of tin to 5, 6 or 7 \[9\].

### 8.4.2 Tributyl Ar Tin (80)

By the use of Bu$_3$SnAr (80) it was hoped to reduce and possibly eliminate the problem of smaller group migration, since $^n$Bu appeared to form the most stable "tin-carbon" bond in the sequence (Section 8.4.1) \[9\]. Butyl with a larger steric requirement will make it more difficult for the two species to approach in the postulated transition state (Figure 8.11).
Bu₃SnAr (80) was isolated and vacuum distilled as a clean oil and as a new Ar-containing tin derivative. In ether no exchange with BCl₃ was observed, as expected from the previous example [10]. With CH₂Cl₂ even by refluxing no Ar or Bu group transference was apparent.

In both reactions involving Bu₃SnAr (80) and Me₃SnAr (78) with BCl₃ a symmetrical peak at ca. -64 ppm in the ¹⁹F NMR appeared, indicative of ArH, a possible result of destannylation.

8.4.3 Other Possible Tin Derivatives

The synthesis of ArSnCl₃, Ar₂SnCl₂ (which may also be a precursor for a diaryl substituted phosphastannene), Ar₄Sn etc. would eliminate the complications of methyl group migrations. However, their use as synthons would be dependent on the ability of the aryl group to migrate in these systems, and a plausible synthetic route to their preparation. For example, there may be steric limitations to the formation of Ar₄Sn, and once prepared, for example with (C₆F₅)₄Sn [7] it may be too unreactive to provide a useful route to Ar'BCl₂ (Ar' = C₆F₅). However, this would be an interesting system for further investigation.
It is appropriate to mention here the observed reaction of \( \text{ArSnMe}_3 \) (78) with iodine, and a possible rationalisation of its lack of reactivity. The reaction is outlined in Figure 8.12.

\[
\begin{align*}
\text{F}_3\text{C}-\text{Sn} & \text{(CH}_3\text{)}_3 \quad \text{I}_2 & \xrightarrow{\text{CHCl}_3 \text{ reflux} \quad 60 \text{ mins.}} & \text{F}_3\text{C}-\text{Sn} & \text{(CH}_3\text{)}_3 \text{I}
\end{align*}
\]

\textbf{Figure 8.12: Attempted reaction of ArSnMe}_3 \text{ with iodine.}

It was reported \(^{[12a]}\) that even after refluxing, neither dissipation of the iodine colouration nor formation of the iodo derivative was observed. The tin-carbon bond strength may be enhanced by the three trifluoromethyl groups, as the reaction is an example of electrophilic aromatic substitution which is hindered by electron withdrawing substituents. The cyclic transition state proposed (Figure 8.13) would also be difficult to achieve in the presence of two bulky ortho substituents \(^{[12b]}\).

\[
\begin{align*}
\text{I} & \quad \text{I} \quad \text{Sn} \quad \text{I} \quad \text{I}_2
\end{align*}
\]

\textbf{Figure 8.13: Interaction of iodine with ArSnMe}_3 \text{ (78); (aromatic electrons omitted for simplicity).}

With the boron trichloride reaction, however, its greater electrophilicity and smaller size, together with its ability to partially complex with fluorine drawing it into the reaction, were anticipated to overcome some of the problems observed in the iodine case (\(\text{ie.}\) repulsion by large diffuse electron clouds). The poor yields obtained in the boron case (Section 8.4.1) may be a direct result of the high tin-carbon bond strength.
Figure 8.15: Mass spectral data for Ar₃B (75).
8.5 PREPARATION OF Ar$_3$B (75)

The new aryl zinc compound, ArZnCl (81) was prepared by classical methods [13] and reacted stoichiometrically with BCl$_3$. Vacuum distillation of this mixture however, yielded a low melting point solid which was characterised as Ar$_3$B (75) (Equation 8.10).

$$3\text{ArBCl}_2 \overset{(73)}{\rightarrow} \text{Ar}_3\text{B} \overset{(75)}{+} 2\text{BCl}_3 \overset{(v)}{\rightarrow}$$ (8.10)

Many such disproportionation reactions are known in organohalo boron chemistry [14,15]. A possible mechanism is shown in Figure 8.14, and Figures 8.15 and 8.16 illustrate, respectively, mass spectral and $^{13}$C NMR data for the Ar$_3$B species.

![Figure 8.14: Possible reaction mechanism for formation of Ar$_3$B.](image)

Addition of ArZnCl (81) to BCl$_3$ gave no apparent reaction at room temperature. No "B-F" decomposition species were evident. Refluxing may promote the required substitution reaction. However, these results appear to suggest that an organometallic derivative of intermediate reactivity between the organolithium and organozinc species is required. Attempts to generate the ArMgCl Grignard by ArLi addition to magnesium chloride failed (Section 8.9.9.1).

Recently a possible route to the Grignard ArMgBr was discovered in the literature [16] generating MgBr$_2$ in situ (Section 9.9.9.2). This may also be via the formation of ArBr, however the synthetic route to ArBr via the direct action of bromine on ArLi gave consistently low yields.
Figure 8.16: Partially decoupled $^{13}C$ NMR spectrum for $Ar_3B$ (75) in CDCl$_3$. 
[A possible steric limitation to Grignard formation may also exist]. This organometallic reagent should be further pursued to allow a possible high yield synthetic route to $\text{Ar}_3\text{BX}_n$ by preventing decomposition via attack at the trifluoromethyl groups.

8.6 HYDROLYSIS OF $\text{Ar}_2\text{BCl}$ (4)

$\text{Ar}_2\text{BCl}$ was hydrolysed (Equation 8.11) and the $^{19}\text{F}$ NMR spectrum was monitored, with no attempt made to isolate the product. The ortho-$\text{CF}_3$ groups appeared to be equivalent although, of course, the rings may still be spatially inequivalent and simply have coincident chemical shifts.

$$\text{Ar}_2\text{BCl} (74) + \text{H}_2\text{O} \rightarrow \text{"Ar}_2\text{B-OH"}$$ (8.11)

8.7 COMPARISON OF $\text{Ar}_3-n\text{BCl}_n\ (n = 1-3)$ SPECIES: STRUCTURE AND NMR PARAMETERS

A direct comparison of the physical data of the three Ar-substituted derivatives is presented in Table 8.1.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>$^{11}\text{B} (\delta/\text{ppm})$</th>
<th>$^{19}\text{F} (\delta/\text{ppm})$</th>
<th>MPt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{ArBCl}_2$ (73)</td>
<td>27 (Et$_2$O)</td>
<td>-56.3 (o-$\text{CF}_3$)</td>
<td>62-64</td>
</tr>
<tr>
<td></td>
<td>31 (CH$_2$Cl$_2$)</td>
<td>-63.9 (p-$\text{CF}_3$)</td>
<td></td>
</tr>
<tr>
<td>$\text{Ar}_2\text{BCl}$ (74)</td>
<td>47 (Et$_2$O)</td>
<td>-57.5 (o-$\text{CF}_3$)</td>
<td>71-73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-57.6 (o-$\text{CF}_3$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-64.6 (p-$\text{CF}_3$)</td>
<td></td>
</tr>
<tr>
<td>$\text{Ar}_3\text{B}$ (75)</td>
<td>31 (Et$_2$O)</td>
<td>-63.3 (o-$\text{CF}_3$)</td>
<td>40-41 †</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-64.8 (p-$\text{CF}_3$)</td>
<td></td>
</tr>
</tbody>
</table>

Table 8.1: Comparative physical data for the three Ar-substituted boron derivatives; †compare with Mes$_3\text{B}$ (190 °C) (ref.4).
Figure 8.18: (a) $^{19}F$ and (b) $^{11}B$ NMR spectra of $Ar_2BCl$ (4) in CDCl$_3$. 
The graph represents the trend in $^{11}$B NMR shifts on progressive substitution of chlorine for Ar in BCl$_3$. Values for the corresponding ethyl and diethylamino derivatives are given for comparative purposes (Figure 8.17).

![Graph showing NMR shifts](image)

**Figure 8.17:** Correlation of $^{11}$B NMR shifts in the Ar ($x$), Et$_2$N ($\bullet$) and Et ($\ast$) systems.

The unexpected shielding of the $^{11}$B NMR value for compound (73) is attributed to occupancy of the fourth valency of boron by electron donation from the ortho fluorine atoms.

The $^{19}$F NMR spectrum of (4) (Figure 8.18) clearly shows two distinctive types of ortho-CF$_3$ group. The MNDO calculation diagnoses this effect to two inequivalent rings. The results of these calculations are shown in Figure 8.19.

The equivalence of the ortho-CF$_3$ groups in Ar$_3$B (75) is attributed to the symmetrical orientation of the three rings (twisting out of plane), cf. Mes$_3$B (82) (Figure 8.20) [4]. The low melting point of Ar$_3$B may be attributed to a crystal-packing effect.
Figure 8.19: Results of MNDO calculation on $\text{Ar}_2\text{BCl} (4)$.
Figure 8.19: Results of MNDO calculation on Ar\textsubscript{2}BCl (4).
8.8 $^{11}$B NMR SPECTRA: A GENERAL DISCUSSION

Broad signals were obtained for all the Ar containing organoboron species. This is due to the quadrupolar relaxation of the boron nucleus ($I = 3/2$), although more serious quadrupolar relaxation is seen in trigonal than in tetrahedral derivatives. It is interesting to compare the line widths obtained in these systems with those for isolated borates (Chapter 10). The electron density is important in determining the shifts but both the inductive (-I) and perhaps most significantly the mesomeric effects also play their part [4].

8.9 EXPERIMENTAL DETAILS

8.9.1 Preparation of ArBCl$_2$ (73)

8.9.1.1 With Excess BCl$_3$

ArLi (100 ml, 45 mmol, 0.45 M in Et$_2$O) was added dropwise over 5 minutes to a stirred solution of BCl$_3$ (5.0 ml, 6.8g, 58 mmol) condensed into Et$_2$O (70 ml) at -40 °C, and the mixture was maintained at this temperature during addition. Copious amounts of white solid were precipitated. The solution was allowed to reach room temperature over a period of one hour and stirred continuously. Removal of the solid by filtration gave a clear yellow-green coloured solution. The $^{11}$B NMR
spectrum showed clear evidence of "B-F" species. $^{19}$F NMR $\delta$: -114.2 (4 equal lines) $^1J_{BF}$ 58 Hz, -128.4 (unresolved), -152 (s), -54.1 (t, o-CF$_3$) $^5J_{FF}$ 15.8 Hz, -64.2 (s, p-CF$_3$), "ArBF$_2$". The large singlet at -64.0 ppm present was attributed to ArH (1).

The solution was pumped under hard vacuum (0.01 mm Hg) for 1 hour to remove all the volatile material. The resulting sticky green residue could be redissolved in CH$_2$Cl$_2$ (ca. 10 ml), or alternatively diethyl ether, and cooled overnight to -40 °C (if no solid precipitated at low temperature the solvent could be slowly removed in vacuo and the product fell out of the solution as a whitish/yellow solid). The solid was isolated by filtration under rigorously anhydrous conditions and washed to pure white crystals by several aliquots of pentane. Very poor yields were obtained, approximately 1.9g (12%) (for improved yields see Section 8.9.1.2). The precipitate obtained at the first stage was analysed and found to contain lithium, fluorine and chlorine, attributed to LiF and LiCl elimination. Mpt. 62-64 °C; Analysis found: C, 29.58; H, 0.52; Required for C$_9$H$_2$F$_9$BCl$_2$: C, 29.79; H, 0.55%; IR (Nujol) $\nu_{\max}$: 3100 ($\omega$, ArCH), 1630 and 1570 (s, ArC=C), 1400-1000 (s, C-F, CF$_3$), ~900 (m, ArCH), 1037 (m, B-Cl), 705 and 690 (m, CF$_3$) cm$^{-1}$; MS (Intensity%) EI: 362 (low intensity, ArBCl$_2^+$), 262 (100, Ar-F), 243 (ring fragmentation), 212; Cl$^+$: 379 (0.51, ArBCl$_2^+$NH$_3$); $^{11}$B (Et$_2$O) $\delta$: 27 ppm, (CH$_2$Cl$_2$) $\delta$: 32 (s, broad) ppm; $^{19}$F (CH$_2$Cl$_2$) $\delta$: -56.3 (6F, o-CF$_3$), -63.9 (3F, p-CF$_3$) ppm; (Et$_2$O) $\delta$: -57.4 (6F, o-CF$_3$), -64.4 (3F, p-CF$_3$) ppm; (THF) $\delta$: -56.4 (6F, o-CF$_3$), -62.7 (3F, p-CF$_3$) ppm.

$^{1}$ F$^-$: Fe(NCS)$_6^{2-}$ test; Cl$^-$: silver nitrate test; Li$^+$: flame test.
8.9.1.2 Improved Synthesis of ArBCl₂

ArLi (100 ml, 45 mmol, 0.45 M in Et₂O) was added dropwise over 10 minutes to a stirred solution of BCl₃ (45 ml, 45 mmol, 1 M solution in hexane) at -10 °C. This was stirred for 30 minutes and allowed to reach room temperature. The ¹¹B NMR spectrum confirmed the presence of ArBCl₂, BFCl₂·Et₂O and BF₃·Et₂O. A greater attack at CF₃ results in the presence of an excess (1.3 equivalents) of boron trichloride (Section 8.9.1.1). The solid filtered from the reaction was found to contain fluorine, reinforcing the belief that the reaction mechanism involved LiF and LiCl elimination (Section 8.2.1). ArBCl₂ was isolated as described earlier (Section 8.9.1.1), and the yield was 5.2g (32%).

8.9.2 Reaction of BF₃·Et₂O and BCl₃·Et₂O

BF₃·Et₂O (0.2 ml, 1.63 mmol) was added dropwise over 2 minutes to a stirred solution of BCl₃·Et₂O (1.63 ml, 1.63 mmol, 1 M) in ether (10 ml) at room temperature. The mixture was stirred for 10 minutes before the ¹¹B NMR spectrum was recorded. ¹¹B δ: 10.62 (s, BCl₃·Et₂O), 7.87 (d, BCl₂F·Et₂O) ¹JBF 57.0 Hz, 3.88 (t, BClF₂·Et₂O) ¹JBF 29.1 Hz, 0.0 (s, BF₃·Et₂O) ppm.

8.9.3 Reaction of ArH and BCl₃

ArH + BCl₃ →

BCl₃ (1.72g, 1.26 ml, 14.7 mmol) was condensed into a stirred solution of ArH (4.1g, 14.6 mmol) in Et₂O (30 ml) at -10 °C. The reaction mixture was allowed to reach room temperature and stirred for 4
hours. There was no visible reaction, even after refluxing for 2 hours. 

$^{19}F\ (Et_2O) \, \delta: -62 \text{ ppm (s, ArH)}$; $^{11}B\ (Et_2O) \, \delta: 11 \text{ ppm (unreacted BCl}_3)^{[4]}$.

8.9.4 Preparation of 'ArBF$_2$'

8.9.4.1 From ArBCl$_2$

$$\text{ArBCl}_2 + \text{SbF}_3 \rightarrow \text{ArBF}_2$$

ArBCl$_2$ (0.42g, 1.2 mmol) in Et$_2$O (25 ml) was added to a stirred suspension of SbF$_3$ (0.24g, 1.32 mmol) in Et$_2$O (10 ml) at room temperature. This mixture was brought gradually to reflux for 2 hours. 

$^{19}F \, \delta: -54.1 \text{ (t, o-CF}_3) \, 5J_{FF} 15.8 \text{ Hz, -64.2 (s, p-CF}_3) \text{ ppm.}$

8.9.4.2 Attempt From ArLi and BF$_3$·Et$_2$O

ArLi (17.2 ml, 7.74 mmol, 0.45 M) was added dropwise to a stirred solution of BF$_3$·Et$_2$O (0.95 ml, 7.74 mmol) in Et$_2$O (35 ml) at -20 °C. The reaction mixture was stirred for 1/2 hour at -20 °C and then warmed to room temperature. The $^{19}F$ spectrum was very complex in the "CF$_3$" region (from -55 to -65 ppm) with a large peak at -151 ppm attributed to BF$_3$·Et$_2$O (see Figure 8.8). BF$_3$·Et$_2$O appeared to catalyse decomposition of ArLi (2).
8.9.5 Preparation of Ar$_2$BCl (74)

8.9.5.1 From ArLi and BCl$_3$

$$3\text{ArLi} (2) + \text{BCl}_3 \rightarrow \text{Ar}_2\text{BCl} (74) \text{ (major product)}$$

A solution of BCl$_3$ (22 ml, 22 mmol, 1 M in hexane) was added dropwise over 5 minutes to a stirred solution of ArLi (67 mmol, 0.45 M) in Et$_2$O (150 ml) at -10 °C. A visible precipitate was formed instantly on addition. The reaction mixture was allowed to reach room temperature. The $^{11}$B NMR showed the presence of two boron species assigned to ArBCl$_2$ and Ar$_2$BCl. The insoluble solid (LiCl/LiF) was removed by filtration and the pale brown filtrate concentrated in volume on the vacuum line. With about 30 ml Et$_2$O remaining, the solution was cooled to -40 °C. Ar$_2$BCl (pale brown solid) precipitated immediately. The solution was maintained at low temperature for 2 hours to maximise yields, filtered at low temperature, and the resultant solid washed with a small volume of petrol, giving a pure white solid which was fully characterised. Yield was 5.2g (39%). Mpt. 71-73 °C. Ar$_2$BCl was also stable to sublimation at 38 °C (0.5 mm Hg). Analysis found: C, 35.81; H, 0.31; B, 1.26; Cl, 5.23; Required for C$_{18}$H$_{14}$F$_{18}$BCl: C, 35.53; H, 0.66; B, 1.77; Cl, 5.82%; IR (Nujol) $\nu_{\text{max}}$: 3640 (m,OH hydrolysis), 3100 (w,ArCH), 1400-1000 (s,C-F), 1350 (m,B-Cl), 700 (m,CF$_3$) cm$^{-1}$; UV-Visible (CCl$_4$) $\lambda_{\text{max}}(\epsilon)$: 270 (2200) nm; MS (Intensity%) EI: 608 (12.1,Ar$_2$BCl$^+$), 262 (100,Ar-F$^+$), [peak higher masses: 871 (1B, 1Cl) 4.0 low intensity]; Cl$^+$: 573 (1.4,Ar$_2$B$^+$), 248 (100); $^{11}$B (CH$_2$Cl$_2$)$_2$ $\delta$: 47 ppm (s,broad); $^{19}$F $\delta$: -57.5 (s), -57.6 (s) (12F,o-CF$_3$), -64.6 (s,3F,p-CF$_3$) ppm.

A small sample (2.1g, 3.5 mmol) was recrystallised from CH$_2$Cl$_2$ (5 ml) at -40 °C to give crystals suitable for X-ray analysis. These
were mounted for this purpose.

8.9.5.2 From ArLi and ArBCl₂

It was thought that, to avoid the problem of excess BCl₃, it would be possible, despite its isolation in low yield, to use ArBCl₂ in a direct reaction with ArLi (Section 8.2.2). An ether solution of ArLi (6.2 ml, 3.4 mmol, 0.55 M) was added dropwise over 5 minutes to a stirred solution of ArBCl₂ (1.1 g, 3.0 mmol) in Et₂O (50 ml) at -10 °C. The formation of Ar₂BCl was confirmed by ¹⁹F and ¹¹B NMR data only, and some "B-F" species were also present in solution.

8.9.6 Reactions of ArSnMe₃ (78) with BCl₃

ArSnMe₃ was made and isolated according to Chambers et al. [⁹], distilled as a colourless oil, bpt. 50 °C (0.5 mm Hg); ¹⁹F δ: -58.5 (6F, o-CF₃), -64.4 (3F, p-CF₃) ppm.

ArSnMe₃ (2.62 g, 5.9 mmol) in CH₂Cl₂ (20 ml) was added dropwise over 5 minutes to a stirred solution of BCl₃ (6 ml, 6 mmol, 1 M in CH₂Cl₂) in additional CH₂Cl₂ (10 ml) at -40 °C. The solution immediately turned blue-green on addition. It was stirred for 1/2 hour, allowed to reach room temperature and stirred for a further 2 hours. ¹¹B δ: 62 ppm ("MeBCl₂") [⁴]; ¹⁹F δ: -57.4 (6F, o-CF₃), -64.4 (3F, p-CF₃) ppm ("Me₂SnArCl") (no coupling by ¹¹⁹Sn was observed). All volatiles were removed in vacuo by pumping for 30 minutes. The ¹¹B NMR peak at +62 ppm almost disappeared.

A further portion of BCl₃ (6 ml, 6 mmol, 1M solution in CH₂Cl₂) was added dropwise to the stirred solution, cooled to -20 °C. This was allowed to reach room temperature over 20 minutes and a ¹¹B signal
11 corresponding to ArBCl₂ was observed. 

\[ ^{11}\text{B (CH}_2\text{Cl}_2) \delta: +31 \text{ (s, broad),} \]

\[+42.6 \text{ (s, broad, unreacted BCl}_3\text{)}, +62.3 \text{ (s, weak, MeBCl}_2 \text{) ppm} \]

The excess BCl₃ and the remaining MeBCl₂ was removed in vacuo over 1 hour to yield Me₂SnCl₂, Me₂SnArCl and ArBCl₂ as a black oil. It did not appear worthwhile to isolate ArBCl₂ from this mixture.

8.9.7 Preparation of Bu₃SnAr (80)

\[
\text{Bu}_3\text{SnCl} + \text{ArLi} \longrightarrow \text{Bu}_3\text{SnAr (80)}
\]

ArLi (47 ml, 36 mmol, 0.77 M solution in Et₂O) was added dropwise over 5 minutes to a stirred solution of Bu₃SnCl (9.8 ml, 11.7g, 36 mmol) in diethylether (120 ml) at -10 °C. A white precipitate was formed immediately. This was removed by filtration and the filtrate concentrated to yield a heavy yellow oil, purified by vacuum distillation, bpt. 124 °C (0.1 mm Hg). Yield was 17.4g (85%). \n
\[ ^{119}\text{Sn} \delta: -11.8 \text{ (s) ppm;} \]

\[^{13}\text{C (CDC}_1\text{)} \delta: 125.1 \text{ (ArCH ring),} 137.5 \text{ (o-CF}_3\text{)} \]

\[^{1}J\text{CF} 33 \text{ Hz,} \]

\[^{130.2} \text{ (p-CF}_3\text{)} \]

\[^{1}J\text{CF} 35 \text{ Hz, ca. 40 (C on Sn) }^{1}J\text{CSn not resolved,} 28.7 \text{ ppm (C Bu);} \]

\[^{19}\text{F} \delta: -56.1 \text{ (6F, o-CF}_3\text{), -64.0 \text{ (3F, p-CF}_3\text{) ppm.} \]

8.9.8 Reaction of Bu₃SnAr (80) with BCl₃

\[
\text{Bu}_3\text{SnAr (80) + BCl}_3 \longrightarrow \text{X} \longrightarrow \text{ArBCl}_2 + \text{Bu}_3\text{SnCl}
\]

ArSnBu₃ (5.62g, 9.8 mmol) in CH₂Cl₂ (10 ml) was added dropwise to a stirred solution of BCl₃ (0.93 ml, 1.27g, 10.8 mmol, 1.1 equivalents) in CH₂Cl₂ (50 ml). This solution was refluxed overnight and no evidence of butyl group transfer was observed. \n
\[^{11}\text{B (CH}_2\text{Cl}_2) \delta: 42.6 \text{ ppm (unreacted BCl}_3\text{);} \]

\[^{19}\text{F} \delta: -56.1, -64.0 \text{ ppm (ArSnBu}_3\text{).} \]
8.9.9 Attempted Preparation of a Grignard Reagent

8.9.9.1 From ArLi and MgCl₂

\[
\text{ArLi} + \text{MgCl}_2 \rightarrow \text{ArMgCl} + \text{LiCl}
\]

ArLi/\text{Et}_2\text{O} (0.57 M, 7.3 mmol) was added dropwise to a stirred suspension of anhydrous \text{MgCl}_2 (0.7 g, 7.3 mmol) in \text{Et}_2\text{O} (20 ml) at room temperature. The reaction mixture was stirred for 1 hour. The \(^{19}\text{F NMR}\) showed complete hydrolysis of the ArLi forming ArH. \(^{19}\text{F (Et}_2\text{O)} \) \(\delta\): -64 ppm (ArH). \text{MgCl}_2 was rigorously dried by heating to 110 °C \textit{in vacuo} for 6 hours. However, the solid appeared to retain sufficient water of crystallisation to make this reaction ineffective.

8.9.9.2 Possible Generation of ArMgBr

Anhydrous MgBr₂ may be prepared \textit{in situ} by the reaction of magnesium with bromine, 1,2 dibromoethane or HgBr₂·THF, to give a two phase system, the dense lower phase containing a MgBr₂·THF complex [16].

8.9.10 Preparation of ArZnCl (81)

\[
\text{ArLi} + \text{ZnCl}_2 \rightarrow \text{ArZnCl (81)}
\]

ArLi (50 ml, 35 mmol, 0.7 M) was added dropwise over 5 minutes to a stirred solution of \text{ZnCl}_2 (4.8 g, 35 mmol) in ether (50 ml) at room temperature. This mixture was stirred for two hours. \(^{19}\text{F NMR}\) \(\delta\): -62.0 (6F, o-CF₃), -64.1 (3F, p-CF₃) ppm. Quantitative conversion with respect to
the $^{19}\text{F}$ NMR. This reagent was used *in situ*.

8.9.11 Preparation of $\text{Ar}_3\text{B}$ (75)

\[3\text{ArZnCl} + \text{BCl}_3 \rightarrow [\text{ArBCl}_2] \rightarrow \text{Ar}_3\text{B} + 3\text{ZnCl}_2\]

The ArZnCl-ether solution (ca. 35 mmol) was added dropwise to a stirred solution of BCl$_3$ (4.1g, 3.0 ml, 35 mmol) in ether (70 ml) at -10 $^\circ$C. This mixture was allowed to reach room temperature and stirred for 2 hours. The Et$_2$O was removed *in vacuo* and the residue distilled to give a pale yellow oil, bpt. 84 $^\circ$C (0.1 mm Hg), which solidified in the receiving vessel. This appeared to be Ar$_3$B (75) presumably formed via the disproportionation of ArBCl$_2$. No B-F species were observed. Yield was 4.2g (42% w.r.t ArZnCl). Mpt. 40-41 $^\circ$C. Analysis found (%C is slightly low): C, 36.08; H, 0.72; B, 1.26; Cl, 0%; Required for C$_{27}$H$_6$B: C, 37.97; H, 0.71; B, 1.27%; UV-Visible (CCl$_4$) $\lambda_{\text{max}}$ ($\varepsilon$): 262.5 (3975.5) nm; MS (Intensity%) EI: 573 (10.2, Ar$_2$B$^+$), 310 (65, ArBF$^+$), 261 (25) and 243 (100, ring fragmentation); CI$^+$: 573 (0.18, Ar$_2$B$^+$), 279 (25) and 240 (100, ring fragmentation); CI$: 591 (100, \text{Ar}_2\text{BF}^-)$; $^{11}$B (CDCl$_3$) $\delta$: 31 ppm (s, broad); $^{19}$F (CDCl$_3$) $\delta$: -63.32 (s, 6F), -64.76 (s, 3F) ppm; $^1$H (CDCl$_3$) $\delta$: 8.1 (s) ppm; $^{13}$C (CDCl$_3$) $\delta$: 144.62 (s, broad, B-C), 139.80 $^1$J$_{CF}$ 31.51 Hz (q, CF$_3$C), 132.88 $^1$J$_{CF}$ 34.47 Hz (q, CF$_3$C), 124.91 $^1$J$_{CH}$ 270.58 Hz (d, CH), 120.76 (s, CF$_3$-C), 118.05 (s, CF$_3$-C), 116.45 (s, CF$_3$-C) ppm (Figure 8.16).
8.9.12 Hydrolysis of $\text{Ar}_2\text{BCl}$ (4)

$$\text{Ar}_2\text{BCl} \xrightarrow{\text{H}_2\text{O}} \text{"Ar}_2\text{BOH"}$$

Excess $\text{H}_2\text{O}$ (5 ml) was added to a stirred solution of $\text{Ar}_2\text{BCl}$ (0.25g, 0.4 mmol) in $\text{CH}_2\text{Cl}_2$ (10 ml). The $^{19}\text{F}$ NMR was recorded. The $\text{o-CF}_3$ groups appear to be equivalent. $^{19}\text{F} \delta$: -57.1 ($\text{o-CF}_3$), -64.1 ($\text{p-CF}_3$) ppm.

8.10 REFERENCES


CHAPTER NINE

BORINIUM CHEMISTRY
9.1 INTRODUCTION

The most prolific researchers within the field of borinium chemistry are H. Nöth and co-workers. Recently (1985) he has provided a comprehensive review on borinium R-B⁺R (83) and borenium R₂B⁺—D (84) ions [1]. The boron cation (−B⁺) has only two electrons available for bonding, therefore, in the case of (84) an electron pair must be supplied by a suitable ligand. It is clear that the coordination of boron is correlated with the size and nature of R, D and X [2]. Studies on systems of type (84) have been carried out to define a three coordinate range in the ¹¹B NMR spectrum [2] [X = Cl⁻, SO₂CF₃⁻]. The molecular orbital approach to these structures has been explored by Nöth and Kölle (1985) [1]. The importance of back-bonding from π-electron rich species and a steric shield for stability is emphasised. This situation is exactly paralleled with phosphenium cations [3].

Aromatic species also seem capable of some degree of stabilisation [1,4]. Borinium ion preparations can be classified into four groups. A brief survey under each classification is given below.

9.1.1 Boron-Halogen Heterolysis

\[ R₂BX + MX₃ \rightarrow R₂B⁺MX₄^- \]

This method, which involves the use of a Lewis acid to remove a halogen as X⁻ [1], is employed in this work. Further examples are illustrated in Figure 9.1.
9.1.2 Electrophilic Attack

This includes, for example, attack on aminoboranes by the use of a suitable electrophile \[1,6\] (Equation 9.1).

\[
\begin{align*}
\text{Me}_3\text{SiX} & \quad \text{Me}_3\text{SiX} \\
\end{align*}
\]

9.1.3 Nucleophilic Attack

Addition of a nucleophile may form borenium ions by displacement of a good anionic leaving group \[1,9\] (Equation 9.2).

\[
\begin{align*}
\text{R}_2\text{BX} + \text{D} & \quad \Rightarrow \quad \text{R}_2\text{B} \xrightarrow{\text{D}} \text{X} \\
\end{align*}
\]
9.1.4 Metathesis

The bulk of tmp is essential for this reaction; (Equation 9.3) \([1,10]\) (for example with \(\text{iPr}_2\text{N}\) the bisamino boron triflate is formed) (see also Chapter 11).

\[
\begin{align*}
\text{N-} & \quad + \quad \text{AgOSO}_2\text{CF}_3 \\
\text{B-Cl} & \quad \rightarrow \quad \text{N=} & \quad \text{B=+} & \quad \text{N=} & \quad \text{OSO}_2\text{CF}_3
\end{align*}
\]

(9.3)

9.2 OVERVIEW

Routes to stable two coordinate boron cations similar to those prepared by Nöth 1985 \([1]\) have been investigated. A range of Lewis acids were used for the abstraction of \(\text{Cl}^-\) from \(\text{R}_2\text{BCl}\). The potential of \(\text{Ar} [2,4,6\text{-tris(trifluoromethyl)phenyl}]\) as a steric shield has been recognised (Chapters 1, 3 and 4). It was of interest to see if it could stabilise the respective borinium ion, i.e. \(\text{Ar}_2\text{B}^+\) (85).

9.3 MNDO CALCULATION ON \(\text{Ar}_2\text{B}^+\) (85)

An MNDO calculation related these properties and allowed an insight into the feasibility of the proposed structure of \(\text{Ar}_2\text{B}^+\) (85). The results are given in Figure 9.2.
Figure 9.2: MNDO calculation results for the postulated borinium ion, \( \text{Ar}_2\text{B}^+ \) (85).
\[
\text{Ar-} \text{B-} \text{Ar} \quad \text{Ar-B length 1.474Å}
\]

9.4 BORINIUM ION SYNTHESIS

To allow a direct comparison of techniques and NMR interpretation a series of borinium ions were synthesised. The bis amino substituted boron halide was prepared either by simple addition of the amine to BCl\(_3\), where the steric strain was low enough to allow this \([4h,11]\), or by the addition of the lithium derivative to BCl\(_3\) (in the cases of tmp and Ar) \([10]\). The resulting compounds (Table 9.1) were treated with SbCl\(_5\), AlCl\(_3\), TiCl\(_4\) and BCl\(_3\).

In cases with tmp\(_2\)BCl (86) and \((^1\text{Pr}_2\text{N})_2\text{BCl} \) (87), the best results were achieved with AlCl\(_3\), although SbCl\(_5\) was also effective in a number of examples (see Table 9.1). However, this often gave intractable black solids which appeared to contain the borinium ion with respect to the \(^{11}\text{B}\) NMR, but purification from these systems proved difficult. The
driving force of these reactions is the thermodynamic favourability of
the formation of a 4th bond to aluminium, or a 6th bond to antimony.
With the use of \( \text{BCl}_3 \) as the Lewis acid, B-Cl bond forming counteracts
B-Cl breaking \[2\].

<table>
<thead>
<tr>
<th>LEWIS ACID</th>
<th>SOLVENT (25°C)</th>
<th>(^{11}B \delta )</th>
<th>SPECIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>([(iPr_2N)_2BCl] )</td>
<td>( \text{CH}_2\text{Cl}_2 )</td>
<td>30.7</td>
<td>((iPr_2N)_2\text{BCl} ) (87)</td>
</tr>
<tr>
<td>( \text{AlCl}_3 )</td>
<td>( \text{CH}_2\text{Cl}_2 )</td>
<td>37.0</td>
<td>((iPr_2N)_2\text{B}^+\text{AlCl}_4^- ) (88)</td>
</tr>
<tr>
<td>( \text{SbCl}_5 )</td>
<td>( \text{CH}_2\text{Cl}_2 )</td>
<td>30.7</td>
<td>((iPr_2N)_2\text{BCl} ) (87)</td>
</tr>
<tr>
<td>( \text{SbCl}_5 )</td>
<td>no solvent</td>
<td>36.4</td>
<td>((iPr_2N)_2\text{B}^+\text{SbCl}_6^- ) (89)</td>
</tr>
<tr>
<td>( \text{BCl}_3 )</td>
<td>( \text{CH}_2\text{Cl}_2 )</td>
<td>42.6</td>
<td>\text{BCl}_3</td>
</tr>
<tr>
<td>( \text{CH}_2\text{Cl}_2 )</td>
<td>30.7</td>
<td>((iPr_2N)_2\text{BCl} ) (87)</td>
<td></td>
</tr>
</tbody>
</table>

\( [(\text{tmp})_2\text{BCl}] \)

| \( \text{CH}_2\text{Cl}_2 \) | 34.5 | \((\text{tmp})_2\text{B}^+ \) (90) |
| \( \text{CH}_2\text{Cl}_2 \) (40°C) | 26.0 | \( n\text{tmp}_2\text{BCl}_2^-n \) (90) |
| \( \text{AlCl}_3 \) | \( \text{CH}_2\text{Cl}_2 \) | 35.6 | \((\text{tmp})_2\text{B}^+\text{AlCl}_4^- \) (91) |
| \( \text{SbCl}_3 \) | \( \text{CH}_2\text{Cl}_2 \) | 35.6 | \((\text{tmp})_2\text{B}^+\text{SbCl}_6^- \) (92) |

Table 9.1: Experimental results for borinium ion synthesis (refs.4h,10); \( \dagger \)small peak: possibly hydrolysis.

9.5 STRUCTURAL CONSIDERATIONS

A downfield shift relative to that of the 3-coordinate precursor
(86) or (87) is indicative of two coordinate cation formation, although
the magnitude is less than that which might have been expected. This is
attributed to electron donation by the amine groups into both vacant
orbitals \[1,4h,10\].

In the starting bisaminoboron chloride, nitrogen to boron \( \pi-\pi \)
backbonding is reduced \[1,4h\]. A theoretical study of electron
delocalisation in the amino-borane system is available \[12\]. On
abstraction of \( X^- \) a geometric change to linearity decreases the steric
strain with concomitant increase in stabilisation by \( \pi-\pi \) backbonding.
Figure 9.4: $^{11}B$ NMR Spectrum of (tmp)$_2$BCl (90) (298K, CH$_2$Cl$_2$).

Figure 9.5: $^{11}B$ NMR Spectrum of (tmp)$_2$B\textsuperscript{+}AlCl$_4$ (91) (298K, CH$_2$Cl$_2$).
The situation for \((\text{tmp})_2B^+\) is exactly analogous (Figure 9.3) \(^{[10]}\).

![Diagram]

**Figure 9.3:** Borinium ion stabilisation by \(\pi-\pi\) backbonding.

It is of interest to note that, in the case of \((\text{tmp})_2BCl\) (86), the cation appeared to be present at normal temperatures in the absence of a Lewis acid (Figure 9.4). The more shielded species may be attributed to \((\text{tmp})_2BCl_2^–\), although on the basis of the results obtained in Chapter 6, the chloroboron species (86) would not be expected to accept \(Cl^–\). The \(^{11}\)B chemical shift is not as shielded as would be anticipated for a 4-coordinate boron species. Raising the temperature to 40 °C gave coalescence of these two peaks yielding an \(^{11}\)B peak corresponding to the expected shift for \((\text{tmp})_2BCl\) (86) \(^{[10]}\). Further temperature dependent studies to low values may prove interesting. On addition of \(\text{AlCl}_3\) the characteristic deshielded peak due to the cation was observed \(^{[10]}\) (Figure 9.5). The general reaction \(R_2BCl\) with Lewis acid was found to be most efficient at low temperature.

The two coordinate boron cations (88) and (91) did not decompose significantly when left in solution-\(\text{CH}_2\text{Cl}_2\) for two weeks at ambient temperature. The results (Table 9.1) indicate \(\text{AlCl}_3\), \(\text{CH}_2\text{Cl}_2\) and low temperatures gave superior results. These were therefore the conditions used in the attempted generation of \(\text{Ar}_2B^+\text{AlCl}_4^-\) (85) from \(\text{Ar}_2BCl\) (74).
9.6 ATTEMPTED SYNTHESIS OF $\text{Ar}_2\text{B}^+$

The solution of $\text{Ar}_2\text{BCl}$ in $\text{CH}_2\text{Cl}_2$ turned black on addition of $\text{AlCl}_3$, but both $^{11}\text{B}$ NMR and $^{19}\text{F}$ NMR showed only the characteristics of unchanged $\text{Ar}_2\text{BCl}$, (ie. an equivalence of o-CF$_3$ groups on borinium ion formation, releasing the steric strain would be predicted). Notwithstanding the bulk of the Ar group and the electron clouds around the fluorines which could act to stabilise the two coordinate cation, the instability may arise from the electron withdrawing nature of the ring. In previous examples (Table 9.1) $\pi$-electron donation stabilised the two coordinate boron. The carbon fragment can play a stabilising role $^4$, for example the downfield $^{13}\text{C}$ shift of the system shown in Figure 9.6 $^4b$ not only indicates cation formation but also charge delocalisation with a considerable contribution of the canonical forms (C) and (F) $^4b$.

![Figure 9.6: A contribution to borinium ion stabilisation by a carbon substituent.](image)

A similar stabilisation by a carbon fragment in a borinium system $^4i$ is shown in Figure 9.7. This moiety has been shown also to stabilise a boron-carbon double bond $^4a$.

![Figure 9.7](image)
The Ar₂B⁺ cation does not form in this way but it is evident in the mass spectra of both Ar₂BCl (74) and Ar₃B (75), illustrating that Ar₂B⁺ can be formed by electron bombardment of these organoboron species. This is an interesting observation but proves only that the lifetime of this species is sufficient to be detected by the mass spectrometer, i.e. of the order of approximately $10^{-10} \rightarrow 10^{-3}$ seconds [13].

It would be interesting to study these systems with a "C-B-C" backbone, and of particular interest to succeed with the reaction:

$$\text{Mes}_2\text{BF} + \text{AlCl}_3 \rightarrow \text{Mes}_2\text{B}^+\text{AlCl}_3\text{F}^-$$

So far [2] a bis tertiary butyl boron or even a bis mesityl boron has eluded detection. SbF₅ or even PF₅ may prove better F⁻ acceptors than AlCl₃. Perhaps by the use of the more bulky supermesityl group this may be possible. However, a synthetic route to the starting material must be available, and possibly this area of work should initially be attempted at low temperature.

Preparation of the initial R₂BF derivative may be advantageous for two reasons: (i) the limited space around B in the initial R₂BX starting material, and (ii) thermodynamic favourability of M⁻F bond formation (where M = Sb, Al).

Large groups, e.g. Supermes, Mes are already known in the stabilisation of two coordinate B (Figure 9.8).

$$R_1 \text{Ph}=\text{B}=\bigtriangleup \text{Mes}$$

**Figure 9.8:** A phosphaborene; $R_1 = \text{Supermes}$ (ref.14); $R_2 = \text{tmp.}$
9.7 EXPERIMENTAL DETAILS

9.7.1 Synthesis of \( \text{R}_2\text{BCl} \) and \( \text{R}_2\text{B}^+\text{AlCl}_4^- \) (\( \text{R} \equiv \text{tmp}, \text{^3Pr}_2\text{N} \))

\( \text{(} \text{^3Pr}_2\text{N})_2\text{BCl} \) and \( \text{(} \text{^3Pr}_2\text{N})_2\text{B}^+\text{AlCl}_4^- \) were synthesised according to Higashi et al.\([4h]\) and \( \text{(tmp)}_2\text{BCl} \) and \( \text{(tmp)}_2\text{B}^+\text{AlCl}_4^- \) according to Nöth et al.\([10]\). The two borinium ions were isolated pure from low temperature crystallisation from \( \text{CH}_2\text{Cl}_2 \). \( \text{^13C} \) and \( \text{^1H} \) data are presented in Table 9.2 and \( \text{^11B} \) NMR data in the text.

<table>
<thead>
<tr>
<th>( \text{^1H} (\delta/\text{ppm}) )</th>
<th>( \text{^13C} (\delta/\text{ppm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{(} \text{^3Pr}_2\text{N})_2\text{BCl} ) (C( \text{D}_6 )) (87)‡</td>
<td></td>
</tr>
<tr>
<td>3.3 (1H, sept, 7.0Hz)</td>
<td>60.9 (s)</td>
</tr>
<tr>
<td>1.0 (6H, d, 7.0Hz)</td>
<td>55.0 (s)</td>
</tr>
<tr>
<td>( \text{(tmp)}_2\text{BCl} ) (C( \text{D}_6 )) (86)</td>
<td></td>
</tr>
<tr>
<td>1.4 (24H, CH\text{\textsubscript{3}})</td>
<td>40.4 (ring C)</td>
</tr>
<tr>
<td>1.5 (24H, CH\text{\textsubscript{3}})</td>
<td>32.8 (CH\text{\textsubscript{3}})</td>
</tr>
<tr>
<td></td>
<td>17.9 (ring C)</td>
</tr>
<tr>
<td>( \text{tmp}_2\text{B}^+\text{AlCl}_4^- ) (91)</td>
<td></td>
</tr>
<tr>
<td>1.7 (12H, ring H)</td>
<td>58.1 (C-CH\text{\textsubscript{3}})</td>
</tr>
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<td>37.3 (ring C)</td>
</tr>
<tr>
<td></td>
<td>30.9 (CH\text{\textsubscript{3}})</td>
</tr>
<tr>
<td></td>
<td>16.1 (ring C)</td>
</tr>
</tbody>
</table>

Table 9.2: \( \text{^1H} \) and \( \text{^13C} \) NMR data for compounds (86)–(88) and (91); agrees well with Nöth et al.\((\text{ref.4h,10})\); \( \text{^1H} \)MS (Intensity%) \( \text{EI: 247 [50,(M+1)\text{\textsuperscript{+}}]} \), 211 [100, (M-Cl)\text{\textsuperscript{-}}], 102; \( \text{CI: 269 [100, rearrangement of } \text{^3Pr}_2\text{N groups on boron}.\)
9.7.2 Preparation of \( \text{^{iPr}_2N}_2B^+\text{SbCl}_6^- \) (89)

The best synthetic route to this borinium ion was by mixing in 1:1 stoichiometry at room temperature \( \text{SbCl}_5 \) (2.79g, 9.3 mmol) and \( \text{^{iPr}_2N}_2\text{BCl} \) (2.3g, 9.3 mmol) as neat liquids (no results were obtained in solution - see Table 9.1).

9.7.3 Preparation of \( \text{(tmp)}_2B^+\text{SbCl}_6^- \) (92)

\( \text{SbCl}_5 \) (3.3g, 11.0 mmol) in \( \text{CH}_2\text{Cl}_2 \) (15 ml) was added dropwise to a stirred solution of \( \text{(tmp)}_2\text{BCl} \) (3.6g, 11.0 mmol) in \( \text{CH}_2\text{Cl}_2 \) (40 ml) at room temperature. This yielded a deep brown/black solution, with quantitative conversion to the borinium ion according to the \( ^{11}\text{B} \) NMR [4h].

9.7.4 Attempted Preparation of \( \text{R}_2B^+\text{BCl}_4^- \) (R = \( \text{^{iPr}_2N} \), tmp)

Reaction of \( \text{(tmp)}_2\text{BCl} \) and \( \text{^{iPr}_2N}_2\text{BCl} \) with \( \text{BCl}_3 \) respectively at room temperature (1:1 stoichiometry) 12 mmol quantities in \( \text{CH}_2\text{Cl}_2 \) (60 ml) gave no evidence of cation formation [2] (Table 9.1).

\( \text{Ar}_2\text{BCl} \) (4) was synthesised via the route described in Section 8.9.5.

9.7.5 Attempted Preparation of \( \text{Ar}_2B^+\text{AlCl}_4^- \) (85)

\[
\text{Ar}_2\text{BCl} \ (4) \xrightarrow{\text{AlCl}_3} \text{Ar}_2B^+\text{AlCl}_4^- \ (85)
\]

Freshly sublimed \( \text{AlCl}_3 \) (ca. 0.4g, 3 mmol) was added as a slurry in \( \text{CH}_2\text{Cl}_2 \) (10 ml) to a stirred solution of \( \text{Ar}_2\text{BCl} \) (1.71g, 2.8 mmol) in \( \text{CH}_2\text{Cl}_2 \) (15 ml) at -20 °C. The reaction mixture became deep brown. It
was allowed gradually to reach room temperature and stirred for 4 hours. Any unreacted AlCl₃ and other solids were removed by filtration, and the ¹¹B solution spectrum of the filtrate recorded (CH₂Cl₂).

This gave ¹¹B +47 ppm (broad singlet) and a characteristic ¹⁹F NMR indicative of unreacted starting material. ¹⁹F δ: -58.4, -58.5 ppm (o-CF₃) and -65.2 ppm (p-CF₃). No borinium ion formation, i.e. no apparent Cl⁻ abstraction, was observed. A few peaks (-137, -131 ppm) in the ¹⁹F NMR may be indicative of AlCl₃ attack at the fluorine site (CF₃) on the ring.

9.8 REFERENCES


   b) Dr. Bartsch (University of Sussex), Seminar at Durham University, 6th May, 1987 "Low Coordinated Phosphorus Compounds".


CHAPTER TEN

NMR STUDY OF TETRAHEDRAL COMPLEXES OF BORON(III)
10.1 INTRODUCTION

The aim of these preliminary investigations was to detect substitution products by $^{11}$B NMR, and to study factors which affect exchange within four coordinated borate anions, for example, solvent, temperature, substituents, cation and concentration. If the exchange rate is slow on the NMR timescale, each species possesses a distinctive chemical shift which can be predicted by the pairwise interaction calculation, provided that the shifts of three members of the series are known (Section 10.12) [1].

The present study involved the observation of $\text{BX}_4^-$ (X = F, Cl, Br, I) with a variety of counterions [eg. $\text{Bu}_4\text{N}^+$, $\text{Et}_4\text{N}^+$, $\text{C}_6\text{F}_5\text{PX}_3^+$ (X = Br or Cl)]. The major interest was their behaviour in the presence of the anions competing for coordination (NCS$^-$, CN$^-$, N$_3^-$, NCO$^-$). Three approaches were used to prepare the substitution products:

1. Addition of a metal (Ag$^+$, Cs$^+$) salt of the anion required, to $\text{R}_4\text{N}^+\text{BX}_4^-$ (X = Cl, Br, I). This is preferred when the substitution product is to be isolated, as it is easy to remove the insoluble metal halide.

2. The reaction of the three-coordinated boron species, for example $\text{BI}_3$ or $\text{BBr}_3$ with $\text{Z}^{\oplus}\text{X}^\ominus$ where X is one of the substituting anions.

3. With the B/F system the strength of the B–F bond may preclude substitution into the boron fluorides, i.e. $\text{BF}_4^-$, hence "reverse" substitution was employed in which fluoride was substituted into the $\text{B(NCS)}_4^-$ system. It was however possible to establish this system via $\text{BF}_3\cdot\text{Et}_2\text{O} + \text{LiNCS}$ (see Section 10.9.1).
10.2 SOLVENT TYPE

The original solvent used in the $\text{BCl}_4^-$ systems was nitromethane, but with $\text{BI}_4^-$ complex spectra were observed, possibly due to solvent interaction yielding black insoluble products. This led to an exploration of a range of solvents (Table 10.1) in an attempt to diagnose their effect, and ultimately obtain a solvent of optimum utility - allowing sufficient solubility of the reactants (possessing a high enough dielectric constant), while not becoming too involved in the reaction by either coordination to the boron [Figure 10.1(a)], or by reaction with one of the pseudo-halogeno anions: $\text{CN}^-$ interaction with $\text{CH}_2\text{Br}_2$ may generate the $\text{CH}_2\text{BrCN}$ species which could act as a coordinating moiety and become involved in the system [Figure 10.1(b)]. Any attack of the anion on the solvent will reduce the concentration of the anion. Its effective concentration may therefore become insufficient to make formation of the four-coordinated species possible. Halogen exchange is significant with $\text{BBr}_4^-$ in $\text{CH}_2\text{Cl}_2$ (Table 10.1).

![Figure 10.1](image.png)

The reverse substitution of $\text{F}^-$ into $\text{R}_4\text{N}^+\text{B(NCS)}_4^-$ involved the use of caesium fluoride for which the optimum solvent was tetraglyme, since CsF is sufficiently soluble in it, and $\text{F}^-$ is not too solvated to prevent its action as a nucleophile. Thus the choice of solvent is crucial if unwanted interactions are to be minimised.
<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>COMMENTS</th>
</tr>
</thead>
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<td>CH₂Cl₂</td>
<td>Best results with R₄N⁺BCl₄⁻.</td>
</tr>
<tr>
<td></td>
<td>With R₄N⁺BI₄⁻, R₄N⁺BBr₄⁻, same chloride ion incorporated into the system, see effect on ¹¹B NMR (below).</td>
</tr>
<tr>
<td></td>
<td>With the cyanide system, CN⁻ attack on the solvent is possible.</td>
</tr>
<tr>
<td>CH₂Br₂</td>
<td>Best results with R₄N⁺BBr₄⁻.</td>
</tr>
<tr>
<td>CH₂I₂</td>
<td>Best results with R₄N⁺BI₄⁻.</td>
</tr>
<tr>
<td>PhNO₂</td>
<td>Best results in the case of C₆F₅PB₃⁺, C₆F₅PCl₃⁺, ArPCl₃⁺ etc. Large cations which are of very limited solubility in the halogenated solvents.</td>
</tr>
<tr>
<td>PhCN</td>
<td>These solvents strongly interact with 3-coordinate boron species.</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>Good solvent for R₄N⁺BX₄⁻ (X ≡ I, Br, Cl) No apparent interaction.</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>Ideal for F⁻ (see Section 10.9.1).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>SOLVENT</th>
<th>³¹P δ(ppm)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>BI₃</td>
<td>CH₃CN</td>
<td>-85.1</td>
<td>coordinates: CH₃CN·BI₃</td>
</tr>
<tr>
<td>BI₃</td>
<td>PhCN</td>
<td>-85.3</td>
<td>coordinates: PhCN·BI₃</td>
</tr>
<tr>
<td>BI₃</td>
<td>CH₂Cl₂</td>
<td>7.1</td>
<td>left overnight ≡ BCl₄</td>
</tr>
<tr>
<td>BI₃</td>
<td>CH₂I₂</td>
<td>-5.6</td>
<td></td>
</tr>
<tr>
<td>BI₄⁻</td>
<td>Hexane</td>
<td>16.2</td>
<td>Decomposition (BI)ₓ ! [4]</td>
</tr>
<tr>
<td>BI₄⁻</td>
<td>CH₃CN</td>
<td>16.0</td>
<td>Decomposition !</td>
</tr>
<tr>
<td>BI₄⁻</td>
<td>PhCN</td>
<td>-127.7</td>
<td></td>
</tr>
<tr>
<td>BI₄⁻</td>
<td>CH₂Cl₂</td>
<td>-127.7</td>
<td></td>
</tr>
<tr>
<td>BI₄⁻</td>
<td>CH₂I₂</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td>BI₄⁻</td>
<td>CH₂Cl₂</td>
<td>-126.7</td>
<td>Stable at RT &gt; 1 week</td>
</tr>
<tr>
<td>Bi₄⁻</td>
<td>CH₂I₂</td>
<td>-126.7</td>
<td></td>
</tr>
<tr>
<td>BBr₃</td>
<td>PhCN</td>
<td>-19.8</td>
<td>coordinates: PhCN·BBr₃</td>
</tr>
<tr>
<td>BBr₃</td>
<td>CH₃CN</td>
<td>-19.8</td>
<td>coordinates: CH₃CN·BBr₃</td>
</tr>
<tr>
<td>BBr₄⁻</td>
<td>CH₂Cl₂</td>
<td>-24.5</td>
<td>BBr₄⁻ (left overnight) [2]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-14.9</td>
<td>BBr₃Cl⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-6.5</td>
<td>BBr₂Cl₂⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.71</td>
<td>BBrCl₃⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.6</td>
<td>BCl₄⁻</td>
</tr>
</tbody>
</table>

Table 10.1: General solvent properties (above); solvent effects on ¹¹B chemical shifts (below).
Several possible methods have been postulated [2] including (i) dissociation to produce the trihalide and free anion, \( \text{BX}_4^- \rightleftharpoons \text{BX}_3^+ + \text{X}^- \) and (ii) nucleophilic attack of \( \text{X}^- \) on \( \text{BY}_4^- \). The former can be followed by recombination (Equation 10.1) or exchange via a bridged species (Equation 10.2), whilst the latter would clearly involve a double negative charge in the transition state (Equation 10.3).

\[
\text{BX}_3 + \text{Y}^\ominus \rightleftharpoons \text{BX}_3\text{Y}^\ominus \tag{10.1}
\]

\[
\text{BX}_3 + \text{BY}_4^\ominus \rightleftharpoons \left[ \text{X}_3\text{B}\text{Y}\text{BY}_3 \right]^\ominus \rightleftharpoons \text{BX}_3\text{Y}^\ominus + \text{BY}_3 \tag{10.2}
\]

\[
\text{X}^- + \text{BX}_4^- \longrightarrow \left[ \begin{array}{c}
\text{X}^\delta^- \\
\text{X}^\delta^-
\end{array} \right] \longrightarrow \tag{10.3}
\]

In the present work initial investigations involved the salt \( R_4\text{N}^+\text{BBr}_4 \) (\( R = \text{Et} \)) with \( \text{CN}^- \), \( \text{NCO}^- \) and \( \text{N}_3^- \). Results are presented in Section 10.4.1. A small number of averaged peaks was obtained and no pairwise correlation fitted [1], hence an exchanging process was postulated. Similar exchanging systems were found with \( R_4\text{N}^+\text{BI}_4^- \) and \( \text{CN}^- \), \( \text{NCO}^- \) and \( \text{N}_3^- \) respectively, for which results are described in Section 10.4.2.
Selected results are presented (Table 10.2) for the $\text{Et}_4\text{NBBr}_4$ system with the anions $\text{CN}^-$, $\text{NCO}^-$ and $\text{N}_3^-$ competing for coordination.

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>SOLVENT</th>
<th>$^{11}$B NMR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Et}_4\text{N}^+\text{BBr}_4^- + \text{AgCN}$</td>
<td>$\text{CH}_3\text{CN}$</td>
<td>$+2.0(\text{m}), +0.2(\text{m}), -24.0(\text{s})$</td>
</tr>
<tr>
<td>$\text{Et}_4\text{N}^+\text{BBr}_4^- + \text{Bu}_4\text{NN}_3$</td>
<td>$\text{CH}_2\text{Br}_2$</td>
<td>$+2.2(\text{m}), -2.2(\text{m}), -10.0(\text{m}), -24.1(\text{s})$</td>
</tr>
<tr>
<td>$\text{Et}_4\text{N}^+\text{BBr}_4^- + \text{AgNCO}$</td>
<td>$\text{CH}_2\text{Br}_2$</td>
<td>$-14.5(\text{m}), -19.0(\text{m}), -24.5(\text{m})$</td>
</tr>
</tbody>
</table>

Table 10.2: The bromoborate systems with $\text{CN}^-$, $\text{N}_3^-$, $\text{NCO}^-$; parentheses indicate signal intensity.

In the cyanide system the results (Table 10.2) illustrate the effect of addition of 1 equivalent of cyanide. If two equivalents are added, signals on average occur at $+4.0$, $+0.2$ and $-23.0$ ppm. In the postulated exchange equilibrium (Equation 10.4) stabilisation of the three coordinate boron by $\pi$-bonding may be effected, via the possible resonance form $\overset{\pi}{\text{B}}\equiv\text{C}=$N$^\ominus$. 

$$\text{BBr}_3\text{CN}^- \rightleftharpoons \text{BBr}_3 + \text{CN}^- \rightleftharpoons \text{BBr}_2\text{CN} + \text{Br}^- \quad (10.4)$$

Attempts to generate the $\text{BBr}_4^-$ systems by addition of the anion to $\text{BBr}_3$ in PhCN failed. The solvent appeared to compete effectively with the anion for the three-coordinate boron species, complicating the spectral interpretation (Table 10.1).
10.4.2 Tetrapropylammonium Tetraiodoborate

Selected results are presented (Table 10.3) for the \( \text{Pr}_4\text{N}^+\text{BI}_4^- \) system with the anions \( \text{CN}^- \), \( \text{NCO}^- \) and \( \text{N}_3^- \) competing for coordination. \( \text{BI}_4^- \) decomposes in acetonitrile (see Table 10.1). It should be noted here that the thiocyanate (NCS) ligand substituted into all the haloboron systems to yield the complete set of anions in each case, however thiocyanate (NCS) appears to be an exceptional ligand and will be considered separately (Section 10.9).

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>SOLVENT</th>
<th>(^{11}\text{B NMR (ppm)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pr}_4\text{N}^+\text{BI}_4^- + \text{AgCN} )</td>
<td>( \text{CH}_2\text{I}_2 )</td>
<td>-128.7(m), -89.0(w)<em>, -84.0(w)</em></td>
</tr>
<tr>
<td>( \text{BI}_3^+ + \text{Bu}_4\text{N}^+\text{CN}^- )</td>
<td>( \text{CH}_2\text{I}_2 )</td>
<td>-101.1(m), -88.7(w)<em>, -84.9(m)</em></td>
</tr>
<tr>
<td>( \text{BI}_3^+ + \text{Bu}_4\text{N}^+\text{N}_3^- )</td>
<td>( \text{CH}_2\text{I}_2 )</td>
<td>-126.3(m), -85.8(m)*</td>
</tr>
<tr>
<td>( \text{BI}_3^+ + \text{Et}_4\text{N}^+\text{NCO}^- )</td>
<td>( \text{CH}_2\text{I}_2 )</td>
<td>-126.0(m), -89(m)<em>, -84(m)</em>, -49(m)</td>
</tr>
</tbody>
</table>

Table 10.3: The iodoborate systems with \( \text{CN}^- \), \( \text{N}_3^- \), \( \text{NCO}^- \); \( ^\dagger \)parentheses indicate signal intensity; \( ^* \)signals are unassigned but are common to each system.

In view of the fact that R. Ali \[3\] had not observed the exchange phenomenon in her experiment with \( \text{BCl}_4^- \) and AgCN, the rapid exchange observed here was somewhat surprising. Initially it was postulated that the difference could be due to the lower strengths of the boron-bromine and boron-iodine bonds, in comparison with boron-chlorine. However, when the system \( \text{R}_4\text{N}^+\text{BCl}_4^- \) was investigated (Section 10.4.3) similarly rapid exchange was again observed.
Figure 10.1a: One dimensional $^{11}$B NMR spectra for the system $\text{BCl}_4^{-} \cdot \text{Et}_4\text{N}^+ \cdot \text{Et}_4\text{N}^+ \cdot \text{NCO}^{-}$ in $\text{CH}_2\text{Cl}_2$. 
10.4.3 Tetraethylammonium Tetrachloroborate

Selected results are presented (Table 10.4) for the $\text{Et}_4\text{N}^+\text{BCl}_4^-$ system with the anions $\text{CN}^-$, $\text{NCO}^-$ and $\text{N}_3^-$ competing for coordination.

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>SOLVENT</th>
<th>$^{11}\text{B NMR (ppm)}$</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Et}_4\text{N}^+\text{BCl}_4^- + \text{AgCN}$</td>
<td>$\text{CH}_3\text{CN}$</td>
<td>+2.0(m), -2.0(m)</td>
<td>[4]</td>
</tr>
<tr>
<td>$\text{Et}_4\text{N}^+\text{BCl}_4^- + \text{Bu}_4\text{N}^+\text{N}_3^-$</td>
<td>$\text{CH}_2\text{Cl}_2$</td>
<td>0.0(m), -4.2(m)</td>
<td></td>
</tr>
<tr>
<td>$\text{Et}_4\text{N}^+\text{BCl}_4^- + \text{Et}_4\text{N}^+\text{NCO}^-$</td>
<td>$\text{CH}_2\text{Cl}_2$</td>
<td>7.6(m), 6.9(s), 1.0(w,br), -1.1(m), -11.7(m)$^\dagger$</td>
<td></td>
</tr>
</tbody>
</table>

**Table 10.4**: The chloroborate systems with $\text{CN}^-$, $\text{N}_3^-$, $\text{NCO}^-$; $^\dagger$parentheses indicate signal intensity; $^\ddagger$See Figure 10.1;

In the isocyanate system there exists the possibility of coordination through oxygen or nitrogen, *linkage isomerism* [5], since the donor atoms are both hard centres. None of the peaks could be assigned to definite substitution products by application of the pairwise interaction calculation. For example, if the assumption of unique nitrogen coordination is made and the signal at 7.6 ppm is assigned to $\text{BCl}_4^-$, -11.7 ppm to $\text{B(NCO)}_4^-$ and +6.9 ppm to the first substitution product $\text{B(NCO)}\text{Cl}_3^-$, the calculated values for the two intermediate substitution products are 3.6 ppm [$\text{B(NCO)}_2\text{Cl}_2$] and -2.6 ppm [$\text{B(NCO)}_3\text{Cl}^-$]. (In principle, of course, $\text{NCO}^-$ could give $^{14}\text{N}$ coupling, and may provide a means of distinguishing oxygen and nitrogen bonded isomers, if J-values could be measured).

The $^{11}\text{B 2-D NMR}$ [6-10] spectrum confirmed the presence of seven different boron species and the existence of exchange. A possible exchange mechanism is shown in Equation 10.5. The $^{11}\text{B NMR}$ spectrum is illustrated in Figure 10.1(a) and the 2D NMR spectrum in Figure 10.1(b).
Figure 10.1b: Two dimensional $^{11}B$ NMR spectra for the system $BCl_3$·$Et_2O$ + $Et_4N$·$NCO^-$ in $CH_2Cl_2$. 
10.5 EFFECT OF CHANGING TEMPERATURE AND CONCENTRATION

Warming gave no change in the NMR for any of the systems where it was attempted. It was avoided for the tetraiodoborate systems since decomposition of this species is inevitable. The effect of cooling the system \( \text{Et}_4\text{N}^+\text{BB}r^-/\text{AgCN} \) in \( \text{CH}_2\text{Br}_2 \) to \(-60^\circ\text{C}\) was also investigated, in an attempt to slow the exchange sufficiently to allow the observation of the substitution products. No change was detected from the results given in Section 10.2.1.

Variation in concentration from 0.5 equivalent with respect to the tetrahaloborate present to a three-fold excess gave an exactly similar exchange phenomenon, with peaks slightly shifted (see example, Section 10.4.1). The concentrations used in a typical exchange experiment were in general of the order of 50-70 mg cm\(^{-3}\).

10.6 EFFECT OF CHANGING COUNTERION WITH THE \( \text{BCl}_4^- \) SYSTEM

Since R. Ali \(^3\) had used \( \text{C}_6\text{F}_5\text{PCl}_3^+ \) as the counterion it seemed that it could be the nature of the counter-cation, rather than the halogen involved which affects the tendency of the \( \text{X}^- \) ion to exchange with other ligands in the \( \text{BX}_4^- \) anion. The next obvious step was to investigate the effect of changing the cation.
Figure 10.2a: One dimensional $^{11}$B NMR spectra for the system $\text{Ph}_4\text{P}^+\text{BCl}_4^- + \text{AgCN}$ in $\text{CH}_3\text{CN}$. 
10.6.1 Ph₄P⁺ Cation

Ph₄P⁺BCl₄⁻ (93) was synthesised. This appeared to reduce the exchange rate with CN⁻, since five peaks were evident (Table 10.5), but shifted slightly downfield from their expected positions (as calculated from pairwise interactions) [see Figure 10.2(a)]. A two-dimensional (2-D) NMR spectrum of this system [Figure 10.2(b)] showed evidence of exchange. Exchange is evident between 'BCl₄⁻' and the first substitution species, and between 'BCl₄⁻' and the second species. All the exchange has been associated with 'BCl₄⁻', possibly because of its greater intensity observed in the 1-D NMR spectrum [Figure 10.2(a)]. Exchanges between other species may not be detectable due to their relatively low concentrations.

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>SOLVENT</th>
<th>¹¹B NMR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₄P⁺BCl₄⁻ (93)</td>
<td>CH₃CN</td>
<td>7.1(s), 1.7(w), -0.9(w), -2.1(w), -3.6(w)</td>
</tr>
</tbody>
</table>

Table 10.5: The chloroborate system (93) with CN⁻ (Ph₄P⁺ counterion); ‡Values calculated by pairwise interactions assuming BCl₄⁻ 7.1 ppm; B(CN)₄⁻ -3.6 ppm; BCl₃CN⁻ 1.7 ppm; BCl₂(CN)₂⁻ -1.9 ppm and B(CN)₃Cl⁻ -3.6 ppm; parentheses indicate signal intensity;.

10.6.2 C₆F₅PCl⁺ Cation

The reaction shown in Equation 10.6 was carried out, and results were exactly analogous to those reported by R. Ali [3], namely, B(CN)⁻ -9.0 ppm, B(CN)₃Cl⁻ -3.4(ppm), B(CN)₂Cl₂⁺0.6(s) ppm, B(CN)Cl₃⁺4.5(s) ppm and BCl₄⁺7.7(m) ppm [assuming B(CN)₄⁻ -9.0 ppm, B(CN)₃Cl⁻ -3.4 ppm and BCl₄⁺7.7 ppm]. The calculated results for B(CN)₂Cl₂⁺0.7 ppm) and B(CN)Cl₃⁺(+4.5 ppm) from pairwise interaction, agree well with
Figure 10.2b: Two dimensional $^1$H NMR spectra for the system $\text{Ph}_4\text{P}^-\text{BCl}_4^- + \text{AgCN}$ in $\text{CH}_3\text{CN}$. 
the data obtained by experiment, and with previous reported data [2].

\[
C_{6}F_{5}PCl_{3}^{+}BCl_{4}^{-} (94) + AgCN \xrightarrow{PhN02} \tag{10.6}
\]

10.6.3 ArPCl\textsuperscript{+}\textsubscript{3} Cation

Because of the significant interest in the Ar substituent, 2,4,6-
tristrifluoromethylphenyl, the system ArPCl\textsuperscript{+}DCl\textsuperscript{-} (95) was explored with
cyanide, and three of the substitution products were observed in the \textsuperscript{11}B
NMR at ambient temperature (Table 10.6). It should be noted that with a
large excess of CN\textsuperscript{-}, substitution into ArPCl\textsuperscript{+} causes decomposition to
ArPCl\textsubscript{2} (12) [verified by the \textsuperscript{31}P NMR data \(\delta +145\) ppm (septet) \(^4J_{PF} +62.4\)
Hz (see Chapter 2)], possibly via the elimination of ClCN.

<table>
<thead>
<tr>
<th>\textsuperscript{11}B NMR (\delta)(ppm)</th>
<th>EXPT</th>
<th>CALC\textsuperscript{‡}</th>
<th>ANIONIC SPECIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>-9.5</td>
<td>-9.5</td>
<td>B(CN)\textsubscript{4}</td>
<td></td>
</tr>
<tr>
<td>-3.4</td>
<td>-3.4</td>
<td>B(CN)\textsubscript{3}Cl\textsuperscript{-}</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>1.5</td>
<td>B(CN)\textsubscript{2}Cl\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>5.2</td>
<td>B(CN)Cl\textsubscript{3}</td>
<td></td>
</tr>
<tr>
<td>7.7</td>
<td>7.7</td>
<td>BCl\textsubscript{4}</td>
<td></td>
</tr>
</tbody>
</table>

Table 10.6: \textsuperscript{11}B NMR data for ArPCl\textsuperscript{+}DCl\textsuperscript{-} (95) + AgCN (PhN02);
\textsuperscript{‡}calculated by pairwise interaction (ref.1)
using the bracketed values.

10.7 BROMINE SYSTEMS: C\textsubscript{6}F\textsubscript{5}PBr\textsuperscript{+}\textsubscript{3} Cation

To investigate BBr\textsubscript{4} systems, C\textsubscript{6}F\textsubscript{5}PBr\textsuperscript{+}BBr\textsubscript{-} (96) was prepared
according to Equation 10.7 [3].

\[
C_{6}F_{5}Br \xrightarrow{Mg} C_{6}F_{5}MgBr + PBr_{3} \xrightarrow{PBr_{2}} C_{6}F_{5}PBr_{2} \xrightarrow{Br_{2}} C_{6}F_{5}PBr_{4} \xrightarrow{BBr_{3}} C_{6}F_{5}PBr_{3}BBr\textsubscript{4}^{-} (96) \tag{10.7}
\]
Figure 10.3: \(^{11}B\) NMR data for \(\text{C}_6\text{F}_5\text{PBr}_3 \cdot \text{BBr}_4^- + \text{Ag}^+\text{CN}^-\) in \(\text{PhNO}_2\); the observed broad background was attributed to the poor solubility of the salt.
Additionally it was hoped, by synthesis of $\text{C}_6\text{F}_5\text{P}^+\text{BI}_4^-$ (97) to extend this work to the iodide systems. Unfortunately, the instability of these P(V) cations severely limited their usefulness. In PhNO$_2$ apparent dissociation of the tetrabromoborate salt occurred, giving a signal at +21 ppm in the $^{31}$P NMR. This suggested the formation of $\text{C}_6\text{F}_5\text{PBr}_2$ which then complexed with the BBr$_3$ present (Equation 10.8).

$$\text{C}_6\text{F}_5\text{PBr}_3^+\text{BBr}_4^- \rightarrow \text{C}_6\text{F}_5\text{PBr}_2 + \text{BBr}_3 + \text{Br}_2 \rightarrow \text{C}_6\text{F}_5\text{PBr}_2 \cdot \text{BBr}_3 \quad (98) \quad (10.8)$$

This agreed well with data obtained by R. Ali [3]. Numerous efforts were made to generate $\text{C}_6\text{F}_5\text{PBr}_3^+\text{BBr}_4^-$ and to substitute with CN$^-$. On one occasion the P(V) cation remained intact while all the substitution products in the $^{11}$B NMR spectrum were observed (Figure 10.3). (Table 10.7)

<table>
<thead>
<tr>
<th>$^{11}$B NMR $\delta$(ppm)</th>
<th>ANIONIC SPECIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXPT</td>
<td>CALC‡</td>
</tr>
<tr>
<td>-9.0</td>
<td>(-9.0)</td>
</tr>
<tr>
<td>-11.1</td>
<td>(-11.1)</td>
</tr>
<tr>
<td>-13.8</td>
<td>-14.3</td>
</tr>
<tr>
<td>-19.5</td>
<td>-18.7</td>
</tr>
<tr>
<td>-24.2</td>
<td>(-24.2)</td>
</tr>
</tbody>
</table>

Table 10.7: $^{11}$B NMR data for $\text{C}_6\text{F}_5\text{PBr}_4^+\text{BBr}_4^- + \text{AgCN (PhNO}_2)$; $‡$calculated by pairwise interaction methods (ref.1) using the bracketed values.

10.8 THE WHOLE SYSTEM

10.8.1. Introduction

$$A^+ + BX^- \rightarrow C^+D^-$$

If $A^+$ can affect the exchange rate then the added cation $C^+$ must also be considered. It has already been seen that the rate of exchange
can be affected by the B-X (X = I, Br, Cl, F) bond strength, and the ability of X to back-donate \( \pi \)-electrons \[2\]. D\(^-\) can also affect the rate of exchange. For example, the properties of NCS\(^-\) make it an exceptional nucleophile (Section 10.9). Substitution into the cationic species, C\(_6\)F\(_5\)PCl\(_3\)\(^+\), ArPCl\(_3\)\(^+\), is inevitable in the presence of powerful nucleophiles. This inherent change in the cation affects its nature, and therefore presumably its effect on BX\(_n\)Y\(_{4-n}\).

The discussion which follows is highly speculative and requires more experimental work before it can be considered complete. However, since this piece of work was not the focus of the thesis it was not considered appropriate to pursue this further in the limited time available.

### 10.8.2 Discussion of the Results

The most prominent difference between the two groups is the much larger proportion of halogen in the Type 2, and thus presumably the presence of electron withdrawing groups makes the P\(^+\) centre more electropositive (i.e. an increase in the formal positive charge at phosphorus). The cations in this latter group also appear to be larger.

\[
\begin{align*}
\text{Et}_4\text{N}^+ & \quad \text{TYPE 1} \\
\text{Ph}_4\text{P}^+ & \quad \text{allows rapid exchange in anion} \\
\text{C}_6\text{F}_5\text{PX}_3^+ & \quad \text{TYPE 2} \\
\text{C}_6\text{H}_2(\text{CF}_3)_3\text{PX}_3^+ & \quad \text{inhibits rapid exchange in anion}
\end{align*}
\]

It may well be that the smaller cations also allow a close approach of boron, helping to remove \( X^- \) from it (see possible exchange mechanism, Section 10.3), whereas the larger cations cannot associate so readily with the borate anion (reduced polarisation) (Figure 10.4). On the other hand the cations in the second group might have been expected to
be effective in X⁻ removal from boron, in view of the greater electron withdrawing nature of the halogen atoms. (There could however be more repulsion between X on boron and electronegative ligands on phosphorus, which would more than counteract the increased positive charge at phosphorus mentioned above. The ions are $\varphi$-tetrahedral, so the P⁺ would be quite well shielded. This does not accord with the following proposal).

\[ (a) \quad + \rightarrow X-B-X \]
\[ (b) \quad + \rightarrow X-B-X \]

\textbf{Figure 10.4: Cation/anion association; (a) allows a close approach; (b) very little association.}

It is hard to envisage why these halogenated cations should inhibit the exchange unless somehow they stabilise a very strong ion pairing with the counterion, possibly \textit{via} a halogen bridge (Figure 10.5). Thus, if the electron withdrawal from phosphorus were sufficiently strong this would also inhibit the loss of a chloride ion from boron either directly, or \textit{via} a bridging mechanism as required by the exchange mechanism (Section 10.3). The existence of such a large attachment to one side of the $\text{BCl}_4^-$ anion would also block the formation, (unlikely in any case), of the transition state required by Method 2. Such an arrangement could explain the inhibition of rapid exchange and still permit substitution to take place at a much lower rate. Indeed, since the overall ion pair is neutral, (hence removing the objection to Method 2), the whole cation with Cl⁻ could act as a leaving group in a possible $S_{N2}$ substitution process.
Figure 10.5: Proposed ion-pair with a halogen bridge.

If these cations of Type 2 do indeed form such stable ion pairs, this would explain why the subsequent addition of a Type 1 cation to the system, for example in the form \( R_4N^+CN^- \), does not cause exchange to commence. It would be possible to check this hypothesis further by adding Type 2 cations (with a convenient anion also) to an exchanging system when the exchange should be inhibited. This has not yet been attempted.

10.9 THE THIOCYANATE SYSTEM

The thiocyanate anion, \( NCS^- \), substitutes into \( BX_4^- (X = F, Cl, Br \) and I), exchanging on a slow enough timescale with respect to the NMR to allow the observation of the \( ^{11}B \) NMR signals corresponding to all of the substitution products. These systems will now be considered.

10.9.1 The \( F^-/NCS^- \) Borate System

This was achieved by the addition of LiNCS to \( BF_3 \cdot Et_20 \), and conversely by the addition of \( F^- (CsF) \) in tetraglyme to \( Et_4N^+B(NCS)_4^- \). Initially, only signals corresponding to \( B(NCS)F_3, BF_4^- \) and \( B(NCS)_4^- \) were present, but after warming to 35 °C all the substitution products were clearly observed. The shifts agree well with those calculated by the pairwise interaction method. A 2-D NMR spectrum showed no evidence of
Figure 10.6: One dimensional 1H-NMR data for Et₄N⁺B(NCS)₄⁻ + Cs⁺F⁻ in tetracycline, illustrating J(DN) coupling.
exchange, as expected.

Boron-nitrogen \(^{(1)}J_{BN}\) coupling was evident in the 1-D \(^{11}\)B NMR spectrum (Figure 10.6). This phenomenon was previously observed in the similar system boron-chlorine-NCS \([3]\). Assignment was made (Table 10.8) entirely to boron-nitrogen coupling, since no \(^{1}J_{BF}\) could be resolved in the \(^{19}\)F NMR spectrum. However, before a final conclusion can be reached, further work would be desirable on resolution in the \(^{19}\)F NMR since the possibility may exist of the observed splitting pattern resulting from both \(^{1}J_{BF}\) and \(^{1}J_{BN}\). The \(^{1}J_{BN}\) values derived look reasonable by comparison with those for \(\text{BCl}_4^-/\text{NCS}^-\), where B-F coupling is impossible.

The sharp signal of \(\text{BF}_4^-\) is in agreement with its high symmetry, and the small coupling constants associated with highly fluorinated boron systems \([2]\).

<table>
<thead>
<tr>
<th>(^{11})B NMR (\delta)(ppm)</th>
<th>ANIONIC SPECIES</th>
<th>(^{1}J_{BN}) (Hz)</th>
<th>(^{19})F NMR (/ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXPT</td>
<td>CALC†</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-17.4</td>
<td>(-17.4)</td>
<td>B(NCS)_4^-</td>
<td>20.1</td>
</tr>
<tr>
<td>-11.7</td>
<td>(-11.7)</td>
<td>B(NCS)_3F^-</td>
<td>22.4</td>
</tr>
<tr>
<td>-7.0</td>
<td>-7.2</td>
<td>B(NCS)_2F^-</td>
<td>26.9</td>
</tr>
<tr>
<td>-3.9</td>
<td>-3.8</td>
<td>B(NCS)F^-</td>
<td>27.6</td>
</tr>
<tr>
<td>-1.6</td>
<td>(-1.6)</td>
<td>BF_4^-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 10.8: \(^{11}\)B NMR data for \(\text{Et}_4\text{N}^+\text{B(NCS)}_4^- + \text{CsF (tetracylglyme)}\); †calculated by pairwise interaction methods (ref.1) using the bracketed values; *no \(^{1}J(BF)\) resolved.

10.9.2 \(\text{Et}_4\text{N}^+\text{BCl}_4^-\) with \(\text{NCS}^-\)

The full set of substitution products was obtained from the tetra-alkylammonium tetrachloroborate system with thiocyanate. This data has been previously reported by R. Ali \([3]\), however her work involved the cation \(\text{C}_6\text{F}_5\text{PCl}_3^+\). The results here (Table 10.9) agree well with this
data. A 2-D NMR was carried out on this system and no evidence of exchange was observed. This system was also achieved with the new cation ArPCl$_3^+$ and the results are presented in Table 10.10.

<table>
<thead>
<tr>
<th>11B NMR $\delta$(ppm)</th>
<th>ANIONIC SPECIES</th>
<th>$^1$JBN * (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXPT</td>
<td>CALC†</td>
<td></td>
</tr>
<tr>
<td>-17.1</td>
<td>(-17.1)</td>
<td>B(NCS)$_4^-$</td>
</tr>
<tr>
<td>-12.7</td>
<td>(-12.7)</td>
<td>B(NCS)$_3Cl^-$</td>
</tr>
<tr>
<td>-7.2</td>
<td>-7.2</td>
<td>B(NCS)$_2Cl_2$</td>
</tr>
<tr>
<td>-0.7</td>
<td>-0.6</td>
<td>B(NCS)$_Cl_3$</td>
</tr>
<tr>
<td>7.0</td>
<td>(7.0)</td>
<td>BCl$_4$</td>
</tr>
</tbody>
</table>

Table 10.9: 11B NMR data for Et$_4N^+BCl_4^-$ + AgNCS (CH$_2$Cl$_2$); ‡calculated by pairwise interaction methods (ref.1) using the bracketed values; *$^1$J(BN) resolved only for the first substitution product in this system.

<table>
<thead>
<tr>
<th>11B NMR $\delta$(ppm)</th>
<th>ANIONIC SPECIES</th>
<th>$^1$JBN (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXPT</td>
<td>CALC†</td>
<td></td>
</tr>
<tr>
<td>-17.2</td>
<td>(-17.2)</td>
<td>B(NCS)$_4^-$</td>
</tr>
<tr>
<td>-12.9</td>
<td>-15.6</td>
<td>B(NCS)$_3Cl^-$</td>
</tr>
<tr>
<td>-7.2</td>
<td>-10.9</td>
<td>B(NCS)$_2Cl_2$</td>
</tr>
<tr>
<td>-3.2</td>
<td>(-3.2)</td>
<td>B(NCS)$_Cl_3$</td>
</tr>
<tr>
<td>+7.7</td>
<td>(+7.7)</td>
<td>BCl$_4$</td>
</tr>
</tbody>
</table>

Table 10.10: 11B NMR data for ArPCl$_3^+$BCl$_4^-$ + AgNCS (CH$_2$Cl$_2$); ‡calculated by pairwise interaction methods (ref.1) using the bracketed values; NR=not resolved.

10.9.3 Et$_4N^+BBr_4^-$ With NCS$^-$

The analogous system with bromide was obtained by the addition of AgNCS to Et$_4N^+BBr_4^-$ in CH$_2$Br$_2$. J($^{11}$B−$^{14}$N) coupling was observed in this system (Table 10.11) but only for the first substitution product.
Figure 10.7: One dimensional $^{11}B$ NMR spectra for the system $BI_3 + Et_4N^+NCS^-$ in $CH_2I_2$. 
<table>
<thead>
<tr>
<th>EXPT</th>
<th>CALC‡</th>
<th>ANIONIC SPECIES</th>
<th>†JBN (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-17.7</td>
<td>(-17.7)</td>
<td>B(NCS)(^-)</td>
<td></td>
</tr>
<tr>
<td>-17.0</td>
<td>(-17.0)</td>
<td>B(NCS)(_3)Br(^-)</td>
<td>*</td>
</tr>
<tr>
<td>-18.5</td>
<td>-17.9</td>
<td>B(NCS)(_2)Br(_2)</td>
<td>*</td>
</tr>
<tr>
<td>-20.9</td>
<td>-20.3</td>
<td>B(NCS)Br(_3)</td>
<td>21.0</td>
</tr>
<tr>
<td>-24.3</td>
<td>(-24.3)</td>
<td>BBr(_4)</td>
<td></td>
</tr>
</tbody>
</table>

Table 10.11: \(^{11}\)B NMR data for Et\(_4\)N\(^+\)Br\(_4\)\(^-\) + AgNCS (CH\(_2\)Br\(_2\)); ‡calculated by pairwise interaction methods (ref.1) using the bracketed values; * no †J(BN) coupling resolved.

10.9.4 Et\(_4\)N\(^+\)NCS\(^-\) With BI\(_3\)

The iodo-thiocyanatoborate system was produced by the addition of Et\(_4\)N\(^+\)NCS\(^-\) to BI\(_3\) in CH\(_2\)I\(_2\) and the results are presented in Table 10.12.

<table>
<thead>
<tr>
<th>EXPT</th>
<th>CALC‡</th>
<th>ANIONIC SPECIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>-17.9</td>
<td>(-17.9)</td>
<td>B(NCS)(^-)</td>
</tr>
<tr>
<td>-27.3</td>
<td>(-27.3)</td>
<td>B(NCS)(_3)I(^-)</td>
</tr>
<tr>
<td>-47.5</td>
<td>-48.4</td>
<td>B(NCS)(_2)I(_2)</td>
</tr>
<tr>
<td>-81.7</td>
<td>-81.3</td>
<td>B(NCS)I(_3)</td>
</tr>
<tr>
<td>-125.8</td>
<td>(-125.8)</td>
<td>BI(_4)</td>
</tr>
</tbody>
</table>

Table 10.12: \(^{11}\)B NMR data for Et\(_4\)N\(^+\)NCS\(^-\) + BI\(_3\) (CH\(_2\)I\(_2\)); ‡calculated by pairwise interaction methods (ref.1) using the bracketed values; for 1-D spectrum see Figure 10.7.

The two intermediate substitution products Et\(_4\)N\(^+\)B(NCS)\(_2\)I\(_2\) and Et\(_4\)N\(^+\)B(NCS)\(_3\)I\(^-\) were not always observed, although they must have been formed to allow the generation of B(NCS)\(^-\)\(_4\). Heating was avoided, because of the inherent instability of BI\(_4\)\(^-\).
No $^{1}J_{BN}$ coupling was observed. This was attributed to the greater quadrupolar relaxation induced by $^{127}$I ($I = 5/2$) compared with $^{35}$Cl ($I = 3/2$), and $^{79}$Br or $^{81}$Br ($I = 3/2$).

10.10 THE $F^−/CN^−$ BORATE SYSTEM

The first cyano-substituted product was obtained by the addition of LiCN to BF$_3$·Et$_2$O. An excess of lithium cyanide gave no evidence of further substitution, but the addition of Bu$_4$N$^+$CN$^−$ caused this to take place (see Table 10.13).

<table>
<thead>
<tr>
<th>EXPT</th>
<th>$^{1}J_{BF}$ (multiplicity)</th>
<th>CALC</th>
<th>ANIONIC SPECIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>-9.0†</td>
<td>---</td>
<td>(-9.0)</td>
<td>B(CN)$_4^−$</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>-7.4</td>
<td>B(CN)$_3F^−$</td>
</tr>
<tr>
<td>-6.6</td>
<td>41.4 triplet</td>
<td>-5.5</td>
<td>B(CN)$_2F_2^−$</td>
</tr>
<tr>
<td>-3.4</td>
<td>27.1 quartet</td>
<td>(-3.4)</td>
<td>B(CN)F$_3^−$</td>
</tr>
<tr>
<td>-1.1</td>
<td>1.0 singlet $^{[2]}$</td>
<td>(-1.1)</td>
<td>BF$_4^−$</td>
</tr>
</tbody>
</table>

Table 10.13: $^{11}$B NMR data for BF$_3$·Et$_2$O + LiCN + Bu$_4$N$^+$CN$^−$ (Et$_2$O/CH$_2$Cl$_2$); †obtained from C$_6$F$_5$PCl$_3^+$ B(CN)$_4^−$ (ref. 3); ‡by pairwise interaction.

Addition of Et$_4$N$^+$NCO$^−$ and Bu$_4$N$^+$CN$^−$ respectively to BF$_3$·Et$_2$O gave in each case a few peaks around 0 ppm, attributed to exchange.

In the systems with counterions such as ArPCl$_3^+$ or C$_6$F$_5$PBr$_3^+$ this work could be extended to observe directly, anion substitution into these cations, using $^{31}$P NMR.
Graph 10.1: $^{11}B$ NMR data for the $BX_4^-$ ($X = F, Cl, Br, I$) and NCS$^-$ systems.

Substitution in tetra-halogeno borate anions by thiocyanate
10.11 SPECTRAL CHARACTERISTICS

10.11.1 Introduction

The shift pattern $\text{BX}_4^-$, $\text{BX}_3Y^{-}$, ..., $\text{BY}_4^-$ inclusive should not be assumed to be sequential. For example, this is illustrated in the $\text{BBr}_4^-$-NCS$^-$ system: -17.7, -17.0, -18.5, -20.9 and -24.3 ppm.

The quadrupolar moment of boron ($I = 3/2$) tends to broaden the lines in the NMR, with the sharpest lines corresponding to the most symmetrically substituted systems. Some of the results of this work have been presented in graphical form (Graphs 10.1-10.4). No variation in linewidth with the nature of the attached halogens was observed. This may be compared with P(III) halides, in which iodides give sharper lines than bromides, which in turn are sharper than those from chlorides. This is attributed to the size of the quadrupole moments.

10.11.2 Graph 10.1: $\text{BX}_4^-$ (X = Cl, Br, I, F) and NCS$^-$

This displays data for the tetrafluoro-, chloro-, bromo- and iodo-borate systems with thiocyanate anions. It clearly illustrates the variation in chemical shift range for the different halogeno compounds. The much larger span for the iodide containing system is evident. The non-sequential shift order for the bromide species has been noted above.

In general for the series chloride, bromide and iodide, there is a greater degree of shielding as the halogen group is descended. An exception exists for the fluoride, whereby towards the end of the substitution system (more fluorine) the species become more shielded than for the analogous chloride compounds. As fluorine is smaller and more electron withdrawing this must be attributed to an increase in the
Substitution in Tetrahalogenoborate Anions by Cyanide and Thiocyanate

Graph 10.2: $^{11}B$ NMR data for the $BX_4^-$ ($X = Cl, Br, I$), $CN^-$ and $NCS^-$ systems.
effective p-orbital overlap with boron. This is also illustrated by $\text{BF}_4^-$ (+1.5) being more shielded than $\text{BCl}_4^-$ (+6.6).

10.11.3 Graph 10.2: $\text{BX}_4^-$ ($X = F, \text{Cl}, \text{Br}$) and $\text{CN}^-, \text{NCS}^-$

This displays substitution in tetrahalogenoborate anions by thiocyanate and cyanide respectively. The graph allows a direct comparison of the thiocyanate and cyanide systems. The iodo-derivatives are omitted since values for the iodo-cyanoborate species were unobtainable.

The order of the cyano systems is chloride, fluoride and bromide, with respect to an increase in shielding at the boron centre: for exactly similar reasons as proposed in the thiocyanate system.

10.11.4 Graph 10.3: $^1J_{\text{BN}}$ Coupling in the B/F/NCS System

This illustrates the novel $^1J_{\text{BN}}$ coupling in the thiocyanate borate system, with fluoride, chloride and limited data with the bromide system. In the fluoride system an apparent decrease in $^1J_{\text{BN}}$ coupling exists, as the number of nitrogen atoms increases.

10.11.5 Graph 10.4: $^1J_{\text{BF}}$ Coupling in the B/F/CN System

This shows $^1J_{\text{BF}}$ coupling in the new cyano-fluoroborate system. The well-known phenomenon is illustrated, of coupling constant decrease with an increase in the number of fluorine atoms $[^2]$.  

- 235 -
Graph 10.3: $^1J(BN)$ coupling in $BX_4^-$ ($X = \text{F, Cl}$) and NCS$^-$ systems.
Graph 10.4: $^1J(BF)$ coupling values for the B/F/NCS system.
10.12 CALCULATION OF CHEMICAL SHIFTS FROM PAIRWISE ADDIIVITY CONSTANTS

Chemical shifts of various nuclei have been observed which are pairwise additive with respect to the substituent groups [1]. For example the chemical shift can be expressed as:

\[ \delta = \sum \eta_{i,j} \]

where \( \eta_{i,j} \) is a parameter associated with substituents i and j and independent of all other substituents. The sum is taken over all substituents about a central atom excluding the nucleus observed in the NMR experiment, for example:

\[ {}^{11}\text{B}\delta = \eta_{F,F} + 4\eta_{F,NCS} + \eta_{NCS,NCS} \]

where \( \eta_{i,j} \) is different for each nucleus observed - theoretical justification for this rule is given in detail elsewhere [11]. Pairwise contributions arise because the wave function of each substituent group suffers a linear correction due to the presence of each neighbouring substituent group [1]. This work involves the use of the pairwise substitution products in the system \( BX_4/Y^- \). Errors in these calculations may originate from deviations in the geometry of the species under consideration. This correlation by pairwise additivity relations provides useful confirmations of the resonance assignments. (The pairwise interaction calculation is obviously more useful for the octahedral systems, because more predictions can be made from the same amount of data.)
2-D correlated experiments have been used to provide a map of coherent interactions, for example $^{11}$B NMR for boranes [12-15]. Two dimensional exchange spectroscopy provides a map of incoherent interactions such as chemical exchange or magnetisation exchange arising from the Nuclear Overhauser Effect (NOE). Many examples of the elucidation of chemical exchange networks by 2-D NMR spectroscopy are known, for example using the techniques for proton [6], deuterium [7] and carbon ($^{13}$C) [8].

An additional fixed time, called the mixing time, $T_m$, is introduced in 2-D exchange spectroscopy to allow exchange of magnetisation via incoherent interactions. The pulse sequence for 2-D exchange spectroscopy is shown in Figure 10.8.

![Figure 10.8: The basic 2-D exchange pulse sequence.](image)

The first 90° pulse flips the net magnetisation vector in the x-y plane and causes each spin to precess at its characteristic frequency during the evolution period. This effectively labels each spin according to its initial precession frequency during $t_1$. In a 2-D NOE experiment, dipole-dipole coupled nuclei exchange magnetisation via the NOE during the mixing period $T_m$. This period has a constant value, chosen to be approximately equal to the spin-lattice relaxation time $T_1$. In this work, a chemical exchange experiment, magnetisation exchange occurs during the mixing period as a consequence of chemical exchange.
In both cases, the final frequency is detected during the detection period of length $t_2$ (2-D spectrum obtained by running this sequence at many values of $t_1$). The species which did not exchange magnetisation during the mixing period have the same initial and final frequencies. Hence, diagonal peaks occur along the diagonal line. This is clearly illustrated in Figures 10.1(b) and 10.2(b). [NB. Figure 10.1(b) shows more than five species present on the diagonal as a consequence of ligand isomerisation]. Those species exchanging magnetisation during the mixing period have final frequencies that differ from their initial frequencies. This exchange gives rise to off-diagonal peaks connecting spins related by a NOE or chemical exchange. The latter is clearly illustrated in Figures 10.1(b) and 10.2(b). These off-diagonal peaks generally occur in pairs that are symmetric about the diagonal peaks.

By matching all pairs of off-diagonal peaks, the complete exchange network can be seen in a single experiment.

The resultant exchange spectrum depends critically on the magnitude of the mixing time, and the cross-peak intensities reflect the amount of exchange that takes place during $\tau_m$. Hence, an interesting development of this work would be an investigation of the build-up rate of cross-peak intensities in 2-D exchange spectra obtained with different mixing times, providing a direct measure of the exchange rate [10].

NB. The pulse sequence (Figure 10.8) used in this work is identical to NOESY, but for the modification of the mixing time. For NOESY this is the spin-lattice relaxation time, and for the 2-D exchange experiment, as applied here for the pseudohaloborate system, it is simply guesswork to obtain a mixing period of the same sort of order as the exchange process.
10.14 EXPERIMENTAL

10.14.1 General Points

Lithium azide (LiN₃) was prepared according to the method of A.W.G. Platt [16], a method adapted by Dr. C. Ludman (University of Durham, 1980). Tetrabutylammonium azide (Bu₄NN₃) and lithium thiocyanate (LiNCS) were prepared as described by A. Marshall [17].

In the simple tetrahalogenoborate salt preparations, at the final stage of solvent removal, the solid appeared to be oily. A small volume of petroleum ether (30-40) was therefore added. The resulting suspension was stirred for several hours, before the petrol was removed in vacuo to yield a pure dry powdery solid.

10.14.2 Preparation of Et₄N⁺BCl₄⁻

\[
\text{Et}_4\text{N}^+\text{Cl}^- + \text{BCl}_3 \rightarrow \text{Et}_4\text{N}^+\text{BCl}_4^- 
\]

Boron trichloride (1.41g, 1.0 ml, 12 mmol) was condensed into a stirred solution of tetraethylammonium chloride (2.0g, 12 mmol) at -20 °C. The reaction mixture was stirred for 1 hour at room temperature. The solvent was removed in vacuo to yield a pure white salt Et₄N⁺BCl₄⁻. Yield was 2.5g (74%). ¹¹B (CH₂Cl₂) δ: + 6.6 ppm. This agrees well with known data [2,3].
10.14.3 Preparation of Et$_4$N$^+$BBr$_4^-$

Et$_4$N$^+$Br$^-$ + BBr$_3$ $\longrightarrow$ Et$_4$N$^+$BBr$_4^-$

Boron tribromide (1.5 ml, 15.9 mmol) in CH$_2$Br$_2$ (15 ml) was added dropwise over 5 minutes to a stirred solution of tetraethylammonium bromide (3.3g, 15.9 mmol) in CH$_2$Br$_2$ (20 ml) at room temperature. The mixture was stirred for 1 hour. The solvent was removed in vacuo to yield a pale brown powdery solid. This was washed with 4 aliquots of cold pentane (5 ml) to give a pure white salt. Yield was 6.2g (84%). $^{11}$B NMR (CH$_2$Br$_2$) $\delta$: -24 ppm, cf. published data [2,3]. The use of CH$_2$Br$_2$ in place of CH$_2$Cl$_2$ prevented chloride incorporation into the product [2].

10.14.4 Preparation of Pr$_4$N$^+$BI$_4^-$

Pr$_4$N$^+$I$^-$ + BI$_3$ $\longrightarrow$ Pr$_4$N$^+$BI$_4^-$

A solution of tetrapropyramidonium iodide (1.9g, 6.1 mmol) in CH$_2$I$_2$ (35 ml) was added dropwise over 5 minutes to a stirred solution of boron triiodide (2.4g, 6.1 mmol) in CH$_2$I$_2$ (20 ml) at 0 °C (the mixture became pale purple attributed to the evolution of iodine, though this was minimised by keeping the reaction mixture in the dark). The mixture was stirred at 0 °C for 30 minutes, before the solvent was removed in vacuo yielding a pale purple/brown solid. This was washed with 2 aliquots (10 ml) cold pentane to give a yellow solid. Yield was 2.2 g (51%). $^{11}$B (CH$_2$Cl$_2$) $\delta$: -127 ppm, cf. published data [2,3].
10.14.5 Preparation of $\text{Et}_4\text{N}^+\text{B}(\text{NCS})_4^-$

$$\text{Et}_4\text{N}^+\text{BCl}_4^- \xrightarrow{4\text{AgNCS}} \text{Et}_4\text{N}^+\text{B}(\text{NCS})_4^- + 4\text{AgCl}$$

AgNCS (2.90g, 17.5 mmol) was added to a stirred solution of $\text{Et}_4\text{N}^+\text{BCl}_4$ (1.21g, 4.3 mmol) in CH$_2$Cl$_2$ (35 ml) at room temperature. This was stirred for four hours. The completion of the reaction was confirmed by $^{11}$B NMR -17.0 ppm [3,18]. AgCl was removed by filtration, and the dichloromethane in vacuo, to yield a pale yellow solid. Yield was 1.24g (77%). $^1\text{J}_{\text{BN}}$ 23.2 Hz [3] (9 lines).

10.14.6 Preparation of $\text{Ph}_4\text{P}^+\text{BCl}_4^-$ (93)

$$\text{Ph}_4\text{PCl}^- + \text{BCl}_3 \longrightarrow \text{Ph}_4\text{P}^+\text{BCl}_4^-$$

Tetraphenylphosphonium chloride (7.96g, 21.3 mmol) in CH$_2$Cl$_2$ (25 ml) was added dropwise over 10 minutes to a stirred solution of boron trichloride (2.5g, 1.8 ml, 21.3 mmol) which had been condensed into CH$_2$Cl$_2$ (35 ml) at -20 °C, and maintained at this temperature. The reaction mixture was allowed to reach room temperature, and stirred for 1 hour before the removal of the solvent in vacuo to yield a white solid. Yield was 6.7g (64%). $^{11}$B NMR (CH$_2$Cl$_2$) $\delta$: +6.6 ppm, cf. published data [2,3].

10.14.7 Preparation of $\text{ArPCl}_3^+\text{BCl}_4^-$ (95)

$$\text{ArPCl}_2 \xrightarrow{\text{Cl}_2} \text{ArPCl}_4 \xrightarrow{\text{BCl}_3} \text{ArPCl}_3^+\text{BCl}_4^-$$ (95)

This was prepared by T.Straw [19]. $^{31}\text{P}$ (CH$_2$Cl$_2$) $\delta$: 97.1 ppm; $^{11}$B (CH$_2$Cl$_2$) $\delta$: +6.6 ppm.
10.14.8 Preparation of $C_6F_5PBr_3^{+}BBr^-_4$ (96)

This reaction followed work by R. Ali [3]. It consisted of four stages:

\[
\begin{align*}
C_6F_5Br + Mg & \xrightarrow{Et_2O} C_6F_5MgBr \\
C_6F_5MgBr + PBr_3 & \xrightarrow{Et_2O} C_6F_5PBr_2 + MgBr_2 \\
C_6F_5PBr_2 + Br_2 & \xrightarrow{CCl_4} C_6F_5PBr_4 \\
C_6F_5PBr_4 + BBr_3 & \rightarrow C_6F_5PBr_3^{+}BBr^-_4 (96)
\end{align*}
\]

It was observed that the use of dibromomethane in the place of dichloromethane at stage 4 allowed higher yields of the order of 65% - avoiding any incorporation of chloride by exchange with the solvent. $C_6F_5PBr_3^{+}BBr^-_4$: $^{11}B$ (PhNO$_2$) $\delta$: -24 ppm; $^{31}P$ (PhNO$_2$) $\delta$: -38 ppm; MS (Intensity%) EI: 438 ($20, C_6F_5PBr_3^{+}$), 358 ($100, C_6F_5PBr_2^{+}$), 277 ($22, C_6F_5PBr^{+}$).

10.14.9 Chloride Systems

10.14.9.1 Reaction of $Et_4N^{+}BCl^-_4$ With $AgNCS$ (CH$_2$Cl$_2$)

$AgNCS$ (0.85g, 5.12 mmol) was added to a stirred solution of $Et_4N^{+}BCl^-_4$ (1.45g, 5.12 mmol) in CH$_2$Cl$_2$ (10 ml) at room temperature. Results are described in Section 10.9.2.

10.14.9.2 Reaction of $Et_4N^{+}BCl^-_4$ With $AgCN$ (CH$_3$CN)

$AgCN$ (0.47g, 3.51 mmol) was added to a stirred solution of $Et_4N^{+}BCl^-_4$ (0.99g, 3.51 mmol) in CH$_3$CN (15 ml) at room temperature. The mixture was filtered and the $^{11}B$ NMR of the filtrate showed two major
peaks (which could not be assigned to any of the expected substitution products) near 0 ppm \[^4\]. Results are described in Section 10.4.3.

10.14.9.3 Reaction of Et\(_4\)N\(^{+}\)BCl\(_4\) With Et\(_4\)N\(^{+}\)NCO\(^{-}\) (CH\(_2\)Cl\(_2\))

Et\(_4\)N\(^{+}\)NCO \((0.87\, g, 5.06\, \text{mmol})\) was added to a stirred solution of Et\(_4\)N\(^{+}\)BCl\(_4\) \((1.43\, g, 5.06\, \text{mmol})\) in CH\(_2\)Cl\(_2\) \((35\, \text{ml})\) at room temperature. The reaction mixture was stirred for 30 minutes. More than five peaks were observed in the \(^{11}\)B NMR. Results are described in Section 10.4.3.

10.14.9.4 Attempted Preparation of B(CN)\(_4\) Salts

It was not possible to isolate Et\(_4\)N\(^{+}\)B(CN)\(_4\)^\(-\) by the addition of four equivalents of cyanide to Et\(_4\)N\(^{+}\)BCl\(_4\)^\(-\) in acetonitrile, since the substitution products exchange. The same problem was encountered with KCN and BCl\(_3\). Signals in the \(^{11}\)B NMR were observed at 0 and -4.1 ppm (Section 10.4.3)

An exactly similar phenomenon exists on refluxing 4.1 equivalents AgCN and Et\(_4\)N\(^{+}\)BCl\(_4\)^\(-\) in PhNO\(_2\). This gave an average \(^{11}\)B NMR chemical shift of -0.51 ppm indicative of rapid exchange:

\[
BX_3(C_6H_5NO_2) + Y^- \rightleftharpoons BX_2Y^- + BX_2Y_2 + BXY_3 + BY_4 + C_6H_5NO_2 \quad [4]
\]

10.14.9.5 Preparation of Ag\(^{+}\)B(CN)\(_4\)^\(-\)

This was carried out according to Bessler \textit{et al.}\[^{[20]}\] using BCl\(_3\) \((1.42\, g, 1.0\, \text{ml}, 12.1\, \text{mmol})\) and AgCN \((6.5\, g, 49\, \text{mmol})\) \textit{(ie. in the ratio 1:4)} in a carius tube at 150-160 °C for 2 hours. The solid obtained was insoluble and had a very poor analysis; Found: C, 6.39; H, 2.05; N,
By following the procedure \cite{21} with \( \text{BCl}_3 \) in slight excess, similarly poor results were obtained.

10.14.9.6 Reaction of \( \text{Ph}_4\text{P}^+\text{BCl}_4^- \) With \( \text{AgCN} \) (CH\(_3\)CN)

\( \text{AgCN} \) (0.35g, 2.58 mmol) was added to a stirred solution of \( \text{Ph}_4\text{P}^+\text{BCl}_4^- \) (1.27g, 2.58 mmol) in CH\(_3\)CN (25 ml) at room temperature. The \( ^{11}\text{B} \) NMR showed 5 peaks (discussed in Section 10.6.1).

10.14.9.7 Reaction of \( \text{ArPCl}_3\text{BCl}_4^- \) With \( \text{AgNCS} \) (PhNO\(_2\))

\( \text{AgNCS} \) (0.35g, 2.1 mmol) was added to a stirred solution of \( \text{ArPCl}_3\text{BCl}_4^- \) (1.2g, 2.1 mmol) in PhNO\(_2\) (20 ml). \( ^{11}\text{B} \) data is detailed in Section 10.9.2. Thiocyanate substitution in the \( \text{P}(\text{V}) \) cation was also observed: \( ^{31}\text{P} \) (PhNO\(_2\)) \( \delta: +97 \text{ [ArPCl}_3^+ \), +26 [ArPCl}\(_2\)(NCS)]\(^+ \), +2.2 ['ArPCl(NCS)\(_2\)']\(^+ \), -30.1 ['ArP(NCS)\(_3\)']\(^+ \) ppm. An excess of thiocyanate resulted in decomposition, and the observation of \( \text{ArPCl}_2 \) \( ^{31}\text{P} \) NMR \( \delta: +145 \text{ ppm, } ^4\text{J}_{\text{PF}} 62.4 \text{ Hz} \).

10.14.9.8 Reaction of \( \text{ArPCl}_3\text{BCl}_4^- \) With \( \text{AgCN} \) (PhNO\(_2\))

\( \text{AgCN} \) (0.34g, 2.54 mmol) was added to a stirred solution of \( \text{ArPCl}_3\text{BCl}_4^- \) (1.45g, 2.54 mmol) in PhNO\(_2\)\(^2\) (15 ml). This mixture was filtered and the \( ^{11}\text{B} \) NMR of the filtrate recorded. Results are discussed in Section 10.6.3. An excess of silver cyanide caused decomposition of the cation (ArPCl\(_3^+\)) generating ArPCl\(_2 \) \( ^{31}\text{P} \) NMR \( \delta: +145 \text{ ppm, } ^4\text{J}_{\text{PF}} 62 \text{ Hz} \) possibly via CNCl elimination.

\(^2\text{PhNO}_2\) is required to bring the salt into solution.
10.14.10 Bromide Systems

10.14.10.1 Reaction of Et₄N⁺BBr₄⁻ With AgNCS (CH₂Br₂)

AgNCS (0.25g, 1.5 mmol) was added to a stirred solution of Et₄N⁺BBr₄⁻ (0.69g, 1.5 mmol) in CH₂Br₂ (20 ml). The solution was stirred at room temperature for 10 minutes before filtration, and recording the ¹¹B NMR. Addition of further AgNCS (0.75g, 4.5 mmol) and stirring at room temperature for 1 hour showed quantitative conversion to Et₄N⁺B(NCS)₄ with respect to the ¹¹B NMR. (Section 10.9.3)

10.14.10.2 Reaction of Et₄N⁺BBr₄⁻ With AgCN (CH₃CN)

AgCN (0.17g, 1.3 mmol) was added to a stirred solution of Et₄N⁺BBr₄⁻ (0.60g, 1.3 mmol) in CH₃CN (25 ml) at room temperature. The reaction mixture was stirred for 10 minutes. Results are discussed in Section 10.4.1. After a further 2 hours there was no change in the ¹¹B NMR.

10.14.10.3 Reaction of Et₄N⁺BBr₄⁻ With Bu₄N⁺N₃⁻ (CH₂Br₂)

Bu₄NN₃⁻ (0.2g, 0.7 mmol) was added to a stirred solution of Et₄N⁺BBr₄⁻ (0.33g, 0.7 mmol) in CH₂Br₂ (20 ml) at room temperature. The reaction mixture was stirred for 30 minutes. Results are described in Section 10.4.1. The peaks to higher field may indicate loss of nitrogen (i.e. via Br₃B–N–N⁺≡N).
10.14.10.4 Reaction of $\text{Et}_4\text{N}^+\text{BBr}_4^-$ With $\text{Et}_4\text{N}^+\text{NCO}^-$ ($\text{CH}_2\text{Br}_2$)

$\text{Et}_4\text{N}^+\text{NCO}^- (0.63\text{g}, 3.7\text{ mmol})$ was added to a stirred solution of $\text{Et}_4\text{N}^+\text{BBr}_4^- (1.72\text{g}, 3.7\text{ mmol})$ in $\text{CH}_2\text{Br}_2 (25 \text{ ml})$ at room temperature. The reaction mixture was stirred for 30 minutes. The results are discussed in Section 10.4.1.

10.14.10.5 Reaction of $\text{C}_6\text{F}_5\text{PBr}_3^+\text{BBr}_4^-$ With AgCN ($\text{PhNO}_2^+$)

The salt was prepared according to R. Ali [3]. AgCN (0.3g, 2.2 mmol) was added to a stirred solution of $\text{C}_6\text{F}_5\text{PBr}_3^+\text{BBr}_4^- (1.67\text{g}, 2.2\text{ mmol})$ in $\text{PhNO}_2^3 (20 \text{ ml})$ at 0 °C. This mixture was allowed to reach room temperature and its $^{11}$B NMR was recorded immediately. Results are discussed in Section 10.7.

10.14.11 Iodide Systems

10.14.11.1 Reaction of $\text{Pr}_4\text{N}^+\text{BI}_4^-$ With AgNCS ($\text{CH}_2\text{I}_2$)

AgNCS (0.26g, 1.6 mmol), was added to a stirred solution of $\text{Pr}_4\text{N}^+\text{BI}_4^- (1.1g, 1.6\text{ mmol})$ in $\text{CH}_2\text{I}_2 (25 \text{ ml})$ at 0 °C. This reaction mixture was allowed to reach room temperature and stirred for 30 minutes. Results are discussed in Section 10.9.4.

---

$^3\text{PhNO}_2$ was required to dissolve $\text{C}_6\text{F}_5\text{PBr}_3^+\text{BBr}_4^-$ salt.
10.14.11.2 Reaction of BI$_3$ With Et$_4$N$^+$NCS$^-$ (CH$_2$I$_2$)

Et$_4$NCS (1.2 g, 6.4 mmol) was added to a stirred solution of BI$_3$ (2.5 g, 6.4 mmol) in CH$_2$I$_2$ (25 ml) at 0 °C. This was stirred at room temperature for 30 minutes. Results are discussed in Section 10.9.4. Decomposition within the cyanoiodo systems was minimised by weighing out the required quantities of R$_4$N$^+$BI$_4^-$ or BI$_3$, and AgCN or Bu$_4$NCN in one vessel at 0 °C under nitrogen. The required solvent was then added by syringe or condensed into the mixture. (The two solids do not react until they are brought into solution).

10.14.11.3 Reaction of Pr$_4$N$^+$BI$_4^-$ With AgCN (CH$_2$I$_2$)

CH$_2$I$_2$ (25 ml) was condensed onto a mixture of Pr$_4$N$^+$BI$_4^-$ (1.1 g, 1.6 mmol) and AgCN (0.21 g, 1.6 mmol) at -78 °C. The reaction mixture was allowed to gradually reach room temperature and stirred for 30 minutes. Results are discussed in Section 10.4.2.

10.14.11.4 Reaction of BI$_3$ With Bu$_4$N$^+$CN$^-$ (CH$_2$I$_2$)

CH$_2$I$_2$ (25 ml) was condensed onto a mixture of BI$_3$ (0.9 g, 2.3 mmol) and Bu$_4$N$^+$CN$^-$ (0.62 g, 2.3 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. Results are discussed in Section 10.4.2.
10.14.11.5 Reaction of BI₃ With Bu₄N⁺N₃⁻ (CH₂I₂)

CH₂I₂ (25 ml) was condensed onto a mixture of BI₃ (1.0g, 2.6 mmol) and Bu₄N⁺N₃⁻ (0.74g, 2.6 mmol) at -78 °C. The reaction mixture was stirred and allowed to reach room temperature. Results are discussed in Section 10.4.2.

10.14.11.6 Reaction of BI₃ With Et₄N⁺NCO⁻ (CH₂I₂)

CH₂I₂ (25 ml) was condensed onto a mixture of BI₃ (0.62g, 1.6 mmol) and Et₄N⁺NCO⁻ (0.27g, 1.6 mmol) at -78 °C. The reaction mixture was stirred and allowed to reach room temperature. Results are discussed in Section 10.4.2.

10.14.12 Fluoride Systems

10.14.12.1 Reaction of Et₄N⁺B(NCS)₄⁻ With CsF (tetraglyme)

CsF (0.68g, 4.5 mmol) was added to a stirred solution of Et₄N⁺B(NCS)₄⁻ (1.67g, 4.5 mmol) in tetraglyme (25 ml) at room temperature. The reaction mixture was stirred for 1 hour. Results are discussed in Section 10.9.1.

10.14.12.2 Reaction of BF₃·Et₂O With LiCN and Bu₄NCN (DMF/Et₂O)

LiCN (0.5 M solution in DMF, 7.04 ml, 3.5 mmol) was added dropwise to a stirred solution of BF₃·Et₂O (0.5g, 0.4 ml, 3.5 mmol) in CH₂Cl₂ (15 ml) at room temperature. The reaction mixture was stirred for 30 minutes. Results are discussed in Section 10.10. The first
substitution product NCBF$_3$ Li$^+$ was observed. For further substitution Bu$_4$N$^+$CN$^-$ (0.94 g, 3.5 mmol) was added, and stirred for 30 minutes. Results are discussed in Section 10.10.

10.14.12.3 Reaction of BF$_3$·Et$_2$O With Bu$_4$N$^+$N$_3$ (CH$_2$Cl$_2$)

BF$_3$·Et$_2$O (0.62 g, 0.54 ml, 4.4 mmol) in CH$_2$Cl$_2$ (10 ml) was added dropwise over 5 minutes to a stirred solution of Bu$_4$NN$_3$ (1.25 g, 4.4 mmol) in CH$_2$Cl$_2$ (15 ml) at room temperature. The reaction mixture was stirred for 30 minutes before recording its $^{11}$B NMR. A peak at +3.2 ppm was observed, and attributed to loss of Et$_2$O coordination of the BF$_3$ in CH$_2$Cl$_2$. (Section 10.10)

10.14.12.4 Reaction of BF$_3$·Et$_2$O With Et$_4$N$^+$NCO$^-$ (CH$_2$Cl$_2$)

Et$_4$N$^+$NCO$^-$ (0.70 g, 4.1 mmol) was added to a stirred solution of BF$_3$·Et$_2$O (0.58 g, 0.50 ml, 4.1 mmol) in CH$_2$Cl$_2$ (15 ml) at room temperature. The solution was stirred for 30 minutes. An $^{11}$B NMR signal at +3.27 ppm was attributed to BF$_3$ in solution. Results are discussed in Section 10.10.

10.15 REFERENCES


CHAPTER ELEVEN

THE CHEMISTRY OF BORON IN NITRILEIMINES
11.1 INTRODUCTION TO NITRILEIMINES

This section is prefaced with a brief historical perspective on nitrileimine chemistry.

1934 The action of triphenylmethylsodium on diazomethane resulted in the discovery of the linear isomer iso-diazomethane 

\[ \text{H-C=N=N-H} \rightarrow \text{H-C=N-N-H} \rightarrow \text{H-C≡N-N-H} \]

1959 Thermal breakdown of 2,5-disubstituted tetrazoles yields nitrileimines as reactive intermediates 

This method has developed as a usual route to unstable nitrileimines and has been used recently (1989) in the generation of the following bis-nitrileimine:

\[ \text{C₆H₅-C≡N-N-R} \rightarrow \text{C₆H₅-C=N-N-R} \rightarrow \text{C₆H₅-C≡N-N-R} \]

The same workers showed that nitrileimines can also be formed by 1,3-dehydrochlorination of a suitable compound:

\[ \text{C₆H₅-C≡N-NH-C₆H₅} \rightarrow \text{C₆H₅-C≡N-N-C₆H₅} \]

1966 The chemistry of iso-diazomethane was reviewed.
Pyrolysis of potassium mesitylazomesityl-nitromethane generated a non-isolable nitrileimine which was trapped by 1,3-dipolar cycloaddition and identified [6]:

\[
\begin{align*}
\text{Mes} & \quad \text{C} \quad \text{N} = \quad \text{N} \quad \text{Mes} & \quad \Delta \quad & \quad \text{Mes} \quad \text{C} = \quad \text{N} \quad \text{N} \quad \text{Mes} \\
\text{NO}_2^* & \quad k^+ & \quad & \quad \\
\end{align*}
\]

The first nitrileimine to be generated by photolysis was characterised spectroscopically [7]:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{C} \quad \text{N} = \quad \text{N} \quad \text{NC}_6\text{H}_5 & \quad \text{hv} \quad \lambda \quad 250\text{nm} & \quad \text{C}_6\text{H}_5\text{C} \quad \text{N} \quad \text{NC}_6\text{H}_5 \\
\end{align*}
\]

The first direct spectroscopic characterisation of a substituted nitrileimine generated thermally. Spectroscopic evidence for the existence of discrete nitrileimine molecules in the gas phase was obtained. The problem of isomerisation of N-substituted compounds to azines and carbodiimides was overcome by the use of a silyl derivative [8]:

\[
\begin{align*}
\text{Ph} \quad \text{N} = \quad \text{N} \quad \text{N} \quad \text{SiMe}_3 & \quad \Delta \quad & \quad \text{Ph} \quad \text{C} = \quad \text{N} \quad \text{N} \quad \text{SiMe}_3 \\
\end{align*}
\]

Synthesis of the first stable nitrileimine via the phosphorus diazo compound:

\[
\begin{align*}
{\text{iPr}_2\text{N}} & \quad \text{S} & \quad \text{P} \quad \text{Cl}^+ & \quad + & \quad {\text{iPr}_2\text{N}} & \quad \text{S} & \quad \text{P} \quad \text{Cl} & \quad \rightarrow & \quad {\text{iPr}_2\text{N}} & \quad \text{S} & \quad \text{P} \quad \text{C} = \quad \text{N} \quad \text{N} \quad \text{P} \quad \text{N}^{\text{Pr}_2} & \quad {\text{iPr}_2\text{N}} \\
\end{align*}
\]

In summary, the parent nitrileimine was discovered in 1934 [1], the first substituted nitrileimine was shown to have independent existence spectroscopically in 1980 [7] and a report of the first stable nitrileimine to be successfully isolated was made in 1988 [9].
The chemistry of the nitrileimines is multifaceted. They have the potential to behave as acids or bases, as electrophiles or nucleophiles, as 1,3-dipoles or a carbene source (see Section 11.8).

### 11.2 Carbodiimides

1980 Carbodiimides are accessible *via* a Wolff rearrangement of a nitrileimine (Section 11.7) \[10\], *eg.*

1988 A direct synthesis for carbodiimides is *via* the following route \[11\]:

1989 The discovery of a synthesis for C=C conjugated carbodiimides by aza-Wittig reaction of iminophosphoranes with isocyanate \[12\]:

The preferred geometry of carbodiimides is analogous to that found in allenes \[13\] with orthogonal \(\pi\)-systems:

A brief consideration of the reactivity of carbodiimides should include its use in the synthesis of phosphaalkenes (Chapter 4) by the route shown below \[14\]:

- 254 -
An interesting use for carbodiimides is in the alignment of peptides in a mi cellular system [15].

The current study aimed to cover stable nitrileimine synthesis, including their rearrangement to carbodiimides and their reactivity as 1,3-dipoles. An attempt was also made to form a boron diazo species.

11.3 BORON DIAZO COMPOUNDS

Boron diazo compounds to date have only been postulated as reactive intermediates [16] for example:

A number of different avenues have been explored in the attempt to obtain diazo compounds of boron and, although success cannot be claimed in the overall goal many interesting and novel observations have been possible en route (Section 11.10).

The main reason for attempting such a synthesis is that a stable diazo compounds could provide a starting point for a wide range of boron compounds. It could provide, above all in line with the interest in the chemistry of low coordinated species, a possible route via the carbene to a B=C double bond, ie.
Recent work in this area includes the synthesis of alkylalkylideneboranes \([R-B=CA_2]\) where \(R = \text{Me, } t\text{Bu; } A = \text{SiMe}_3\) by elimination of \(\text{AOMe}\) at 560 °C and 490 °C respectively \([17]\):

Other work includes the synthesis of aminomethylene boranes \([18]\):

Helm and Nöth \([19]\) demonstrated the high reactivity of \(\text{B}=\text{C}\) double bonds towards 2+2 and 2+3 cycloaddition. Berndt et al.\([20]\) have developed the chemistry of borolithium alkanes [postulated as boron stabilised carbanions with a boratoalkene structure (11.1a)], and have prepared the first stable diboryldilithiomethane established as having a 1,3-diboratoallene structure (11.1b):

11.4 NITRILEIMINES VIA DIAZO COMPOUNDS

One of the principal routes to nitrileimines is via the diazo compound \([9]\).

11.4.1 Synthesis of Diazocompounds

A major problem in the synthesis of diazo compounds is their susceptibility to the Staudinger reaction \([21]\). This was comprehensively reviewed up to 1981 \([22]\). In order to prevent \(\text{P(III)}\)-diazo compounds
following the Staudinger process (Figure 11.1) bulky substituent groups must be employed to block reaction with the lone electron pair on the phosphorus atom [23]. The bisdiisopropylamino group is frequently used for this purpose [23].

![Figure 11.1: The Staudinger process.](image)

It is interesting to contrast this problem with the facile synthesis of P(V)-diazo compounds [24] (Figure 11.2).

![Figure 11.2: P(V) diazo compound synthesis.](image)

In this case the R groups can be small since there is no lone pair of electrons on the phosphorus atom to permit the Staudinger reaction to interfere. However, the "Curtius" rearrangement [25-27] is still possible as in the P(III) case on generation of the carbene, and is prevented by the use of R groups such as -OEt [28].

11.4.2 The Diazo Route to Nitrileimines

The diazo compounds described here are from work of the Toulouse research group led by G. Bertrand [24,29], with whom the author has collaborated.

The starting material is usually diazomethane itself prepared by a standard reaction (Equation 11.1) [30]. The diazomethane in ether is then silylated using trimethyl-silyltriflate (Equation 11.2) [31]. The diazo compound is then lithiated. At this stage there are theoretically
two possible sites for electrophilic attack, the carbon or nitrogen as indicated (Equation 11.3). As the reaction scheme shows the product is formed entirely by electrophilic attack at the carbon.

\[
\begin{align*}
\text{CH}_3\text{SO}_2-N-\text{NO} + \text{KOH} + \text{ROH} & \xrightarrow{\text{Et}_2\text{O}} \text{CH}_2\text{N}_2 + \text{H}_2\text{O} + \text{CH}_3\text{SO}_2\text{OR} \quad (11.1) \\
\text{CH}_2\text{N}_2 + \text{Me}_3\text{Si-OSO}_2\text{CF}_3 & \xrightarrow{i\text{Pr}_2\text{NET}^+\text{CF}_3\text{SO}_3^-} \text{Me}_3\text{SiCH(N}_2\text{)} (99) + i\text{Pr}_2\text{NHEt}^+\text{CF}_3\text{SO}_3^- (11.2)
\end{align*}
\]

The \text{Me}_3\text{Si-} group is easily cleaved by aqueous methanol to generate the required compound, \((i\text{Pr}_2\text{N})_2\text{P-CH=N}_2\) (102). The chemistry of this compound was explored in relation to its reactions with boron derivatives (Experimental data, Section 11.13). Previous work by Bertrand et al.\cite{9} clearly showed that in reactions with acyl chlorides, \(\text{N-acylation strongly competes with C-acylation. In the case of the P(III) compound the final product is partly the result of attack at C (Figure 11.3). The P(V) analogue with S attached to the lone pair of P} [Figure 11.3(ii)] provides an example of the N-acylated product.

\[
\begin{align*}
\text{R}_2\text{P-C Li}^+ + \text{R'}\text{C-Cl} & \quad \xrightarrow{(i)} \text{R}_2\text{P-C-N-C-R'} + \text{R}_2\text{P-C-CR'} \quad 75\% \\
\text{R}_2\text{P-C Li}^+ + \text{R'}\text{C-Cl} & \quad \xrightarrow{(ii)} \text{R}_2\text{P-C-S-N-C-R'} + \text{R}_2\text{P-C-CR'} \quad 25\%
\end{align*}
\]

\textbf{Figure 11.3: Reaction of the lithio derivative of a phosphorus diazo compound with acyl chloride; (i) }X = \text{lone pair (103); (ii) }X = (\equiv\text{S}) (105)\text{.}
An exactly parallel pair of reactions is shown with P(III) monochlorides [9] (Figure 11.4). In the case of these compounds it is clear that in terms of the final product, P(V) gives result of attack at nitrogen and P(III) gives result of attack at carbon.

\[
\begin{align*}
R_2P&\underset{\Theta}{\equiv}CLi^+ + R_2P-Cl \\
&\xrightarrow{(i)} R_2P-C\equiv PR_2 \quad (106) \\
&\xrightarrow{(ii)} \quad \begin{array}{c} S \\
R_2P&\underset{\Theta}{\equiv}C=N\equiv N=PR_2 \quad (107)
\end{array}
\end{align*}
\]

Figure 11.4: Reaction of the lithio derivative of a phosphorus diazo compound with a P(III) monochloride; (i) \(X = \text{lone pair}\) (103); (ii) \(X = (=S)\) (105).

11.4.3 Extension to Boron-Containing Compounds

The reaction between the lithio P(III) diazo compound with bis-diisopropylaminoboron chloride was explored. This resulted in the formation of the new stable nitrileimine (Equation 11.4).

\[
\begin{align*}
iPr_2N\quad P-C&\equiv Li + iPr_2N\quad B-Cl \\
&\xrightarrow{} iPr_2N\quad P&\underset{\Theta}{\equiv}C=N\equiv N&\equiv B\quad iPr_2N \\
\quad (103) &\quad (108) &\quad (109)
\end{align*}
\]

Selected spectroscopic data for the nitrileimine (109) are presented in Table 11.1, and full experimental details are given in Section 11.13.1.

The formation of compound (109) by the reaction sequence above illustrates quite a different behaviour of the P(III) compound from that described in Figure 11.4. Perhaps this reaction may be attributed to the high level of crowding around the boron. This is further evidence that the nitrileimine is the kinetically stabilised/preferred product [1,32].
<table>
<thead>
<tr>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$ /ppm</td>
<td>Coupling /Hz</td>
</tr>
<tr>
<td>3.36 (sept,4H,CH/B)</td>
<td>$^3$J(HH) 6.7</td>
</tr>
<tr>
<td>3.37 (d/s,4H,CH/P)</td>
<td>$^3$J(HH) 6.6</td>
</tr>
<tr>
<td>1.33 (d,24H,CH$_3$/B)</td>
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<tr>
<td>1.16 (d,12H,CH$_3$/P)</td>
<td>$^3$J(HH) 6.6</td>
</tr>
<tr>
<td>1.05 (d,12H,CH$_3$/P)</td>
<td>$^3$J(HH) 6.6</td>
</tr>
</tbody>
</table>

Table 11.1: $^1$H and $^{13}$C NMR data (C$_6$D$_6$) for nitrileimine (109); $d/s$=doublet of septets.

The addition of a stoichiometric equivalent of sulphur to (109) gave nitrileimine (110) (Equation 11.5).

$$
\begin{align*}
\text{iPr}_{2}N & \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2} \\
= & \text{iPr}_{2}N \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2} \\
\text{S} \text{S} & \text{iPr}_{2}N \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2} \\
\text{iPr}_{2}N & \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2} \\
\text{iPr}_{2}N & \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2} \\
\text{iPr}_{2}N & \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2}
\end{align*}
$$

(11.5)

Furthermore, the P(V)-diazo compound (104) was synthesised via the three stages described above (Section 11.4.2) followed by the addition of sulphur and purification by column chromatography [9] before lithiation. Nitrileimine (110) was also synthesised independently (Equation 11.6). This also led to attack at nitrogen. Selected spectroscopic data on nitrileimine (110) are given in Table 11.2, and full experimental details in Section 11.13.2.

$$
\begin{align*}
\text{iPr}_{2}N & \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2} \\
= & \text{iPr}_{2}N \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2} \\
\text{S} \text{S} & \text{iPr}_{2}N \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2} \\
\text{iPr}_{2}N & \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2} \\
\text{iPr}_{2}N & \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2} \\
\text{iPr}_{2}N & \text{P} \text{-} \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \text{N} \text{iPr}_{2}
\end{align*}
$$

(11.6)
<table>
<thead>
<tr>
<th></th>
<th>( ^1H ) NMR</th>
<th>( ^{13}C ) NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta ) /ppm</td>
<td>Coupling /Hz</td>
<td>( \delta ) /ppm</td>
</tr>
<tr>
<td>3.60 (mult,6H,4CH/B, 2CH/P)</td>
<td>57.42 (d,1C,C=N)</td>
<td>1J(PC) 125.28</td>
</tr>
<tr>
<td>3.39 (mult,2H,CH/P)</td>
<td>47.27 (d,4C,CH/P)</td>
<td>2J(PC) ~40.0</td>
</tr>
<tr>
<td>1.34 (d,12H,CH₃/P)</td>
<td>( ^3J(HH) ) 6.5</td>
<td>46.66 (s,4C,CH/B)</td>
</tr>
<tr>
<td>1.28 (d,24H,CH₃/B)</td>
<td>( ^3J(HH) ) 6.6</td>
<td>23.72 (s,8C,CH₃/B)</td>
</tr>
<tr>
<td>1.19 (d,12H,CH₃/P)</td>
<td>( ^3J(HH) ) 6.7</td>
<td>23.70 (s,2C,CH₃/P)</td>
</tr>
</tbody>
</table>

Table 11.2: \( ^1H \) and \( ^{13}C \) NMR data (C₆D₆) for nitrileimine (110).

11.5 NITRILEIMINES WITH CARBON SUBSTITUENTS ON BORON

It was of interest to look at the behaviour of groups on boron forming B-C bonds, *eg.*

\[
\begin{align*}
\text{(1) Mes}_2\text{BF} & \quad \text{+ Pr}_2\text{N} \quad \text{P-C-Li} \quad (103) \\
\text{(2) Ar}_2\text{BCl} & \quad \text{+ Pr}_2\text{N} \quad \text{P-C-Li} \quad (103)
\end{align*}
\]

where Ar = 2,4,6-tris(trifluoromethyl)phenyl.

Both of these groups are relatively large and hence would be expected to stabilise the nitrileimine structure. In (1) with (103), the reaction mixture turned deep pink with an infra-red absorption characteristic of a nitrileimine, a \( ^{31}P \) shift of +44ppm, but lithium fluoride did not separate (Experimental, Section 11.13.5).
Reaction (2) with (103) formed a black oil which was attributed to the attack of the lithium compound on the CF$_3$ groups. Even the reverse addition of the lithium compound to the boron monochloride gave a similar decomposition product (Section 11.13.6).

It is unfortunate that separation and full characterisation of these products did not prove to be possible.

11.6 BORON AND SILICON CONTAINING STABLE NITRILEIMINES

In a similar way the first nitrileimine containing both boron and silicon was prepared (Equation 11.7).

\[
\text{iPr}_2\text{N} \quad \text{B-Cl} + \quad \text{iPr}_3\text{Si-Cl-Li} \quad \xrightarrow{N_2} \quad \text{iPr}_2\text{N} \quad \text{B-N=N=C-Si} \quad \text{iPr}_3
\]

Selected spectroscopic data for the nitrileimine (113) are presented in Table 11.3, and full experimental details are given in Section 11.13.7. The size of the groups attached to silicon appears to control the course of the reaction since when isopropyl groups are replaced by methyl, completely different products are obtained (See Section 11.13.19).

<table>
<thead>
<tr>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$ /ppm</td>
<td>Coupling /Hz</td>
</tr>
<tr>
<td>3.61 (sept,2H,CH/B)</td>
<td>$^3J$(HH) 6.9</td>
</tr>
<tr>
<td>3.41 (sept,2H,CH/B)</td>
<td>$^3J$(HH) 6.9</td>
</tr>
<tr>
<td>1.31 (d,12H,CH$_3$/B)</td>
<td>$^3J$(HH) 6.6</td>
</tr>
<tr>
<td>1.19 (d,12H,CH$_3$/B)</td>
<td>$^3J$(HH) 6.8</td>
</tr>
<tr>
<td>1.04 (s,18H,CH$_3$/Si)$\dagger$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 11.3: $^1$H and $^{13}$C NMR data (C$_6$D$_6$) for nitrileimine (113); $\dagger$Underneath the propyl signal, 3H.
Irradiation of nitrileimines (109), (110) and (113) at 300 nm and 250 nm gave carbodiimides (114), (115) and (116) respectively. Formulae and selected spectroscopic data for these are given in Tables 11.4-11.6, with full experimental details in Sections 11.13.8 (114), 11.13.9 (115) and 11.13.10 (116).

\[
i_{\text{Pr}_2\text{N}}\text{P}^{-\text{N}}\text{C}==\text{N}^{-\text{B}}\text{N}^{i\text{Pr}_2}_{\text{N}} (114)
\]

\[
i_{\text{Pr}_2\text{N}}\text{S}^{-\text{N}}\text{C}==\text{N}^{-\text{B}}\text{N}^{i\text{Pr}_2}_{\text{N}} (115)
\]

[also via (114) + 1/8S8]

<table>
<thead>
<tr>
<th>( ^1\text{H NMR} )</th>
<th>( ^{13}\text{C NMR} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta /\text{ppm} )</td>
<td>Coupling /Hz</td>
</tr>
<tr>
<td>3.61 (d,sept,4H,CH/P)</td>
<td>( ^3J(\text{HH}) \sim 6 )</td>
</tr>
<tr>
<td>3.39 (sept,8H,CH/B)</td>
<td>( ^3J(\text{HH}) \sim 6 )</td>
</tr>
<tr>
<td>1.35 (d,12H,CH\text{P})</td>
<td>( ^3J(\text{HH}) 6.7 )</td>
</tr>
<tr>
<td>1.24 (d,24H,CH\text{B})</td>
<td>( ^3J(\text{HH}) 6.7 )</td>
</tr>
<tr>
<td>1.20 (d,12H,CH\text{P})</td>
<td>( ^3J(\text{HH}) 6.3 )</td>
</tr>
</tbody>
</table>

Table 11.4: \( ^1\text{H} \) and \( ^{13}\text{C} \text{NMR data } (\text{C}_6\text{D}_6) \) for carbodiimide (114); \( \ ^3J(\text{PH}) \) is not resolved; \( \dagger\)Inequivalent.

<table>
<thead>
<tr>
<th>( ^1\text{H NMR} )</th>
<th>( ^{13}\text{C NMR} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta /\text{ppm} )</td>
<td>Coupling /Hz</td>
</tr>
<tr>
<td>3.53 (d,sept,8H,CH/P)</td>
<td>( ^3J(\text{HH}) \sim 6 )</td>
</tr>
<tr>
<td>3.32 (sept,8H,CH/B)</td>
<td>( ^3J(\text{HH}) \sim 6 )</td>
</tr>
<tr>
<td>1.18 (d,12H,CH\text{P})</td>
<td>( ^3J(\text{HH}) 6.6 )</td>
</tr>
<tr>
<td>1.13 (d,24H,CH\text{B})</td>
<td>( ^3J(\text{HH}) 6.7 )</td>
</tr>
<tr>
<td>1.02 (d,12H,CH\text{P})</td>
<td>( ^3J(\text{HH}) 6.3 )</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 11.5: \( ^1\text{H} \) and \( ^{13}\text{C} \text{NMR data } (\text{C}_6\text{D}_6) \) for carbodiimide (115); \( \ ^3J(\text{PH}) \) is not resolved; \( \dagger\)Or small \( ^3J(\text{PC}) \) and 2 singlets.
A possible mechanism for this rearrangement has been proposed [10] which postulates an aziridine intermediate. This is outlined in Figure 11.5. It seems likely that the rearrangement of the B/Si nitrileimine (113) occurs similarly.

**Table 11.6:** $^1H$ and $^{13}C$ NMR data ($C_6D_6$) for carbodiimide (116); *not well defined*; †possibly CH/Si carbon.

<table>
<thead>
<tr>
<th>$^1H$ NMR</th>
<th>$^{13}C$ NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta /ppm$</td>
<td>$\delta /ppm$</td>
</tr>
<tr>
<td>Coupling /Hz</td>
<td></td>
</tr>
<tr>
<td>3.46 (mult, 8H, CH/B)</td>
<td>84.6 (weak*, 1C, N=(\equiv)N?)</td>
</tr>
<tr>
<td>1.93 (mult, 8H, CH/Si)</td>
<td>~48 (s's, 11C, CH/\textsuperscript{2}Pr, B/Si)</td>
</tr>
<tr>
<td>1.18 (d's, 24H, CH$_3$/B)</td>
<td>20 (s, 8C, CH$_3$/B)†</td>
</tr>
<tr>
<td>3J(HH) 2.9</td>
<td>~14 (s, 6C, CH$_3$/Si)</td>
</tr>
<tr>
<td>1.13 (d, 18H, CH$_3$/Si)</td>
<td>11</td>
</tr>
</tbody>
</table>

**Figure 11.5:** Proposed mechanism for rearrangement of (109) to (104).

Further information has been sought from a theoretical perspective using MNDO calculations. The details of the calculation and further discussion are given in Section 11.12. They predict a significant
interaction between C(1) and N(3) with a partial bond of order 0.3, \( ie. \)

\[
\begin{array}{c}
i\Pr_2N \\
\cdots
\end{array}
\begin{array}{c}
N_2 \\
\cdots
\end{array}
\begin{array}{c}
C_1 \\
\cdots
\end{array}
\begin{array}{c}
N_1 \\
\cdots
\end{array}
\begin{array}{c}
i\Pr_2 \\
\cdots
\end{array}
\]

Thus, in the ground state, the C(1)-N(3) bond required in the rearrangement has already begun to form.

The nitrileimine rearrangement to carbodiimide via the nitrene intermediate is very similar to the well-known Wolff rearrangement (which involves the migration of an alkyl or aryl group to an electron deficient carbon centre), and the analogous migration to an electron deficient nitrogen \( eg. \) a nitrene which is a feature of the Hofmann reaction. Both of these are discussed by Sykes \[34\] and are represented in Figure 11.6.

\[ \begin{array}{c}
(a) \quad \text{O} \\
\quad \text{R} \\
\quad \text{C} \\
\quad \text{R} \\
\quad \text{C} \\
\quad \text{O}
\end{array} \quad \longrightarrow \quad \text{R} \quad \text{C} \quad \text{C} \quad \text{O} \]

\[ \begin{array}{c}
(b) \quad \text{O} \\
\quad \text{R} \\
\quad \text{N} \\
\quad \text{R} \\
\quad \text{N} \\
\quad \text{C} \quad \text{O}
\end{array} \quad \longrightarrow \quad \text{R} \quad \text{N} \quad \text{C} \quad \text{O} \]

Figure 11.6: (a) The Wolff rearrangement; (b) The Hofmann reaction.

In contrast to the expected rearrangement of nitrileimine (109) to the carbodiimide (114), on one occasion, photolysis at 250 nm resulted in a species with \( ^{31}\text{P} \) shift at +139 ppm \[35\] possibly in line with the proposed structure (117):

\[
\begin{array}{c}
\Theta \\
\text{P} \\
\Theta
\end{array}
\quad (117)
\]

An alternative synthesis of this proposed structure (117) involved the addition of an electron donating substituent to boron thus increasing the negative charge here and forcing the rearrangement to this part of the molecule. The reaction of nitrileimine (109) with triethylamine after several days stirring at room temperature gave a \( ^{31}\text{P} \)
shift of +139 ppm. The nitrileimine absorption was also found to be absent from the infrared spectrum. By using a smaller attacking amine (trimethylamine), it was hoped to increase the rate of reaction. However, decomposition resulted and the product was not identified (Section 11.13.11/12).

The rearrangement from nitrileimine to the postulated carbene species may proceed via the diazo compound (118) as a key intermediate, followed by the loss of nitrogen [Figure 11.7 J.

\[
\begin{align*}
\text{(109)} & \quad \rightarrow \quad \left[ \begin{array}{c}
R_2N\text{P} & \text{C=} & \text{N} & \text{N} & \text{B} & \text{NR}_2 \\
\text{NR}_2 & & & & & \\
\end{array} \right] \\
\text{(118)} & \quad \rightarrow \quad \text{N}_2 \\
\text{(117)} & \quad \end{align*}
\]

Figure 11.7: Possible mechanism for conversion of (109) to (117).

11.8 1,3-DIPOLAR CYCLOADDITION CHEMISTRY

1,3 dipolar cycloaddition is a versatile method for the stereo- and regio-selective synthesis of penta-atomic heterocyclic rings [9,36-40]. The nitrileimine structure has four delocalised electrons distributed over three atoms and thus is electron rich. Consequently some of the higher energy orbitals are occupied. Nitrileimines readily form cycloadducts with electron poor alkenes (dienophiles). Consider the series of dienophiles (Figure 11.8).
Donation of electrons occurs from HOMO of the nitrileimine to the LUMO of the alkene. Hence, the greater the electron deficiency of the alkene, the smaller the value of $\Delta \varepsilon$ and the more favourable is the reaction.

Cycloaddition reactions were studied with nitrileimines (109), (110) and (113) in conjunction with the dienophiles—methyl fumarate (119) and methyl acrylate (120), e.g. nitrileimine (109) with methyl fumarate gave cyclo-adduct (121) (Equation 11.8). Selected spectroscopic data for the cycloadduct (121) are presented in Table 11.7 with full experimental details in Section 11.13.13.

The P(V) species (110) reacts similarly to give (122) (Equation 11.9). The boron-silicon containing nitrileimine (113) produces an analogous adduct (123) (Equation 11.10). Cycloadduct (122) can also be made by reaction of (121) and sulphur (Equation 11.11).
Selected spectroscopic data for the cycloadducts (122) and (123) are presented in Table 11.8 with full experimental details in Sections 11.13.14 and 11.13.15 respectively.

<table>
<thead>
<tr>
<th></th>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$/ppm</td>
<td>Coupling /Hz</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.74</td>
<td>(d.d, 1H, H$_a$)</td>
<td>$^3$J(H$_a$H$_b$) 7.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^3$J(PH$_a$) 1.44</td>
</tr>
<tr>
<td>3.97</td>
<td>(d.d, 1H, H$_b$)</td>
<td>$^3$J(H$_a$H$_b$) 6.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^4$J(PH$_b$) 1.42</td>
</tr>
<tr>
<td>3.73</td>
<td>(s, 3H, CO$_2$Me)</td>
<td></td>
</tr>
<tr>
<td>3.65</td>
<td>(s, 3H, CO$_2$Me)</td>
<td></td>
</tr>
<tr>
<td>3.57</td>
<td>(mult, 8H, CH/CH$+$)</td>
<td></td>
</tr>
<tr>
<td>1.23</td>
<td>(d, 6H, CH$_3$/P)</td>
<td>$^3$J(HH) 7.06</td>
</tr>
<tr>
<td>1.18</td>
<td>('d', 6H, CH$_3$/P)</td>
<td>---</td>
</tr>
<tr>
<td>1.15</td>
<td>(d, 24H, CH$_3$/P)</td>
<td>$^3$J(HH) 7.03</td>
</tr>
<tr>
<td>1.06</td>
<td>(d, 6H, CH$_3$/P)</td>
<td>$^3$J(HH) 6.61</td>
</tr>
<tr>
<td>1.02</td>
<td>(d, 6H, CH$_3$/P)</td>
<td>$^3$J(HH) 6.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 11.7: $^1$H and $^{13}$C NMR data (C$_6$D$_6$) for cycloadduct (121); †all singlet peaks (CH$_3$/P).
<table>
<thead>
<tr>
<th></th>
<th><strong>δ /ppm</strong></th>
<th><strong>Coupling /Hz</strong></th>
<th></th>
<th><strong>δ /ppm</strong></th>
<th><strong>Coupling /Hz</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1H NMR</strong></td>
<td></td>
<td></td>
<td><strong>13C NMR</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.62</td>
<td>(d.d,1H,Ha)</td>
<td>3J(HaHb) 4.5‡</td>
<td>172.19</td>
<td>(s,1C,C=0)</td>
<td></td>
</tr>
<tr>
<td>4.22</td>
<td>(d.d,1H,Ha)</td>
<td>3J(HaHb) 4.5‡</td>
<td>171.38</td>
<td>(s,1C,C=0)</td>
<td></td>
</tr>
<tr>
<td>4.06</td>
<td>(mult,6H,*)</td>
<td>3J(HH) 7.0</td>
<td>143.27</td>
<td>(d,1C,C=N)</td>
<td>1J(PC) 158.2</td>
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<tr>
<td>3.82</td>
<td>(mult,2H,CH/P)</td>
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<td>66.05</td>
<td>(d,1C,C-ring)</td>
<td>3J(PC) 3.6</td>
</tr>
<tr>
<td>3.73</td>
<td>(s,3H,CO₂Me)</td>
<td></td>
<td>56.97</td>
<td>(d,1C,C-ring)</td>
<td>2J(PC) 26.0</td>
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<tr>
<td>3.69</td>
<td>(s,3H,CO₂Me)</td>
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<td>52.35</td>
<td></td>
<td>48.13</td>
</tr>
<tr>
<td>1.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2xs,2C,OMe)</td>
</tr>
<tr>
<td>1.37</td>
<td>(d,24H,CH₃/P)</td>
<td>3J(HH) ~7†</td>
<td>47.14</td>
<td>(d,2C,CH/P)</td>
<td>2J(PC) 5.1</td>
</tr>
<tr>
<td>1.34</td>
<td></td>
<td></td>
<td>46.98</td>
<td>(d,2C,CH/P)</td>
<td>2J(PC) 6.9</td>
</tr>
<tr>
<td>1.26</td>
<td></td>
<td></td>
<td>26.76</td>
<td>(s,4C,CH/B)</td>
<td></td>
</tr>
<tr>
<td>1.15</td>
<td>(d,24H,CH₃/B)</td>
<td>3J(HH) 6.7</td>
<td>24.34, 24.28,</td>
<td>(4xs,6C,CH₃/P)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24.22, 24.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23.32</td>
<td>(s,8C,CH₃/B)</td>
<td></td>
</tr>
<tr>
<td>5.01</td>
<td>(d,1H,Ha)</td>
<td>3J(HaHb) 4.8</td>
<td>172.71</td>
<td>(s,1C,C=0)</td>
<td></td>
</tr>
<tr>
<td>4.24</td>
<td>(d,1H,Ha)</td>
<td>3J(HaHb) 4.8</td>
<td>171.03</td>
<td>(s,1C,C=0)</td>
<td></td>
</tr>
<tr>
<td>3.85</td>
<td>(sept,2H,CH/B)</td>
<td>3J(HH) ~6</td>
<td>164.93</td>
<td>(s,C=0,***)</td>
<td></td>
</tr>
<tr>
<td>3.40</td>
<td>(sept,2H,CH/B)</td>
<td>3J(HH) ~6</td>
<td>143.26</td>
<td>(s,1C,C=N)</td>
<td></td>
</tr>
<tr>
<td>3.31</td>
<td>(s,3H,OMe ring)</td>
<td></td>
<td>133.40</td>
<td>(s,C=C,sym. fumarate)</td>
<td></td>
</tr>
<tr>
<td>3.29</td>
<td>(s,3H,OMe ring)</td>
<td></td>
<td>64.13</td>
<td>(s,2C,CH/B)</td>
<td></td>
</tr>
<tr>
<td>3.26</td>
<td>(s,***)</td>
<td></td>
<td>61.32</td>
<td>(s,2C,CH/B)</td>
<td></td>
</tr>
<tr>
<td>~1.5</td>
<td>(mult,3H,CH/Si)</td>
<td></td>
<td>51.58</td>
<td>(s,1C,OMe ring)</td>
<td></td>
</tr>
<tr>
<td>1.37</td>
<td>(d,6H,CH₃/B)</td>
<td>3J(HH) 6.58</td>
<td>48.47</td>
<td>(s,OMe,***)</td>
<td></td>
</tr>
<tr>
<td>1.29</td>
<td>(d,6H,CH₃/B)</td>
<td>3J(HH) 6.88</td>
<td>47.29</td>
<td>(s,1C,CH/B)</td>
<td></td>
</tr>
<tr>
<td>1.18</td>
<td>(d,6H,CH₃/B)</td>
<td>3J(HH) 6.78</td>
<td>27.10</td>
<td>(s,2C,CH₃/B)</td>
<td></td>
</tr>
<tr>
<td>1.14</td>
<td>(d,6H,CH₃/B)</td>
<td>3J(HH) 5.71</td>
<td>23.79</td>
<td>(s,2C,CH₃/B)</td>
<td></td>
</tr>
<tr>
<td>1.05</td>
<td>(d,18H,CH₃/Si)</td>
<td>3J(HH) 5.88</td>
<td>23.48</td>
<td>(s,6C,CH₃/Si)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18.90</td>
<td>(s,2C,CH₃/B)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18.80</td>
<td>(s,2C,CH₃/B)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.13</td>
<td>(s,3C,CH/Si)</td>
<td></td>
</tr>
</tbody>
</table>

**Table 11.8:** 1H and 13C NMR data (C₆D₆) for cycloadducts (122) (above) and (123) (below); ‡3J(PH) not resolved; *Ratio CH/B:CH/P = 2:1; **unreacted fumarate starting material; †Complex.
11.8.1 Stereochemical Considerations

The methyl fumarate molecule has the trans configuration [Figure 11.9(a)]. If a single stage reaction occurs it would be expected that the trans configuration would be preserved in the product (121) [Figure 11.9(b)].

Evidence that this is the case is provided by the large coupling constant of $^3J_{HaHb}$ (Table 11.9) (values are of the order of staggered hydrogen atoms in iso-propyl).

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>$^3J(H_aH_b)/Hz$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_2$P--C/N--BR$_2$</td>
<td>(121) ~ 7.0</td>
</tr>
<tr>
<td>H$_a$</td>
<td>C--CO$_2$Me</td>
</tr>
<tr>
<td>MeO$_2$C--H$_b$</td>
<td></td>
</tr>
<tr>
<td>R$_2$P(S)--C/N--BR$_2$</td>
<td>(122) 4.5</td>
</tr>
<tr>
<td>H$_a$</td>
<td>C--CO$_2$Me</td>
</tr>
<tr>
<td>MeO$_2$C--H$_b$</td>
<td></td>
</tr>
<tr>
<td>R$_2$B--N--C/SiR$_3$</td>
<td>(123) 4.8</td>
</tr>
<tr>
<td>H$_a$</td>
<td>C--CO$_2$Me</td>
</tr>
<tr>
<td>MeO$_2$C--H$_b$</td>
<td></td>
</tr>
</tbody>
</table>

Table 11.9: $J(H_aH_b)$ coupling constants for cycloadducts (121)-(123).
11.8.2 Regiospecificity

Reactions with the unsymmetrical methyl acrylate (120) allowed a study of regiospecificity in this system. Isomers were formed in the ratio 3:1 (Figure 11.10). Selected spectroscopic data for the cycloadducts (124) and (125) are presented in Table 11.10 with full experimental details in Section 11.13.16.

Figure 11.10: Reaction of nitrileimine (109) with methyl acrylate (120).

<table>
<thead>
<tr>
<th>1H NMR</th>
<th>Coupling /Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ /ppm</td>
<td></td>
</tr>
<tr>
<td>4.58 (d.d, 1H, Hx)</td>
<td>3J(HbHx) 7.58</td>
</tr>
<tr>
<td>~3.8 (mult, 8H, CH/B+P)</td>
<td></td>
</tr>
<tr>
<td>~3.5 (mult, 2H, HbHb)</td>
<td></td>
</tr>
<tr>
<td>3.33 (s, 3H, CO2Me)</td>
<td>3J(PC) 12.06</td>
</tr>
<tr>
<td>~1.3 (s, 18H, CH3/P)</td>
<td></td>
</tr>
<tr>
<td>~1.3 (s, 18H, CH3/B)</td>
<td></td>
</tr>
<tr>
<td>*3.4 (s, 3H, OMe)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>13C NMR</th>
<th>Coupling /Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ /ppm</td>
<td></td>
</tr>
<tr>
<td>174.47 (s, 1C, C=O)</td>
<td>3J(PC) 5.68</td>
</tr>
<tr>
<td>152.06 (d, 1C, C=N)</td>
<td></td>
</tr>
<tr>
<td>60.36 (d, 1C, C=O/CO2Me)</td>
<td>3J(PC) 5.38</td>
</tr>
<tr>
<td>48.28 (s, 1C, CO2Me)</td>
<td></td>
</tr>
<tr>
<td>42.53 (d, 1C, CH2•)</td>
<td>2J(PC) 41.12</td>
</tr>
<tr>
<td>~48 (d's, 8C, CH/P)</td>
<td></td>
</tr>
<tr>
<td>~27 (s, 8C, CH/B)</td>
<td></td>
</tr>
<tr>
<td>24 (8xs, 16C, CH3/P)</td>
<td></td>
</tr>
<tr>
<td>23 (s, 16C, CH/B)</td>
<td></td>
</tr>
<tr>
<td>*172.70 (s, 1C, C=O)</td>
<td></td>
</tr>
<tr>
<td>*150.22 (d, 1C, C=N)</td>
<td>1J(PC) 13.9</td>
</tr>
<tr>
<td>* 54.61 (d, 1C, CH2•)</td>
<td>2J(PC) 6.9</td>
</tr>
<tr>
<td>* 52.46 (d, 1C, CO2Me•)</td>
<td>3J(PC) 2.97</td>
</tr>
<tr>
<td>* 51.3 (s, 1C, CO2Me)</td>
<td></td>
</tr>
</tbody>
</table>

Table 11.10: 1H and 13C NMR data (C6D6) for cycloadduct (124); *Data for 25% isomer (125); • = on ring.
The formation of these two regioisomers may be explained by consideration of the HOMO of the nitrileimine (Figure 11.11).

The large coefficients on C(1) and N(3) allow the alkene to add in either orientation. The site of the larger HOMO density coefficient corresponds to the more electronegative terminus (the expected site of attack by the electrophile). The site of the largest LUMO coefficient is the least negative terminus and provides the site for attack by the nucleophile \[^{[41]}\]. The isomers (124) and (125) can be distinguished by \(^{13}\)C NMR spectroscopy. In (124), C(3) is more deshielded with a smaller \(^{3}\)J\(_{PC}\) coupling constant. In (125), the most deshielded carbon is C(4) and this has the larger coupling with phosphorus [cf. C(3)] (see Figure 11.10, and for spectra, Figure 11.20).

With the presence of boron it is important to consider electron back-donation from nitrogen to boron. The geometry at the nitrogen is determined by the degree to which the nitrogen lone pair back-donates. The possibility of two rotamers exists, with boron fixed up or down with respect to the nitrileimine backbone. However since these could not be detected in the case of the reaction with methyl fumarate, the diagnosis of the presence of two regioisomers in this case is justified (together with the \(^{13}\)C NMR evidence).

Since (124) is the predominant isomer, 'fixing' of the geometry at boron does not appear to be significant. The isomers were not separated but each was distinguished by \(^{13}\)C NMR spectroscopy. Separation using
column chromatography was considered but was judged inappropriate owing to the sensitivity of the boron to air and traces of moisture. Removing the boron from the system by cleaving the B-N bond (Figure 11.12) may provide a possible route to adduct separation and isolation.

![Figure 11.12: Possible removal of boron from the compound.](image)

It is very interesting to note that in the case of the sulphur containing P(V) nitrileimine (110) only one isomer was formed by cycloaddition with methyl acrylate (120) (Equation 11.12, R = 1Pr). This [and the predominance of isomer (124) with the P(III) nitrileimine] is attributed to the steric bulk at phosphorus. In the case of P(V) the presence of the sulphur atom provides sufficient bulk to prevent the formation of any of the isomer with the ester group on the same side of the molecule as the phosphorus.

The addition of elemental sulphur to isomers (124) and (125) in the P(III) case produced one isomer only (Equation 11.13). It seems that the cycloaddition may be reversible thus providing the route for the conversion of isomer (125) into the more stable form (Equation 11.14). If sulphur only added to isomer (124), it would have been expected that the phosphorus shift of (125) would still have been evident. This was not observed.

\[
\begin{align*}
\text{(110)} & \quad \text{C=N=N-B} \quad \text{NR}_2 \\
\text{(120)} & \quad \text{CH}_2=\text{CHCO}_2\text{Me} \\
\text{(11.12)} & \quad \text{S} \\
\text{(124)} & \quad \text{SR}_2 \\
\text{(125)} & \quad \text{SR}_2
\end{align*}
\]
Selected spectroscopic data for the cycloadduct (126) are presented in Table 11.11 with full experimental details in Section 11.13.17.

<table>
<thead>
<tr>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$ /ppm</td>
<td>Coupling /Hz</td>
</tr>
<tr>
<td>4.55 (d.d, 1H, $H_x$)</td>
<td>$^3$J($H_b$,$H_x$) 5.3</td>
</tr>
<tr>
<td></td>
<td>$^3$J($H_a$,$H_x$) 13.4</td>
</tr>
<tr>
<td>3.9 (mult, 8H, CH/P)</td>
<td>$^3$J(HH) ~6.6</td>
</tr>
<tr>
<td>3.7 (mult, 8H, CH/B)</td>
<td>$^3$J(HH) ~6.6</td>
</tr>
<tr>
<td>3.5 (mult, 2H, CH$_3$•)</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>3.28 (s, 3H, CO$_2$Me)</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>1.3 (d's, 24H, CH$_3$/P)</td>
<td>$^3$J(HH) ~6.8</td>
</tr>
<tr>
<td>1.2 (d, 24H, CH$_3$/B)</td>
<td>$^3$J(HH) ~6</td>
</tr>
</tbody>
</table>

Table 11.11: $^1$H and $^{13}$C NMR data (C$_6$D$_6$) for cycloadduct (126); •=ring.

An interesting extension of this work would involve a study of the reaction of nitrileimine (113) with CH$_2$=CO$_2$Me (120) in order to investigate the regiochemistry involved.
Orthoquinones are known to react across double bonds and to form P(V) species \([42]\). Nitrileimine (109) was reacted successively with sequential molar equivalents of tetrachloroorthoquinone (127). No products were isolated, so the attempted rationalisation is based on \(31^P\) NMR and infrared data only (Table 11.12).

### 11.9.1 Results

Addition of one equivalent of (127) caused loss of the nitrileimine absorption in the infrared and a \(31^P\) NMR shift was obtained in the P(III) region. Two equivalents gave a characteristic P(V) \(31^P\) chemical shift at -36 ppm. In addition, a white precipitate was formed too insoluble to allow solution NMR spectroscopy.

![Diagram](image)

<table>
<thead>
<tr>
<th>EQUIV. OF (127)</th>
<th>(31^P) NMR (δ/ppm)</th>
<th>IR OBSERVATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+103</td>
<td>No NI absorption</td>
</tr>
<tr>
<td>2</td>
<td>-36</td>
<td>No NI absorption</td>
</tr>
<tr>
<td>3</td>
<td>+19</td>
<td>Decomposition</td>
</tr>
</tbody>
</table>

Table 11.12: Addition of TCOQ to nitrileimine (NI) (109).

### 11.9.2 Possible Reaction Mechanism

A possible reaction mechanism for this system is presented in Figure 11.13(a). From a model of this system it appears that this seven membered ring would be possible without substantial strain [Figure
11.13(b). Other possibilities to account for the observed experimental data include 6 membered rings [Figure 11.13(c)].

(a) \[ \text{Reaction 1} \]

(b) \[ \text{Reaction 2} \]

(c) \[ \text{Reaction 3} \]

(d) \[ \text{Reaction 4} \]

Figure 11.13: Proposed reaction mechanism for TCOQ (127) and nitrileimine (109).
To date, no stable boron diazo species are known, some possible guidelines for their synthesis are considered here.

11.10.1 Increasing Negative Charge at Boron

Increasing the negative charge at the boron of the nitrileimine can be achieved, for example, by reaction with a tertiary amine. It appears that this causes rearrangement to \( \hat{\text{P}}\text{C} \hat{\text{B}} \) (117), possibly via an unstable diazo compound which eliminates \( \text{N}_2 \) (Section 11.7). It is difficult to see how the diazo compound can be stabilised at the same time as destabilisation of the nitrileimine. A similar reaction could be tried with nitrileimine (113):

\[
\begin{align*}
\text{iPr}_2\text{N} & \quad \text{B} \quad \text{N} \quad \text{N} \quad \text{C} \quad \text{Si} \quad \text{iPr}_3 \\
\text{iPr}_2\text{N} & \quad \oplus \\
\end{align*}
\]

(113)

11.10.2 Reduction in Substituent Size

Reduction of the group size on boron was done in an attempt to disfavour the formation of a nitrileimine. A direct analogy to work by Bertrand et al.\(^{[32]}\), with the phosphorus derivatives [Figure 11.14(a)]. With smaller dimethylamino groups on phosphorus, the reaction proceeds as shown in Figure 11.14(b).
The reaction of \((i\text{Pr}_2\text{N})_2\text{PC(N}_2\text{)}\text{Li}(103)\) with \((\text{Me}_2\text{N})_2\text{BCl}(130)\) did not give the expected results (Section 11.13.20). A peak at +139 ppm in the \(^{31}\text{P} \text{NMR}\) was observed, thought possibly to be due to \(\overset{\text{>}}{\text{P}}=\text{C}(\text{N}_2)\overset{\text{<}}{\text{P}}\) (117). On cooling crystals were formed and isolated. The NMR shift varied depending on the solvent: 135.0 ppm (THF), 138.5 ppm (pentane) and 140.5 ppm (CDCl\(_3\)). The \(^1\text{H}\) and \(^{13}\text{C} \text{NMR}\) data clearly indicated that the solid was \((i\text{Pr}_2\text{N})_2\text{PCl}(100)\).

Repetition of this experiment gave a diazo absorption in the infrared and a \(^{31}\text{P} \text{NMR}\) shift as expected for \(\overset{\text{>}}{\text{P}}=\text{C}(\text{N}_2)\overset{\text{<}}{\text{P}}\) (106). This was further identified by its characteristic shift on addition of sulphur, giving two further \(^{31}\text{P} \text{NMR}\) signals corresponding to \(\overset{\text{>}}{\text{P}}(\text{S})=\text{C}(\text{N}_2)\overset{\text{<}}{\text{P}}\) (129) and \(\overset{\text{>}}{\text{P}}(\text{S})=\text{C}(\text{N}_2)\overset{\text{<}}{\text{P}}(\text{S})\) (131) \(^{[32]}\). On addition of sulphur another peak also formed upfield at +50 ppm, presumably due to the phosphorus and boron containing material. A shift to high field on addition of sulphur appears to be characteristic of a diazo species \(^{[32]}\), and to low field of a nitrileimine species, \textit{cf.} compounds (107) and (129). The infrared spectrum showed a broad absorption centred around 2100 cm\(^{-1}\) (it may be the nitrileimine species had formed due to B-N thermodynamic favourability).
In the presence of sulphur it was hoped to isolate the phosphorus-boron containing material by low temperature crystallisation, but no solid was obtained. Repetition of this experiment gave totally reproducible results.

It has proved very difficult to postulate a mechanism with the formation of bis(diisopropylamino)phosphorus(III) chloride, \((\text{Pr}_2\text{N})_2\text{PCl}\) (100). This reaction does not occur with the larger diisopropylamino groups on boron, only with the smaller dimethylamino groups, hence with more room around the boron, a 4-coordinated intermediate may be postulated (cf. Equations 11.15 and 11.16). A possible mechanism is shown in Figure 11.15. This rearrangement would also explain the appearance of \(>\text{PC(N}_2\text{P}<\) (106) by coupling of bis(diisopropylamino)phosphorus(III) chloride (100) with \(>\text{PC(N}_2\text{P}<\)Li (103). The other \(^{31}\text{P}\) NMR signal must be generated via a different route.

\[
(\text{Pr}_2\text{N})_2\text{BCl} \xrightarrow{\text{AlCl}_3} (\text{Pr}_2\text{N})_2\text{B}^+\text{AlCl}_4^- \quad (11.15)
\]

\[
(\text{Me}_2\text{N})_2\text{BCl} \xrightarrow{\text{AlCl}_3} (\text{Me}_2\text{N})_2\text{BCl} \cdot \text{AlCl}_3 \quad (11.16)
\]

Figure 11.15: Proposed mechanism for reaction of the phosphorus diazo compound (103) with \((\text{Me}_2\text{N})_2\text{BCl}\) (130).

It may be possible to prevent rearrangement via a four-coordinate intermediate by starting with four-coordinate boron (Equation 11.17).
The reaction of the lithio diazo compound (112) with the boron halide has previously been shown to give a stable nitrileimine (Equation 11.7, see Section 11.6). Reduction of the size of the groups on silicon (e.g. replacing \(-\text{Si}^3\text{Pr}_3\) with \(-\text{SiMe}_3\)) gave a complex reaction mixture, which had a broad absorption in the infrared around 2400-2000 cm\(^{-1}\), and many peaks around 30-20 ppm in the \(^{11}\text{B}\) NMR spectrum (possibly due to some diazo compound and some nitrileimine).

With the phosphorus diazo compound (103), reducing the size of the groups on boron has been investigated. This also led to a mixture of products (see earlier in this section).

In support of this experimental data an interesting reaction to try would involve reduction of the group size at silicon and boron, possibly kinetically favouring the diazo compound (Equation 11.18). The presence of smaller groups may prevent bulky groups "pushing off" the \(N_2\).

\[
\begin{align*}
\text{Me}_2\text{N} & \quad \text{B-Cl (130)} + \text{Me}_3\text{Si-CLi (133)} \rightarrow \text{Me}_2\text{N} \quad \text{Me}_3\text{Si-CLi (133)} \\
\end{align*}
\]

11.10.4 Reaction Between Boron Triflate and Diazomethane

A reaction analogous to that used to form \(\text{Me}_3\text{SiC}(N_2)\text{H}\) (99), by direct interaction of a covalent boron triflate \(^{[43]}\) with diazomethane was attempted (Equation 11.19).
PrNEt\textsubscript{2} was added to scavenge for triflate, as for the trimethylsilyl derivative (99), preventing the following displacement of N\textsubscript{2} by precipitation of the salt:

\[
\begin{array}{c}
\text{PrNEt}_2 + \underset{\text{CH}_2\text{-N=N}}{\text{OSO}_2\text{CF}_3} \\
\rightarrow \underset{\text{N=N}}{\text{CH}_2\text{-N=N}}
\end{array}
\]  

On reaction at -78 °C a yellow solution was formed with a white precipitate. As the temperature rose > -20 °C an apparent rapid polymerisation occurred, yielding a white apparently 'air stable' solid with a clear overlying liquid. The insoluble nature of this polymer limited spectroscopic data (Section 11.13.21).

It is known that if R\textsubscript{2}BCl acts as an electron pair acceptor, formation of polymethylene may result with the initial step involving the coordination of the -CH\textsubscript{2} group of the diazomethane with the acceptor orbital (Equation 11.20) \[44\].

\[
\begin{array}{c}
\Theta \oplus \\
\text{X}_3\text{B} + \underset{\text{H}_2\text{C-N=N}}{\text{CH}_2\text{-N=N}} \\
\rightarrow \underset{\Theta}{\text{X}_3\text{B-CH}_2\text{-N=N}}
\end{array}
\]  

This is followed by fast subsequent steps by elimination of N\textsubscript{2} and polymerisation. It is therefore clear that the less the boron species acts as an electron acceptor, the more likely it is to prevent this reaction.

Nitrogen: electron-donating substituents, bis(diisopropylamino), (\textsuperscript{1}Pr\textsubscript{2}N) groups on boron are already in use. However, perhaps the bulk of the groups could be increased, for example to tetramethylpiperidine (tmp) groups. This will donate to the empty orbital on boron, and may be large enough to prevent polymerisation. However, the use of tmp
groups makes the triflate ionic: \([(\text{tmp})_2\text{B}^+][\text{CF}_3\text{OSO}_2^-]\) \[^{[43]}\]. It is debatable whether this will make it more susceptible to attack since once the \(\text{CH}_2\text{N}_2\) has reacted, the molecule will be covalent.

11.10.5 Conclusion

There appears to be a conflict as to whether small groups or large groups (Sections 11.10.3 and 11.10.4 respectively) would stabilise the boron-diazo compound.

11.11 DIAZO-CARBENE CHEMISTRY WITH Ar GROUPS ON PHOSPHORUS

Photolysis of the diazo compound \((^1\text{Pr}_2\text{N})_2\text{PC(N}_2\text{)SiMe}_3\) (101) or thermal elimination of \(\text{N}_2\) at 250 °C under vacuum generates the stable carbene (Equation 11.21) \[^{[45-47]}\]. It was of interest to look at the possible electronic and steric stabilisation of a carbene bearing the Ar group, 2,4,6-tris(trifluoromethyl)phenyl. The reaction (Equation 11.22) was therefore undertaken.

\[
\begin{align*}
(11.21) \quad ^1\text{Pr}_2\text{N} & \quad \text{P-Cl (14) + Me}_3\text{Si-CLi (133)} \quad \text{Ar} \\
& \quad \text{Ar} \\
(11.22) \quad ^1\text{Pr}_2\text{N} & \quad \text{P=Cl} (14) + \text{Me}_3\text{Si-CLi} (133) \quad \text{Ar} \\
& \quad \text{Ar} \\
& \quad \text{N}_2
\end{align*}
\]

On dropwise addition of the \(\text{Ar}_2\text{PCl (14)}\) solution in ether to (133) at -78° in THF, a black oil was obtained which was attributed to possible 'Li' attack at the Ar ring fluorine atoms. There may also be a steric barrier to the introduction of this group, since the synthesis of 'Ar_3P' is not possible (attributed to the limited room around the
tetrahedral phosphorus, see Chapter 2).

To avoid the Ar compound being in an excess of the lithium species, reverse addition was carried out with exactly similar results. The LiCl was inseparable. The $^{31}$P NMR spectrum showed a 13 line splitting pattern at -8 ppm and a similar multiplet signal at -70 ppm. (A diazo absorption was present in the infrared spectrum).Attributing the former to Ar$_2$P-C(N$_2$)SiMe$_3$ (136), the peak at -70 ppm may correspond to a stable carbene (137) formed at room temperature.

Gentle heating and also photolysis of this mixture caused the signal at -8 ppm to disappear, reinforcing the diazo nature of this species. However, a marked increase in the signal at -70 ppm was not clear, perhaps due to the low concentration involved (Section 11.13.22).

This synthetic route is not satisfactory and the possibility of the peak at -70 ppm corresponding to Ar$_2$PH cannot be ruled out. It may be possible to avoid attack at the fluorine atom by generating a less reactive derivative, for example via a Grignard reagent [the solution put forward for a high yield synthetic route to Ar containing organaboron species (Chapter 8)]. The steric bulk of the Ar group may stabilise carbene (137) and aid its formation by N$_2$ elimination:

$$\Phi \Theta$$ Ar$_2$P=CsSiMe$_3$ ---- Ar$_2$P=C-SiMe$_3$ (137)

11.12 MNDO CALCULATIONS

11.12.1 Introduction

The following calculations were done using MNDO as implemented in MOPAC version 5. In order to keep the calculations tractable, the model fragments (138), (139) and (140) have been used. This has the implicat-
ion that the results have qualitative rather than quantitative value.

\begin{align*}
H_2P-C-N-N-BH_2 & \quad \text{H}_2P-C-BH_2 \quad (139) \quad \text{H}_2P-C-BH_2 \quad (140) \\
(138) & \quad \text{triplet (t)} \\
& \quad + \text{singlet (s)}
\end{align*}

MNDO does not take into account contributions from d-orbitals [48-50], but it is known to give good results for P(III) species. H-substituents were used in the three systems, since with diisopropylamino there are too many atoms to carry out a reasonable calculation.

By replacing \( \text{IP}_2N \) with H, the steric effects of this group have been lost, together with the electronic effect of the nitrogen back-donating into boron. Although these parameters may alter the situation, a concept of the bonding involved is possible. The geometry has been optimised with no initial symmetry parameters.

11.12.2 Nitrileimine (138)

A previous calculation has been carried out on the parent nitrileimine, \( H_2CNNH \) [51].

For nitrileimine (138) the predicted final heat of formation is +56.8 kcal mol\(^{-1}\) and its ionisation potential is 10.16 eV.

\textit{Final Geometry}

\begin{center}
\begin{tikzpicture}
\node (P) at (0,0) [circle, fill=white, label=above:$P$]{}
\node (C) at (0.5,0) [circle, fill=white, label=above:$C$]{}
\node (N1) at (1.5,0) [circle, fill=white, label=above:$N$]{}
\node (N2) at (2,0) [circle, fill=white, label=above:$N$]{}
\node (B) at (2.5,0) [circle, fill=white, label=above:$B$]{}
\node (H1) at (3.5,0) [circle, fill=white, label=above:$H$]{}
\node (H2) at (3.5,-1) [circle, fill=white, label=above:$H$]{}
\node (H3) at (3.5,-2) [circle, fill=white, label=above:$H$]{}
\draw (P) -- (C) -- (N1) -- (N2) -- (B) -- (H1)
\draw (P) -- (H2)
\draw (P) -- (H3)
\end{tikzpicture}
\end{center}

\textit{HOMO (delocalised)}

To summarise the nature of the HOMO, N(3): node (no contribution); N(6): large negative value, bigger and opposite to C(2); B: contribution in phase with nitrogen but a smaller value.
Bond Order

Calculated bond orders are: C(2)-N(3) = 2.5; C(2)-N(6) = 0.3 and N(6)-B(7) = 1.32.

Valency

This indicates that the nitrogen lone pair is donating into the boron, however with \( (^{1}\text{PrN})_2 B \), with two nitrogens already donating into boron this may be significantly lower. To summarise the results, N(3): expanded valency (more like the nitrilium ion); C(2): reduced valency (3.8) and N(6): reduced valency (2.86).

Localised Bonding Orbitals

(A consideration of orbitals lower in energy than these involves the \( \sigma \)-framework.)

<table>
<thead>
<tr>
<th>Energy/eV</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>-11.63</td>
<td>(N lone pair)</td>
</tr>
<tr>
<td>-15.27</td>
<td>(C-N ( \pi ) bond)</td>
</tr>
<tr>
<td>-15.75</td>
<td>(2 degenerate B-H bonds)</td>
</tr>
<tr>
<td>-16.24</td>
<td>(2 degenerate P-H bonds)</td>
</tr>
</tbody>
</table>

The boron-nitrogen bond \( (1.71\text{\AA}) \) has contributions from the nitrogen lone pair and the \( \sigma \)-bond. The rest are effectively 2 centre bonds. The
top localised orbital is the nitrogen lone pair donating into the boron. The orbital below this in energy is the C(2)-N(3) \( \pi \)-bond. The most representative structure can be drawn with nitrogen in an expanded valency:

\[
\begin{array}{c}
P_1 - C_2 \equiv N_3 \\
N_6 \rightarrow B_7
\end{array}
\]

However, other canonical forms are important, for example, \( \equiv N \rightarrow N \).

**Nitrideimine Molecular Charge**

This charge distribution will change with \( \text{\textsuperscript{1}} \text{Pr}_2 \text{N} \) groups on the boron and phosphorus. The boron here is not charged. When amine substituents are present on boron this may not be the case. Perhaps by making the boron negatively charged the nitrideimine could be destabilised to form the diazo. This argument has been discussed previously (Section 11.1.1).

\[
\begin{array}{c}
P_1 - C_2 \equiv N_3 \\
0.534 \quad 0.21 \quad 0.26 \\
N_6 \rightarrow B_7
\end{array}
\]

The next stage would be to do a similar calculation but with nitrogen substituents in place of the hydrogen atoms, i.e. using the nitrideimine compound \((\text{H}_2\text{N})_2\text{P-C=}=\text{N} \rightarrow \text{N}(\text{H}_2)\text{P}\). This work is at present underway.

**11.12.3 Calculation on Diazo (139)**

The calculated heat of formation = 43.73 kcal mol\(^{-1}\), \( nb. \) the diazo is 13 kcal more stable than the nitrideimine (however, the more steric demand of \( \text{\textsuperscript{1}} \text{Pr}_2 \text{N} \) and its inductive effect may counteract this, hence the
difference in heats of formation of the two structures may not be so pronounced).

The calculated ionisation energy is 9.6 eV, cf. 10.1 eV for the nitrileimine (in the diazo compound the slightly higher lying orbitals make it easier to ionise by 0.5 eV).

**Molecular Geometry**

Calculated bond lengths and angles are as follows: P-H = 1.34 Å and B-H = 1.16 Å (cf. 1.33 Å and 1.17 Å respectively in the nitrileimine); P-C = 1.72 Å (larger than in the nitrileimine). The carbon atom is effectively flat with the P, B, N and C all in the same plane. The C(2)-N(3)-N(6) fragment is virtually linear. The C-N bond (1.36 Å) is short, with some double-bonded character, and the N-N (1.12 Å) close to that of molecular nitrogen, so it appears that the structure can be represented by the fragment, C-N=N. The C-B bond is short (1.46 Å) due to the negative charge donated from carbon to the boron vacant orbital. This effect would probably be reduced with nitrogen substituents on the boron.

\[
\begin{align*}
\text{P} & \quad 1.72 \\
\text{C} & \quad 1.36 \\
\text{B} & \quad 1.46 \\
\text{N} & \quad 1.12 \\
\end{align*}
\]

**Highest Delocalised Molecular Orbital**

The C-N-N \( \pi \)-system is basically delocalised into the boron atom. The next orbital energy level down is the phosphorus lone pair, followed by the B-H bonds in the delocalised orbital scheme.

\[
\begin{align*}
\text{C} & \quad +0.78 \\
\text{B} & \quad +0.45 \\
\text{N} & \quad +0.3 \\
\text{N} & \quad -0.45
\end{align*}
\]
Charges

Here the carbon is more negatively charged than in the nitrileimine species.

\[
P{-0.38} \quad \overset{\text{neutral}}{\text{C}_2} \quad B
\]

\[
\begin{array}{c}
N_3 \quad +0.20 \\
N_6 \quad +0.05
\end{array}
\]

Bond Order and Valencies

The structure is almost \(N\equiv N\) so it is fairly unstable to the loss of \(N_2\). \(N(3)\): has expanded valency, \(N^+ (3.7)\); \(P\): normal valence; \(C\): valence is reduced (3.58), it is on its way to becoming a carbene.

Diazo Localised Molecular Orbital

The electrons on carbon donate into boron (cf. the nitrileimine in which the nitrogen lone pair donates to the boron).

It appears that the diazo fragment is thermodynamically more stable than the nitrileimine. There is no information on the potential surface connecting the nitrileimine and the diazo species.
11.12.4 Triplet State \( \text{P-C-B<} (140^t) \) (UHF)

This system has already been calculated using the 3-21G 2nd order Moller-Plesset theory \([52]\), which is a much more rigorous calculation than that used here. However, very similar results have been obtained showing that the MNDO is comparable, and is an acceptable method for this system.

The unrestricted Hartree-Fock method treats up and down spin electrons differently with different energies and different orbital shapes, whereas the RHF system treats the up and down spin electrons equally. In this UHF system there are 7 \( \beta \)-electrons and 9 \( \alpha \)-electrons, i.e. 9 up, 7 down occupying different orbitals. The calculated heat of formation is 45.67 kcal mol\(^{-1}\). Its geometry is nearly linear (175\(^\circ\)):

\[
\begin{array}{c}
\text{P} \\
\text{C} \\
\text{B}
\end{array}
\]

\[ \text{H} 1.65 \text{H} 1.45 \text{H} \]

**Highest Occupied Molecular Orbital**

The two highest (singly occupied) orbitals have energies of -9.6 and -10.9, both \( \alpha \)(up) spin. They are not degenerate. There is one electron in C(y), and one in C(z) and the latter can donate into the boron empty orbital so its energy is slightly lower.

---

\(^2\)The heats of formation here cannot be compared with the nitrileimine and the diazo compounds as these were calculated with RHF. Unrestricted Hartree-Fock (UHF) is used here since it gives an accurate picture of the electron spin distribution.
Charges

The C-B bond is $\sigma$-polarised, the negative charge resides on the carbon, $\pi$-donation is possible from only one electron to boron. With the Unrestricted Hartree-Fock (UHF) treatment, the amount bond orders are inaccurate is proportional to the amount of spin. The spin is significant here and therefore bond orders cannot be accurately determined.

\[
\begin{array}{c}
\text{P} \\
\text{C} \\
\text{B}
\end{array}
\]

Spin and Valency

Some spin is transferred to boron from donation by the $p_z$ orbital on carbon. The expected value of the spin is 2, in the calculation it appears as 2.0239, hence there is no substantial spin contamination. The C($p_z$) orbital has slightly less spin than the C($p_y$) as it has transferred some spin to the boron.

11.12.5 Singlet State $\text{P-C-B} \rangle (140^S) \ (\text{UHF})$

A comparison of UHF type calculations can only be made with similar UHF calculations, cf. the triplet state. Heat of formation is 44 kcal mol$^{-1}$, so the singlet state is calculated to be slightly more stable than the triplet state. [8 doubly filled energy levels - all electron paired and therefore a different geometry is obtained]. The C-B bond length is shortened as the two electrons on the carbene carbon atom can
donate into the boron empty orbital, increasing the bond order and hence the negative charge at boron.

**Geometry and HOMO**

Molecular geometry and the highest occupied molecular orbital are depicted below. Two electrons overlap with the boron orbital. The HOMO-1 (next highest molecular orbital) is the lone pair on the phosphorus.

\[
P-C-B
\]

Geometry

\[
\begin{align*}
\text{P} & \quad \text{C} & \quad \text{B} \\
1.63
\end{align*}
\]

HOMO

**Atomic Charges, Bond Order and Valency**

More negative charge resides on boron due to more \( \pi \)-donation (cf. the triplet case). Bond orders for the singlet case cannot be compared with those in the triplet, since the UHF treatment for the triplet state precluded their calculation (Section 11.12.4). The bond order of P-C is 1.12 (slightly multiple bonded) whilst for B-C it is 1.74 (almost a B=C bond). The carbon valency of 3.09 corresponds to a significant valency decrease (ie. singlet carbon). The boron valency is 3.6 (ie. significantly increased). There are no unpaired electrons therefore it is possible to consider the *localised orbitals*, as represented by a lone pair of electrons on carbon donating into boron. The next energy level down is the phosphorus lone pair.

The heat of formation for the diazo species (139) cannot be directly compared to that of the carbene (140) since even though by *definition* the heat of formation of \( \text{N}_2 \) is zero, the entropy must also be taken into account which will be large and positive.
11.13 EXPERIMENTAL DETAILS

11.13.1 Preparation of (109)

\[
\begin{align*}
(102) & \quad \text{iPr}_2N\text{CH}_2 \quad \text{BuLi/THF} \quad -78^\circ\text{C} \\
(103) & \quad \text{iPr}_2N\text{Li} \quad -78^\circ\text{C} \\
(108) & \quad \text{>B-Cl} \\
(109) & \quad \text{LiCl} \quad \text{LiCl} \\
\end{align*}
\]

A solution of (102) (2g, 7.4 mmol) in THF (25 ml) was cooled to -78 °C and to it was added n-BuLi (4.6 ml, 7.4 mmol, 1.6 M), dropwise via syringe. The solution was stirred at -78 °C for 30 min, followed by the dropwise addition of bis-(diisopropylamino)boron chloride (108) (2 ml, 1.8g, 7.4 mmol, 1 equivalent) in THF (20 ml). The temperature was maintained at -78 °C until the addition was complete (15 mins) and then was allowed to slowly return to ambient temperature over a period of 2h. The THF was removed \textit{in vacuo} and pentane (20 ml) was added to precipitate the LiCl formed in the reaction. The salts were removed by filtration and the filtrate was concentrated \textit{in vacuo} to give (109) as a yellow oil (pure by $^{31}\text{P}$ NMR). Yield was 3.5g (98%) with some unreacted ($\text{iPr}_2\text{N}_2$)BCl (108); bpt. 113 °C (0.2 mm Hg); IR (pentane) $\nu_{\text{max}}$: 2100 cm$^{-1}$; MS (Intensity%) EI: 282 [100,$\text{iPr}_2\text{N-PC(N}_2\text{)B-N}\text{iPr}_2$]; $^{11}\text{B}$ δ: 29 ppm (s,broad); $^{31}\text{P}$ δ: 45.1 ppm. $^1\text{H}$ and $^{13}\text{C}$ NMR spectral data are presented in Table 11.1 (Section 11.4.3) (see also Figure 11.16).
11.13.2 Preparations of (110)

11.13.2.1 From Nitrileimine (109) and Sulphur

\[
\text{iPr}_2\text{N} - \overline{\text{C}} - \text{N} - \text{N} - \text{B} - \text{N} - \text{iPr}_2 \xrightarrow{1/8\text{S}_8, \text{benzene}} \text{iPr}_2\text{N} - \overline{\text{C}} - \text{N} - \text{N} - \text{B} - \text{N} - \text{iPr}_2
\]

A solution of nitrileimine (109) (1g, 2.1 mmol) in benzene (25 ml) was placed in a 100 ml Schlenk tube. To this solution was added sulphur (0.074g, 2.18 mmol, 1.1 equivalents). The reaction mixture was stirred for 1 hour at room temperature, after which complete conversion to (110) was noted by \( {^3}\text{P} \) NMR spectroscopy. The solvent was removed \textit{in vacuo} and the product separated from excess sulphur by cooling to -30°C in pentane (30 ml). Concentration of the filtrate allowed isolation of the pure nitrileimine (110). Yield was 900 mg (83% by weight) with some unreacted \((\text{iPr}_2\text{N})_2\text{BCl} \) (108).

11.13.2.2 From \((\text{iPr}_2\text{N})_2\text{P(S)CHN}_2 \) (104)

\[
\text{iPr}_2\text{N} - \overline{\text{P}} - \text{CH} - \overline{\text{S}} - \text{Li} \xrightarrow{-78°C} \text{iPr}_2\text{N} - \overline{\text{P}} - \text{Cl} - \text{Li} \xrightarrow{(\text{iPr}_2\text{N})_2\text{BCl}, -78°C} \text{iPr}_2\text{N} - \overline{\text{P}} - \text{C} - \text{N} - \text{N} - \text{B} - \text{N} - \text{iPr}_2
\]

A solution of the yellow crystalline diazo compound (104) (500 mg, 1.6 mmol) in THF (25 ml) was cooled to -78°C and to it was added \( \text{^nBuLi} \) (1 ml, 1.6 mmol, 1 equivalent, 1.6 M) dropwise \textit{via} syringe. The solution was stirred at -78°C for 30 min followed by dropwise addition of bis(diisopropylamino)boron chloride (0.4g, 1.6mmol) in THF (10 ml). The temperature was maintained at -78°C until the addition was complete (10 min), and then was allowed to slowly return to ambient temperature over a period of 2 hours. The THF was removed \textit{in vacuo} and pentane (20
ml) was added to precipitate the LiCl formed in the reaction. The salts were removed by filtration and the product (110) was isolated as a white solid in pure form by crystallisation from pentane. Yield was 500 mg (61%); IR (C₆D₆) νmax: 2095 cm⁻¹; ¹¹B δ: 27.8 ppm (s,broad); ³¹P δ: 31.8 ppm (pentet) ³¹P 19.7 Hz. ¹H and ¹³C NMR spectral data are presented in Table 11.2 (Section 11.4.3) (see also Figure 11.17).

11.13.3 Preparation of Mes₂BF

Very low yields were obtained by the use of organozinc compounds and other classical routes to organoboron species (Section 8.1). Higher yields (ca. 70%) were obtained by the preparative route, and use of specific apparatus designed by Professor Pelter [53].

Mes₂BF: air sensitive white solid, mpt. 70-72⁰C; bpt. 120-122⁰C (0.1 mm Hg); ¹¹B (CH₂Cl₂) δ: 53.5 ppm (s,broad).

11.13.4 Attempted Reaction of (111) with (101)

\[
\begin{align*}
\text{Mes}_2\text{BF} \; (\text{111}) + \text{Me}_3\text{SiCl}_2 \rightleftharpoons \text{X} \rightarrow \text{Me}_3\text{SiF}
\end{align*}
\]

Mes₂BF (0.8g, 3 mmol) in THF (10 ml) was added to a solution of phosphorus diazo compound (101) (1.0g, 3 mmol) at room temperature with stirring. After 1 hour, the ³¹P NMR indicated that no reaction had taken place. The reaction mixture was warmed to 35 °C, and stirred at this temperature for 2 hours and no reaction occurred. The ³¹P NMR signal (+54 ppm) corresponds to the starting material (101), with the corresponding diazo absorption in the infrared at 2020 cm⁻¹.
11.13.5 Reaction of (102) with (111)

\[
\begin{align*}
{^i\text{Pr}_2\text{N}}_{\text{P-CH}} \quad & \xrightarrow{\text{BuLi}} \quad {^i\text{Pr}_2\text{N}}_{\text{P-CLi}} \\
{^i\text{Pr}_2\text{N}}_{\text{N}_2} \quad & \xrightarrow{\text{Mes}_2\text{BF}} \\
\end{align*}
\]

A solution of diazo compound (102) (0.51g, 1.9 mmol) was cooled in THF (25 ml) to -78 °C. BuLi (0.83 ml, 2.1 mmol, 1.1 equivalents, 2.5 M) was added dropwise, and the solution stirred at -78 °C for 20 mins. Mes₂BF (0.51g, 1.9 mmol) in THF (15 ml) was added dropwise. On addition the solution turned bright pink. The THF was removed in vacuo to yield a pink oil. Addition of pentane gave no visible precipitate, and no lithium fluoride was separable. Cooling in pentane to -20 °C gave an apparent precipitate (LiF!). Filtration gave a pink solution, from which no crystalline product was obtained by cooling to -40 °C. IR (pentane) \( \nu_{\text{max}} = 2120 \text{ cm}^{-1} \); \( ^{31}\text{P} \delta: +44.97 \text{ ppm}; ^{11}\text{B} \delta: -40 \text{ ppm}; (\text{br}) \) \(^1\text{H} \) NMR spectroscopy indicated a mixture of products.

11.13.6 Reaction of (103) with (4)

\[
\begin{align*}
{^i\text{Pr}_2\text{N}}_{\text{P-CH}} \quad & \xrightarrow{\text{BuLi}} \quad {^i\text{Pr}_2\text{N}}_{\text{P-CLi}} \\
{^i\text{Pr}_2\text{N}}_{\text{N}_2} \quad & \xrightarrow{\text{Ar}_2\text{BCl}} \quad (4) \\
\end{align*}
\]

\( \text{Ar} = 2,4,6\text{-tris(trifluoromethyl)benzene} \)

A solution of diazo compound (102) (1.1g, 4.0 mmol) was cooled to -78 °C in THF (20 ml). BuLi (1.78 ml, 4.5 mmol, 1.1 equivalents, 2.5 M) was added dropwise, and the solution was stirred at -78 °C for 20 mins, followed by the dropwise addition of \( \text{Ar}_2\text{BCl} \) (4) (2.43g, 4.0 mmol) dissolved in THF (10 ml). Following the first drop of \( \text{Ar}_2\text{BCl} \) solution, the solution turned black. After complete addition the THF was removed in vacuo, and addition of pentane (20 ml) gave no LiCl precipitate. It
was inseparable from the black oil. The very poor broad signal in the $^{31}$P NMR spectrum (42 ppm) was attributed to decomposition. IR $\nu_{\text{max}}$: 1160 cm$^{-1}$ (broad). Reverse addition of the lithio compound to Ar$_2$BCl gave the same black oil attributed to the same decomposition process.

11.13.7 Preparation of (113)

\[
\begin{align*}
\text{iPr}_3\text{Si-CH} & \xrightarrow{\text{BuLi, -78}^\circ\text{C}} \text{iPr}_3\text{Si-Cl} \xrightarrow{\text{iPr}_2\text{N}_2\text{BCl, -78}^\circ\text{C}} \text{iPr}_3\text{Si-} + \text{N}=\text{N-B} \xrightarrow{\text{N}^\text{iPr}_2} \text{(113)}
\end{align*}
\]

A solution of the diazo compound (142) (0.41g, 2.07 mmol) in THF (25 ml) was cooled to -78 °C, and to it was added $^n$BuLi (1.29 ml, 2.07 mmol, 1 equivalent, 1.6 M) dropwise by syringe. The solution was stirred at -78 °C for 30 min followed by the dropwise addition of bis(diisopropylamino)boron chloride (0.51 ml, 2.07 mmol, 1 equivalent) in THF (10 ml). The temperature was maintained at -78 °C until the addition was complete (10 min) and then was allowed to slowly return to ambient temperature over a period of 2 hours. The THF was removed $\text{in vacuo}$, and pentane (10 ml) was added to precipitate the LiCl formed in the reaction. No immediate precipitation occurred, so the solution was cooled to -30 °C overnight to allow its separation. [This problem may have been overcome by the use of a crown ether]. The salts were removed by filtration. The filtrate was concentrated $\text{in vacuo}$ to give (113) as a pale yellow oil (purified by crystallisation from CDCl$_3$). Yield was 800 mg (95%); IR $\nu_{\text{max}}$: 2100 (C=N) cm$^{-1}$; Mass spectrum (EI) showed small fragments: 96 [100, $^3\text{Pr-Si}$]; $^{11}$B (C$_6$D$_6$) $\delta$: +28.1 (s, broad) ppm; $^{29}$Si (C$_6$D$_6$) $\delta$: 0.726 (s) ppm. $^1$H and $^{13}$C NMR spectral data are presented in Table 11.3 (Section 11.6) (see also Figure 11.18).
11.13.8 Preparation of (114)

\[
\begin{align*}
\text{iPr}_2\text{N} & \quad \Theta \quad \Phi \\
\text{iPr}_2\text{N} & \quad \text{C} \quad \text{N} \quad \text{N} \quad \text{B} \quad \text{iPr}_2 \quad \stackrel{\text{h} \nu}{\longrightarrow} \quad \text{iPr}_2\text{N} & \quad \text{P} \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{B} \quad \text{iPr}_2 \\
& \quad \text{N} \quad \text{iPr}_2 & \quad \text{N} \quad \text{iPr}_2 \\
\text{(109)} & & \text{(114)}
\end{align*}
\]

A solution of nitrileimine (109) (200 mg, 0.41 mmol) in d$_6$-benzene (5 ml) in a 10 mm pyrex NMR tube was irradiated at 300 nm for 12 hours. After irradiation was stopped the $^{31}$P NMR spectrum showed complete conversion to a single new product. Removal of the solvent in vacuo gave carbodiimide (114) in quantitative yield as a pale yellow oil. Yield was 200 mg (100% by weight); IR (benzene) $\nu_{\text{max}}$: 2200 (N=C=N) cm$^{-1}$; MS (Intensity%) EI: 257 [100, (iPr$_2$N)$_2$P-N=C]; 211 [65, (iPr$_2$N)$_2$B]; $^{11}$B $\delta$: +23 ppm (s, broad); $^{31}$P $\delta$: +82 ppm. $^1$H and $^{13}$C NMR spectral data are presented in Table 11.4 (Section 11.7).

11.13.9 Preparations of (115)

11.13.9.1 From Carbodiimide (114) and Sulphur

\[
\begin{align*}
\text{iPr}_2\text{N} \quad \text{P} \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{B} \quad \text{iPr}_2 \quad \stackrel{1/8\text{S}_8}{\longrightarrow} \quad \text{iPr}_2\text{N} \quad \text{P} \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{B} \quad \text{iPr}_2 \\
\text{(114)} & & \text{(115)} \\
\text{benzene} & & \text{benzene}
\end{align*}
\]

To a solution of the carbodiimide (114) (300 mg, 0.62 mmol) in benzene (15 ml) was added sulphur (22 mg, 0.68 mmol, 1.1 equivalents). The reaction mixture was stirred for 1 hour at room temperature. Quantitative conversion to (115) was noted by $^{31}$P NMR spectroscopy. The solvent was removed in vacuo, and the excess sulphur removed by crystallisation at -30 °C in pentane. The carbodiimide (115) was isolated as a yellow oil. Yield was 290 mg (91% by weight).
11.13.9.2 Via Photolysis of Nitrileimine (110)

\[
\begin{array}{c}
\text{iPr}_2N^+\text{C}^=\text{N}^+\text{N}^+\text{B}^+\text{N}^+\text{iPr}_2 \\
\text{iPr}_2N^+\text{C}^=\text{N}^+\text{N}^+\text{B}^+\text{N}^+\text{iPr}_2 \\
\text{benzene} \\
\text{300 nm} \\
\end{array}
\]

A solution of nitrileimine (110) (400 mg, 0.78 mmol) in d\text{6}-benzene (5 ml) in a 10 mm pyrex NMR tube was irradiated at 300 nm for 12 hours. The solvent was removed \textit{in vacuo}. Addition of pentane and cooling allowed the removal of any impurity by precipitation. Concentration of the filtrate gave the carbodiimide (115) in 60\% yield (240 mg); IR (pentane) \( \nu_{\text{max}} \): 2200 (N=C=N) cm\textsuperscript{-1}; \( ^{11}\text{B} \) \( \delta \): 22 (broad) ppm; \( ^{31}\text{P} \) \( \delta \): 54.5 (pentet) ppm \( ^{3}J_{\text{PH}} \) 19.4 Hz. \( ^{1}\text{H} \) and \( ^{13}\text{C} \) NMR spectral data are presented in Table 11.5 (Section 11.7).

11.13.10 Preparation of (116)

\[
\begin{array}{c}
\text{iPr}_2N^+\text{B}^=\text{N}^+\text{C}^=\text{Si}^+\text{iPr}_3 \\
\text{iPr}_2N^+\text{B}^=\text{N}^+\text{C}^=\text{Si}^+\text{iPr}_3 \\
\text{300nm} \\
\end{array}
\]

A solution of nitrileimine (113) (400 mg, 0.98 mmol) in d\text{6}-benzene (5 ml) in a 10 mm Pyrex NMR tube was irradiated at 300 nm for 12 hours. The solvent was removed \textit{in vacuo}. Addition of pentane and cooling allowed the removal of a small amount of solid material. The filtrate was concentrated to give the carbodiimide (116). Yield was 344 mg (86\%). IR \( \nu_{\text{max}} \): 2200 cm\textsuperscript{-1}; \( ^{11}\text{B} \) (C\text{6}D\text{6}) \( \delta \): 22.2 ppm; \( ^{1}\text{H} \) and \( ^{13}\text{C} \) NMR spectral data are presented in Table 11.6 (Section 11.7).
11.13.11 Reaction of (109) with Et₃N

\[
\begin{align*}
\text{iPr}_2\text{N} & - \Theta - \Theta - \text{N} - \text{B} - \text{N} & \text{iPr}_2 \\
\text{iPr}_2\text{N} & - \Theta - \Theta - \text{N} - \text{B} - \text{N} & \text{iPr}_2 \\
\text{iPr}_2\text{N} & - \Theta - \Theta - \text{N} - \text{B} - \text{N} & \text{iPr}_2 \\
\text{iPr}_2\text{N} & - \Theta - \Theta - \text{N} - \text{B} - \text{N} & \text{iPr}_2
\end{align*}
\]

A solution of the nitrileimine (109) (0.40g, 0.83 mmol) in THF (25 ml) was reacted with Et₃N (0.5g, 5.0 mmol) at room temperature. After stirring for 2 hours there was no evidence of any reaction in the \(^{31}\text{P} \text{NMR}\) spectrum. After stirring overnight a small peak at +139 ppm was observed and the solution became coloured red. Addition of a further amount of Et₃N (0.5g, 5.0 mmol) and stirring for 2 days gave an apparent quantitative conversion by \(^{31}\text{P} \text{NMR}\) to a species with a chemical shift of +139 ppm. No absorption remained in the infrared spectrum corresponding to the nitrileimine starting material. The signal at +139 ppm was attributed to the \(\text{P} \equiv \text{C} \equiv \text{B}\) moiety (see Section 11.7).

11.13.12 Reaction of (109) with Me₃N

\[
\begin{align*}
\text{iPr}_2\text{N} & - \Theta - \Theta - \text{N} - \text{B} - \text{N} & \text{iPr}_2 \\
\text{iPr}_2\text{N} & - \Theta - \Theta - \text{N} - \text{B} - \text{N} & \text{iPr}_2 \\
\text{iPr}_2\text{N} & - \Theta - \Theta - \text{N} - \text{B} - \text{N} & \text{iPr}_2 \\
\text{iPr}_2\text{N} & - \Theta - \Theta - \text{N} - \text{B} - \text{N} & \text{iPr}_2
\end{align*}
\]

A ten-fold excess of Me₃N (0.62g, 10.5 mmol) was bubbled through a THF solution (25 ml) containing nitrileimine (109) (0.51g, 1.06 mmol) at room temperature with stirring. No apparent reaction was observed. The solution remained yellow. The \(^{31}\text{P} \text{NMR}\) signal at \(\sim 4\) ppm however, showed complete decomposition, and the nitrileimine absorption in the infrared spectrum was lost.
11.13.13 Preparation of (121)

\[
\begin{align*}
\text{iPr}_2\text{N} & \overset{\text{CHCO}_2\text{Me}}{\text{C}} \overset{\text{N}}{\text{C}} \overset{\text{N}}{\text{N}} \text{N} \text{Pr}_2 \\
\text{iPr}_2\text{N} & \text{MeO}_2\text{C} \overset{\text{C}}{\text{C}} \overset{\text{C}}{\text{H}} \overset{\text{N}}{\text{N}} \text{Pr}_2
\end{align*}
\]

A solution of nitrileimine (109) (0.37g, 0.77 mmol) in benzene (15 ml) was placed in a 100ml Schlenk tube. To this solution was added solid dimethyl fumarate (122 mg, 1.1 equivalents). The reaction mixture was stirred at ambient temperature for 6 hours, after which complete conversion to (121) was noted by $^{31}$P NMR spectroscopy. The solvent was removed in vacuo and the product was separated from the excess fumarate by crystallisation at -30 °C from pentane. The cycloadduct (121) was isolated as a pale yellow oil. Yield was 480 mg (99% by weight); IR (pentane) $\nu_{\text{max}}$: 1730 (broad,CO$_2$Me) cm$^{-1}$; $^{11}$B $\delta$: 27.7 ppm (s, broad); $^{31}$P $\delta$: 26.7 ppm. $^1$H and $^{13}$C NMR spectral data are presented in Table 11.7 (Section 11.8) (see also Figure 11.19).

11.13.14 Preparations of (122)

11.13.14.1 From Nitrileimine (110) and (CHCO$_2$Me)$_2$ (119)

\[
\begin{align*}
\text{iPr}_2\text{N} & \overset{\text{S}}{\text{C}} \overset{\text{N}}{\text{C}} \overset{\text{N}}{\text{N}} \text{Pr}_2 \\
\text{iPr}_2\text{N} & \text{MeO}_2\text{C} \overset{\text{C}}{\text{C}} \overset{\text{C}}{\text{H}} \overset{\text{N}}{\text{N}} \text{Pr}_2
\end{align*}
\]

A solution of nitrileimine (110) (500 mg, 0.97 mmol) in benzene (15 ml) was placed in a 100 ml Schlenk tube. To this solution was added solid dimethyl fumarate (0.15g, 1.07 mmol, 1.1 equivalents). The reaction mixture was stirred at ambient temperature for 6 hours, after which the complete conversion to (122) was noted by $^{31}$P NMR spectro-
scopy. The solvent was removed \textit{in vacuo} and the product was separated from the excess fumarate by crystallisation at -30 °C. Cycloadduct (122) was isolated as a pale yellow oil. Yield was 620 mg (97%). A small impurity was detected from the $^{13}$C NMR spectrum.

11.13.14.2 From Cycloadduct (121) and Sulphur

\[
\begin{align*}
\text{iPr}_2\text{N} & \quad \text{N} \quad \text{B} & \quad \text{iPr}_2 \\
\text{iPr}_2\text{N} & \quad \text{N} \quad \text{C} & \quad \text{CO}_2\text{Me} \\
\text{MeO}_2\text{C} & \quad \text{H} \quad \text{H} \\
(121)
\end{align*}
\]

\[
\begin{align*}
\text{iPr}_2\text{N} & \quad \text{N} \quad \text{B} & \quad \text{iPr}_2 \\
\text{iPr}_2\text{N} & \quad \text{N} \quad \text{C} & \quad \text{CO}_2\text{Me} \\
\text{MeO}_2\text{C} & \quad \text{H} \quad \text{H} \\
(122)
\end{align*}
\]

To a solution of cycloadduct (121) (200 mg, 0.32 mmol) in benzene (15 ml) was added sulphur powder (11.2 mg, 0.35 mmol, 1.1 equivalents). The reaction mixture was stirred for 1 hour at room temperature. Quantitative conversion to (122) was noted by $^{31}$P NMR spectroscopy. The solvent was removed \textit{in vacuo} and the excess sulphur removed by crystallisation at -30 °C in pentane. Compound (122) was isolated as a pale yellow oil. Yield was 0.20g (97%); IR (pentane) $\nu_{\text{max}}$: 1740 (d, C=O) cm$^{-1}$; $^{11}$B $\delta$: +27 ppm (s, broad); $^{31}$P $\delta$: +57 ppm (pentet) $^{3}J_{PH}$ 15.9 Hz. $^{1}$H and $^{13}$C NMR spectral data are presented in Table 11.8 (Section 11.8) (see also Figure 11.20).

11.13.15 Preparation of (123)

\[
\begin{align*}
\text{iPr}_2\text{N} & \quad \text{N} \quad \text{N} \quad \text{C} & \quad \text{Si} \quad \text{iPr}_3 \\
\text{iPr}_2\text{N} & \quad \text{N} \quad \text{N} \quad \text{C} & \quad \text{Si} \quad \text{iPr}_3 \\
(113)
\end{align*}
\]

\[
\begin{align*}
\text{iPr}_2\text{N} & \quad \text{N} \quad \text{N} \quad \text{C} & \quad \text{Si} \quad \text{iPr}_3 \\
\text{iPr}_2\text{N} & \quad \text{N} \quad \text{N} \quad \text{C} & \quad \text{Si} \quad \text{iPr}_3 \\
(123)
\end{align*}
\]

A solution of nitrileimine (113) (500 mg, 1.2 mmol) in benzene (15 ml) was placed in a 100 ml Schlenk tube. To this solution was added solid dimethyl fumarate (194 mg, 1.34 mmol, 1.1 equivalents). The
reaction mixture was stirred at ambient temperature for 6 hours, after which complete conversion to (123) was noted by $^{31}$P NMR spectroscopy.

The solvent was removed \textit{in vacuo}, and the product was separated from the excess fumarate by crystallisation at -30 °C. The cycloadduct (123) was isolated as a pale yellow oil. Yield was 800 mg (spectroscopy suggested that not all the excess fumarate had been removed); IR $\nu_{\text{max}}$: 1740 cm$^{-1}$; $^{11}$B ($C_6D_6$) $\delta$: +28 (s, broad) ppm; $^{29}$Si ($C_6D_6$) $\delta$: 0.705 (s) ppm. $^1$H and $^{13}$C NMR spectral data are presented in Table 11.8 (Section 11.8) (see also Figure 11.22).

11.13.16 Preparation of (124) and (125)

A solution of nitrileimine (109) (500 mg, 1.0 mmol) in benzene (20 ml) was placed in a 100 ml Schlenk tube. To this solution was added dropwise by syringe methyl acrylate (0.09 g, 0.1 ml, 1.1 mmol, 1.1 equivalent). The reaction mixture was stirred at ambient temperature for 6 hours after which complete conversion to (124) and (125) was noted by $^{31}$P NMR spectroscopy. The solvent and any excess trapping agent was removed \textit{in vacuo}. A mixture of the cycloadduct isomers (124) and (125) was isolated as a pale yellow oil. Yield was 500 mg (88% by weight); IR (pentane) $\nu_{\text{max}}$: 1735 (C=O) cm$^{-1}$; MS EI: 568 [M$^+$], 468 [(M-$^{i}$Pr$_2$N)$^+$]; $^{11}$B ($C_6D_6$) $\delta$: 27.9 ppm (broad, both isomers); $^{31}$P ($C_6D_6$) $\delta$: 36.47 $^3$J$_{PH}$ 9.4 Hz.
(75% isomer), 34.43 ppm (25% isomer). $^1$H and $^{13}$C NMR spectral data for both isomers are presented in Table 11.10 (Section 11.8.2).

See also figure 11.20

11.13.17 Preparations of (126)

11.13.17.1 From Nitrileimine (110) and CH$_2$=CHCO$_2$Me (120)

A solution of nitrileimine (110) (450 mg, 0.87 mmol) in benzene (15 ml) was placed in a 100 ml Schlenk tube. To this solution was added dropwise by syringe methyl acrylate (0.09 ml, 1.1 equivalents). The reaction mixture was stirred at ambient temperature for 6 hours after which complete conversion to (126) was noted by $^{31}$P NMR spectroscopy. The solvent and any excess trapping agent was removed in vacuo. The cycloadduct (126) was isolated as a pale yellow oil. Yield was 525 mg (100% by weight) with a small impurity detected from the $^{13}$C NMR spectrum.

11.13.17.2 From Cycloadduct (124)/(125) and Sulphur

The cycloadduct (126) was also formed by the addition of sulphur (1.1 equivalents) with stirring at ambient temperature for 1 hour to a benzene solution of the isomers (124) and (125). IR (pentane) $\nu_{\text{max}}$: 1745 (C=O) cm$^{-1}$; $^{11}$B (C$_6$D$_6$) $\delta$: ~28 ppm; $^{31}$P (C$_6$D$_6$) $\delta$: 57.16 ppm (pentet)
\(^3J_{PH} 16.3\) Hz. \(^1H\) and \(^{13}C\) NMR spectral data are presented in Table 11.11 (Section 11.8.2).

11.13.18 Reaction of (109) with (127)

\[
\begin{align*}
\text{iPr}_2N & \quad \Theta \quad \Theta \\
\text{iPr}_2N & \quad \text{P} \quad \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{B} \quad \text{N} \text{iPr}_2 \\
(109) & \quad \text{TCOQ} \quad (127)
\end{align*}
\]

Successive volumes (2 ml) of a solution of the tetrachloroortho-quinone (TCOQ) (0.47 g, 1.9 mmol) in benzene were added to a solution of the nitrileimine (109) (900 mg, 1.9 mmol) with stirring at room temperature. The results are shown in Table 11.13.

<table>
<thead>
<tr>
<th>EQUIV. OF TCOQ</th>
<th>COLOUR OF SOLUTION</th>
<th>(^{31}P) NMR (\delta/\text{ppm})</th>
<th>IR OBSERVATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>green</td>
<td>+103</td>
<td>No NI absorption</td>
</tr>
<tr>
<td>2</td>
<td>red</td>
<td>-36</td>
<td>No NI absorption</td>
</tr>
<tr>
<td>3</td>
<td>deep brown</td>
<td>+19</td>
<td>Apparent decomposition</td>
</tr>
</tbody>
</table>

Table 11.13: The reaction of TCOQ with nitrileimine (NI) (109).

11.13.19 Reaction of (133) with (108)

\[
\begin{align*}
\text{Me}_3\text{Si-CH} (99) & \xrightarrow{\text{BuLi}} \text{Me}_3\text{Si-CLi} (133) \\
\big\downarrow \text{N}_2 & \quad \quad \big\downarrow \text{N}_2 \\
(108) & \quad (\text{iPr}_2N)_2\text{BCl}
\end{align*}
\]

A solution of trimethylsilyl-diazo compound (99) (820 mg, 7.2 mmol) in THF (25 ml) was cooled to -78 °C. BuLi (3.2 ml, 7.95 mmol, 1.1 equivalent, 2.5 M) was added dropwise. The reaction mixture was stirred at -78 °C for 20 min before the addition of \((\text{iPr}_2N)_2\text{BCl}\) (1.77 g, 7.2 mmol) in THF (10 ml). After complete addition it was allowed to warm to room temperature. The THF was removed \textit{in vacuo} before the addition of
pentane (20 ml). A white insoluble precipitate was removed by filtration and the filtrate concentrated by removal of pentane in vacuo. IR $\nu_{\text{max}}$: 2100-2200 cm$^{-1}$ (broad); $^{11}$B $\delta$: 30-35 ppm (many broad peaks).

11.13.20 Reaction of (103) with (130)

\[
\begin{align*}
\text{iPr}_2\text{N} \quad \text{P-CH} & \quad \text{(102)} \quad \quad \text{BuLi/THF} \quad \quad -78^\circ\text{C} \\
\text{iPr}_2\text{N} \quad \text{P-CLi} & \quad \quad \text{(103)} \quad \quad \text{(Me}_2\text{N)}_2\text{BCl} \quad \quad \text{(130)}
\end{align*}
\]

Phosphorus diazo compound (102) (0.52g, 1.9 mmol) was dissolved in THF (25 ml) and cooled to -78 °C. BuLi (0.84 ml, 2.1 mmol, 1.1 equivalents, 2.5 M) was added, followed by stirring at -78 °C for 20 mins. A solution of (Me$_2$N)$_2$BCl (0.26g, 1.9 mmol) in THF (15 ml) was added dropwise with stirring. The reaction mixture was allowed to reach room temperature and the THF removed in vacuo. Addition of pentane (20 ml) produced a white precipitate. $^{31}$P NMR of the resultant filtrate showed a peak at +139 ppm. No diazo or nitrileimine absorptions were observed in the infrared. Cooling the solution to -40 °C gave a crystalline solid whose analysis corresponded to (iPr$_2$N)$_2$PCl (100); mpt. 96-98°C. A repeat of this preparation showed the presence of compound (iPr$_2$N)$_2$PC(N$_2$)PN(iPr$_2$N)$_2$ (106) with a characteristic IR absorption at 2010 cm$^{-1}$. This was further verified by the addition of an excess of elemental sulphur, which was stirred in pentane at room temperature for 1 hour. $^{31}$P NMR spectroscopy showed characteristic shifts at 74.5, 72.39 ($^{1}$J$_{PP}$ 140.1 Hz) and 71.44 ppm [9] corresponding to compounds (129) and (131) respectively, and another peak at +50 ppm thought to correspond to the boron and phosphorus containing species.

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By cooling the solution to -40 °C it was hoped to separate the product as a solid, however no precipitation occurred. IR $v_{\text{max}}$: 2780 (N-Me), 2010 (sharp, diazo), 2040, 2095, 2160 (broad) cm$^{-1}$.

11.13.21 Attempted Reaction of (134) with Diazomethane

\((\text{iPr}_2\text{N})_2\text{B(OSO}_2\text{CF}_3)\) was synthesised by a route analogous to that used by Narula and Nöth (Equation 11.23) [55].

\[
(\text{iPr}_2\text{N})_2\text{BCl} + \text{CF}_3\text{O}_2\text{SO}^-\text{Ag}^+ \xrightarrow{\text{CH}_2\text{Cl}_2} (\text{iPr}_2\text{N})_2\text{B(OSO}_2\text{CF}_3) + \text{AgCl} \quad (11.23)
\]

Bis(diisopropylamine)boron triflate (134) (1g, 2.8 mmol) was dissolved in Et$_2$O (50 ml) followed by the addition of PrNEt$_2$ (0.32g, 2.8 mmol). This mixture was cooled to -78 °C. Diazomethane was generated by the standard route (Section 11.4.2) and obtained as an ether solution (2g in 150 ml, 0.32 M), some of which (10 ml, 3.2 mmol, 1.1 equivalents) was added dropwise by syringe with continual stirring. The solution turned yellow with a white precipitate. On warming to approximately -20 °C there was an apparent rapid polymerisation forming a white solid and clear overlying liquid. The insolubility of the polymer limited the spectral data which could be obtained. The infrared spectrum of the overlying liquid showed no diazo absorption.
11.13.22 Reaction of (133) with (14)

\[
\text{Me}_3\text{Si-CH}_2 (99) \xrightarrow{\text{BuLi, THF}} \text{Me}_3\text{Si-CLi (133)} \xrightarrow{\text{Ar}_2\text{PCl}} (14)
\]

\(\text{Ar} = 2,4,6\text{-tris(trifluoromethyl)benzene}\)

Trimethylsilyldiazo compound (99) (0.5g, 4.4 mmol) was dissolved in THF (25 ml) and cooled to -78 °C. This was stirred continuously while BuLi (1.93 ml, 4.82 mmol, 1.1 equivalents, 2.5 M) was added dropwise. After stirring at -78 °C for 20 mins \(\text{Ar}_2\text{PCl (14) (2.77g, 4 mmol) as a solution in THF (20 ml) was added dropwise. The solution turned black after the addition of just one drop of the phosphorus compound. When addition was complete, the solution was allowed to warm to room temperature and the THF was removed \textit{in vacuo}. On addition of pentane the LiCl appeared inseparable from the viscous black oil. IR \(\nu_{\text{max}}: 2010\ \text{cm}^{-1}\) (diazo absorption); \(^{31}\text{P} \delta: +77 J_{\text{PF}} 41 \text{ Hz}, -8.15 [\text{Me}_3\text{SiC(N}_2\text{)PAr}_2 (106)], -70.1 [\text{carbene (137) ppm}]\).

Warming the reaction mixture to 35 °C caused the signal at -8.15 ppm to disappear. The same result was obtained by exposure to radiation for 30 mins.

Using the same quantities but reversing the addition (to avoid \(\text{Ar}_2\text{PCl being in excess of the lithio compound}) gave a similar black oil with the same spectroscopic data.

11.14 SUMMARY OF SPECTROSCOPIC DATA AND SELECTED SPECTRA

A summary of the NMR data of some of these species is presented in Table 11.14, and some selected spectra are shown in Figures 11.16-11.22.
Figure 11.16: (i) $^1H$ NMR and (ii) IR (pentane) spectra of nitrileimine (109)
Figure 11.16: (iii) $^{13}$C NMR spectrum of nitrileimine (109) in $C_6D_6$. (cont'd)
Figure 11.17: (i) $^{31}P$ and (ii) $^1H$ NMR spectra of nitrileimine (110) in $C_6D_6$. 
Figure 11.17: (iii) $^{13}$C NMR spectra of nitrileimine (110) in $C_6D_6$. (cont'd)
Figure 11.17: (iv) IR spectrum of nitrileimine (109) (pentane). (cont'd)
Figure 11.18: (i) $^{11}$B and (ii) $^{29}$Si NMR spectra of nitrileimine (113) in C$_6$D$_6$. 
Figure 11.18: (iii) $^1H$ NMR ($C_6D_6$) and (iv) IR (pentane) spectra (cont'd) of nitrileimine (113).
Figure 11.18: (v) $^{13}C$ NMR spectrum of nitrileimine (113) in $C_6D_6$.
(cont'd)
Figure 11.19: (i) $^{31}P$ and (ii) $^{11}B$ NMR spectra of cycloadduct (121) in CDCl$_3$. 
Figure 11.19: (iii) $^1H$ NMR spectrum of cycloadduct (121) in CDCl$_3$. (cont'd)
Figure 11.19: (iv) $^{13}C\{^{1}H\}$ NMR spectrum of cycloadduct (121) in CDCl$_3$. (cont'd)
Figure 11.19: (v) *IR spectrum of cycloadduct (121) (pentane). (cont'd)
Figure 11.20: (i) $^{31}P (CDCl_3)$ and (ii) IR (pentane) spectra of cycloadduct (122).
Figure 11.20: (iii) $^1$H NMR spectrum of cycloadduct (122) in CDCl$_3$. (cont'd)
Figure 11.21: (i) IR (pentane) and (ii) $^{31}P$ NMR (CDCl$_3$) spectra of cycloaducts (124, 125).
Figure 11.21: (iii) $^1$H NMR spectrum of cycloadducts (124,125) in CDCl$_3$. (cont'd)
Figure 11.21: (iv) $^{13}$C NMR spectrum of cycloadducts (124,125) (cont'd) in CDCl$_3$. 
Figure 11.2: (v) Mass spectrum cycloadduct mixture (124, 125).
Figure 11.22: (i) $^1H$-NMR ($C_6D_6$) and (ii) IR (pentane) spectra of cycloadduct (129).
Figure 11.22: (iii) $\text{^{13}C}^1H$ NMR spectrum of cycloadduct (123) in CDCl$_3$. (cont'd)
Figure 11.22: (iv) $^{29}$Si NMR spectrum of cycloadduct (123) in CDCl$_3$. (cont'd)
<table>
<thead>
<tr>
<th>CPD</th>
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<th>31P (3JPH)</th>
<th>13CCN (1JCP)</th>
<th>IR</th>
</tr>
</thead>
<tbody>
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<td>29.07</td>
<td>45.14(----)</td>
<td>61.87(48.3)</td>
<td>2100</td>
</tr>
<tr>
<td>110</td>
<td>27.75</td>
<td>31.8 (19.7)</td>
<td>57.42(125)</td>
<td>2095</td>
</tr>
<tr>
<td>113</td>
<td>28.1</td>
<td>0.726*</td>
<td></td>
<td>2100</td>
</tr>
<tr>
<td>114</td>
<td>23.06</td>
<td>82.96(----)</td>
<td>(-----------)</td>
<td>2200</td>
</tr>
<tr>
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<td>'84</td>
<td>2200</td>
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<tr>
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<td>146.7 (17.4)</td>
<td>1730</td>
</tr>
<tr>
<td>122</td>
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<td>57.1 (16.4)</td>
<td>143.27(158)</td>
<td>1750</td>
</tr>
<tr>
<td></td>
<td>123</td>
<td>28</td>
<td>0.705*</td>
<td>143.26</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>27.9</td>
<td>36.4 (9.4)</td>
<td>152 (~6)</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>~25</td>
<td>34.43(----)</td>
<td>~152 (~5)</td>
</tr>
<tr>
<td></td>
<td>126</td>
<td>27</td>
<td>57.16(16.2)</td>
<td>147.45(150)</td>
</tr>
</tbody>
</table>

Table 11.14: NMR parameters for nitrileimines (109)-(113); carbodiimides (114),(116) and cycloadducts (121)-(126); *29Si data.

11.15 REFERENCES


CHAPTER TWELVE

CONCLUSION
12.1 CONCLUSION

The Ar group has been shown to be effective in stabilising low coordinate phosphorus compounds. Some interesting coordination complexes have been isolated, and the crystal structure of ArPCI$_2$[Pt(PEt$_3$)Cl$_2$] (57) has been obtained.

Work has begun in the area of low coordinate compounds containing boron and antimony, and some potentially useful starting materials have been obtained. Some progress has been made in the areas of halogenoborate and phosphoranide chemistry.

It is perhaps noteworthy that many of the Ar compounds illustrate 'through space coupling' some of the values of which are presented in Table 12.1. This data has been provided to a student of Stafford Polytechnic to help with a more direct study on the specific properties which influence these values.

Some new nitrileimines and heterocycles derived from these starting materials have been obtained, and the rearrangement of nitrileimines to carbodiimides by photolysis has been explored. This work has been extended to phosphorus and boron diazo compounds. Much of the above investigation has been supported by a parallel theoretical calculation of the molecular parameters by MNDO.
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<tr>
<th>COMPOUND</th>
<th>NUMBER</th>
<th>$^4J_{PF}$</th>
<th>$^5J_{PF}$</th>
<th>$^5J_{FH}$</th>
<th>$^5J_{FF}$</th>
<th>$^5J_{PtF}$</th>
</tr>
</thead>
<tbody>
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<td>(16)</td>
<td>40.6</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>ArPF$_2$</td>
<td>(3)</td>
<td>50.6</td>
<td></td>
<td>5.5</td>
<td></td>
<td>18.6</td>
</tr>
<tr>
<td>ArP(C)Cl$_2$</td>
<td>(12)</td>
<td>62.0</td>
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<td>ArP(Me)Cl</td>
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<tr>
<td>ArP(Et)Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArP(Bu)Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArP(PhCH$_2$)$_2$Cl</td>
<td>(3)</td>
<td>43.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArP(Me)$_2$</td>
<td></td>
<td>33.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArP(PhCH$_2$)$_2$Cl</td>
<td>(36)</td>
<td>40.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArP(CH$_2$SiMe$_3$)$_2$</td>
<td></td>
<td>46.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArP(PhCH$_2$)$_2$Cl</td>
<td>(57)</td>
<td>34.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArP(Me)$_2$</td>
<td></td>
<td>43.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArP(PhCH$_2$)$_2$Cl</td>
<td>(40)</td>
<td>45.0</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>ArP=CH(Ph)</td>
<td>(31)</td>
<td>21.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArP=CH(SiMe$_3$)</td>
<td>(33)</td>
<td>26.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArP=C(Cl)$_2$</td>
<td>(32)</td>
<td>23.7</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>ArP=C(Cl)[Pt(PEt$_3$)$_2$]Cl$_2$</td>
<td>(15)</td>
<td>32.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArP[Mo(CO)$_5$]</td>
<td>(56)</td>
<td>24.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArBF$_2$</td>
<td>(57)</td>
<td>15.8</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 12.1: Through-space coupling constants; ‡side product only.
APPENDIX A

CHARACTERISATION METHODS
A.1 COMPOUND IDENTIFICATION

A.1.1 Mass Spectrometry (MS)

Three techniques were employed: Electron Impact (EI), Positive Ion Chemical Ionisation (CI+) and Negative Ion Chemical Ionisation (CI-). For each example the technique used has been specified. Where an isotopic distribution pattern exists the most intense peak has been reported.

A.1.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

Unless otherwise stated, where NMR shifts are quoted these have been obtained on a Bruker AC250 (250 MHz) machine. Frequencies used for specific nuclei include: $^{31}$P 101.256 MHz; $^{11}$B 80.239 MHz; $^{13}$C 62.896 MHz; $^1$H 250.133 MHz; $^{19}$F 235.360 MHz; $^{119}$Sn 93.275 MHz and $^7$Li 97.206 MHz with the following references: $^{31}$P $\mathrm{H}_3\mathrm{PO}_4$ (external); $^{11}$B BF$_3$·Et$_2$O (external); $^1$H TMS (internal); $^{13}$C (internal deuterated solvent); $^{19}$F (internal CFCl$_3$); $^{119}$Sn (external Me$_4$Sn) and $^7$Li (1M LiI solution). In Chapter 11, work was carried out in Toulouse and the spectra were recorded on a Bruker AC200 (200 MHz) machine; $^{11}$B 96.295 MHz; $^{31}$P 121.496 MHz; $^{13}$C 75.469 MHz; $^1$H 300.133 MHz and $^{29}$Si 39.761 MHz.

A.1.3 Vibrational Spectra (IR)

Infrared spectra were recorded on a Perkin-Elmer 577 instrument. The solids were prepared as Nujol mulls between KBr/ CsI plates, or as a KBr disc when considered appropriate. The liquids were recorded as thin films, and the solutions in 0.05 mm solution cells with a KBr window.
A.1.4 Ultraviolet-Visible Spectra

The UV-visible spectra were recorded as solutions in CCl$_4$ or CHCl$_3$ in quartz cells with the solvent system in the reference beam, between 200 nm and 450 nm.

A.1.5 Chemical Analysis

C, H and N analysis 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 mls with distilled water. For phosphorus a suitable aliquot was treated with ammonium molybdate/ammonium vanadate reagent and the absorbance measured at 420 $\mu$m 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. Bromine and iodine were determined iodometrically following a Schoniger oxygen flask combustion. Metal analysis was achieved by atomic absorption spectrometry.

A.2 APPARATUS

A.2.1 Glove Box

Due to the moisture-sensitive nature of many of the compounds studied, manipulation of materials was carried out under an atmosphere of dry nitrogen. A dry box was used, equipped with two ports. The large port, for sizeable apparatus, was purged for at least 30 minutes
before opening to the box. A smaller 'quick-entry' port, suitable for removal of NMR sample tubes and other small apparatus, was purged by excess internal pressure. The laboratory supply of piped nitrogen was further dried by passage through a tower packed with $P_2O_5$ about 1 metre in length. The external water pump, used for filtering solutions in the box, was protected by a calcium chloride trap, to prevent any water vapour diffusion into the dry box. A further precaution was a dish of $P_2O_5$ kept exposed in the box to remove any traces of water admitted through the entry ports.

A.2.2 Vacuum and High Pressure Apparatus

Standard vacuum line equipment, and high pressure apparatus (discussed in Chapter 1) was employed.

A.3 REAGENTS

A.3.1 Diazomethane Synthesis

$CH_2N_2$ was generated by the standard procedure (Chapter 11), using apparatus specially designed to avoid the use of ground glass joints.

A.3.2 Solvent and Reagent Purification

All solvents were dried and purified by standard techniques. For example, chlorocarbons were dried over 4Å mesh molecular sieve and stored under nitrogen. Hydrocarbon solvents were first dried over sodium wire and then stored under nitrogen over freshly activated molecular sieve. Diethylcarbonate was dried over $MgSO_4$. Nitrobenzene
was distilled from P2O5 and stored over molecular sieve before use. All amines, for example i-Pr2NH, were dried by distillation from, and storage over, KOH pellets.

The drying procedure for DBU involved refluxing with benzene and subsequent distillation onto activated 4Å molecular sieve. AlCl3 was used directly after sublimation. The deliquescent tetraalkylammonium salts were dried by dissolving them in methanol, stirring, filtering off any insoluble impurities and removing the methanol in vacuo. Any residual methanol/water was removed by addition of toluene to form a slurry. This was stirred for 1 hr. before the toluene was removed in vacuo. The solid was pumped to dryness. In order to minimise borate hydrolysis, this procedure was repeated several times. Caesium fluoride was finely ground under nitrogen, and dried in vacuo at temperatures exceeding 100 °C for 2 hr. Specific cases in which further purification has been effected have been indicated.

A.4 MNDO CALCULATIONS

The calculations carried out in this work were done using MNDO as implemented in MOPAC version 5.
APPENDIX B

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES
The Board of Studies in Chemistry requires that each postgraduate research thesis contains an Appendix listing:

(A) All research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student, including lectures organised by Durham University Chemical Society;

(B) All research conferences attended and work presented by the author during the period when research for the thesis was carried out and

(C) Details of the postgraduate induction course.
RESEARCH COLLOQUIA, SEMINARS AND LECTURES ORGANISED

DURING THE PERIOD: 1986-1987

* ALLEN, Prof. Sir G. (Unilever Research) 13th November 1986
  Biotechnology and the Future of the Chemical Industry

* BARTSCH, Dr. B. (University of Sussex) 6th May 1987
  Low Co-ordinated Phosphorus Compounds

BLACKBURN, Dr. M. (University of Sheffield) 27th May 1987
  Phosphonates as Analogues of Biological Phosphate Esters

BORDWELL, Prof. F.G. (Northeastern University, USA) 9th March 1987
  Carbon Anions, Radicals, Radical Anions and Radical Cations

CANNING, Dr. N.D.S. (University of Durham) 26th November 1986
  Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis

CANNON, Dr. R.D. (University of East Anglia) 11th March 1987
  Electron Transfer in Polynuclear Complexes

CLEGG, Dr. W. (University of Newcastle-upon-Tyne) 28th January 1987
  Carboxylate Complexes of Zinc; Charting a Structural Jungle

DÜPP, Prof. D. (University of Duisburg) 5th November 1986
  Cyclo-additions and Cyclo-reversions Involving Captodative Alkenes

DORFMÜLLER, Prof. T. (University of Bielefeld) 8th December 1986
  Rotational Dynamics in Liquids and Polymers

GOODGER, Dr. E.M. (Cranfield Inst. Technology) 12th March 1987
  Alternative Fuels for Transport

GREENWOOD, Prof. N.N. (University of Leeds) 16th October 1986
  Glorious Gaffes in Chemistry

* HARMER, Dr. M. (I.C.I. Chemicals & Polymer Group) 7th May 1987
  The Role of Organometallics in Advanced Materials

HUBBERSTEY, Dr. P. (University of Nottingham) 5th February 1987
  Demonstration Lecture on Various Aspects of Alkali Metal Chemistry

* HUDSON, Prof. R.F. (University of Kent) 17th March 1987
  Aspects of Organophosphorus Chemistry

- 322 -
HUDSON, Prof. R.F. (University of Kent)  
Homolytic Rearrangements of Free Radical Stability  
18th March 1987

JARMAN, Dr. M. (Institute of Cancer Research)  
The Design of Anti Cancer Drugs  
19th February 1987

KRESPAN, Dr. C. (E.I. Dupont de Nemours)  
Nickel(0) and Iron(0) as Reagents in Organofluorine Chemistry  
26th June 1987

KROTO, Prof. H.W. (University of Sussex)  
Chemistry in Stars, between Stars and in the Laboratory  
23rd October 1986

LEY, Prof. S.V. (Imperial College)  
Fact and Fantasy in Organic Synthesis  
5th March 1987

* MILLER, Dr. J. (Dupont Central Research, USA)  
Molecular Ferromagnets; Chemistry and Physical Properties  
3rd December 1986

WILNE/CHRISTIE, Dr. A./Mr. S. (International Paints)  
Chemical Serendipity: A Real Life Case Study  
20th November 1986

NEWMAN, Dr. R. (University of Oxford)  
Change and Decay: A Carbon-13 CP/MAS NMR Study of humification and Coalification Processes  
4th March 1987

* OTTEWILL, Prof. R.H. (University of Bristol)  
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WONG, Prof. E.H. (University of New Hampshire, USA) 17th February 1987
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BAILEY, Dr. P.D. (University of York) November 1987
Uncogenes

* BIRCHALL, Prof. D. (I.C.I. Advanced Materials) 25th April 1988
Environment Chemistry of Aluminium

* BORER, Dr. K. (University of Durham Industrial Research Laboratories) 18th February 1988
The Brighton Bomb - (A Forensic Science View)

BOSSONS, L. (Durham Chemistry Teachers' Centre) 16th March 1988
GCSE Practical Assessment

* BUTLER, Dr. A.R. (University of St. Andrews) 5th November 1987
Chinese Alchemy

* CAIRNS-SMITH, Dr. A. (Glasgow University) 28th January 1988
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Liquid Crystals and their Applications

HARTSHORN, Prof. M.P. (University of Canterbury, New Zealand) 7th April 1988
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GCE Chemistry A-Level Post-mortem

KOCHE, Prof. H.F. (Ithaca College, U.S.A.) 7th March 1988
Does the E2 Mechanism Occur in Solution?
LACEY, Mr. (Durham Chemistry Teacher's Centre)  
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9th February 1988

* LUDMAN, Dr. C.J. (Durham University)  
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10th December 1987

McDONALD, Dr. W.A. (I.C.I. Wilton)  
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11th May 1988

* MAJORAL, Prof. J.-P. (Université Paul Sabatier)  
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DINGWALL, Dr. J. (Ciba Geigy)  
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18th October 1988

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*STIBR, Dr. R. (Czechoslovak Academy of Sciences)  
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16th May 1989

VON RAGUE SCHLEYER, Prof. P. (Universitat Erlangen Nurnberg)  
The Fruitful Interplay Between Calculational and Experimental Chemistry  
21st October 1988

*WALKER, Dr. R.W. and Dr. R.R. (University of Hull)  
Combustion - Some Burning Problems  
24th November 1988

- 328 -
* Indicates Colloquia attended by the author.

(B) CONFERENCES

The author attended and presented a summary of her current research at the Euchem Conference Psiblocs in Paris-Palaiseau (August 1988).

The research work carried out in Toulouse on Nitrileimine and Carbodiimide chemistry was presented at the Conseil Scientifique at the CNRS (June 1989).

The Durham Graduate Symposium was also attended (April 1987).

(C) FIRST YEAR INDUCTION COURSE (OCTOBER 1986)

This course consisted of a series of one hour lectures on the services available in the department:

Departmental Organisation
Safety Matters
Electrical Appliances
Chromatography and Microanalysis
Atomic Absorption and Inorganic Analysis
Library Facilities
Mass Spectrometry
Nuclear Magnetic Resonance Spectroscopy
Glass Blowing Technique

Dr. E.J.F. Ross
Dr. M.R. Crampton
Mr. B.T. Barker
Mr. T.F. Holmes
Mr. R. Coult
Mr. R.B. Woodward
Dr. M. Jones
Dr. R.S. Matthews
Mr. R. Hart
Mr. G. Haswell