

Durham E-Theses

Synthesis and characterisation of some novel low-coordinate phosphorus compounds containing bulky electron-withdrawing substituents

Roden, M. D.

How to cite:

Roden, M. D. (1998) Synthesis and characterisation of some novel low-coordinate phosphorus compounds containing bulky electron-withdrawing substituents, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/4692/

Use policy

 $The full-text\ may\ be\ used\ and/or\ reproduced,\ and\ given\ to\ third\ parties\ in\ any\ format\ or\ medium,\ without\ prior\ permission\ or\ charge,\ for\ personal\ research\ or\ study,\ educational,\ or\ not-for-profit\ purposes\ provided\ that:$

- a full bibliographic reference is made to the original source
- a link is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the full Durham E-Theses policy for further details.

Academic Support Office, Durham University, University Office, Old Elvet, Durham DH1 3HP e-mail: e-theses.admin@dur.ac.uk Tel: +44 0191 334 6107 http://etheses.dur.ac.uk Synthesis and Characterisation of some Novel Low-Coordinate Phosphorus Compounds containing Bulky Electron-Withdrawing Substituents

by

M. D. Roden B.Sc., M. Sc., (Dunelm) Hatfield College

A thesis submitted for the degree of Doctor of Philosophy at the University of Durham

The copyright of this thesis rests with the author. No quotation from it should be published without the written consent of the author and information derived from it should be acknowledged.

September 1998



Statement of Copyright

The copyright of this thesis rests with the author. No quotation from it should be published without the prior written consent and information derived from it should be acknowledged.

Declaration

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham between October 1994 and October 1997. All the work is my own unless stated to the contrary, and it has not been submitted previously for at this or any other University.

Abbreviations

Ar, Fluoromes,	1,3,5-tris(trifluoromethyl)phenyl
Ar', Fluoroxyl	1,3-bis(trifluoromethyl)phenyl
Ar''	1,3-bis(trifluoromethyl)phenyl
CCD	Charge Couple Device (Area Detector)
DBU	1,8-diazabicyclo[5,4,0]undec-2-ene
dppe	diphenylphosphinoethane
ESD	Estimated Standard Deviations
IR	Infra Red
LUMO	Lowest Unoccupied Molecular Orbital
NQR	Nuclear Quadropole Resonance
PMDETA	Pentamethyldiethylenediamine
Supermes	1,3,5-tris(tertiarybuty)phenyl
THF	Tetrahydrofuran
UV	Ultra Violet

Acknowledgements

I would like to thank Dr K. B. Dillon for his patience, understanding and encouragement through my time in Durham. Over the past five years, Dr Dillon has been a great influence on me; working with him has been great fun.

I would also like to thank Professor J. A. K. Howard for allowing me access to the X-ray facilities at Durham University and to the rest of her team for explaining time and time again the fundamentals of crystallography, which just never seemed to stick, particularly Janet Moloney.

Thanks also go to Mr D. Hunter, without whom the synthesis of Fluoromes would have been impossible. His experience with the high-pressure facilities was invaluable.

I would like to thank all the Ph.D. students in the Inorganic Section with whom I worked. Their encouragement over the odd jar or two was equally invaluable.

I would like to say a special thank you to my wife Kayo. Her encouragement, love and patience have been invaluable.

Abstract

The synthesis of several new phosphorus derivatives including new monophosphanes of the type RPX₂ (X = F, Cl and H), containing either the Fluoromes $[2,4,6-(CF_3)_3C_6H_2]$ or Fluoroxyl $[2,6-(CF_3)_2C_6H_3]$ group has been carried out successfully.

The synthesis of a number of *Cis*-Platin analogous has been facilitated by the reaction of these new monophosphanes with a platinum dimer $[(PCl_2(PEt_3)_2]_2]_2$. These compounds are of the type $PtCl_2(PEt_3)RPX_2$ (X = Cl, H and F, R = 2,6-bis(trifluoromethyl)phenyl). These compounds have shown an interesting correlation between bond length and ${}^1J_{P-Pt}$ NMR coupling.

Disubstituted phosphanes (RPX₂, X = Cl, H) have also been synthesised and subsequent reaction has facilitated the formation, characterisation and structure solution of a new phosphorus (I) species (RP₂⁽⁻⁾)(Ph₃PCH₃)¹ (R = Fluoromes).

Attempts have been made to synthesise the first phosphaalkyne containing a bulky electron withdrawing ligand. This involved the reaction of $RP=CCl_2$ (R = 2,6-bis(trifluoromethyl)phenyl) with a number of Pt(0) and Pd(0) species.

³¹P NMR studies have been used extensively throughout the project to help characterise and identify the products. The single crystal, solid state structures of many of the new species were elucidated by X-ray diffraction using a Siemens Smart CCD.

Mark Roden (November 1998)

v

¹ M. G. Davidson., K. B. Dillon., J. A. K., Howard., M. D. Roden., S. Lamb., J. Organometallic Chemistry, 1998, **550** 481

To Laura and my Parents

My 2nd Book

Contents for Chapter 1

-	3,5-tris(trifluoromethyl)benzene [Fluoromes (ArH)] 2 Reasons and advantages for using Fluoromes rather than other aryl species Compounds containing Fluoromes Fluoromes bonded to metals Fluoromes bonded to phosphorus	3 4 4 4
1.2 1,5-	bis(trifluoromethyl)benzene [Fluoroxyl (Ar'H)]	4
	nparisons between Fluoromes and Fluoroxyl	5
1.3.1	One substitution site or three?	5
	Formation of mono and di-substituted product upon further reaction	7
1.3.3	NQR studies on electronegativity	8
1.4 Pre	cautions necessary when working with fluorinated aryl groups	8
1.5 Ste	ric bulk in low coordinate phosphorus species	9
1.6 Lov	v coordinate phosphorus species	10
1.6.1	Three coordinate phosphorus species	10
1.6.2	Two coordinate phosphorus species	12
1.6.2.1	Diphosphenes	12
1.6.2.2	Phosphaalkenes	12
1.6.2.3		13
1.6.2.4	Metal phosphides	13
1.6.3		14
1.6.3.1	Phosphaalkynes	14
1.7 Exp	perimental	15
1.7.1	Preparation of 1,3,5-tris(trifluoromethyl)benzene	15

List of Figures

Figure 1.1 – Substitution sites in Fluoroxyl and Fluoromes	5
Figure 1.2 – Probable lithiation sites for Fluoroxyl	6
Figure 1.3 – Possible disubstituted products, in the reaction between Fluoroxyl, $Li^{(+)}$ and PCl_3	7
Figure 1.4 – Orbitals involved in bonding between phosphines and metal centres	
Figure 1.5 - Back donation of electron density into unoccupied orbitals on the phosphorus atom	
Figure 1.6 – Teflon lined steel vacuum line	
Figure 1.7 – Teflon lined steel bottle	
Figure 1.8 – Safety, Bursting disc assembly.	
Figure 1.9 – Scrubbing system used to neutralise acidic waste gases	

List of Equations

Equation 1.1 – Synthesis of 1,3,5-tris(trifluoromethyl)benzene	2
Equation 1.2 – Formation of lithiated 1,3,5-tris(trifluoromethyl)benzene	
Equation 1.3 – Formation of diphosphenes using transition metal catalysed metathesis	
Equation 1.4 – Trimerisation of a diphosphene	
Equation 1.5 – Formation of mono substituted phosphanes	
Equation 1.6 – Synthesis of the first symmetrical diphosphene	
Equation 1.7 – Synthesis of a phosphaalkene (RP=CHCl)	
Equation 1.8 – Formation of $Li(PPh_3)_2^{(-)}$	
Equation 1.9 - Formation of a metal diphosphide	
Equation 1.10 – Formation of a phosphaalkyne (R= 'Bu, Adamantyl, Supermes)	
Equation 1.11 – Synthesis of Fluoromes	

List of Tables

I

Table 1.1 – Number of CF_3 groups in the ortho and meta positions, relative to sites A, B, C, and D.	5
Table 1.2 – Structures of various substituted P(V) species, ascertained using NQR	8
Table 1.3 – Stability of diphosphenes	9

Contents for Chapter 2

2.1 Int	roduction	20
2.1.1	Synthesis of P(III) species of the type RPX ₂	20
22 No	vel phosphanes with bulky electron-withdrawing substituents .	20
2.2.1	Ar'PCl ₂	
2.2.1	¹⁹ F Spectroscopic study on the reaction intermediates in the reaction of BuLi and Ar'H	
2.2.2	Ar"PCl ₂	
2.2.2	Ar'PH ₂	
2.2.3	Ar'PF ₂	
2.2.4	$Ar'PBr_2 (Ar''PBr_2)$	
2.2.5	$Ar'P(Cl)CHCl_2$	
2.2.7	Ar'P=CCl ₂	
2.2.8	Ar' ₂ PCl (Ar'Ar''PCl) Attempted formation of Ar' ₂ PCl	
2.2.8.1 2.2.8.2	Variable temperature ¹⁹ F NMR studies on Ar'Ar''PC1	
2.2.8.3	X-ray structure of Ar'Ar''PCl.	
2.2.9	Ar'Ar''PH	
2.2.10		
2.2.11	Ar ₂ PCl	
	Ar ₂ PH	
2.2.12.1	-	
	Attempted preparation of Ar ₂ PF	
	ArP(Cl)CHCl ₂	
	$ArP=CCl_2$	
2.2.15		00
		~ ~
2.3 Th	e resistance of Ar'PH $_2$ and ArPH $_2$ to reaction	64
2.4 Ex	perimental	
2.4.1	Synthesis of Ar'Li and Ar''Li	
2.4.2	Synthesis of Ar'PCl ₂ /Ar''PCl ₂	66
2.4.3	Synthesis of Ar'Ar''PC1	
2.4.4	Synthesis of Ar'PH ₂	
2.4.5	Synthesis of Ar'PF ₂	
2.4.6	Synthesis of Ar'PBr ₂ and Ar''PBr ₂	
2.4.7	Synthesis of Ar'P(Cl)CHCl ₂	
2.4.8	Synthesis of Ar'P=CCl ₂	
2.4.9	Synthesis of Ar'Ar''PH	
2.4.10	5	
2.4.10	Synthesis of ArP(Cl)CHCl ₂	
2.4.11	•	
	Synthesis of Ar ₂ PCl	
2.4.14	Synthesis of Ar ₂ PH	12

List of Figures

Figure 2.1 – Two possible products formed in the reaction between BuLi and Ar'H	_ 22
Figure 2.2 – Inequivalence of CF ₃ groups in the products caused by lithiation of different sites	_ 22
Figure 2.3 – Differences in products upon reaction of the lithiated products with PCl ₃	_23
Figure 2.4 – Possible products (mono and disubstituted) formed in the between Ar'H, BuLi and PCl3	_ 29
Figure 2.5 – Expected NMR signals for Ar'Ar''PCl	_ 31
Figure 2.6 – Equivalent CF ₃ groups shown in the NMR at 100°C of Ar'Ar''PCl	_ 32
Figure 2.7 – Inequivalent CF ₃ groups shown by NMR at -78°C	_ 33
Figure 2.8 – Thermal Ellipsoid diagram at 150K (50% probability) for Ar'Ar''PCl	_ 34
Figure 2.9 – Thermal ellipsoid diagram at 150 (50% probability) showing the inequivalence of the Ch	53
groups on the Ar' group in the solid state	_ 35
Figure 2.10 – P-F interactions in the solid-state structure of Ar'Ar''PCl	_ 35
Figure 2.11 – Thermal ellipsoid diagram at 150 (50% probability) showing the interaction between the	ie
chlorine atom and the adjacent hydrogen atom on the aryl group Ar".	_ 37
Figure 2.12 – Thermal ellipsoid diagram at 150 (50% probability) showing the P-ClH hydrogen bor	ıd
it's effect on the structure of the molecule	_ 37
Figure 2.13 – Thermal Ellipsoid diagram at 150K (50% probability)	_ 48

List of Equations

and the state

ŕ

The second

ł

*

Equation 2.1 – Synthesis of a mono substituted phosphane	20
Equation 2.2 – Synthesis of Ar'PCl ₂	21
Equation 2.3 – Synthesis of Ar' PCl ₂	24
Equation 2.4 – Synthesis of Ar'PH2	24
Equation 2.5 – Synthesis of Ar'PF ₂	25
Equation 2.6 – Synthesis of Ar'PBr ₂	26
Equation 2.7 – Synthesis of Ar''PBr ₂	26
Equation 2.8 – Synthesis of Ar'PCl(CHCl ₂)	27
Equation 2.9 – Synthesis of Ar'P=CCl ₂	28
Equation 2.10 – Synthesis of Ar'Ar''PCl	30
Equation 2.11 – Synthesis of Ar'Ar''PH	44
Equation 2.12 – Synthesis of ArPCl ₂	45
Equation 2.13 – Synthesis of Ar ₂ PCl	46
Equation 2.14 – Synthesis of Ar ₂ PH	47
Equation 2.15– Synthesis of Ar ₂ PF	62
Equation 2.16– Synthesis of ArPCl(CHCl ₂)	63
Equation 2.17- Synthesis of ArP=CCl ₂	64

List of Tables

Table 2.1 - P-F bond lengths in Ar'Ar''PCl	36
Table 2.2 - Crystal data and structure refinement for Ar'Ar''PCl	38
Table 2.3 - Atomic coordinates (x 10 ⁴) and equivalent isotropic displacement parameters ($Å^2 x 10^3$)) for
Ar'Ar''PCl. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor	39
Table 2.4 - Bond lengths [Å] and angles [°] for Ar'Ar''PCl	42
Table 2.5 - Anisotropic displacement parameters $(\hat{A}^2 \times 10^3)$ for Ar'Ar''PCl. The anisotropic	
displacement factor exponent takes the form: $-2\pi^2 [h^2 a^2 U_{11} + 2h k a^* b^* U_{12}]$	43
Table 2.6 - Hydrogen coordinates $(x \ 10^4)$ and isotropic displacement parameters $(A^2 \ x \ 10^3)$ for	
Ar'Ar''PCl.	44
Table 2.7 - Crystal data and structure refinement for Ar_2PH .	50
Table 2.8 - Atomic coordinates (x 10 ⁴) and equivalent isotropic displacement parameters ($A^2 \times 10^3$)) for
Ar ₂ PH, U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.	53
Table 2.9 - Bond lengths $[Å]$ and angles $[°]$ for Ar_2PH .	59
Table 2.10 - Anisotropic displacement parameters $(A^2 \times 10^3)$ for Ar_2PH . The anisotropic displacement	<i>ient</i>
factor exponent takes the form: $-2 \pi^2 [h^2 a^2 U + 2 h k a^* b^* U]$	61

Contents for Chapter 3

3.1 Int	roduction	75
3.1.1	The "Pt dimer"	76
3.2 Ne	ew phosphorus analogues of <i>cis</i> –platin	77
3.2.1	Reaction between the "Pt dimer" and low coordinate phosphorus	
3.2.2	Reaction between $[PtCl_2(PEt_3)]_2$ and $(C_8H_3F_6)PCl_2$	•
3.2.2.1	Molecular structure of $[PtCl_2(PEt_3)]_2$ and $(\odot_8^{-1})_3^{-1} \odot_2^{-1}$	
3.2.3	Reaction between [PtCl ₂ (PEt ₃)] ₂ and (C ₈ H ₃ F ₆)PH ₂	
3.2.3.1	The molecular structure of $[PtCl_2(PEt_3)(C_8H_3F_6)PH_2]$	
3.2.4	Reaction between [PtCl ₂ (PEt ₃)] ₂ and (C ₈ H ₃ F ₆)PF ₂	
3.2.4.1	The molecular structure of [PtCl ₂ (PEt ₃)(C ₈ H ₃ F ₆)PF ₂]	
3.2.5	Reaction between [PtCl ₂ (PEt ₃)] ₂ and (C ₈ H ₃ F ₆)P=CCl ₂	112
3.2.5.1	The molecular structure of $[PtCl_2(PEt_3)(C_8H_3F_6)P=CCl_2]$	
3.2.6	Reaction between [PtCl ₂ (PEt ₃)] ₂ and (C ₈ H ₃ F ₆) ₂ PCl	123
3.2.7	Attempted reaction between [PtCl ₂ (PEt ₃)] ₂ and Ar'Ar''PH	125
3.2.8	Attempted reaction between [PtCl ₂ (PEt ₃)] ₂ and Ar ₂ PH	125
	-	
3.3 Re	esults	
3.3.1	A comparison of coupling constants	
24 04	annamican between counting constants and Dt. D band (math 407
3.4 Co	omparison between coupling constants and Pt–P bond le	engtn 127
3.5 Cł	nanges in the chemical shifts upon bonding	
3.5.1	Change in chemical shift upon bonding to platinum	129
3.6 Va	ariations in the delocalisation of electrons in the aryl ring	1
		,
97 E.		
		420
3.7.1		
3.7.1.1	The "Platinum dimer" trans-[PtCl ₂ (PEt ₃)] ₂	
2717	The "Platinum dimer" <i>trans</i> –[PtCl ₂ (PEt ₃)] ₂ Synthesis of cis–[PtCl ₂ (PhCN) ₂]	
3.7.1.2	The "Platinum dimer" <i>trans</i> –[PtCl ₂ (PEt ₃)] ₂ Synthesis of cis–[PtCl ₂ (PhCN) ₂] Synthesis of cis–[PtCl ₂ (PEt ₃) ₂]	
3.7.1.3	The "Platinum dimer" <i>trans</i> –[PtCl ₂ (PEt ₃)] ₂ Synthesis of cis–[PtCl ₂ (PhCN) ₂] Synthesis of cis–[PtCl ₂ (PEt ₃) ₂] Synthesis of trans–[PtCl ₂ (PEt ₃)] ₂	
3.7.1.3 3.7.2	The "Platinum dimer" <i>trans</i> –[PtCl ₂ (PEt ₃)] ₂ Synthesis of cis–[PtCl ₂ (PhCN) ₂] Synthesis of cis–[PtCl ₂ (PEt ₃) ₂] Synthesis of trans–[PtCl ₂ (PEt ₃)] ₂ Synthesis of cis–[PtCl ₂ (PEt ₃)(Ar'PCl ₂)]	
3.7.1.3 3.7.2 3.7.3	The "Platinum dimer" <i>trans</i> –[PtCl ₂ (PEt ₃)] ₂ Synthesis of cis–[PtCl ₂ (PhCN) ₂] Synthesis of cis–[PtCl ₂ (PEt ₃) ₂] Synthesis of trans–[PtCl ₂ (PEt ₃)] ₂ Synthesis of <i>cis</i> –[PtCl ₂ (PEt ₃)(Ar'PCl ₂)] Synthesis of <i>cis</i> –[PtCl ₂ (PEt ₃)(Ar'PH ₂)]	
3.7.1.3 3.7.2 3.7.3 3.7.4	The "Platinum dimer" $trans$ –[PtCl ₂ (PEt ₃)] ₂ Synthesis of cis–[PtCl ₂ (PhCN) ₂] Synthesis of cis–[PtCl ₂ (PEt ₃) ₂] Synthesis of trans–[PtCl ₂ (PEt ₃)] ₂ Synthesis of cis–[PtCl ₂ (PEt ₃)(Ar'PCl ₂)] Synthesis of cis–[PtCl ₂ (PEt ₃)(Ar'PH ₂)] Synthesis of cis–[PtCl ₂ (PEt ₃)(Ar'PF ₂)]	
3.7.1.3 3.7.2 3.7.3 3.7.4 3.7.5	The "Platinum dimer" $trans$ –[PtCl ₂ (PEt ₃)] ₂ Synthesis of cis–[PtCl ₂ (PhCN) ₂] Synthesis of cis–[PtCl ₂ (PEt ₃) ₂] Synthesis of trans–[PtCl ₂ (PEt ₃)(Ar'PCl ₂)] Synthesis of cis–[PtCl ₂ (PEt ₃)(Ar'PH ₂)] Synthesis of cis–[PtCl ₂ (PEt ₃)(Ar'PF ₂)] Synthesis of cis–[PtCl ₂ (PEt ₃)(Ar'PF ₂)]	
3.7.1.3 3.7.2 3.7.3 3.7.4	The "Platinum dimer" $trans$ –[PtCl ₂ (PEt ₃)] ₂ Synthesis of cis–[PtCl ₂ (PhCN) ₂] Synthesis of cis–[PtCl ₂ (PEt ₃) ₂] Synthesis of trans–[PtCl ₂ (PEt ₃)] ₂ Synthesis of cis–[PtCl ₂ (PEt ₃)(Ar'PCl ₂)] Synthesis of cis–[PtCl ₂ (PEt ₃)(Ar'PH ₂)] Synthesis of cis–[PtCl ₂ (PEt ₃)(Ar'PF ₂)]	132 132 132 132 132 133 133 133 134 134 134 135

List of Equations

Equation 3.1 – Synthesis of $[(PtCl_2)PEt_3]_2$	
Equation 3.2 – Synthesis of trans Ar'PCl ₂ and Ar''PCl ₂ derivatives of the dimer	
Equation 3.3 – Re–arrangement of trans $(Ar'PCl_2)PtCl_2(PEt_3)$	32
Equation 3.4 – Synthesis of cis $(Ar'PH_2)PtCl_2(PEt_3)$	
Equation 3.5 – Rearrangement of trans $(Ar'PF_2)PtCl_2(PEt_3)$	
Equation 3.6 – Re-arrangement of trans [PtCl ₂ (PEt ₃) (Ar'P=CCl ₂)]	
Equation 3.7 – Synthesis of trans (Ar'Ar''PCI)PtCl ₂ (PEt ₃)	

List of Figures

Figure 3.1 – Electron pairing in a square planar complex	75
Figure 3.2 – Formation of two possible isomers upon initial reaction between Ar'PCl ₂ and the dimer	77
Figure 3.3 – Rearrangement of the initial trans product to give the kinetically more stable cis product.	80
Figure 3.4 – Thermal ellipsoid diagram at 150K (50% Probability) for [PtCl ₂ (PEt ₃)(Ar'PCl ₂)]	83
Figure 3.5 – Back donation of electron density from the metal centre to unoccupied orbitals on the	
phosphorus atom	94
Figure 3.6 – Thermal ellipsoid diagram at 150K (50% Probability) for [PtCl ₂ (PEt ₃)(Ar'PH ₂)]	95
Figure 3.7 – Thermal ellipsoid diagram at 150K (50% Probability) showing the interactions between	
hydrogen and fluorine atoms in the molecule	96
Figure 3.8 – Thermal ellipsoid diagram at 150K (50% probability) for [PtCl ₂ (PEt ₃)(Ar'PF ₂)]1	05
Figure 3.9 – Thermal ellipsoid diagram at 150K (50% probability) for [PtCl ₂ (PEt ₃)(Ar'P=CCl ₂)]1	14
Figure 3.10 – $Trans - [PtCl_2(PEt_3)(Ar'Ar''PCl)]$.	24

ļ

List of Tables

Table 3.1 – Crystal data and structure refinement for (Ar'PCl ₂)PtCl ₂ (PEt ₃)	. 84
Table 3.2 – Atomic coordinates (x 10 ⁴) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for a second	or
(Ar'PCl ₂)PtCl ₂ (PEt ₃).U(eq) is defined as one third of the trace of the orthogonalized Uij tensor	. 86
Table 3.3 – Atomic Selected bond lengths [Å] and angles [°] for (Ar'PCl ₂)PtCl ₂ (PEt ₃)	. 89
Table 3.4 –Anisotropic displacement parameters $(A^2 \times 10^3)$ for $(Ar'PCl_2)PtCl_2(PEt_3)$. The anisotropic	с
displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + 2h k a^* b^* U_{12}]$. 91
Table 3.5 – Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters ($A^2 \ x \ 10^3$) for	
$(Ar'PCl_2)PtCl_2(PEt_3)$. 92
Table 3.6 – Crystal data and structure refinement for (Ar'PH ₂)PtCl ₂ (PEt ₃)	. 97
Table 3.7 – Atomic coordinates (x 10 ⁴) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for a second	or
(Ar'PH ₂)PtCl ₂ (PEt ₃).U(eq) is defined as one third of the trace of the orthogonalized Uij tensor	. 98
Table 3.8 – Atomic Selected bond lengths [Å] and angles [°] for (Ar'PH ₂)PtCl ₂ (PEt ₃)	100
Table 3.9 –Anisotropic displacement parameters $(A^2 \times 10^3)$ for $(Ar'PH_2)PtCl_2(PEt_3)$. The anisotropic	2
displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + 2h k a^* b^* U_{12}]$	101
Table 3.10 – Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters ($A^2 \ x \ 10^3$) for	
$(Ar'PH_2)PtCl_2(PEt_3)$	102
Table 3.11 – Crystal data and structure refinement for $[PtCl_2(PEt_3)(C_8H_3F_6)PF_2]$	106
Table 3.12 – Atomic coordinates ($x \ 10^4$) and equivalent isotropic displacement parameters ($A^2 \ x \ 10^3$)	for
$[PtCl_2(PEt_3)(C_8H_3F_6)PF_2].U(eq)$ is defined as one third of the trace of the orthogonalized Uij tensor.	107
Table 3.13 – Atomic Selected bond lengths $[Å]$ and angles $[\degree]$ for $[PtCl_2(PEt_3)(C_8H_3F_6)PF_2]$	109
Table 3.14 –Anisotropic displacement parameters $(A^2 \times 10^3)$ for $[PtCl_2(PEt_3)(C_8H_3F_6)PF_2]$. The	
anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + 2h k a^* b^* U_{12}] \dots$	110
Table 3.15 – Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters ($A^2 \ x \ 10^3$) for	
$L^{-} = 2(1 - 1) (1 - 0 - 1) (1 - 0 - 1) (1 - 0 - 1) (1 - 0) (1 - 1) (1 - 0) (1 - 1)$	111
Table 3.16 - Crystal data and structure refinement for [PtCl ₂ (PEt ₃) (Ar'P=CCl ₂)]	115
Table 3.17 – Atomic coordinates ($x \ 10^4$) and equivalent isotropic displacement parameters ($A^2 \ x \ 10^3$)	for
$[PtCl_2(PEt_3) (Ar'P=CCl_2)].U(eq)$ is defined as one third of the trace of the orthogonalized Uij tensor.	116
Table 3.18 – Atomic Selected bond lengths [Å] and angles [°] for [PtCl ₂ (PEt ₃) (Ar'P=CCl ₂)]	
Table 3.19 – Bond lengths $[Å]$ and angles $[°]$ for $[PtCl_2(PEt_3) (Ar'P=CCl_2)]$	120
Table 3.20 –Anisotropic displacement parameters $(A^2 \times 10^3)$ for $[PtCl_2(PEt_3) (Ar'P=CCl_2)]$. The	
anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + 2h k a^* b^* U_{12}] \dots$	121
Table 3.21 – Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters ($A^2 \ x \ 10^3$) for	
$L = -\frac{1}{2} \sqrt{-1} - \frac{1}{2} \sqrt{-1} - \frac{1}{2} \sqrt{-1} - \frac{1}{2} \sqrt{-1} - \frac{1}{2} \sqrt{-1} \sqrt{-1} - \frac{1}{2} \sqrt{-1} \sqrt{-1} - \frac{1}{2} \sqrt{-1} \sqrt{-1} - \frac{1}{2} \sqrt{-1} \sqrt{-1} \sqrt{-1} - \frac{1}{2} \sqrt{-1} \sqrt$	122
Table 3.22 – Coupling constants and P-Pt bond lengths for a series of synthesised platinum phosphan	
	126
5 5 1 5 1	129
Table 3.24 – Comparison between carbon–carbon bond lengths in the aryl rings	131

Contents for Chapter 4

4.1	Int	roduction	137
4.2	Ph	osphaalkenes	138
4.2	2.1	Synthesis of Ar'P=CCl ₂	138
4.2	.1.1	Ar'P(Cl)CHCl ₂	138
4.2	.1.2	Reaction between Ar'P(Cl)CHCl ₂ and DBU	
4.2	2.2	Formation of ArP=CCl ₂	139
4.3	At	tempted synthesis of η^2 -bonded phosphaalkene complexes	140
4.	3.1	Reaction between Ar'P=CCl ₂ and Pt(PPh ₃) ₄	140
4.3	5.1.1	The molecular structure of [PtCl(CCl=PAr')(PPh ₃) ₂]	142
4.	3.2	Reaction between ArP=CCl ₂ and Pt(PPh ₃) ₄	153
4.3	.2.1	Molecular structure of trans-[PtCl(CC1=PAr)(PPh ₃) ₂]	154
4.	3.3	Reaction between Ar'P=CCl ₂ and Pd(PPh ₃) ₄	155
4.	3.4	Reaction between ArP=CCl ₂ and Pd(PPh ₃) ₄	156
4.4	Sy	nthesis of other phosphaalkenes	157
		Reaction between Ar'P=CCl ₂ , Bu ₃ SnH and DBU	
4.5	Ex	perimental	159
4.:	5.1	Preparation of [PtCl(CCl=PAr')(PPh ₃) ₂]	
	5.2	Preparation of $[PtCl(CCl=PAr)(PPh_3)_2]$	
	5.3	Preparation of [PdCl(CCl=PAr')(PPh ₃) ₂]	
	5.4	Preparation of [PdCl(CCl=PAr)(PPh ₃) ₂]	
	J. 4		100

List of Figures

Figure 4.1 – Thermal ellipsoid diagram 150(2)K (50% probability) showing trans-	
$PtCl(CCl=PAr')(PPh_3)_2$	
Figure 4.2 – Thermal ellipsoid diagram at 150(2)K (50% probability)	
Figure 4.3 – Thermal ellipsoid diagram 150(2)K (50% probability) showing trans-	
$PtCl(CCl=PAr)(PPh_3)_2$	154

List of Equations

<i>Equation 4.1</i> – Proposed mechanism for the synthesis of a phosphaalkyne using PdL ₄ and $RP=CCl_2$	137
Equation 4.2 – Mechanism demonstrated by Angelici with the isolation of intermediates	137
Equation 4.3 – Preparation of Ar'PCl(CHCl ₂)	138
Equation 4.4 – Preparation of Ar'P=CCl ₂	139
Equation 4.5 – Preparation of trans-[PtCl(CCl=PAr')(PPh_3)2]	142
Equation 4.6 – Preparation of trans- $[PtCl(CCl=PAr)(PPh_3)_2]$	154
Equation 4.7 – Preparation of trans-PdCl(PPh ₃)(CCl-PAr')	155
Equation 4.8 – Preparation of trans-PdCl(PPh ₃)(CCl-PAr)	156
Equation 4.9 – Preparation of a number of phosphaalkenes	157

List of Tables

Fable 4.1 - Crystal data and structure refinement for [PtCl(CCl=PAr')(PPh ₃) ₂]	4
Fable 4.2 - Atomic coordinates (x 10 ⁴) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for	
PtCl(CCl=PAr')(PPh ₃) ₂]. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor 14	6
$[A]$ and angles $[\circ]$ for $[PtCl(CCl=PAr')(PPh_3)_2]$ $[A]$	9
Table 4.4 - Anisotropic displacement parameters $(A^2 \times 10^3)$ for $[PtCl(CCl=PAr')(PPh_3)_2]$. The	
inisotropic displacement factor exponent takes the form: -2 pi^2 [$h^2 a^2 U11 + + 2 h k a^* b^* U12$] . 15.	2
Table 4.5 - Hydrogen coordinates (x 10 ⁴) and isotropic displacement parameters ($A^2 \times 10^3$) for	
$PtCl(CCl=PAr')(PPh_3)_2]15$	2

Contents for Chapter 5

5.1	Inti	roduction 1	62
5.2	Sta	arting materials 1	63
	2.1	Fluoroxyl disubstituted phosphanes	
5.2		Fluoromes disubstituted phosphanes	
		·····	
5.3	The	e anionic P(I) species Ar₂P ⁽⁻⁾ 1	63
		The appearance of the blue colour at low temperature	
010			
5.4	Re	actions between Ar₂PH and selected bases	67
5.4		Attempted preparation of Ar ₂ PLi (in hexanes)	
5.4	1.2	Preparation of Ar ₂ PLi (in THF)	
5.4	1.3	Attempted stabilisation of Ar ₂ Li using PMDETA	
5.4	1.4	Reaction between Ar ₂ PH and pyrrolidine	
	4.5	Reaction between Ar_2PH and $Ph_3P=CH_2$	
	.1.1	The molecular structure of $[C_6H_2(CF_3)_3]_2P^{(-)}[Ph_3PCH_3]^{(+)}$	171
5.4	4.6	Reaction between Ar ₂ PH and DBU	
5.5	Re	sults of substitution reactions between Ar ₂ PH and metal amides	5
	18	5	
5.5	5.1	Reaction between Ar_2PH and $Cp_2Zr(NMe_2)_2$	
5.5	.1.1	Mechanism for the substitution of Ar ₂ PH for NMe ₂ H	186
5.5	5.2	Reaction between Ar ₂ PH and Ta(NMe ₂) ₅	187
5.6		action of Ar ₂ PH with low oxidation state transition metals 1	
5.0		Reaction of Ar ₂ PH with Pt(PPh ₃) ₄	
	5.2	Reaction of Ar ₂ PH with Pd(PPh ₃) ₄	
5.0	5.3	Reaction of Ar ₂ PH with Pt(dppe) ₂	190
5.7	٨ 44	empted reaction of Ar ₂ PH and Ar ₂ PCI with Pt(II) compounds 1	104
5.7		Reaction between Ar_2PH and the "Pt Dimer"	
	7.2	Reaction between Ar_2PH and $PtCl_2(PhCN)_2$	
	7.3	Reaction between Ar_2PC1 and $Pt(PPh_3)_4$	
	7.4	Reaction between Ar_2PC1 and $Pt(dppe)_2$	
5.	/.4	Reaction between Ar ₂ rCr and rt(uppe) ₂	192
5.8	Ex	perimental 1	193
	3.1	Attempted synthesis of [Ar ₂ P] ⁽⁻⁾ [Li] ⁽⁺⁾ in Hexanes	
	8.2	Attempted synthesis of $[Ar_2P]^{(\cdot)}[Li]^{(+)}$ in THF	193
	8.3	Attempted synthesis of $[Ar_2P]^{(-)}[Li]^{(+)}(PMDETA)$	193
	8.4	Attempted synthesis of $[DBUH]^{(+)}[Ar_2P]^{(-)}$	194
	8.5	Attempted synthesis of $[Ar_2P]^{(-)}[(C_4H_8NH)H]^{(+)}$	194
	8.6	Synthesis of $[Ar_2P]^{(-)}[Ph_3PCH_3]^{(+)}$	194
	8.7	Attempted synthesis of $ZrCp_2(PAr_2)_2$	
	8.8	Attempted synthesis of Ta(NMe ₃) ₄ (PAr ₂)	
	8.9	Attempted synthesis of $[HPt(PPh_3)_2(Ar_2P)]$	
	8.10	Attempted synthesis of [PtH(dppe)(Ar ₂ P)]	

ļ

:

5.8.11	Attempted synthesis of [PdH(PPh ₃) ₂ (Ar ₂ P)]	196
	Attempted synthesis of [PtCl(PPh ₃) ₂ (Ar ₂ P)]	
5.8.13	Attempted synthesis of [PtCl(dppe)(Ar ₂ P)]	197

List of Figures

Figure 5.1 – A canonical form of RP ⁽⁻⁾ Fmes	165
Figure 5.2 – Equilibrium constants for the reaction between Ar_2PH and NEt_3	
Figure 5.3 – Thermal Ellipsoid diagram for $Ar_2P^{(-)}[PPh_3CCH_3]^{(+)}$	
Figure 5.4 – Superimposition of the two aryl rings, highlighting the distortion from planarity	
Figure 5.5 – The two aryl rings in the compound $Ar_2 P^{(\cdot)}$	
Figure 5.6 – Mechanism for the proton transfer in the reaction between $Cp_2Zr(NMe_2)_2$ and $2Ar_2PH_2$	187

List of Equations

L

Equation 5.1 – Substitution of amines in metal-amide chemistry	162
Equation 5.2 – Synthesis of $PPh_2^{(-)}Li^{(+)}$	164
Equation 5.3 – Equilibrium in the reaction between Ar_2PH and NEt_3	
Equation 5.4 – Possible product formed by the lithiation in hexanes of Ar_2PH at $-78^{\circ}C$	167
Equation 5.5 – Lithiation in THF of Ar_2PH at $-78^{\circ}C$	
Equation 5.6 – Predicted products formed in the lithiation Ar ₂ PH using PMDETA to stabilise the	
ion	169
Equation 5.7 – Speculated products formed in the synthesis of $Ar_2P^{(-)}[pyrrolidineH]^{(+)}$	
Equation 5.8 – Synthesis of $Ar_2 P^{(-)} [PPh_3 CCH_3]^{(+)}$	170
Equation 5.9 – Synthesis of $Ar_2P^{(+)}[DBUH]^{(+)}$	
Equation 5.10 – Proposed synthesis of $Cp_2Zr(PAr_2)_2$	
Equation 5.11 – Proposed synthesis of $Ta(NMe_2)_4(PAr_2)$	
Equation 5.12 – Synthesis of a platinum hydride ⁸	
Equation 5.13 – Possible substitution of dppe ligands in the attempted formation of a platinum hy	
	191

List of Tables

Table 5.1 - Crystal data and structure refinement for (Ar ₂ P)(PPh ₃ CH ₃)	. 172
Table 5.2 - Atomic coordinates $(x \ 10^4)$ and equivalent isotropic displacement parameters $(A^2 \ x \ 10^3)$ f	for
(Ar ₂ P)(PPh ₃ CH ₃). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor	. 174
Table 5.3 - Bond lengths [Å] and angles [°] for (Ar ₂ P)(PPh ₃ CH ₃)	. 178
Table 5.4 - Anisotropic displacement parameters $(A^2 \times 10^3)$ for $(Ar_2P)(PPh_3CH_3)$. The anisotropic	
displacement factor exponent takes the form: $-2\pi^2 / h^2 a^2 U 11 + + 2h k a^* b^* U 12]$. 180
Table 5.5 - Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters ($A^2 \ x \ 10^3$) for	
$(Ar_2P)(PPh_3CH_3)$. 181
Table 5.6 - Comparisons of carbon-carbon bond lengths in the aryl rings	. 183

Contents for Appendix 1

A.1 Crystal growth and crystallographic methods	A.1-2
A.1.1 Growing Crystals	
A.1.1.1 The layering technique	
A.1.1.2 Vacuum sublimation	
A.1.1.3Recrystallisation	A.1-3
A.1.2 Crystallographic methods	

l

Contents for Appendix 2

A.2	OTHER CRYSTALS STRUCTURES 1994-1997	A.2-2
	1 1,2,bisdiphenylphosphoniumethylene hydroxide bromide	
A.2.	2 cis-dibromo(triethylphosphane)(1,1-dihydroxy-2,6-	
bis(rifluoromethyl)phenyl)platinum(II)	A.2 - 9
A.2.	3 1,1-dihydroxy-2,6-bis(trifluoromethyl)phenylphosphane.	A.2-16

List of Figures

Figure $A2.1 - A$ Diagrammatical representation of the product formed in the reaction between PCl ₃ and
dppe
Figure A2.2 – Thermal ellipsoid diagram at 150K (50% Probability) for Ar'P(OH) ₂ [PtBr ₂ (PEt ₃)]A.2-9
Figure A2.2 – Thermal ellipsoid diagram at 150K (50% Probability) for ArP(OH ₂)A.2-16

List of Tables

Table 1 Crystal data and structural refinement A.2-3
Table 2 Atomic coordinates (x 10 ⁴) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for
C26H28Br2OP2. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor
Table 3 - Bond lengths [Å] and angles [°] for C ₂₆ H ₂₈ Br ₂ OP ₂
Table 4 Anisotropic displacement parameters $(A^2 \times 10^3)$ for C ₂₆ H ₂₈ Br ₂ OP ₂ . The anisotropic displacement
factor exponent takes the form: $-2 \pi^2 [h^2 a^2 U 11 + 2h k a^* b^* U 12]$
Table 2.5 Hydrogen coordinates (x 10 ⁴) and isotropic displacement parameters ($A^2 \times 10^3$) for C26H28Br2OP2.
Table 6 Crystal data and structural refinement
Table 7 Atomic coordinates (x 10 ⁴) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for
C14H20Br2F6O2P2Pt. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor
Table 8 - Bond lengths [Å] and angles [°] for C14H20Br2F6O2P2Pt
Table 9 Anisotropic displacement parameters $(A^2 \times 10^3)$ for C ₁₄ H ₂₀ Br ₂ F ₆ O ₂ P ₂ Pt. The anisotropic
displacement factor exponent takes the form: $-2 \pi^2 / h^2 a^2 U I I + 2 h k a^* b^* U I 2]$
Table 2.10 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($A^2 \times 10^3$) for
C14H20Br2F6O2P2Pt
Table 11 Crystal data and structural refinement A.2-17
Table 12 Atomic coordinates (x 10 ⁴) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for
Ar'P(OH) ₂ . U(eq) is defined as one third of the trace of the orthogonalized Uij tensor
Table 13 - Bond lengths [Å] and angles [°] for Ar 'P(OH)2 A.2-20
Table 14 Anisotropic displacement parameters $(A^2 \times 10^3)$ for Ar'P(OH) ₂ . The anisotropic displacement
factor exponent takes the form: $-2 \pi^2 [h^2 a^2 U I I + 2 h k a^* b^* U I 2]$

Contents for Appendix 3

I I

A.3	CO	URSES ATTENDED	A.3-2
A.3	3.1	First Year Induction Courses : October 1993	A.3-2
A.3	3.2	Examined Lecture Courses : October 1993 - April 1994	A.3-2

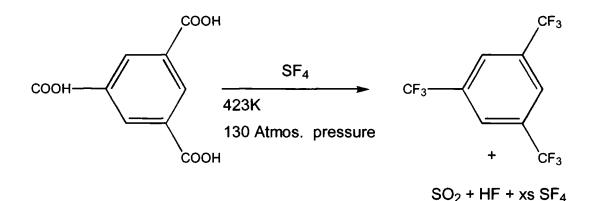
Chapter 1

Introduction

1.1 1,3,5-tris(trifluoromethyl)benzene [Fluoromes (ArH)]

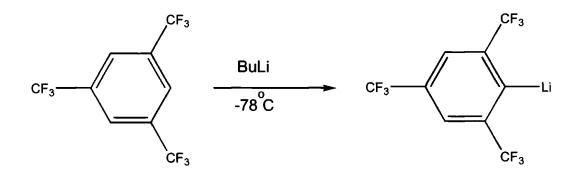
"Fluoromesitylene" (Fluoromes, ArH) was first prepared in 1947 by McBee and Leech¹. This involved the fluorination of 1,3,5-tris(trichloromethyl)benzene and the extensive preparation yielded 49% product.

The modern synthesis for ArH was first described by Chambers *et al.*² involving the reaction of SF₄ and the commercially available trimesic acid $[C_6H_3(COOH)_3]$ (yield 33%). This method was then subsequently improved dramatically by Edelmann *et al.*³, increasing the yield of the reaction to 95%.



Equation 1.1 - Synthesis of 1,3,5-tris(trifluoromethyl)benzene

The chemistry of Fluoromes has since been extensively studied. The reaction of Fluoromes with ⁿBuLi to form the lithiated species 1-lithio-2,4,6-tris(trifluoromethyl)benzene ² (ArLi) has proved to be a very versatile reagent.



Equation 1.2 - Formation of lithiated 1,3,5-tris(trifluoromethyl)benzene

1.1.1 Reasons and advantages for using Fluoromes rather than other aryl species

Fluoromes itself is a colourless liquid which boils at 119°C at 1 atmosphere pressure. It is prepared on an approximately 100g scale in the department using the high pressure facilities available.

The Fluoromes group has a number of advantages over other aryl and alkyl groups in its inclusion in phosphorus (and other main groups element) compounds. The compounds involving phosphorus, are comparatively more oxygen- and moisture-stable than equivalent aryl and alkyl bonded P(III or V) species. In the case of phosphorus multiply bonded to other elements (e.g. RP=PR, RP=CCl₂), these species are more resistant to polymerisation and formation of dimer and trimer products (see Section 1.5). This is a great advantage to preparation in bulk. These properties are due to two main factors regarding the Fluoromes group itself :

- The CF₃ groups bonded to the *ortho* and *para* carbons in the aryl group cause an overall withdrawal of electrons from the element to which the group is bonded. In this case it makes the phosphorus atom to which it is attached less electron rich and less susceptible to electrophilic attack.
- 2) The steric bulk of the CF₃ groups also restricts attack on the phosphorus, particularly in the case of a di-substituted species, i.e. compounds of the type Ar_2PX (X= Cl or H). In the cases where Fluoromes is bonded to main group elements there is a distinct interaction between the fluorine atoms on the *ortho*-CF₃ groups and the element itself through space (visible in the ³¹P NMR as a ⁴J_{P-F} coupling constant through space of approximately 25-70 Hz).

These two effects in tandem cause a greater overall stability of the phosphorus species in question.

1.1.2 Compounds containing Fluoromes

1.1.2.1 Fluoromes bonded to metals

The reaction of ArLi, like other lithiated aryl species, with metal and non-metal halides has led to the synthesis of a wide variety of compounds. There are examples of compounds formed with main group metals, (e.g. In, Ga, Sn)^{4,5,6,7} and transition metals including the type $M(Fluoromes)_2^{8,9}$. Some reactions of Sn(Fluoromes)₂ producing higher oxidation state tin compounds have also been shown by Edelmann¹⁰.

1.1.2.2 Fluoromes bonded to phosphorus

By the same method of reacting ArLi with metal chlorides, Fluoromesphosphorus bonds can be formed by the reaction of ArLi with P-Cl bonds, the typical starting material being PCl₃ itself. This has led to a number of low-coordinate Fluoromes-phosphorus compounds such as $(ArPX_2 - X = Cl, H, F)^{11}$, $ArP=PAr^{12}$ and $ArP=CCl_2^{13}$ and their derivatives. High-coordinate compounds such as $Ar-PCl_4^{14}$ have been also prepared.

1.2 1,5-bis(trifluoromethyl)benzene [Fluoroxyl (Ar'H)]

Fluoroxyl has rarely been used as a ligand in main group chemistry, with only two examples in the Cambridge structural database¹⁵. The first is a chromacene analogue containing two Ar' species in a sandwich complex with chromium¹⁶. The second is the only substituted example, the diphosphene Ar'P=PAr',¹⁷ although it is interesting to note that there has been some chemistry achieved involving the side substituted product¹⁸.

Ar'H was the main aryl group used at the start of the project because of the unavailability of the starting material SF_4 , used for producing Fluoromes. The properties of the two ligands are similar in the respect that they are electron withdrawing and the *ortho* positions are sterically hindering. The deciding factor in using Fluoroxyl initially was the cost. The cost of Fluoroxyl from the chemical suppliers was approximately 1/20th of that of the price of Fluoromes.

1.3 Comparisons between Fluoromes and Fluoroxyl

1.3.1 One substitution site or three?

If we consider the case shown below in Figure 1.1, there are three different carbon atoms on the Fluoroxy group not bonded to CF_3 (A, B and C). In the case of Fluoromes there are three carbon atoms not bonded to CF_3 , however these are all equivalent (D).

In the case of Fluoroxyl, (1), there are three possible reaction sites, (A, B and C). The *para* carbon (C) in the Fluoroxyl group does not have a substituted CF_3 group and this leads to a number of potential reactions. Reaction site C (which is *meta* to both A and B) is the most unlikely substitution site in the reaction with BuLi. Sites A and B are influenced by both groups, thus making these sites more susceptible to reaction.

For Fluoromes, (2), there is only one possible reaction site (D). The D position has two CF₃ groups *ortho* and one CF₃ group *para*. This means that this site is activated equally by all the CF₃ groups in the molecule and substitution has an equal chance at each.

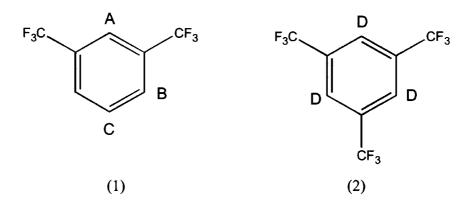


Figure 1.1 - Substitution sites in Fluoroxyl and Fluoromes

	A	В	С	D
Ortho CF ₃	2	1		2
Para CF ₃		1		1

Table 1.1 – Number of CF₃ groups in the ortho and meta positions, relative to sites A, B, C, and D

Because the aryl ring is not symmetrical in the case of Fluoroxyl, there is more than one potential lithiation site upon reaction with BuLi (see Figure 1.2). The CF_3 groups have a directional functionality, which causes the positions *ortho* and *para* to them to become comparatively electron deficient. This in turn makes the hydrogen atom associated with these sites more acidic and susceptible to nucleophilic attack by the butyl group. This preference for nucleophilic attack leads to a number of differences in the species formed.

 There are two possible substitution sites, the first of which is where the lithiation site is *ortho* to both CF₃ groups (i), and the second where the lithiated site is *ortho* to one CF₃ group and *para* to the other (ii). This second lithiation site is similarly activated by the CF₃ groups, as compared to the first case.

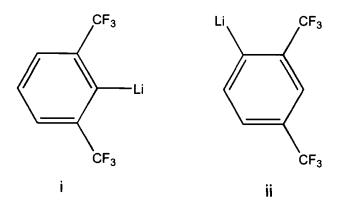


Figure 1.2 – Probable lithiation sites for Fluoroxyl

- 2) The desired product (i) which has the lithiated site ortho to both CF₃ groups retains its symmetry and the lithiated site is sterically hindered by both CF₃ groups. There is also the greatest interaction between the lithium atom and the electron rich fluorine atoms. For the compound ArLi, Helen Goodwin attempted to characterise any interaction between the lithium and the fluorine atoms using ⁷Li NMR, but was unable to observe any.
- The undesired product (ii) is only sterically hindered to one side and the reactivity of the compound is therefore likely to differ markedly.

¹⁹F NMR studies of the reaction mixture formed in the reaction of BuLi and Ar'H have shown that the ratio of species (i) to species (ii) is approximately 50:50; however, once this mixture has been reacted with PCl₃ the ratio of products is approximately 2:1 (see Section 2.2.1.1). This implies that the side substituted Ar''Li (ii), is somehow comparatively more unstable with respect to Ar'Li. Because Ar''Li has only one CF₃ group in the *ortho* position, it has a more exposed lithium atom. This may well lead to side reactions involving the possible formation of LiF (see Section 1.4).

1.3.2 Formation of mono and di-substituted product upon further reaction

The reaction described above involving Ar'Li and PCl₃ yields a number of different products (see Figure 1.3) including the di-substituted mixed aryl species Ar'Ar''PCl which is formed by reaction of the two different lithiated species with PCl₃. There is however, no evidence for the formation of either of the potential di-substituted compounds Ar'₂PCl and Ar''₂PCl (2 and 3 below).

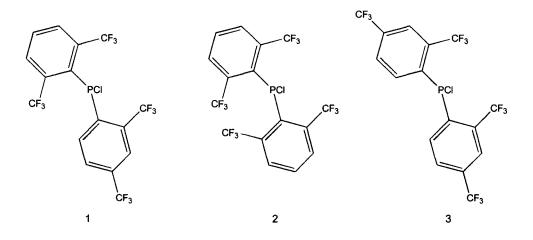


Figure 1.3 - Possible disubstituted products, in the reaction between Fluoroxyl, BuLi and PCl₃

1.3.3 NQR studies on electronegativity

A study had previously been undertaken of P(V) species of the type PCl_4R where R was a number of different electronegative withdrawing aryl groups¹⁴. Using NQR it is possible to show whether the aryl group is in an equatorial or axial position. If the aryl group is more electron withdrawing that chlorine, the group will be axial, otherwise equatorial.

Aryl group (R)	Structure as shown by NQR
C ₆ H ₄ CH ₃ (tolyl)	Equatorial
C ₆ H ₄ CF ₃	Axial
$C_6H_3(CF_3)_2$ (Fluoroxyl)	Axial
$C_6H_2(CF_3)_3$ (Fluoromes)	Axial

Table 1.2 - Structures of various substituted P(V) species, ascertained using NQR

This study shows that Fluoroxyl and Fluoromes are more electron withdrawing than chlorine and thus the relative electronegativity of the group is high.

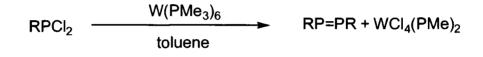
1.4 Precautions necessary when working with fluorinated aryl groups

Addition of an excess of BuLi to a solution containing fluorinated aryl groups can cause the formation of LiF over time. LiF is insoluble in ether and precipitates out of the solution rapidly, causing localised heating in the solution, which in turn causes the ether to boil. This is believed to be the cause of explosions in previous projects.

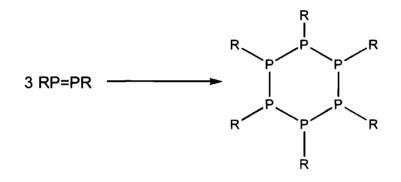
To avoid this, all reactions of this manner are performed with an excess of the Fluoromes or Fluoroxyl and at all times with the system open to the mercury bubbler. In this way there is always a pressure release mechanism.

1.5 Steric bulk in low coordinate phosphorus species

It is interesting to compare the steric properties of the Fluoromes and Fluoroxyl groups with other comparable bulky aryl ligands of the type $C_6H_2R_3$ (R = ^tBu, CH₃ and ⁱPr). In the formation of diphosphenes using transition metal catalysed metathesis¹⁹, the steric bulk of the aryl ligand determines the rate at which the diphosphene trimerises to form the trimer species R₃P₃.



Equation 1.3 – Formation of diphosphenes using transition metal catalysed metathesis



Equation 1.4 – Trimerisation of a diphosphene

Substituent used in C ₆ H ₂ R ₃	Rate of decomposition of diphosphene
CH ₃	No formation of RP=PR observed
ⁱ Pr	8 Hours
^t Bu	RP=PR stable
CF ₃	RP=PR stable

Table 1.3 - Stability of diphosphenes

The steric bulk of CF_3 is much closer to that of CH_3 than to that of the ^tBu group. Table 1.3 illustrates nicely the fact that the steric bulk itself is not the only factor affecting the stability of the compounds formed with Fluoromes and Fluoroxyl.

1.6 Low coordinate phosphorus species

Phosphorus has three common oxidation states (I, III, V) and is known to have coordination numbers from one (RCP) to six ($[PCl_6]^{(-)}$). Low coordinate phosphorus species are considered to be those with coordination number three or lower.

1.6.1 Three coordinate phosphorus species

There is a vast amount of P(III) chemistry, much of which is based around the derivatisation of PX_3 (X = Cl, Br, I) and the formation of P-F and P-H derivatives.

A very common reaction is that between an organolithium species and PCl_3 to form lithium chloride and the desired product $RPCl_2$. This is the reaction which forms the basis for the synthesis of most of the work described in this thesis.

RLi
$$\xrightarrow{\text{PCl}_3}$$
 RPCl₂ + LiCl ether

Equation 1.5 - Formation of mono substituted phosphanes

Phosphorus can be derivatised to form RPX₂, R₂PX and R₃X depending on the steric bulk of the R group (e.g. PPh₃ can be synthesised, however PAr₃ cannot). The formation of di- and tri-substituted phosphanes has become more common over the last few years with the increase of research into organometallic chemistry.

 PR_3 groups bond to metal centres through the lone pair on the phosphorus forming a single σ bond.

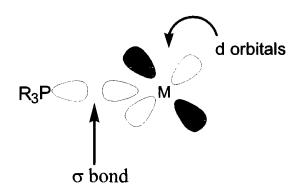


Figure 1.4 - Orbitals involved in bonding between phosphines and metal centres

The donation of the lone pair to a vacant metal orbital is not, however, the only factor that influences the bonding. Back bonding occurs from d-orbitals on the metal to the LUMO on the phosphorus (either a σ^* or π^* orbital) and this is a very important factor in transition metal chemistry. This back donation facilitates the stabilisation of 14 and 16 electron metal centres [e.g. "Wilkinson's catalyst" – RhCl(PPh₃)₃].

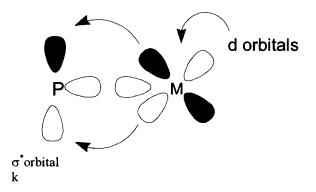


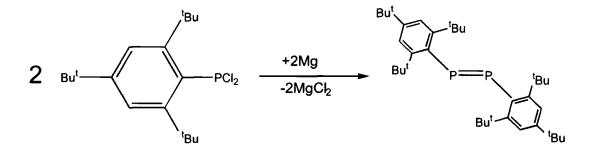
Figure 1.5 - Back donation of electron density into unoccupied orbitals on the phosphorus atom

1.6.2 Two coordinate phosphorus species

1.6.2.1 Diphosphenes

The formation of double bonds between elements outside the first long period of the periodic table was thought for many years to be impossible due to the "classical double bond rule" ²⁰, rationalised by long bond distances and inefficient π -bonding in the second and third row elements.

The first diphosphene was synthesised by Yoshifuji²¹ by the reduction of SupermesPCl₂ with elemental magnesium.

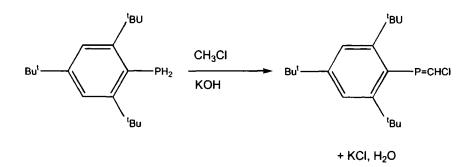


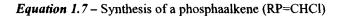
Equation 1.6 - Synthesis of the first symmetrical diphosphene

1.6.2.2 Phosphaalkenes

Phosphaalkenes are normally stabilised by bulky substituents on either the phosphorus, the carbon, or both atoms²². The type of phosphaalkene synthesised here was first prepared using the 2,4,6-tris(tritertiarybutyl)phenyl (Supermes) ligand²³.

One method of preparation is the reaction of RPH₂ with chloroform and alkali.



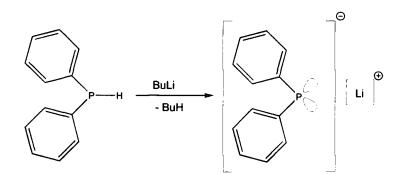


This reaction was not successful for R= Ar' or Ar. Possible reasons for this are given in a later chapter (see Section 2.3). Goodwin did, however, synthesise a Fluoromes containing phosphaalkene, by the removal of HCl from ArP(Cl)CHCl₂ (see Section 2.2.15)

Since this first discovery there have been a number of 2-coordinate phosphorus compounds synthesised including species with P=As, P=C, P=Si, P=Ge, and P=Sn.²⁴

1.6.2.3 P(I) species

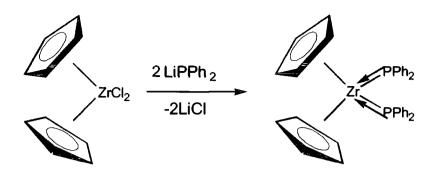
A good example of a phosphorus species in oxidation state (I) was reported by Schmidtpeter *et al*²⁵ with synthesis and X-ray characterisation of $[P(CN)_2]^{(-)}$ in a sodium crown-ether salt. The standard P(I) reagent used in organometallic chemistry is $PPh_2^{(-)}Li^{(+)}$ which is synthesised as a pure yellow solid from the reaction between PPh_2H and BuLi.



Equation 1.8 –Formation of Li(PPh₃)₂⁽⁻⁾

1.6.2.4 Metal phosphides

The discovery of the $PPh_2^{[-]}$ ligand has led to the formation of metal phosphides of the type M=PR₂²⁶. These compounds are analogous to the metal amides formed by the reaction of LiNR₂ and M(Cp)₂Cl₂.



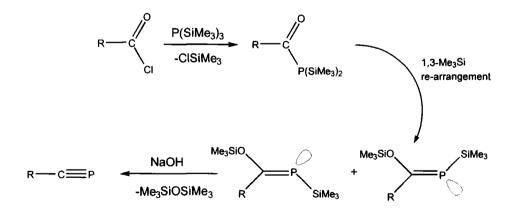
Equation 1.9 – Formation of a metal diphosphide

1.6.3 One coordinate phosphorus species

1.6.3.1 Phosphaalkynes

HCP, the most fundamental of all phosphaalkynes, has been known since 1961 when it was synthesised by the arcing of PH_3 between two graphite electrodes by Gier²⁷. The compound is unstable at room temperature and was characterised by IR spectroscopy.

The synthesis of the first kinetically stable phosphaalkyne was published by Becker *et al* in 1981^{28} and was slightly modified and the current synthetic method published by Regitz²⁹.



Equation 1.10 – Formation of a phosphaalkyne (R= ^tBu, Adamantyl, Supermes)

1.7 Experimental

1.7.1 Preparation of 1,3,5-tris(trifluoromethyl)benzene

The vacuum line used for this reaction was specifically designed for the use and manipulation of SF₄. The inside of the line was coated with Teflon to prevent corrosion of the steel from the highly reactive gas. The vacuum system is outlined below (see Figure 1.6). An upper reservoir of known volume (425cm^3) was filled over a period of 15 minutes with SF₄ from a cylinder. The volume of this gas was equal to approximately 150g. This was subsequently transferred to a small sample bottle (teflon lined steel) using vacuum transfer methods. From the initial tare of the bottle the quantity of SF₄ transferred could be determined. This process was then repeated until the desired quantity of SF₄ (550g, 3.9moles) had been obtained. The bottle was then allowed to warm to room temperature.

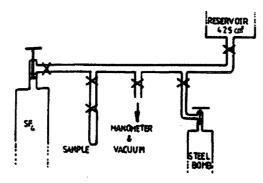


Figure 1.6 - Teflon lined steel vacuum line

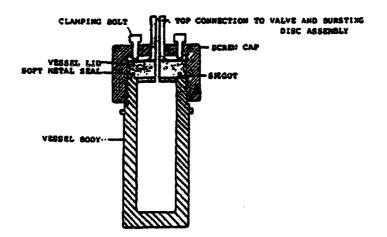


Figure 1.7 – Teflon lined steel bomb

Trimesic acid (benzene-1,3,5-tricarboxylic acid) (150g, 0.71moles) was introduced into a 1000 cm³ bomb. It was then evacuated and cooled to 76K in liquid nitrogen.

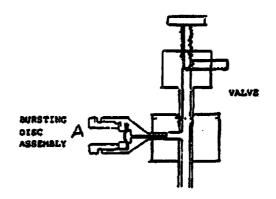


Figure 1.8 – Safety, Bursting disc assembly.

The contents of the steel bottle were then carefully condensed into the bomb and the tare of the bottle checked to ensure that all the SF_4 had been transferred. The bomb was then transferred to the high pressure facilities in a Dewar of liquid N_2 and allowed to warm up to room temperature safely under controlled conditions.

The bomb was then placed in a furnace, with the help of thermocouples heated to a temperature of 150°C which was maintained for the duration of the reaction (12 hours). The reaction was then allowed to cool to room temperature and the bomb was transferred to a fume cupboard.

 $C_{6}H_{3}(COOH)_{3} \xrightarrow{SF_{4}} C_{6}H_{3}(CF)_{3}$ 423K
130 Atmos. Pressure

Equation 1.11 - Synthesis of Fluoromes

The by-products of the reaction are SO_2 , HF, and any unreacted SF_4 . These gases need to be scrubbed, neutralised, and not allowed into the atmosphere. The apparatus used for scrubbing is shown below (Figure 1.9). The gases are slowly passed over a vessel containing a saturated solution of potassium hydroxide. Sodium hydroxide is not used because the solubility of potassium fluoride is three times that of sodium fluoride. The second vessel containing KOH is there for safety should all the KOH in the first vessel is consumed during the scrubbing process.

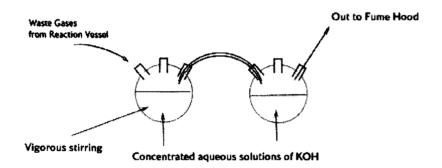


Figure 1.9 - Scrubbing system used to neutralise acidic waste gases

After scrubbing the gases, the contents of the bomb were then tipped onto crushed ice (to remove any unreacted trimesic acid and HF). The mixture was then filtered, treated with NaOH, and left to stir overnight to remove any last acidic impurities. The oily product was then separated and dried over anhydrous magnesium sulphate.

The product was then purified by distillation using a fractionating column to yield a colourless oil Bp 119°C (760mm Hg).

²G. E. Carr., R. D. Chambers., T. F. Holmes., D. G. Parker., J. Organometallic Chem., 1987, 325, 13.

³ M. Scholtz., H. W. Roesky., D. Stalke., K. Keller., F. T. Edelmann., *J Organometallic Chem.*, 1989, **366**, 73.

⁴ R. D. Schulter., A. H. Atwood., R. A. Jones., M. R. Bond., C. J. Carrano., J. Am. Chem. Soc., 1993, 115,

2070; R. D. Shulter., H. S. Isom., A. H. Cowley., D. A. Atwood., R. A. Jones., F. Olbright., S. Corbelin., R. J. Lagow., *Organometallics*, 1994, 13, 4058.

- ⁵ H. Grutzmacher., H. Prizkow., F. T. Edlemann., Organometallics, 1991, 10, 23.
- ⁶ S. Brooker., J-K. Buijink., F. T. Edlemann., Organometallics, 1991, 10, 25.
- ⁷ K. H. Whitmire., D. Labahn., H. W. Roesky., M. Noltemeyer., G. M. Sheldrick., J. Organomet. Chem., 1991, **402**, 55.

⁸ S. Brooker., N. Bertel., D. Stalke., M. Noltemeyer., R. W. Roesky., G. M. Sheldrick. F. T. Edelmann., *Organometallics*, 1992, 11, 192.

- ⁹ M. Belay., F. T. Edelmann., J. Organomet. Chem., 1994, 479, C21.
- ¹⁰ F. T. Edelmann., W. Bruser., P. Poremba., J. Fluorine. Chem., 1997, 82, 43
- ¹¹ K. B. Dillon., H. P. Goodwin., J. Organomet. Chem., 1992, 429, 169.
- ¹² D. Stalke., K. Keller., F. T. Edlemann., M. Scholtz., H. W. Roesky., J. Organomet. Chem., 1989, 366,73
- ¹³ K. B. Dillon., H. P. Goodwin., J. Organomet. Chem., 1994, 469, 125.
- ¹⁴ T. A. Straw., Ph. D Thesis, Durham, 1991.
- ¹⁵ F. H. Allen., O. Kennard., Chemical Design Automation News, 1993, 8(1)1, 31-37
- ¹⁶ M. Y. Eyring., E. C. Zuerner., L. J. Radonovich., Inorg. Chem., 1981, 20, 3405.
- ¹⁷ A. Dubourg., J. P., Declercq., H. Ranaivonjatovo., J. Escudié., C. Couret., M. Lazraq., Acta Crystallographica., Sect. C., 1988, 44, 2004.
- ¹⁸ L. Heuer., P. G. Jones., R. Schmutzler., J. Fluorine Chem., 1990, 46, 243.
- ¹⁹ K. B. Dillon., V. C. Gibson., L. J. Sequeira., J. Chem. Soc. Chem. Comm., 1995, 2429.
- ²⁰ L. E. Gusel'nikov., N. S. Nametkin., Chem. Rev., 1979, 529 and references therein.
- ²¹ M. Yoshifuji., I. Shima., N., Inamoto., K. Hirotsu., T. Higuchi., J. Am. Chem. Soc., 1981, 103, 4587.
- ²² J. F. Nixon., Chem. Rev., 1988, 88, 1327
- ²³ R. Appel., C. Casser., M. Immenkeppel., F. Knoch., Angew. Chem. Ed. Int. Ed. Engl., 1984, 23, 895
- ²⁴ O. J. Scherer., Angew. Chem. Int. Ed. Engl., 1985, 24, 924-943.
- ²⁵ W. S. Sheldick., J. Kroner., F. Zwaschka., A. Schmidtpeter., Angew. Chem. Int. Ed. Engl., 1979, 1979, 934.
- ²⁶ S. R. Wade., M. G. H. Wallbridge., G. R. Willey., J. Chem. Soc. Dalton. Trans., 1983, 2555.
- ²⁷ T. E. Gier., J. Am. Chem. Soc., 1961, 83, 1769.

²⁸ G. Becker., W. Becker., R. Knebl., H. Schmidt., U. Weeber., M. Westerhausen., Nova Acta Leopold., 1985, **59**, 55.

²⁹ M. Regitz., W. Rosch., T. Allspach., U. Annen., K. Blatter., J. Fink., M. Hermesdorf., H. Heydt., U. Vogelbacher., O. Wagner., *Phosphorus Sulfur.*, 1987, **30**, 479.

¹ E. T. McBee., R. E. Leech., Ind. Eng. Chem., 1947, 39, 393.

Chapter 2

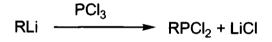
Novel low-coordinate phosphane synthesis

2.1 Introduction

Dichlorophosphanes have been known since the 19th century¹, and form the starting material for the synthesis of other species of the type RPX_2 (where X = H, F) and other phosphanes described in this chapter.

2.1.1 Synthesis of P(III) species of the type RPX₂

A common and convenient method for the preparation of this type of compound is the reaction of a lithiated aryl or alkyl species with PCl₃, forming the desired alkyl/aryl phosphane. During the reaction LiCl precipitates out of solution (ether). The solvent is then removed *in vacuo* and the product is purified by distillation.



Equation 2.1 - Synthesis of a mono substituted phosphane

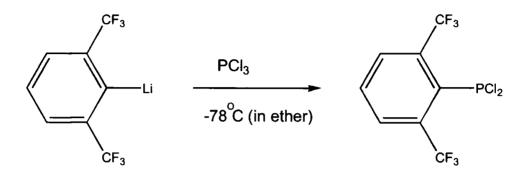
2.2 Novel phosphanes with bulky electron-withdrawing substituents

All the synthetic methods used in this chapter (unless otherwise stated) were similar to those first used by Helen Goodwin during her $Ph.D^2$.

2.2.1 Ar'PCI₂

The $Ar'PCl_2$ compound formed the basic starting material for a number of other phosphanes described later in this chapter. The product was obtained as an impure colourless oil (see Equation 2.2).

The ³¹P NMR spectrum of the compound shows a septet at $\delta = 148.0$ ppm (⁴J_{P-F} = 65.2 Hz). This splitting is caused by the proximity of the fluorines on the CF₃ groups to the phosphorus atom (i.e. an interaction through space rather than through the connecting bonds). The ¹⁹F NMR spectrum for this compound shows a single doublet with a chemical shift $\delta = -53.0$ ppm (⁴J_{P-F} = 65.2 Hz).



Equation 2.2 – Synthesis of Ar'PCl₂

2.2.1.1 ¹⁹F Spectroscopic study on the reaction intermediates in the reaction of BuLi and Ar'H

In the reaction between Ar'H and BuLi there are a number of different possible lithiation sites shown in Figure 2.1. The most probable product, Ar'Li, will only show one resonance in the ¹⁹F NMR because both CF_3 groups are equivalent. This is also true if the lithiation site is on the site *meta* to both CF_3 groups; this is the least likely site of substitution, as discussed earlier. If the *meta* site was lithiated, the resulting species would be very reactive and would then be likely to react in a coupling reaction with another aryl group.

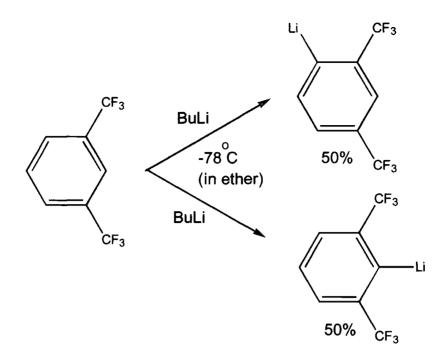
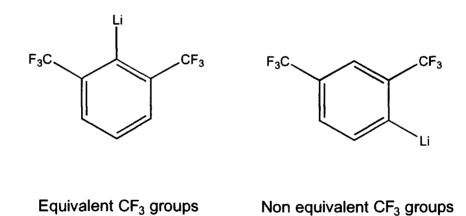
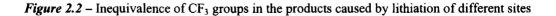


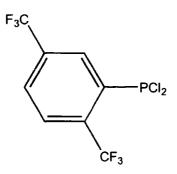
Figure 2.1 - Two products formed in the reaction between BuLi and Ar'H

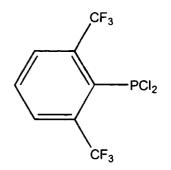
If the lithiation site is *ortho* to one CF_3 group and *para* to the other, then the two CF_3 groups will be inequivalent, and two singlets should be apparent in the ¹⁹F NMR spectrum.

By following the ¹⁹F spectrum over the course of the reaction it is also possible to recognise when the maximum quantity of the lithiated species is present and thus maximise the yield of phosphane products.









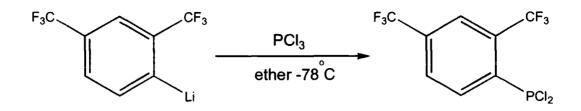
Undesired product [Ar"PCb] Desired product [Ar'PCb]

Figure 2.3 - Differences in products upon reaction of the lithiated products with PCl₃

2.2.2 Ar"PCl₂

The reaction of Ar'H with BuLi causes the formation of two distinct lithiated species. Upon further reaction with PCl₃, this in turn leads to the formation of two distinct RPCl₂ species. The two species (Ar'PCl₂ and Ar''PCl₂) have the same molecular mass and were therefore very difficult to separate. Fractional distillation of the resulting mixture did not separate the two compounds, although it would appear that Ar''PCl₂ boils at a slightly lower temperature than Ar'PCl₂ (the first few fractions contained a much greater percentage of Ar''PCl₂, but were impossible to obtain pure).

The ³¹P NMR spectrum of the resulting mixed oil shows the resonance of Ar''PCl₂ to be a quartet $\delta = 151.1$ ppm (⁴J_{P-F} = 84.5 Hz). The splitting is different to that of Ar'PCl₂ because there is only one CF₃ group in close proximity to the phosphorus atom. The size of the coupling constant is greater than that in the case of Ar'PCl₂, implying that the CF₃ groups are interacting more with the P atom. Knowing this, it is possible to concur that the average distance between the phosphorus atom and the fluorine atoms of the *ortho* CF₃ groups is shorter in Ar''PCl₂ than in Ar'PCl₂. The coupling constant is 29% larger than in the species containing Ar'.

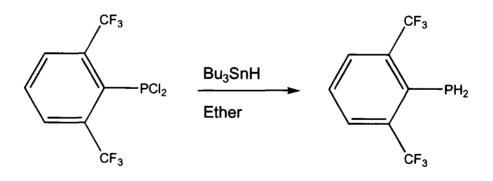


Equation 2.3 – Synthesis of Ar"PCl₂

2.2.3 Ar'PH₂

This phosphane was prepared by the reaction of the mixture of $Ar'PCl_2/Ar''PCl_2$ and Bu_3SnH . The product was purified by distillation and isolated as a clear colourless oil. The product obtained was $Ar'PH_2$ only, and showed no signs in its NMR spectra of $Ar''PH_2$, which remained below the detection limit.

The ³¹P NMR spectrum of this compound shows the chemical shift of the compound has changed quite markedly, ($\delta = -140.3$ ppm) from that of the starting material Ar'PCl₂ There is a distinct phosphorus-hydrogen coupling, giving a triplet of septets (${}^{1}J_{P-H} = 216.7$ Hz, ${}^{4}J_{P-F} = 29.4$ Hz).



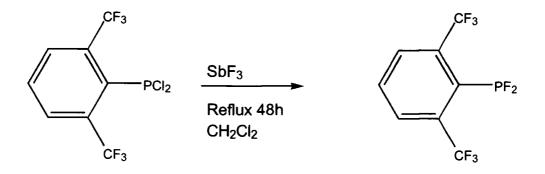
Equation 2.4 – Synthesis of Ar'PH₂

2.2.4 Ar'PF₂

The difluorophosphane was prepared by refluxing a solution of $Ar'PCl_2/Ar''PCl_2$ in ether with solid SbF₃ over 48 hours at atmospheric pressure. The product was purified by distillation and isolated as a clear colourless oil. The product obtained was $Ar'PF_2$ only, and showed no signs in its NMR spectra of $Ar''PF_2$, which remained below the detection limit.

The ³¹P NMR spectrum of the compound shows distinct P-F coupling caused by both the CF₃ groups and the two new fluorines bonded to the phosphorus itself, again giving rise to a doublet of septets with chemical shift $\delta = 193.3$ ppm (¹J_{P-F} = 1224 Hz, ⁴J_{P-F} = 48.3 Hz).

The ¹⁹F NMR spectrum showed a doublet of triplets showing a small amount of F-F interaction and a doublet of septets. The chemical shifts for this compound were $\delta = -55.5$ ppm (⁴J_{P-F} = 48.3 Hz) and $\delta = -91.85$ ppm (¹J_{P-F} = 1224 Hz), (⁵J_{F-F} = 14.1 Hz).



Equation 2.5 – Synthesis of Ar'PF₂

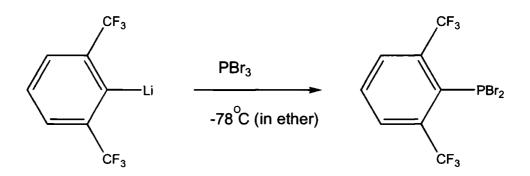
2.2.5 Ar'PBr₂ (Ar''PBr₂)

This compound was prepared in the same manner as $Ar'PCl_2$ except using PBr₃ instead of PCl₃. Although dibromophosphanes are less common than dichlorophosphanes, the preparation is in principle the same. The product was isolated as a very viscous yellow oil.

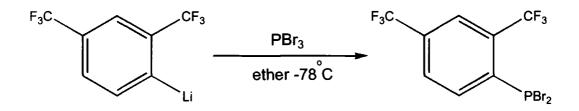
As in the case of the preparation of Ar'PCl₂, there is a mixture of inseparable products formed in this reaction (Ar'PBr₂ and Ar''PBr₂). The ³¹P NMR spectrum of this compounds shows a septet and a quartet, $\delta = 135.8$ ppm (⁴J_{P-F} = 62.8 Hz) and $\delta = 143.9$ ppm (⁴J_{P-F} = 77.0 Hz).

The ¹⁹F NMR spectrum of the two compounds shows two doublets and a singlet. Ar'PBr₂ has one doublet $\delta = -50.70$ ppm (⁴J_{P-F} = 62.8Hz). Ar''PBr₂ shows a doublet and a singlet, $\delta = -54.9$ ppm (⁴J_{P-F} = 77.0 Hz) and $\delta = -61.9$ ppm.

This result confirms the result shown for the Ar'PCl₂/Ar''PCl₂ case where the species containing Ar'' had a larger coupling constant that the species containing Ar'. In this case the coupling constant is 23% larger for Ar''PBr₂.



Equation 2.6 – Synthesis of Ar'PBr₂

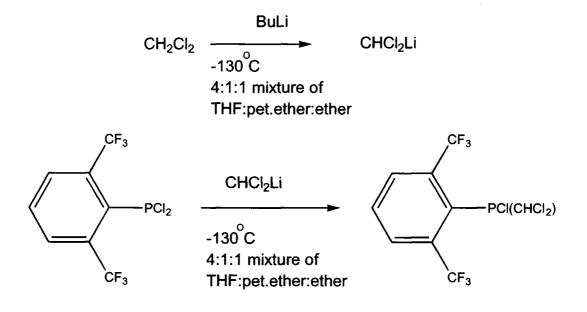


Equation 2.7 – Synthesis of Ar''PBr₂

2.2.6 Ar'P(CI)CHCl₂

This phosphane was produced by the careful reaction of $Ar'PCl_2/Ar''PCl_2$ with a solution of lithiated CH_2Cl_2 at -130°C in a pentane slush bath. The temperature in this reaction is crucial because lithiated dichloromethane decomposes above -120°C. During the reactions, the solutions must be kept from freezing solid because this would not facilitate transfer through a cannular. This was achieved by a combination of solvents and by vigorous mechanical stirring. There were no signs of the $Ar''P(Cl)CHCl_2$ species from the ³¹P NMR spectrum. The compound was isolated by distillation yielding a colourless oil.

The ³¹P NMR spectrum of the product shows a septet with a chemical shift, $\delta = 65.6 \text{ ppm} (^4J_{P-F} = 48.6 \text{ Hz})$. The ¹⁹F NMR spectrum shows a doublet with chemical shift $\delta = -53.6 \text{ ppm} (^4J_{P-F} = 48.6 \text{Hz})$.

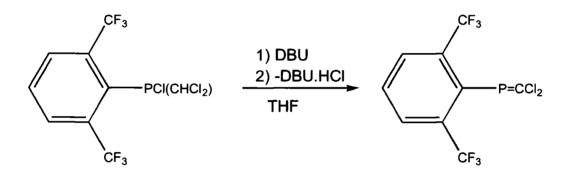


Equation 2.8 – Synthesis of Ar'PCl(CHCl₂)

2.2.7 Ar'P=CCl₂

The synthesis of this compound involves the removal of HCl from $Ar'P(Cl)CHCl_2$ using the tertiary amine base DBU. DBU was used because it is a strong non-nucleophilic base, and as such will not cause a direct reaction with the P-Cl bond. The product is isolated as a colourless oil.

The ³¹P NMR spectrum of this compound showed a septet with a chemical shift, $\delta = 206.8 \text{ ppm} (^4J_{P-F} = 21.5 \text{ Hz})$. The ¹⁹F NMR spectrum showed a doublet with a chemical shift, $\delta = -59.89 \text{ ppm} (^4J_{P-F} = 21.5 \text{ Hz})$.



Equation 2.9 – Synthesis of Ar'P=CCl₂

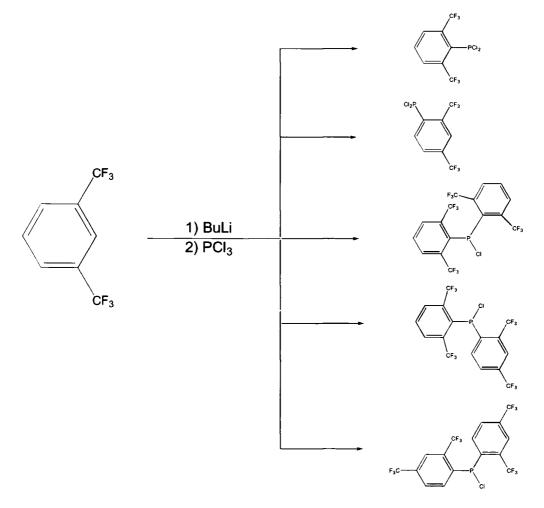
2.2.8 Ar'₂PCI (Ar'Ar''PCI)

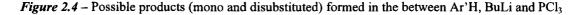
2.2.8.1 Attempted formation of Ar'₂PCl

As shown in Section 2.2.1, when BuLi is added to a solution of Ar'H in ether there are two different lithiated products formed (Ar'Li and Ar''Li). When PCl_3 is added to this solution this facilitates the formation of a number of different products (see Figure 2.4). The formation of the di-substituted products does not appear to be controlled by the ratio of lithiated product to PCl_3 . In the formation of Ar_2PCl (see Section 2.2.11), due to the steric hindrance of surrounding the phosphorus atom with four CF₃ groups, formation of the di-substituted product is difficult and the reaction is slow. In this reaction, however, the formation of the di-substituted product seems to be facilitated more easily than the formation of the mono-substituted product. Even when a large excess of PCl₃ is used a significant quantity of the di-substituted product is formed.

Because Fluoroxyl is more electronegative than chlorine (see Section 1.3.3) the P-Cl bond in RPCl₂ will be weaker than in PCl₃. It is reasonable to assume that the newly formed RPCl₂ species is more reactive to RLi than PCl₃. In the case of R=Ar this effect is tempered by the steric hindrance of both the CF₃ groups, being in the *ortho* position. The steric effect is less of a consideration if there is only one *ortho* CF₃ group as in the case of Ar''.

There are a number of different possible products obtainable by the addition of PCl₃ to the mixture of Ar'Li and Ar''Li.

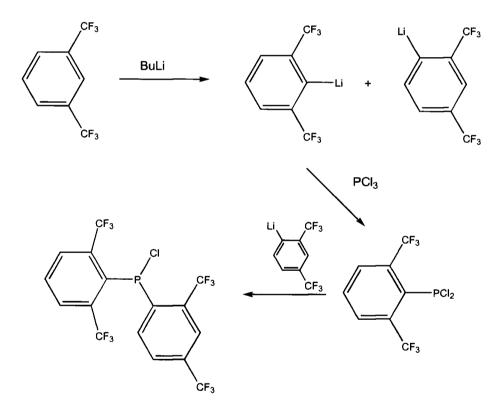




The product was isolated by distillation and a white crystalline solid was purified by recrystallisation from hexanes.

The ³¹P NMR spectrum of the product showed the existence of only one disubstituted product. The spectrum shows a complicated multiplet and although all the expected peaks are not visible it was possible to obtain a chemical shift $\delta = 67.3$ ppm (⁴J_{P-F} = 67.1 Hz). The expected spectrum would be a septet of quartets due to the six equivalent fluorines on the Ar' CF₃ group and the fluorines on the Ar''CF₃ group.

The structure deduced from the NMR spectra was also confirmed by X-ray crystallographic analysis on crystals of the compound (see Section 2.2.8.3). The 19 F spectrum shows a doublet and two singlets (see Equation 2.10).



Equation 2.10 - Synthesis of Ar'Ar''PCl

 19 F NMR studies (see Section 2.2.1.1) have shown that the ratio of lithiated products in the initial reaction is approximately 50:50. This would imply that the most probable di-substituted product would be the mixed Ar'Ar''PCl in preference to Ar''_2PCl or Ar'_2PCl.

After purification by distillation the ratio of $Ar'PCl_2$ to $Ar''PCl_2$ has been reduced from approximately 50:50 to 66:33 in favour of the more sterically hindered product. Whilst it is fortuitous as that is the desired product, there appears to be a deficit in the amount of Ar'' aryl groups present in the products. The less sterically hindered Ar''Li is more likely to be involved in side reactions, with the possible formation of other coupling products and LiF. After purification the mixture left in the reaction vessel contained a number of different fluorinated species but none containing phosphorus (determined from ¹⁹F and ³¹P NMR studies).

2.2.8.2 Variable temperature ¹⁹F NMR studies on Ar'Ar''PCl

The ¹⁹F spectrum of Ar'₂PCl would only show a doublet because all the fluorines are equivalent and the signal is coupled to the phosphorus through space. At room temperature, however, the ¹⁹F NMR spectrum of Ar'Ar''PCl in toluene shows a doublet with a chemical shift $\delta = -59.3$ ppm (⁴J_{P-F} = 59.1 Hz) and two singlets, $\delta = -55.4$ (broad peak) and $\delta = -64.1$ ppm (sharp). These peaks are in the ratio 1:2:1, implying that the broad singlet is indeed due to two CF₃ groups rather than one.

From the diagram (Figure 2.5), it is possible that there are four inequivalent CF_3 groups present if the molecule is rigid on the NMR time scale. In this position we would expect to see three doublets and a singlet.

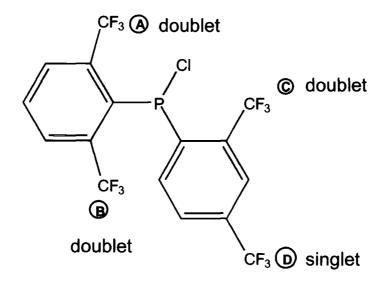


Figure 2.5 - Expected NMR signals for Ar'Ar''PCl

The room temperature spectrum shows three inequivalent CF_3 groups, which can be assigned to a doublet and singlet from the two CF_3 groups on the Ar'' group, and the broad peak arises from both the CF_3 groups from the Ar' group. If these two CF_3 groups were equivalent, a well resolved doublet would be expected; if they were completely (not exchanging), then two doublets would result. What is seen from the resulting spectrum, is that the CF_3 groups become almost equivalent, but not sufficient enough to give a clear doublet in the NMR spectrum.

If the solution (in toluene) is heated to 100° C the ¹⁹F NMR spectrum shows a broad doublet in the position where the broad singlet was ($\delta = -55.0$ ppm ⁴J_{P-F} = 35.3 Hz). This demonstrates that the rotation of the Ar' group about the P-C bond is fast enough on the NMR time scale for the two CF₃ groups to become equivalent.

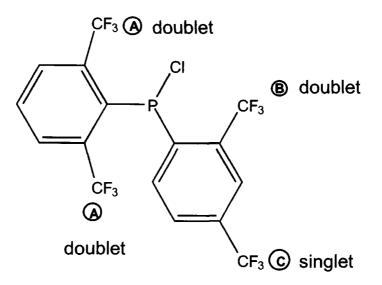


Figure 2.6 - Equivalent CF3 groups shown in the NMR at 100°C of Ar'Ar''PCl

If the solution is cooled and the rotation of the Ar' group around the P-C bond is slowed significantly on the NMR time scale so that the two CF₃ groups become inequivalent, then the expected spectrum would have 3 separate doublets and a singlet. When the solution is cooled down to -78° C, however, the ¹⁹F solution NMR shows two doublets and two singlets. The doublet and singlet, assigned to the Ar'' group from before, are at the same chemical shifts ($\delta = -59.5$ ppm and $\delta = -64.0$ ppm).

The peaks assignable to the CF₃ groups from Ar', however, do not show two separate doublets. The ¹⁹F NMR spectrum shows a doublet ($\delta = -54.5$ ppm, ⁴J_{P-F} = 75.8 Hz) and a singlet ($\delta = -56.6$ ppm). This result implies that not only are the CF₃ groups on the Ar' group inequivalent, it implies that one of the CF₃ groups is significantly further away from the phosphorus atom than the other.

This result is confirmed from the X-ray crystallographic structure of the molecule (see Section 2.2.8.3). The closest contact distance of one of the fluorines in an *ortho* CF₃ group (A) to the phosphorus atom is 2.89Å and the closest distance of a fluorine atom in the CF₃ group (B) is 3.25 Å.

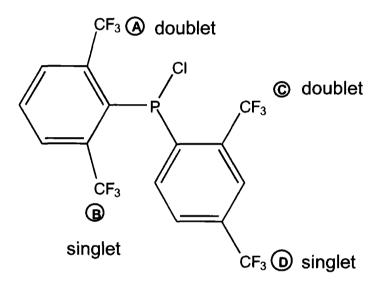


Figure 2.7 - Inequivalent CF₃ groups shown by NMR at -78°C

2.2.8.3 X-ray structure of Ar'Ar''PCl

Data collection and structure solution was performed by Dr A. S. Batsanov.

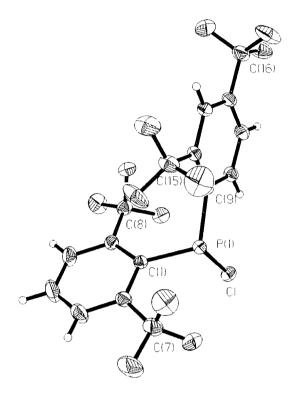


Figure 2.8 - Thermal Ellipsoid diagram at 150K (50% probability) for Ar'Ar''PCl

The structure of this compound shows a number of interesting characteristics. These characteristics are the result of steric interactions and a number of intramolecular interactions between atoms in the same molecule.

• The following diagrams shows differences in the fluorine to phosphorus distances. These differences in distance are shown up in the low temperature solution NMR studies of the compound, which shows two distinct peaks assignable to inequivalent CF₃ groups on the same aryl group (see Section 2.2.8.2).

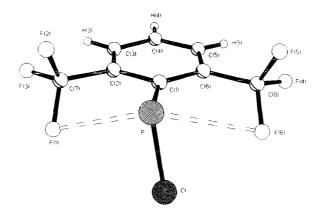


Figure 2.9 – Thermal ellipsoid diagram at 150 (50% probability) showing the inequivalence of the CF₃ groups on the Ar' group in the solid state

Figure 2.10 shows the interactions between some of the fluorine atoms within the CF_3 groups and the phosphorus atom.

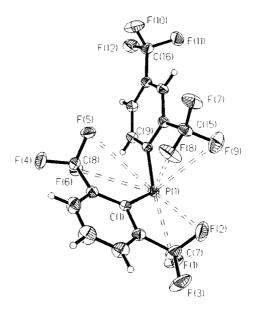


Figure 2.10 – P-F interactions in the solid-state structure of Ar'Ar''PCl (The chlorine atom (Cl1) has been omitted for clarity)

Table 2.1 shows the comparison between phosphorus fluorine distances from a number of atoms on different CF₃ groups within the molecule. What is immediately apparent from the table is that F(1) and F(2) are significantly closer to the phosphorus atom that F(5) and F(6). This demonstrates the inequality in the two CF₃ groups on the Ar' aryl ring. The distance between the nearest fluorine atom on the Ar'' aryl group and the phosphorus atom [F(8)-P(1)] is also significantly shorter than F(6)-P(1).

Fluorine Atom	Distance to P(1) (Å)		
F(1)	2.89		
F(2)	2.89		
F(5)	3.68		
F(6)	3.25		
F(8)	2.89		
F(9)	3.36		

Table 2.1 - P-F bond lengths in Ar'Ar''PCl

• There is an interaction between the chlorine and the adjacent hydrogen atom on the Ar" group. This interaction is possible because the Ar" group does not have two CF₃ groups *ortho* to the phosphorus atom. The distance between the two atoms is 2.52 Å which is close enough to be considered an intramolecular hydrogen bond³.

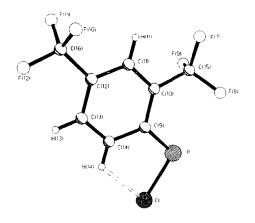


Figure 2.11 – Thermal ellipsoid diagram at 150 (50% probability) showing the interaction between the chlorine atom and the adjacent hydrogen atom on the aryl group Ar''.

• It is also worthy of note that the plane of the aryl ring is the same at the P-Cl...H bond. This is more evidence for the H-Cl interaction as this appears to be determining the conformation of the aryl ring and its position in the structure. The bond angle C(9)-P(1)-Cl(1) is equal to 102° which shows a reduction from the ideal tetrahedral angle of 109°.

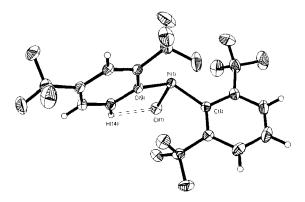


Figure 2.12 – Thermal ellipsoid diagram at 150 (50% probability) showing the P-Cl..H hydrogen bond it's effect on the structure of the molecule

• The steric influences on the molecule are due to the bulky CF₃ groups on the Ar' and Ar'' groups. The angle between the two aryl rings is 94°, which significantly decreases the interaction between the CF₃ groups on different aryl groups.

Crystal data and structure refinement.				
Identification code	Ar'Ar"PCI			
Empirical formula	Gte He CI Ft2 P			
Formula weight	492.63			
Temperature	150/21 K			
Wavelength	0.71073 Å			
Crystal system	Triclinic			
Space group	P-1			
Unit cell dimensions	$a = 7.949(1)$ Å $\alpha = 104.25(1)$			
	b = 9.313(1) Å β = 90.49(1) °.			
	c = 12.369(1) Å = 96.35(1) *			
Volume	881.4(2) Å ³			
Z	2			
Number of reflections used	Calculation of cell = 512			
	Total = 10579			
and the second s	Unique = 4735			
	Obs [I>2σ(I)] = 4285			
Crystal description	needle			
Crystal colour	colourless			
Density (calculated)	1.856 g/cm ³			
Absorption coefficient	4.43 cm ⁻¹			
F(000)	484			
Crystal size	0.2 x 0.2 x 0.3 mm			
Theta range for data collection	1.70 to 30.44 *.			
Index ranges	-11<=h<=10, -13<=k<=12, -17<=l<=16			
Experiment device	Siemens SMART			
Experiment methods	ω scans			
Reflections collected	10579			
Independent reflections	4735 [R(int) = 0.0231]			
Refinement method	Full-matrix least-squares on F ²			
Data / restraints / parameters	4710/0/295			
Goodness-of-fit on F ²	1.094			
Final R indices [I>2o(I)]	$R_1 = 0.0324, wR_2 = 0.0761$			
R indices (all data)	$R_1 = 0.0381, wR_2 = 0.0861$			
Largest diff. peak and hole	0.583 and -0.383 e.Å-3			

Table 2.2 - Crystal data and structure refinement for Ar'Ar''PCl

	X	У	z	U(eq)	
P(1)	6022(1)	3418(1)	3267(1)	19(1)	
CI(1)	8253(1)	4457(1)	4103(1)	26(1)	
C(1)	6803(2)	2747(2)	1825(1)	19(1)	
C(2)	6975(2)	1203(2)	1530(1)	24(1)	
C(3)	7459(2)	490(2)	471(2)	35(1)	
C(4)	7757(3)	1277(2)	-331(2)	41(1)	
C(5)	7625(2)	2792(2)	-69(1)	33(1)	
C(6)	7174(2)	3531(2)	995(1)	22(1)	
C(7)	6644(2)	215(2)	2337(2)	35(1)	
C(8)	7136(2)	5197(2)	1189(1)	25(1)	
C(9)	4803(2)	5012(2)	3308(1)	19(1)	
C(10)	3096(2)	4756(2)	2902(1)	20(1)	
C(11)	2094(2)	5919(2)	3053(1)	22(1)	
C(12)	2748(2)	7352(2)	3647(1)	22(1)	
C(13)	4394(2)	7617(2)	4077(1)	24(1)	
C(14)	5412(2)	6459(2)	3904(1)	22(1)	
C(15)	2254(2)	3215(2)	2335(1)	29(1)	
C(16)	1597(2)	8563(2)	3829(1)	28(1)	
F(1)	7528(2)	744(1)	3306(1)	44(1)	
F(2)	4999(2)	38(1)	2577(1)	48(1)	
F(3)	7076(2)	-1158(1)	1917(1)	61(1)	
F(4)	7938(2)	5736(1)	393(1)	41(1)	
F(5)	5554(1)	5581(1)	1187(1)	31(1)	
F(6)	7904(1)	5961(1)	2166(1)	29(1)	
F(7)	840(1)	3243(1)	1759(1)	45(1)	
F(8)	3259(1)	2427(1)	1616(1)	52(1)	
F(9)	1821(2)	2415(1)	3073(1)	58(1)	
F(10)	958(2)	8714(1)	2860(1)	49(1)	
F(11)	267(1)	8266(1)	4425(1)	47(1)	
F(12)	2378(1)	9895(1)	4366(1)	42(1)	

Table 2.3 - Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for Ar'Ar''PCl. U(eq) is defined as one third of the trace of the *ortho*gonalized Uij tensor

Bond lengths [Å] and a Ar'Ar''PCI.	
P(1)-C(9)	1.8518(14)
P(1)-C(1)	1.8746(14)
P(1)-CI(1)	2.0608(6)
P(1)-F(1)	2,8903(11)
P(1)-F(8)	2.8969(12)
C(1)-C(2)	1.416(2)
C(2)-C(3)	1.394(2)
C(2)-C(7)	1.522(2)
C(3)-C(4)	1.378(3)
C(3)-H(3)	.90(2)
C(4)-C(5)	1.384(3)
C(4)-H(4)	.96(2)
C(5)-H(5)	.90(2)
C(6)-C(8)	1.514(2)
C(7)-F(1)	1.338(2)
C(7)-F(3)	1.340(2)
C(7)-F(2)	1.345(2)
C(8)-F(6)	1.345(2)
C(8)-F(5)	1.345(2)
C(8)-F(4)	1.345(2)
C(9)-C(14)	1.398(2)
C(10)-C(11)	1.392(2)
C(10)-C(15)	1.511(2)
C(11)-C(12)	1.396(2)
C(11)-H(11)	.94(2)
C(12)-C(13)	1.382(2)
C(12)-C(16)	1.506(2)
C(13)-C(14)	1.395(2)
C(13)-H(13)	.93(2)
C(14)-H(14)	1 332(2)
C(15)-F(8)	1.337(2)
C(15)-F(9)	1.339(2)
C(16)-F(12)	1.335(2)
C(16)-F(11)	1.336(2)
C(16)-F(10)	1.343(2)
C(9)-P(1)-C(1)	109.23(6)
C(9)-P(1)-CI(1)	102.10(5)
C(1)-P(1)-Cl(1) C(9)-P(1)-F(1)	100.23(4) 172.45(5)
C(1)-P(1)-F(1)	75.04(5)
Cl(1)-P(1)-F(1)	82.91(3)
C(9)-P(1)-F(8)	71.98(5)
C(1)-P(1)-F(8)	68.11(5)
CI(1)-P(1)-F(8)	163.08(3)

Bond lengths [Å] and a Ar'Ar''PCI.	ngles [º] for
F(1)-P(1)-F(8)	104.75(4)
C(6)-C(1)-C(2).	116.54(12)
C(6)-C(1)-P(1)	129.91(10)
C(2)-C(1)-P(1)	113.50(10)
C(3)-C(2)-C(1)	121.69(14)
C(3)-C(2)-C(7)	115.60(14)
C(1)-C(2)-C(7)	122.70(13)
C(4)-C(3)-C(2)	120,3(2)
C(4)-C(3)-H(3)	119(2)
C(2)-C(3)-H(3)	121(2)
C(3)-C(4)-C(5)	119.7(2)
C(3)-C(4)-H(4)	120.9(14)
C(5)-C(4)-H(4)	119.4(14)
C(4)-C(5)-C(6)	120.8(2)
C(4)-C(5)-H(5)	120(2)
C(6)-C(5)-H(5)	119(2)
C(5)-C(6)-C(1)	120.93(14)
C(5)-C(6)-C(8)	115.71(13)
C(1)-C(6)-C(8)	123.35(12)
F(1)-C(7)-F(3)	105.9(2)
F(1)-C(7)-F(2)	107.3(2)
F(3)-C(7)-F(2)	106.3(2)
F(1)-C(7)-C(2)	112.86(14)
F(3)-C(7)-C(2)	111.82(14)
F(2)-C(7)-C(2)	112.19(14)
F(6)-C(8)-F(5)	107.21(12)
F(6)-C(8)-F(4)	106.26(12)
F(5)-C(8)-F(4)	106.01(12)
F(6)-C(8)-C(6)	112.16(12)
F(5)-C(8)-C(6)	112.85(12)
F(4)-C(8)-C(6)	111.90(12)
C(14)-C(9)-C(10)	117:48(12)
C(14)-C(9)-P(1)	121.50(10)
C(10)-C(9)-P(1)	120.07(10)
C(11)-C(10)-C(9)	120.93(12)
C(11)-C(10)-C(15)	116.81(12)
C(9)-C(10)-C(15)	122.21(12)
C(10)-C(11)-C(12)	119.99(13)
C(10)-C(11)-H(11)	118.6(12)
C(12)-C(11)-H(11)	121.3(12)
C(13)-C(12)-C(11)	119.96(13)
C(13)-C(12)-C(16)	121.82(13)
C(11)-C(12)-C(16)	118.19(13)
C(12)-C(13)-C(14)	120.08(13)
C(12)-C(13)-H(13)	121.7(12)
C(14)-C(13)-H(13)	118.2(12)
C(13)-C(14)-C(9)	121.50(13)
C(13)-C(14)-H(14)	118.2(12)
C(9)-C(14)-H(14)	120.3(12)

Bond lengths [Å] and angles [°] for Ar'Ar''PCI.				
F(7)-C(15)-F(8)	109 (8/44)			
F(7)-C(15)-F(9)	106 40(14)			
F(7)-C(15)-F(9)	106.40(14)			
r(0)-0(10)-r(8)	106.51(14)			
F(7)-C(15)-C(10)	112.86(13)			
F(8)-C(15)-C(10)	112.53(12)			
F(9)-C(15)-C(10)	111.62(13)			
F(12)-C(16)-F(11)	107.12(13)			
F(12)-C(16)-F(10)	106.99(13)			
F(11)-C(16)-F(10)	106.14(14)			
F(12)-C(16)-C(12)	112.84(13)			
F(11)-C(16)-C(12)	111.70(13)			
F(10)-C(16)-C(12)	111.67(13)			
C(7)-F(1)-P(1)	82.33(8)			
C(15)-F(8)-P(1)	89.01(9)			

Table 2.4 - Bond lengths [Å] and angles [°] for Ar'Ar''PCl

	U11	U22	U33	U23	U13	U12
P(1)	20(1)	19(1)	18(1)	4(1)	2(1)	4(1)
CI(1)	22(1)	32(1)	23(1)	5(1)	-5(1)	5(1)
C(1)	17(1)	20(1)	19(1)	4(1)	0(1)	4(1)
C(2)	-26(1)	21(1)	26(1)	3(1)	-1(1)	4(1)
C(3)	44(1)	25(1)	32(1)	-3(1)	4(1)	7(1)
C(4)	55(1)	39(1)	24(1)	-3(1)	9(1)	9(1)
C(5)	41(1)	39(1)	20(1)	7(1)	6(1)	5(1)
C(6)	21(1)	24(1)	20(1)-	5(1)	0(1)	3(1)
C(7)	50(1)	20(1)	37(1)	7(1)	4(1)	9(1)
C(8)	25(1)	27(1)	25(1)	11(1)	2(1)	- 4(1)
C(9)	18(1)	20(1)	17(1)	3(1)	2(1)	3(1)
C(10)	18(1)	21(1)	19(1)	2(1)	2(1)	2(1)
C(11)	19(1)	26(1)	22(1)	6(1)	3(1)	5(1)
G(12)	24(1)	22(1)	22(1)	6(1)	6(1)	7(1)
C(13)	27(1)	20(1)	24(1)	2(1)	3(1)	3(1)
C(14)	21(1)	22(1)	22(1)	1(1)	-1(1)	2(1)
C(15)	19(1)	25(1)	39(1)	-1(1)	-2(1)	2(1)
C(16)	30(1)	25(1)	32(1)	8(1)	6(1)	10(1)
F(1)	63(1)	40(1)	35(1)	15(1)	-4(1)	21(1)
F(2)	54(1)	35(1)	58(1)	20(1)	12(1)	-7(1)
F(3)	105(1)	23(1)	59(1)	11(1)	14(1)	26(1)
F(4)	53(1)	39(1)	40(1)	23(1)	19(1)	6(1)
F(5)	31(1)	34(1)	32(1)	12(1)	-2(1)	12(1)
F(6)	29(1)	23(1)	33(1)	7(1)	-4(1)	-1(1)
F(7)	24(1)	39(1)	61(1)	-9(1)	-16(1)	2(1)
F(8)	24(1)	41(1)	67(1)	-29(1)	-1(1)	3(1)
F(9)	68(1)	32(1)	69(1)	17(1)	-2(1)	-16(1)
F(10)	62(1)	51(1)	42(1)	15(1)	-2(1)	32(1)
F(11)	39(1)	40(1)	68(1)	20(1)	30(1)	19(1)
F(12)	43(1)	23(1)	59(1)	2(1)	4(1)	11(1)

Table 2.5 - Anisotropic displacement parameters (Å² x 10³) for Ar'Ar''PCl. The anisotropic displacement factor exponent takes the form: -2 π² [h² a² U11 + 2 h k a* b* U12]

	x	У	z	U(eq)
H(3)	7525(30)	-494(27)	285(19)	48(6)
H(4)	8075(30)	792/28)	-10E4(20)	50(6)
H(5)	7861(29)	3321(26)	-583(19)	47(6)
H(11)	963(26)	5704(22)	2789 (18)	32(5)
H(13)	4874(24)	8591(22)	4495(16)	29(5)
H(14)	65 (9(25)	6673(21)	4197(10)	27/5

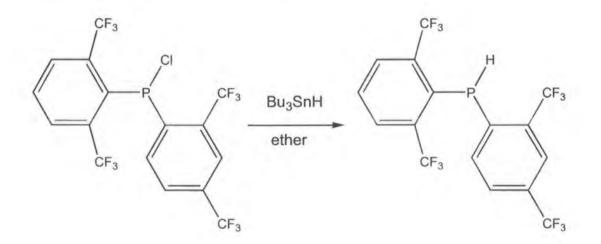
Table 2.6 - Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters (Å² x 10³) for
Ar'Ar''PCI.

2.2.9 Ar'Ar"PH

The synthesis of the disubstituted phosphane was not attempted by Goodwin, and this method is analogous to the synthesis of the mono-substituted phosphane (Ar'PH₂) where P-Cl bonds are replaced by P-H bonds. Bu₃SnH was added dropwise to a solution of Ar'Ar''PCl in ether at room temperature and pressure. The product was recrystallised from hexanes as a white solid.

The proton decoupled ³¹P NMR spectrum of the compound in toluene, appears to be a broad multiplet with chemical shift δ = -45.6ppm (⁴J_{P-F} = 39.4 Hz). Again, the expected coupling pattern for this compound would be a septet of quartets, which would explain why the peaks are broad.

When coupled to the proton, the ³¹P NMR spectrum yields a doublet of multiplets, $\delta = -45.6$ ppm (¹J_{PH} = 232.9 Hz).



Equation 2.11 - Synthesis of Ar'Ar''PH

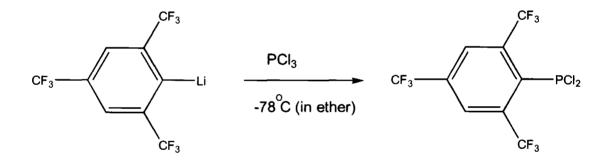
2.2.10 ArPCI₂

The use of Fluoromes as the aryl ligand instead of the Fluoroxyl species has many advantages in product synthesis and yields, due to the existence of only site for lithiation in the molecule. The work on P(I) compounds described in Chapter 5 was all performed using ArPCl₂ as the principal starting material for reasons described therein.

The preparation of $ArPCl_2$ is identical to that of $Ar'PCl_2$ except for the different aryl starting material. There is only one possible lithiation product for Fluoromes which makes the synthesis more efficient and faster.

The ³¹P NMR spectrum of this compound in dichloromethane yielded a septet with a chemical shift, $\delta = 144.5$ ppm (⁴J_{P-F} = 61.5ppm). The ¹⁹F spectrum shows a doublet and a singlet, $\delta = -53.3$ ppm (⁴J_{P-F} = 61.4Hz) and $\delta = -64.5$ ppm.

This NMR data confirms almost exactly the data given by Goodwin in her thesis $({}^{4}J_{P-F} = 61.4 \text{ Hz}).$



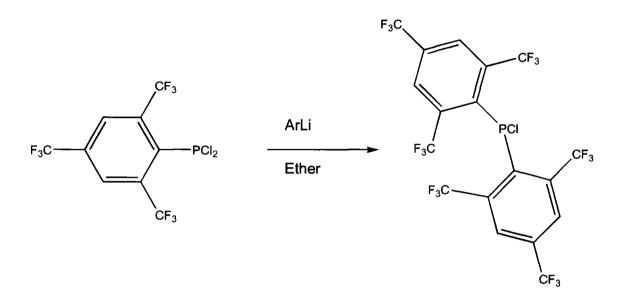
Equation 2.12 – Synthesis of ArPCl₂

2.2.11 Ar₂PCI

During the synthesis of $ArPCl_2$ there was very little formation of the disubstituted product. Even when an excess of the lithiated Fluoromes was added there was very little reaction other than mono-substitution. The most effective synthetic method was the addition of a solution of ArLi at room temperature very slowly to a solution of $ArPCl_2$ in ether. The product was isolated and purified by re-crystallisation from hexanes. Attempts were made to grow crystals suitable for structural X-ray crystallographic analysis, but even after numerous attempts, the crystals grown were unsuitable.

The ³¹P NMR solution spectrum of this compound yielded a multiplet of thirteen lines, with a chemical shift, $\delta = 75.5$ ppm (⁴J_{P-F} = 41.2Hz). The ¹⁹F NMR spectrum showed a doublet and a singlet with chemical shifts $\delta = -55.6$ ppm (doublet), ⁴J_{P-F} = 41.2Hz, and $\delta = -65.2$ ppm (singlet).

These values again relate closely to the results given by Goodwin (³¹P: $\delta = 73.3$ ppm, ⁴J_{P-F} = 42.0 Hz).



Equation 2.13 – Synthesis of Ar₂PCl

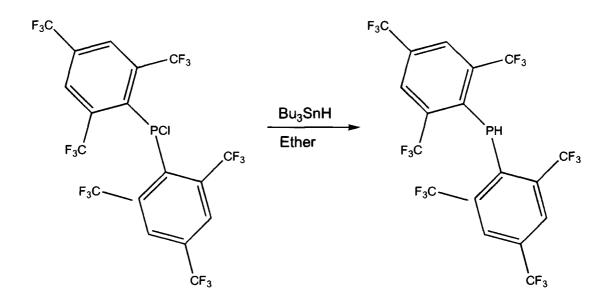
2.2.12 Ar₂PH

This compound is synthesised in the same manner as the analogous compound Ar'Ar''PH. Bu₃SnH is added dropwise to a solution of Ar₂PCl in ether at room temperature and the solution is allowed to stir for 30 minutes. The solvent is removed in *vacuo* and the white crystalline product is isolated by recrystallisation from hexanes.

The ³¹P NMR solution spectrum shows a doublet of multiplets when the experiment is run proton coupled; this gives the chemical shift of the species $\delta = -65.7$ ppm (¹J_{PH} = 249.5Hz) (⁴J_{P-F} = 21.21 Hz). The ¹⁹F NMR solution spectrum shows a distinct F-H coupling, albeit very small. The spectrum shows a doublet of doublets and a singlet, $\delta = -60.8$ ppm (⁵J_{FH} = 7.14 Hz) (⁴J_{P-F} = 21.21 Hz) and $\delta = -64.7$ ppm.

The synthesis of this phosphane was very important because the P(I) species formed when it is deprotonated is much more stable than the equivalent species synthesised with Fluoroxyl.

Crystals of Ar₂PH were grown by vacuum sublimation and were submitted for X-ray characterisation.



Equation 2.14 – Synthesis of Ar₂PH

2.2.12.1 X-ray structure of Ar₂PH

Crystals submitted for X-ray characterisation were mounted on a glass fibre, introduced onto the diffractometer and diffraction data collected. The structure was subsequently solved. The molecular structure of one of the three molecules in the asymmetric unit is shown in Figure 2.13

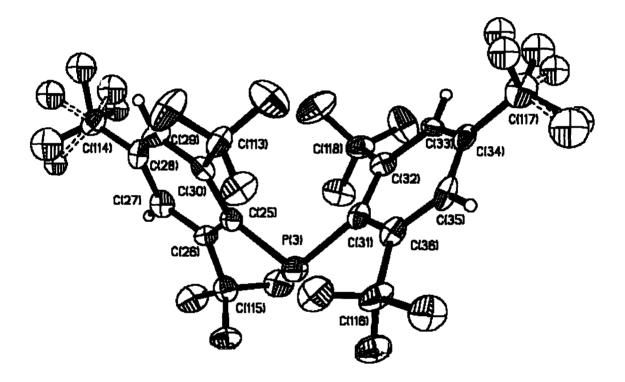


Figure 2.13 – Thermal Ellipsoid diagram at 150K (50% probability) showing one of the three molecules of Ar_2PH in the asymmetric unit.

Unfortunately the structure solution for this compound shows that there are three molecules within the asymmetric unit. With this, there are a number of disordered CF₃ groups on the specific Ar₂PH groups. This leads to problems refining the structure accurately and describing the CF₃ groups accurately. The final R value for the structure using data greater than $2\sigma = 7.15$.

Data were collected on a Siemens 3-circle diffractometer with a CCD area detector, ω scan mode $2\theta \le 60.2^{\circ}$. The structure was solved by direct methods and refined by full-matrix least squares against F^2 . Lists of crystal data and refinement parameters, anisotropic displacement parameters, bond lengths and angles, and atomic coordinates are given in Table 2.7 through Table 2.10.

The initial structure solution yielded three independent molecules in the asymmetric unit and refined all the non-Hydrogen atoms. Upon refinement the best solution attainable was all non-H atoms refined with anisotropic displacement parameters.

All the bond lengths quoted have reasonable estimated standard deviation values, although the numbers quoted in the discussion will be concerned with only one of the three molecules listed in the tables below.

The CF₃ groups are disordered, and although there is a significant amount of residual electron density the best model for the groups in this solution is anisotropic. The presence of dynamic disorder of the CF₃ groups was apparent due to the elongated shape of the thermal ellipsoids. The majority of residual electron density in the compound is associated with the disordered CF₃ groups.

What is interesting to note is that there are three molecules in the asymmetric unit. Although this is rare, it is not unprecedented. There is a question over whether or not the solution is in the correct space group, but searches for higher symmetry did not yield better results. Two of the molecules are of a greater proximity to each other than the third. The distances between the molecules, however, are of the order of 3.0Å and are outside the van der Waals radii for two fluorine atoms (2.85 Å⁴). This closeness would imply that there could have been an interaction between the CF₃ groups on different molecules which is unlikely and adds some weight to the possibility that the space group in this solution may not be correct.

The angle between the planes of the two aryl rings is 67.7° , which is far from ideal. The bulky CF₃ groups on each aryl ring interact with each other due to their close proximity. The conformation of lowest energy, sterically, would be where the two rings are orthogonal to each other.

Crystal data a	nd structure refinement
Identification code	Ar ₂ PH
Empirical formula	Cite Ha Fite P
Formula weight	592.17
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	$a = 16.583(3) \text{ Å} \alpha = 90^{\circ}$.
	b = 23.236(5) Å β = 112.39(3) °.
	c = 17.869(4) Å χ = 90 °.
Volume	5982(2) Å ³
Z sala sala de a nema	12
Number of reflections used	Calculation of cell = 512
	Total = 26813
	Unique = 8348
	Obs [I>2σ(I)] = 3882
Crystal description	needle
Crystal colour	colourless
Density (calculated)	1.973 g/cm ³
Absorption coefficient	3.10 cm ⁻¹
F(000)	3456
Crystal size	0.3 x 0.2 x 0.2 mm
Theta range for data collection	1.48 to 23.02 °.
Index ranges	-17<=h<=12, -25<=k<=25, -19<=l<=19
Experiment device	Siemens SMART
Experiment methods	() SCANS
Reflections collected	26813
Independent reflections	8348 [R(int) = 0.1149]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8339 / 0 / 992
Goodness-of-fit on F2	1.223 D = 0.0745 mD = 0.4400
Final R indices [I>2o(I)]	$R_1 = 0.0715, wR_2 = 0.1493$
R indices (all data)	$R_1 = 0.1768$, $wR_2 = 0.1947$
Largest diff. peak and hole	0.742 and -0.474 e.Å ⁻³

Table 2.7 - Crystal data and structure refinement for Ar_2PH .

an Antonia	and contracts	Strapping and the	an and hand to	
D(4)	X	4044(4)	Z	U(eq)
P(1)	890(2)	1644(1)	1196(1)	33(1)
F(Z)	(2)0000	-14(1)	2/ 15(1)	33(1)
P(3)	6064(2)	-3321(1)	9586(1)	31(1)
0(1)	129(5)	1640(3)	1/33(3)	24(2)
C(2)	350(5)	2335(4)	2239(5)	22(2)
6(3)	-202(5)	2518(4)	2639(5)	28(2)
C(4)	-998(6)	2216(4)	2578(5)	27(2)
C(5)	-1193(6)	1705(4)	2137(5)	20(2)
C(6)	-633(6)	1522(4)	1736(5)	27(2)
C(7)	120(6)	1457(4)	136(5)	25(2)
C(8)	388(6)	984(4)	-220(5)	27(2)
C(9)	-139(6)	811(4)	-1009(5)	32(2)
C(10)	-943(6)	1098(4)	-1479(5)	30(2)
C(11)	-1199(6)	1578(4)	-1147(5)	26(2)
C(12)	-676(6)	1762(4)	-365(5)	29(2)
C(13)	5139(6)	174(4)	1667(5)	25(2)
C(14)	4391(6)	-164(4)	1152(5)	24(2)
C(15)	3834(6)	15(3)	382(5)	22(2)
C(16)	4007(6)	518(4)	59(5)	25(2)
C(17)	4779(6)	836(4)	527(5)	29(2)
C(18)	5331(6)	666(3)	1301(5)	23(2)
C(19)	5219(6)	-220(4)	3290(5)	25(2)
C(20)	5515(6)	-698(3)	3817(5)	22(2)
C(21)	5014(6)		4282(5)	28(2)
C(22)	4225(6)	-608(4)	4250(5)	24(2)
C(23)	3935(6)	-121(4)	3774(5)	21(2)
C(24)	4419(6)	67(3)	3313(5)	27(2)
C(25)	5338(6)	-3109(4)	8535(5)	24(2)
C(26)	5598(5)	-2611(3)	8195(5)	19(2)
C(27)	5108(6)	-2429(4)	7419(5)	28(2)
C(28)	4326(6)	-2723(4)	6931(5)	27(2)
C(29)	4060(6)	-3228(3)	7212(5)	25(2)
C(30)	4571(6)	-3410(3)	7997(5)	22(2)
C(31)	5265(6)	-3524(4)	10102(5)	24(2)
C(32)	4500(6)	-3197(3)	10109(5)	24(2)
C(33)	3963(5)	-3382(4)	10524(5)	= 21(2)
C(34)	4151(6)	-3893(4)	10955(5)	27(2)
C(35)	4939(6)	-4202(4)	11011(5)	27(2)
C(36)	5477(6)	-4027(3)	10600(5)	25(2)
C(101)	-932(7)	943(4)	1296(6)	37(3)
F(11)	-243(3)	655(2)	1216(3)	38(1)
F(12)	-1606(4)	997(2)	580(3)	58(2)
F(13)	-1267(4)	594(2)	1733(4)	60(2)
C(103)	1221(6)	2681(4)	2388(5)	32(2)
F(17)	COMPANY OF A DESCRIPTION OF A DESCRIPTIO	and the second	1758(3)	and the second se
F(17)	1135(3) 1973(3)	3033(2) 2361(2)		49(2)
			2526(3)	34(1)
F(19) C(104)	1424(3)	3022(2)	3034(3)	48(2)
	-1027(7)	2317(4)	-139(6)	35(2)
F(110)	-342(3)	2638(2)	387(3)	40(1)

	- sisteranabemasia	and the other starts	and instruction in the second	Lindersteinen
	X	У	Z	U(eq)
F(111)	-1625(4)	2222(2)	218(4)	56(2)
F(112)	-1449(4)	2649(2)	-769(3)	57(2)
C(105)	-1559(7)	870(5)	-2309(6)	49(3)
F(113)	-1944(8)	1330(5)	-2778(6)	0(3)
F(114)	-2121(9)	513(6)	-2320(7)	- 1(4)
F(1A)	-2301(8)	1204(5)	-2676(7)	6(3)
F(10)	-1900(9)	754(12)	-22/1(7)	((4) C(E)
F(1C)	-1005(17)	754(13)	-2755(14)	6(5)
F(1Z)	-909(15)	619(9)	-2608(14)	38(10)
C(102)	-1609(7)	2446(4)	2970(6)	36(3)
F(14)	-1224(10)	2550(6)	3723(8)	43(5)
F(15)	-2015(7)	1996(5)	3223(6)	35(3)
F(16)	-2232(8)	2787(5)	2545(7)	35(4)
F(1D)	-2359(8)	2116(5)	2848(7)	53(4)
F(1E)	-2013(9)	2983(6)	2630(7)	44(4)
F(1F)	-1074(9)	2723(6)	3694(8)	37(4)
C(106)	1261(6)	649(4)	227(6)	30(2)
F(116)	1237(3)	332(2)	832(3)	45(2)
F(117)	2004(3)	994(2)	525(3)	35(1)
F(118)	1466(3)	289(2)	-272(3)	49(2)
C(107)	6394(7)	-1009(4)	3937(6)	37(3)
F(21)	7123(3)	-669(2)	4113(3)	41(1)
F(22)	6347(3)	-1319(2)	3287(3)	50(2)
F(23)	0024(3)	-1399(2)	4544(3)	53(2)
C(108) F(24)	3670(8) 3461(9)	-867(5)	4706(6) 4533(7)	53(3) 0(3)
F(24A)	3116(9)	-1242(6)	4394(7)	0(3)
F(25)	3056(13)	-481(8)	4764(12)	24(4)
F(25A)	2775(13)	-667(9)	4367(12)	57(6)
F(25B)	3949(18)	-753(12)	5363(17)	77(9)
F(25C)	3408(13)	-385(7)	5077(10)	24(5)
F(26A)	4265(15)	-956(10)	5532(11)	7(5)
F(26B)	4421(15)	-1088(9)	5462(14)	46(10)
C(111)	3403(6)	726(4)	-746(6)	33(2)
F(213)	2910(9)	1180(6)	-713(8)	35(4)
F(214)	3057(9)	309(6)	-1265(8)	44(5)
F(215)	3965(12)	1026(7)	-1105(10)	53(6)
F(2D)	2786(8)	290(5)	-1193(7)	28(4)
F(2E)	2677(9)	1050(5)	-747(7)	31(4)
F(2F)	3789(10)	912(7)	-1205(9)	31(5)
C(109)	4024(7)	616(4)	2826(6)	33(2)
F(27)	3434(4)	512(2)	2075(3)	52(2)
F(28)	4693(3)	961(2)	2769(3) 3180(3)	40(1)
C(112)	3574(4) 6172(6)	929(2) 1044(4)	1721(6)	55(2) 32(2)
F(216)	6953(3)	739(2)	2093(3)	36(1)
F(217)	6071(4)	1381(2)	2289(3)	53(2)
F(218)	6367(3)	1388(2)	1207(3)	49(2)
C(110)	4101(7)	-741(4)	1404(6)	32(2)
		17	17	

-	X	у	z	U(eq)
F(210)	3471(4)	-690(2)	1722(4)	54(2)
F(211)	4834(3)	-1018(2)	1942(3)	40(1)
F(212)	3779(4)	-1095(2)	769(3)	54(2)
C(114)	3798(7)	-2500(4)	6103(6)	35(3)
F(34)	2964(8)	-2771(5)	5759(6)	46(3)
F(34A)	3227(9)	-2102(6)	6032(7)	48(4)
F(35B)	3409(7)	-2931(5)	5566(6)	41(3)
F(35A)	4459(7)	-2304(5)	5753(6)	28(3)
F(35)	4156(10)	-2506(6)	5611(8)	58(4)
F(36)	3532(8)	-1929(5)	6150(6)	30(3)
C(116)	6345(6)	-4389(4)	10728(6)	35(3)
F(310)	7108(3)	-4061(2)	10922(3)	38(1)
F(311)	6280(3)	-4698(2)	10081(3)	44(2)
F(312)	6517(3)	-4751(2)	11351(3)	44(1)
C(118)	4211(6)	-2625(4)	9688(6)	32(2)
F(316)	3590(4)	-2678(2)	8940(3)	54(2)
F(317)	4920(3)	-2325(2)	9628(3)	38(1)
F(318)	3840(4)	-2279(2)	10087(3)	51(2)
C(113)	4208(7)	-3975(4)	8195(6)	35(3)
F(31)	3592(4)	-3892(2)	8551(4)	54(2)
F(32)	4879(3)	-4300(2)	8710(3)	38(1)
F(33)	3784(4)	-4295(2)	7545(3)	53(2)
C(115)	6479(6)	-2278(4)	8671(6)	33(2)
F(37)	6405(3)	-1982(2)	9291(3)	41(1)
F(38)	6676(3)	-1894(2)	8208(3)	42(1)
F(39)	7221(3)	-2618(2)	8987(3)	36(1)
C(117)	3525(7)	-4098(4)	11365(6)	37(3)
F(313)	3977(10)	-4275(6)	12119(9)	36(5)
F(314)	3082(9)	-4568(5)	11011(7)	39(4)
F(315)	2902(9)	-3678(6)	11371(8)	46(4)
F(3D) -	3193(9)	-3683(5)	11655(7)	37(4)
F(3E)	2792(8)	-4408(5)	10875(7)	36(4)
F(3F)	4070(11)	-4428(7)	12034(10)	60(6)

Table 2.8 - Atomic coordinates ($x \ 10^4$) and equivalent isotropic displacement parameters (Å² $x \ 10^3$) for Ar₂PH,. U(eq) is defined as one third of the trace of the *ortho*gonalized Uij tensor.

	Bond lengths [Å] and Angles [°]	
P(1)-C(1)	1.845(9)	C(28)-C(114)	1.485(11)
P(1)-C(7)	1.866(8)	C(29)-C(30)	1.389(11)
P(2)-C(19)	1.846(9)	C(30)-C(113)	1.523(12)
P(3)-C(25)	1.852(8)	C(31)-C(36)	1.429(11)
P(3)-C(31)	1.870(8)	C(32)-C(33)	1.381(11)
C(1)-C(6)	1.400(11)	C(32)-C(118)	1.509(11)
C(1)-C(2) C(2)-C(3)	1.422(10) 1.379(11)	C(33)-C(34)	1.385(11)
C(2)-C(103)	1.512(11)	C(34)-C(35) C(34)-C(117)	1.503(12)
C(3)-C(4)	1.393(11)	C(35)-C(36)	1.370(11)
C(4)-C(5)	1.393(11)	C(36)-C(116)	1.534(12)
C(4)-C(102)	1.481(12)	C(101)-F(12) C(101)-F(11)	1.316(10)
C(6)-C(101)	1.538(12)	C(101)-F(13)	1.361(10)
C(7)-C(8)	1.410(11)	C(103)-F(18)	1.329(10)
C(7)-C(12)	1.413(11)	C(103)-F(19)	1.336(9)
C(8)-C(9)	1.394(11)	C(103)-F(17)	1.355(10)
C(8)-C(106) C(9)-C(10)	1.506(12)	C(104)-F(112) C(104)-F(111)	1.315(10)
C(10)-C(11)	1.391(11)	C(104)-F(110)	1.347(10)
C(10)-C(105)	1.521(12)	C(105)-F(1Y)	1.13(3)
C(11)-C(12) C(12)-C(104)	1.389(11)	C(105)-F(1C)	1.40(3)
C(12)-C(104) C(13)-C(18)	1.404(11)	C(105)-F(114) C(105)-F(113)	1.35(2)
C(13)-C(14)	1.416(11)	C(105)-F(1A)	1.338(14)
C(14)-C(15)	1.382(11)	C(105)-F(1Z)	1.44(3)
C(14)-C(110)	1.536(12)	C(105)-F(1B)	1.37(2)
C(15)-C(16) C(16)-C(17)	1.376(11)	F(113)-F(1A) F(113)-F(1Y)	.711(13) 1.52(3)
C(16)-C(111)	1.468(11)	F(114)-F(1B)	.53(2)
C(17)-C(18)	1.379(11)	F(114)-F(1A)	1.71(2)
C(18)-C(112)	1.518(11)	F(1C)-F(1Z)	.40(4)
C(19)-C(24) C(19)-C(20)	1.429(11) 1.414(11)	F(1C)-F(1Y) F(1Y)-F(1Z)	.45(4) .77(3)
C(20)-C(21)	1.407(11)	C(102)-F(16)	1.259(14)
C(20)-C(107)	1.492(12)	C(102)-F(14)	1.27(2)
C(21)-C(22)	1.368(11)	C(102)-F(1D)	1.345(14)
C(22)-C(23) C(22)-C(108)	1.383(11)	C(102)-F(15) C(102)-F(1F)	1.385(13)
C(23)-C(24)	1.381(11)	C(102)-F(1E)	1.42(2)
C(24)-C(109)	1.536(11)	F(14)-F(15)	1.77(2)
C(25)-C(30)	1.403(11)	F(15)-F(1D)	.735(13)
C(25)-C(26) C(26)-C(27)	1.436(11) 1.371(11)	F(16)-F(1E) F(16)-F(1D)	.55(2) 1.69(2)
C(26)-C(115)	1.523(11)	C(106)-F(116)	1.320(10)
C(27)-C(28)	1.379(11)	C(106)-F(117)	1.341(9)
C(28)-C(29)	1.399(11)	C(106)-F(118)	1.346(9)

	Bond lengths	[Å] and Angles [°]	
C(107)-F(21)	1.320(10)	C(116)-F(310)	1.342(10)
C(107)-F(22)	1.345(10)	C(118)-F(316)	1.323(9)
C(107)-F(23)	1.353(10)	C(118)-F(318)	1.341(10)
C(108)-F(25B)	1.12(2)	C(113)-F(32)	1.333(10)
C(108)-F(24)	1.29(2)	C(113)-F(33)	1.324(10)
C(108)-F(25)	1.35(2)	C(113)-F(31)	1.353(10)
C(108)-F(25A)	1,37(2)	C(115)-F(39)	1.336(9)
C(108)-F(25C)	1.44(2)	C(115)-F(38)	1.331(10)
C(108)-F(26B)	1.50(2)	C(117)-F(3D)	1.293(14)
F(24)-F(24A)	.624(14)	C(117)-F(314)	1.317(14)
F(24A)-F(25A)	1.43(2)	C(117)-F(313)	1.32(2)
F(25)-F(25C)	.65(2)	C(117)-F(3E)	1.353(14)
F(25)-F(25A)	.80(2)	C(117)-F(315)	1.38(2)
F(25A)-F(25C)	1.43(2)	F(314)-F(3E)	.56(2)
F(25B)-F(26A)	.67(3)	F(315)-F(3D)	.54(2)
F(25B)-F(26B)	1.04(3)	C(1)-P(1)-C(7)	107.0(4)
F(25B)-F(25C)	1.17(3)	C(19)-P(2)-C(13)	108.0(4)
C(111)-F(2F)	1.26(2)	C(25)-P(3)-C(31)	107.6(4)
C(111)-F(213)	1.31(2)	C(6)-C(1)-P(1)	125.9(6)
C(111)-F(2E)	1.36(2)	C(2)-C(1)-P(1)	118.9(6)
C(111)-F(2D)	1,42(2)	C(3)-C(2)-C(1)	122.1(8)
C(111)-F(215)	1.45(2)	C(3)-C(2)-C(103)	116.1(8)
C(109)-F(28)	1.349(10)	C(1)-C(2)-C(103)	121.7(8)
C(109)-F(29)	1.325(10)	C(5)-C(4)-C(3)	118.0(8)
C(112)-F(218)	1,337(10)	C(5)-C(4)-C(102)	122.4(8)
C(112)-F(216)	1.344(9)	C(3)-C(4)-C(102)	119.6(8)
C(112)-F(217)	1.337(10)	C(4)-C(5)-C(6)	120.5(8)
C(110)-F(210) C(110)-F(212)	1.313(10) 1.336(10)	C(1)-C(6)-C(5) C(1)-C(6)-C(101)	122.7(8) 123.5(8)
C(110)-F(211)	1.344(9)	C(5)-C(6)-C(101)	113.8(8)
C(114)-F(35)	1.209(14)	C(8)-C(7)-C(12)	116.3(8)
C(114)-F(34A)	1.257(14)	C(8)-C(7)-P(1)	116.9(6)
C(114)-F(34) C(114)-F(35B)	1.362(13)	C(12)-C(7)-P(1) C(9)-C(8)-C(7)	126.6(7)
C(114)-F(36)	1.402(14)	C(9)-C(8)-C(7) C(9)-C(8)-C(106)	121.4(8) 116.9(8)
C(114)-F(35A)	1.466(14)	C(7)-C(8)-C(106)	121.8(8)
F(34)-F(35B)	.958(12)	C(8)-C(9)-C(10)	121.5(9)
F(34)-F(34A)	1.64(2)	C(11)-C(10)-C(9)	117.9(8)
F(34A)-F(36) F(35B)-F(35)	.60(2) 1.51(2)	C(11)-C(10)-C(105) C(9)-C(10)-C(105)	121.2(9) 120.8(9)
F(35A)-F(35)	.64(2)	C(10)-C(11)-C(12)	121.5(8)
C(116)-F(311)	1.331(10)	C(11)-C(12)-C(7)	121.3(8)
C(116)-F(312)	1.338(9)	and the second second	

	Bond lengths	[Å] and Angles [°]	
C(11)-C(12)-C(104)	113.4(8)	C(33)-C(32)-C(31)	121.4(8)
C(7)-C(12)-C(104)	125.2(8)	C(33)-C(32)-C(118)	114.6(8)
C(18)-C(13)-C(14) C(18)-C(13)-P(2)	114.7(7) 118.7(6)	C(31)-C(32)-C(118) C(32)-C(33)-C(34)	124.0(8) 121.5(8)
C(14)-C(13)-P(2)	126.2(7)	C(33)-C(34)-C(35)	118.4(8)
C(15)-C(14)-C(13)	121.9(8)	C(33)-C(34)-C(117)	120.2(8)
C(15)-C(14)-C(110)	114.3(8)	C(35)-C(34)-C(117)	121,3(8)
C(13)-C(14)-C(110) C(16)-C(15)-C(14)	123.7(8) 121.7(8)	C(36)-C(35)-C(34) C(35)-C(36)-C(31)	120.7(8)
C(15)-C(16)-C(17)	117.5(8)	C(35)-C(36)-C(116)	116.2(8)
C(15)-C(16)-C(111)	122.4(8)	C(31)-C(36)-C(116)	121.5(8)
C(17)-C(16)-C(111) C(18)-C(17)-C(16)	120.1(8)	F(12)-C(101)-F(11) F(12)-C(101)-F(13)	109.0(8)
C(17)-C(18)-C(13)	122.5(8)	F(11)-C(101)-F(13)	105.4(8)
C(17)-C(18)-C(112)	115.0(8)	F(12)-C(101)-C(6)	112.8(8)
C(13)-C(18)-C(112)	122.5(8)	F(11)-C(101)-C(6)	113.5(8)
C(24)-C(19)-C(20) C(24)-C(19)-P(2)	114.4(8) 127.9(6)	F(13)-C(101)-C(6) F(18)-C(103)-F(19)	109.5(8) 105.6(7)
C(20)-C(19)-P(2)	117.5(6)	F(18)-C(103)-F(17)	107.1(7)
C(21)-C(20)-C(19)	121.4(8)	F(19)-C(103)-F(17)	106.0(8)
C(21)-C(20)-C(107)	116.9(8)	F(18)-C(103)-C(2)	113.8(8)
C(19)-C(20)-C(107) C(22)-C(21)-C(20)	121.7(8)	F(19)-C(103)-C(2) F(17)-C(103)-C(2)	111.6(8)
C(21)-C(22)-C(23)	119.1(8)	F(112)-C(104)-F(111)	107.1(8)
C(21)-C(22)-C(108)	118.5(8)	F(112)-C(104)-F(110)	106.1(8)
C(23)-C(22)-C(108) C(22)-C(23)-C(24)	122.3(8)	F(111)-C(104)-F(110) F(112)-C(104)-C(12)	105.6(8)
C(23)-C(24)-C(19)	123.4(8)	F(111)-C(104)-C(12)	112.0(8)
C(23)-C(24)-C(109)	114.2(8)	F(110)-C(104)-C(12)	112.8(8)
C(19)-C(24)-C(109)	122.5(8)	F(1Y)-C(105)-F(1C)	16(2)
C(30)-C(25)-C(26) C(30)-C(25)-P(3)	114.5(7) 126.5(7)	F(1Y)-C(105)-F(114) F(1C)-C(105)-F(114)	125(2) 117.2(14)
C(26)-C(25)-P(3)	118.8(6)	F(1Y)-C(105)-F(113)	75(2)
C(27)-C(26)-C(25)	122.6(8)	F(1C)-C(105)-F(113)	91(2)
C(27)-C(26)-C(115)	116.4(8)	F(114)-C(105)-F(113)	112.8(12)
C(25)-C(26)-C(115) C(28)-C(27)-C(26)	120.9(7) 120.3(9)	F(1Y)-C(105)-F(1A) F(1C)-C(105)-F(1A)	101(2)
C(27)-C(28)-C(29)	120.0(8)	F(114)-C(105)-F(1A)	84.5(11)
C(27)-C(28)-C(114)	118.5(8)	F(113)-C(105)-F(1A)	30.7(6)
C(29)-C(28)-C(114)	121.5(8)	F(1Y)-C(105)-F(1Z)	32(2)
C(30)-C(29)-C(28) C(29)-C(30)-C(25)	119.0(8) 123.5(8)	F(1C)-C(105)-F(1Z) F(114)-C(105)-F(1Z)	16.1(14) 108.9(14)
C(29)-C(30)-C(113)	112.2(7)	F(113)-C(105)-F(1Z)	107.5(13)
C(25)-C(30)-C(113)	124.4(8)	F(1A)-C(105)-F(1Z)	130.8(14)
C(32)-C(31)-C(36) C(32)-C(31)-P(3)	115.4(8) 126.1(7)	F(1Y)-C(105)-F(1B) F(1C)-C(105)-F(1B)	113(2) 100.7(14)
C(36)-C(31)-P(3)	118.3(7)	F(114)-C(105)-F(1B)	22.5(8)

	Bond lengths	[Å] and Angles [°]	
F(113)-C(105)-F(1B)	131.6(12)	C(102)-F(14)-F(15)	51.0(7)
F(1A)-C(105)-F(1B)	105.8(11)	F(1D)-F(15)-C(102)	71.4(14)
F(1Z)-C(105)-F(1B)	89.4(12)	F(1D)-F(15)-F(14)	108(2)
F(1Y)-C(105)-C(10)	108 0(11)	C(102)-F(15)-F(14) E(1E) E(16) C(102)	45.4(6)
F(1C)-C(105)-C(10) F(1A)-F(113)-C(105)	108.9(11)	F(1E)-F(16)-C(102) F(1E)-F(16)-F(1D)	96(2)
F(1A)-F(113)-F(1Y)	112(2)	C(102)-F(16)-F(1D)	51.9(7)
C(105)-F(113)-F(1Y)	45.8(13)	F(15)-F(1D)-C(102)	77(2)
F(1B)-F(114)-C(105)	97(3)	F(15)-F(1D)-F(16)	121(2)
F(1B)-F(114)-F(1A)	144(3)	C(102)-F(1D)-F(16) E(16) E(1E) C(102)	4/,4(/)
C(105)-F(114)-F(1A) F(113)-F(1A)-C(105)	51.1(8)	F(16)-F(1E)-C(102) F(116)-C(106)-F(117)	62(2)
F(113)-F(1A)-F(114)	117(2)	F(116)-C(106)-F(118)	106.6(7)
C(105)-F(1A)-F(114)	44.4(7)	F(117)-C(106)-F(118)	104.3(7)
F(114)-F(1B)-C(105)	60(2)	F(116)-C(106)-C(8)	114.9(7)
F(12)-F(1C)-F(1Y) F(12)-F(1C)-C(105)	131(10)	F(117)-C(106)-C(8)	111.7(8)
F(1Z)-F(1C)-C(105) F(1Y)-F(1C)-C(105)	86(6)	F(118)-C(106)-C(8) F(21)-C(107)-F(22)	111.3(7)
F(1C)-F(1Y)-C(105)	119(8)	F(21)-C(107)-F(23)	105.6(7)
F(1C)-F(1Y)-F(1Z)	23(5)	F(22)-C(107)-F(23)	104.2(8)
C(105)-F(1Y)-F(1Z)	96(4)	F(21)-C(107)-C(20)	113.8(8)
F(1C)-F(1Y)-F(113)	1/4(/)	F(22)-C(107)-C(20)	113.0(8)
C(105)-F(1Y)-F(113) F(17)-F(1Y)-F(113)	59(2) 155(5)	F(23)-C(107)-C(20) F(25B)-C(108)-F(24A)	112.9(8)
F(1C)-F(1Z)-F(1Y)	26(6)	F(25B)-C(108)-F(24)	116(2)
F(1C)-F(1Z)-C(105)	78(6)	F(24A)-C(108)-F(24)	28.6(7)
F(1Y)-F(1Z)-C(105)	52(3)	F(25B)-C(108)-F(25)	76(2)
F(16)-C(102)-F(14)	117.7(11)	F(24A)-C(108)-F(25)	96.4(14)
F(16)-C(102)-F(1D) F(14)-C(102)-F(1D)	80.7(10) 108.2(11)	F(24)-C(108)-F(25) F(25B)-C(108)-F(25A)	122.6(14)
F(16)-C(102)-F(15)	109.2(10)	F(24A)-C(108)-F(25A)	67.2(12)
F(14)-C(102)-F(15)	83.6(10)	F(24)-C(108)-F(25A)	95.7(14)
F(1D)-C(102)-F(15)	31.2(6)	F(25)-C(108)-F(25A)	34.3(9)
F(16)-C(102)-F(1F) F(14)-C(102)-F(1F)	108.7(11) 19.8(9)	F(25B)-C(108)-F(25C) F(24A)-C(108)-F(25C)	53(2)
F(1D)-C(102)-F(1F)	126.0(11)	F(24)-C(108)-F(25C)	119.8(13)
F(15)-C(102)-F(1F)	103.3(10)	F(25)-C(108)-F(25C)	26.9(9)
F(16)-C(102)-F(1E)	22.8(7)	F(25A)-C(108)-F(25C)	61.3(11)
F(14)-C(102)-F(1E)	103.8(10)	F(25B)-C(108)-F(26A)	27(2)
F(1D)-C(102)-F(1E)	102.5(10)	F(24A)-C(108)-F(26A)	116.3(13)
F(15)-C(102)-F(1E) F(1F)-C(102)-F(1E)	128.2(10) 90.2(9)	F(24)-C(108)-F(26A) F(25)-C(108)-F(26A)	96.5(13)
F(16)-C(102)-C(4)	115.4(9)	F(25A)-C(108)-F(26A)	131(2)
F(14)-C(102)-C(4)	116.2(10)	F(25C)-C(108)-F(26A)	79.8(14)
F(1D)-C(102)-C(4)	113.0(9)	F(25B)-C(108)-F(26B)	44(2)
F(15)-C(102)-C(4)	109.7(8)	F(24A)-C(108)-F(26B)	110(2)
F(1F)-C(102)-C(4) F(1E)-C(102)-C(4)	109.9(9)	F(24)-C(108)-F(26B) F(25)-C(108)-F(26B)	85.7(13)
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	(in the fact	a feat of 1001 1 (For)	140(4)

	Bond lengths [Å] and Angles [°]	
F(25A)-C(108)-F(26B)	145.6(14)	F(2F)-C(111)-F(2E)	114.4(11)
F(25C)-C(108)-F(26B) F(26A)-C(108)-F(26B)	96.5(13) 17.0(12)	F(213)-C(111)-F(2E) F(214)-C(111)-F(2E)	19.6(8)
F(25B)-C(108)-C(22) F(24A)-C(108)-C(22)	113(2) 119.6(10)	F(2F)-C(111)-F(2D) F(213)-C(111)-F(2D)	105.4(11) 108.4(10)
F(24)-C(108)-C(22)	113.4(9)	F(214)-C(111)-F(2D)	20.1(8)
F(25)-C(108)-C(22) F(25A)-C(108)-C(22)	110.1(11)	F(2E)-C(111)-F(2D) F(2E)-C(111)-F(215)	90.6(9)
F(25C)-C(108)-C(22)	104.9(10)	F(213)-C(111)-F(215)	95.5(11)
F(26A)-C(108)-C(22) F(26B)-C(108)-C(22)	109.5(11) 102.2(12)	F(214)-C(111)-F(215) F(2E)-C(111)-F(215)	101.4(12)
F(24A)-F(24)-C(108)	68(2)	F(2D)-C(111)-F(215)	119.3(11)
F(24)-F(24A)-C(108) F(24)-F(24A)-F(25A)	84(2)	F(2F)-C(111)-C(16) F(213)-C(111)-C(16)	117.5(10)
C(108)-F(24A)-F(25A)	62.1(11)	F(214)-C(111)-C(16)	112.8(10)
F(25C)-F(25)-F(25A)	159(4)	F(2E)-C(111)-C(16)	114.0(9)
F(25C)-F(25)-C(108) F(25A)-F(25)-C(108)	85(3)	F(2D)-C(111)-C(16) F(215)-C(111)-C(16)	111.2(9)
F(25C)-F(25)-F(25B)	46(2)	F(28)-C(109)-F(27)	106.8(7)
F(25A)-F(25)-F(25B) C(108)-F(25)-F(25B)	116(3) 45.2(10)	F(28)-C(109)-F(29) F(27)-C(109)-F(29)	106.0(8)
F(25)-F(25A)-C(108)	71(2)	F(28)-C(109)-C(24)	112.4(7)
F(25)-F(25A)-F(25C) C(108)-F(25A)-F(25C)	9(2)	F(27)-C(109)-C(24)	113.3(8)
F(25)-F(25A)-F(24A)	114(2)	F(218)-C(112)-F(216)	104.7(7)
C(108)-F(25A)-F(24A)	50.7(10)	F(218)-C(112)-F(217)	107.2(8)
F(25C)-F(25A)-F(24A) F(26A)-F(25B)-F(26B)	105.9(14)	F(216)-C(112)-F(217) F(218)-C(112)-C(18)	106.3(7)
F(26A)-F(25B)-C(108) F(26B)-F(25B)-C(108)	103(4) 88(2)	F(216)-C(112)-C(18) F(217)-C(112)-C(18)	112.9(8)
F(26A)-F(25B)-F(25C)	179(4)	F(210)-C(110)-F(212)	108.9(8)
F(26B)-F(25B)-F(25C)	165(3)	F(210)-C(110)-F(211)	107.8(7)
C(108)-F(25B)-F(25C) F(26A)-F(25B)-F(25)	78(2) 158(4)	F(212)-C(110)-F(211) F(210)-C(110)-C(14)	104.8(7)
F(26B)-F(25B)-F(25) C(108)-F(25B)-F(25)	145(3)	F(212)-C(110)-C(14) F(211)-C(110)-C(14)	110.2(7)
F(25C)-F(25B)-F(25)	59(2) 23.5(12)	F(35)-C(114)-F(34A)	116.1(12)
F(25)-F(25C)-F(25B) F(25)-F(25C)-C(108)	111(3) 69(2)	F(35)-C(114)-F(34) F(34A)-C(114)-F(34)	107.0(11) 77.2(9)
F(25B)-F(25C)-C(108)	49.5(14)	F(35)-C(114)-F(35B)	71.6(9)
F(25)-F(25C)-F(25A) F(25B)-F(25C)-F(25A)	12(2)	F(34A)-C(114)-F(35B) F(34)-C(114)-F(35B)	111.3(11) 41.2(6)
C(108)-F(25C)-F(25A)	57.2(10)	F(35)-C(114)-F(36)	106.4(11)
F(25B)-F(26A)-C(108)	50(3)	F(34A)-C(114)-F(36)	25.1(7)
F(25B)-F(26B)-C(108) F(2F)-C(111)-F(213)	48(2) 100.7(11)	F(34)-C(114)-F(36) F(35B)-C(114)-F(36)	102.2(9)
F(2F)-C(111)-F(214)	87.8(11)	F(35)-C(114)-F(35A)	25.6(8)
F(213)-C(111)-F(214)	122.3(11)	F(34A)-C(114)-F(35A)	108.3(10)

	Bond lengths	[Å] and Angles [°]	
F(34)-C(114)-F(35A)	130.9(10)	F(3D)-C(117)-F(313)	87.9(11)
F(35B)-C(114)-F(35A)	97.1(9)	F(314)-C(117)-F(313)	102.1(11)
F(36)-C(114)-F(35A)	90.2(8)	F(3D)-C(117)-F(3E)	106.7(11)
F(35)-C(114)-C(28)	119.2(11)	F(314)-C(117)-F(3E)	24.4(7)
F(34A)-C(114)-C(28)	117.3(10)	F(313)-C(117)-F(3E)	118.9(11)
F(34)-C(114)-C(28) F(35B)-C(114)-C(28)	111.1(9) 112.1(8)	F(3D)-C(117)-F(315) F(314)-C(117)-F(315)	110.4(11)
F(36)-C(114)-C(28)	109.6(8)	F(313)-C(117)-F(315)	108.3(11)
F(35A)-C(114)-C(28)	108.7(8)	F(3E)-C(117)-F(315)	87.6(10)
F(35B)-F(34)-C(114)	69.3(10)	F(3D)-C(117)-F(3F)	105.7(12)
F(35B)-F(34)-F(34A)	110.0(12)	F(314)-C(117)-F(3F)	89.6(10)
C(114)-F(34)-F(34A)	48.5(7)	F(313)-C(117)-F(3F)	17.9(10)
F(36)-F(34A)-C(114)	91(2)	F(3E)-C(117)-F(3F)	110.4(11)
F(36)-F(34A)-F(34) C(114)-F(34A)-F(34)	145(3)	F(315)-C(117)-F(3F)	125.3(12)
F(34)-F(35B)-C(114)	54.3(8) 69.5(10)	F(3D)-C(117)-C(34) F(314)-C(117)-C(34)	113.1(9)
F(34)-F(35B)-F(35)	112.2(13)	F(313)-C(117)-C(34)	113.7(10)
C(114)-F(35B)-F(35)	49.6(7)	F(3E)-C(117)-C(34)	113.5(9)
F(35)-F(35A)-C(114)	54(2)	F(315)-C(117)-C(34)	111.7(9)
F(35A)-F(35)-C(114)	100(2)	F(3F)-C(117)-C(34)	107.2(10)
F(35A)-F(35)-F(35B)	159(2)	F(3E)-F(314)-C(117)	81(2)
C(114)-F(35)-F(35B)	58.9(9)	F(3D)-F(315)-C(117)	69(2)
F(34A)-F(36)-C(114) F(311)-C(116)-F(312)	64(2) 107.9(8)	F(315)-F(3D)-C(117) F(314)-F(3E)-C(117)	88(3)
F(311)-C(116)-F(310)	107.3(8)	F(314)-F(3E)-6(117)	[4]2]-
F(312)-C(116)-F(310)	107.3(7)	STREET, STREET,	CONTRACTOR OF
F(311)-C(116)-C(36)	113.3(7)		
F(312)-C(116)-C(36)	110.7(8)	A REAL PROPERTY AND A REAL PROPERTY AND	That is a second
F(310)-C(116)-C(36)	111.8(8)		
F(316)-C(118)-F(318)	107.2(7)		
F(316)-C(118)-F(317)	106.0(7)		
F(318)-C(118)-F(317) F(316)-C(118)-C(32)	105.4(7) 112.7(7)		
F(318)-C(118)-C(32)	111.7(8)	CONTRACTOR OF THE OWNER	
F(317)-C(118)-C(32)	113.4(7)		
F(32)-C(113)-F(33)	106.6(8)		Barry Inte
F(32)-C(113)-F(31)	105.5(7)		Rest of the second
F(33)-C(113)-F(31)	106.6(8)		
F(32)-C(113)-C(30)	112.7(8)		
F(33)-C(113)-C(30) F(31)-C(113)-C(30)	112.6(7) 112.3(8)		
F(39)-C(115)-F(38)	107.0(7)		A DESCRIPTION OF
F(39)-C(115)-F(37)	106.6(7)		
F(38)-C(115)-F(37)	106.4(7)		- All Lans
F(39)-C(115)-C(26)	112.7(8)		
F(38)-C(115)-C(26)	111.5(7)		Some Train
F(37)-C(115)-C(26)	112.2(7)	south the state of the local division in which the real division in the local division i	and the second

Table 2.9 - Bond lengths [Å] and angles [°] for Ar_2PH .

	U11	U22	U33	U23	U13	U12
P(1)	25(2)	38(2)	33(2)	-13(1)	9(1) 8(1)	-3(1)
P(3)	29(2)	36(2)	28(1)	11(1)	10(1)	0(1)
C(1) C(2)	25(6) 18(5)	11(5) 25(6)	27(5) 23(5)	-5(4) -1(4)	-2(4) 9(4)	-1(4)
C(3)	39(6)	13(5)	23(5)	-5(4)	1(5)	1(4)
C(4)	40(6)	18(6) 13(5)	28(5)	7(4) -3(4)	19(5)	5(4)
C(6)	23(6)	21(6)	32(6)	-8(4)	6(5)	-9(4)
C(7)	34(6)	15(5)	25(5)	-4(4)	10(4)	3(4)
C(8) C(9)	39(6) 38(7)	15(6) 23(6)	30(6) 40(6)	-7(4) -3(5)	15(5) 20(5)	0(4)
C(10)	28(6) 27(6)	34(6) 20(6)	24(5)	2(5)	7(5)	-4(5)
C(12)	28(6)	24(6)	37(6)	-9(5)	16(5)	-6(4)
C(13)	32(6)	17(5)	28(5)	1(4)	12(5)	6(4)
C(14) C(15)	35(6) 25(6)	14(5)	27(6) 26(5)	-1(4) -11(5)	15(5) 12(5)	3(4)
C(16) C(17)	15(5) 35(6)	32(6)	29(6) 47(7)	2(5)	9(4)	7(4)
C(17) C(18)	25(6)	11(6) 12(5)	25(5)	1(4)	22(5)	2(4)
C(19)	29(6)	11(5)	29(5)	1(4)	5(4)	2(4)
C(20) C(21)	22(5) 30(6)	10(5) 16(6)	31(5) 28(5)	2(4)	7(4)	3(4)
C(22)	32(6)	12(5)	29(5)	-3(4)	12(5)	0(4)
C(23) C(24)	25(6) 38(6)	20(6) 10(5)	20(5) 27(5)	0(4) 2(4)	10(4) 6(5)	3(4)
C(25)	25(5)	20(6)	28(5)	-12(4)	10(4)	-1(4)
C(26) C(27)	20(5) 41(6)	8(5) 11(5)	28(5) 35(6)	-2(4) 0(5)	6(4) 16(5)	-3(4)
C(28)	44(6)	15(6)	22(5)	2(4)	13(5)	3(5)
C(29) C(30)	26(6) 26(6)	11(5) 16(5)	31(6) 29(5)	0(4) 2(4)	3(5) 15(5)	-6(4) 1(4)
C(31)	31(6)	19(6)	20(5)	-8(4)	6(4)	-11(4)
C(32) C(33)	25(6)	14(5) 25(6)	29(5)	-3(4)	6(4) 8(4)	-3(4)
C(34)	30(6)	29(6)	17(5)	-4(4)	4(4)	-14(5)
C(35) C(36)	48(7) 35(6)	12(6) 12(5)	16(5) 23(5)	1(4) -3(4)	6(5) 5(5)	-5(5) -1(4)
C(101)	43(7)	29(7)	42(7)	-2(5)	21(6)	-14(5)
F(11) F(12)	44(4) 51(4)	16(3) 35(4)	61(4) 62(4)	-10(3) -23(3)	29(3) -8(3)	-3(2)
F(13)	84(5)	32(4)	89(5)	-21(3)	61(4)	-26(3)
C(103) F(17)	30(6) 46(4)	27(6) 34(4)	28(6) 63(4)	-11(5) 17(3)	-1(5) 15(3)	-11(5) -12(3)
F(18)	25(3)	25(3)	45(3)	-9(3)	6(3)	-5(2)
F(19) C(104)	40(3) 39(7)	38(4) 29(6)	64(4) 34(6)	-31(3) -7(5)	17(3)	-16(3)
F(110)	49(4)	22(3)	40(3)	-10(3)	7(3)	3(3)

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	-						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		U11	U22	U33	U23	U13	U12
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	and the second se			Contraction in the local data and the second se		39(4)	9(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$							25(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				the second s	and the second sec		44(2)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					22(3)		11(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			and the second	and the second se	-0(3)	10[0]	11(3)
F(21)33(3) $36(4)$ $50(4)$ $10(3)$ $12(3)$ $4(3)$ F(22) $51(4)$ $34(4)$ $59(4)$ $-12(3)$ $14(3)$ $14(3)$ F(23) $49(4)$ $38(4)$ $69(4)$ $36(3)$ $19(3)$ $15(3)$ C(108) $55(8)$ $89(11)$ $20(6)$ $9(6)$ $21(6)$ $30(7)$ C(109) $32(6)$ $35(7)$ $35(6)$ $6(5)$ $15(5)$ $6(5)$ F(27) $50(4)$ $38(4)$ $44(4)$ $9(3)$ $8(3)$ $7(3)$ F(28) $47(4)$ $25(3)$ $50(4)$ $10(3)$ $20(3)$ $5(3)$ F(29) $80(4)$ $32(4)$ $80(4)$ $20(3)$ $62(4)$ $28(3)$ C(112) $32(6)$ $21(6)$ $40(6)$ $2(5)$ $11(5)$ $-1(5)$ F(216) $33(3)$ $23(3)$ $48(3)$ $8(3)$ $10(3)$ $2(2)$ F(217) $53(4)$ $33(4)$ $74(4)$ $-28(3)$ $24(3)$ $-11(3)$ F(218) $44(4)$ $35(3)$ $55(4)$ $22(3)$ $5(3)$ $15(3)$ C(110) $42(7)$ $18(6)$ $28(6)$ $4(5)$ $5(5)$ $-1(5)$ F(210) $57(4)$ $36(4)$ $92(5)$ $6(3)$ $52(4)$ $8(3)$ F(211) $44(4)$ $20(3)$ $49(4)$ $8(3)$ $8(3)$ $-3(2)$ F(212) $83(4)$ $24(3)$ $38(3)$ $-7(3)$ $6(3)$ $19(3)$ C(114) $36(7)$ $33(7)$ $30(6)$ $-5(5)$ $7(5)$ $-1(5)$ C(114) <t< td=""><td></td><td></td><td></td><td>39(7)</td><td>1(6)</td><td></td><td>the second se</td></t<>				39(7)	1(6)		the second se
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			and the second se	50(4)	10(3)	and the second	and the second se
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	F(22)	51(4)	34(4)		and the second se		14(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	F(23)	49(4)	38(4)				15(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					9(6)		30(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C(109)	32(6)	35(7)	35(6)	6(5)	15(5)	6(5)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			the second se	and the second	the second s	a set	7(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			25(3)			20(3)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	and the second		the state of the s		A set of the set of th	and the second	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			21(6)	40(6)	2(5)		-1(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	A REAL PROPERTY OF A READ REAL PROPERTY OF A REAL P				8(3)	and the second	-2(2)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					-28(3)	24(3)	-11(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	the second se		a state the second		22(3)	5(3)	10(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	A REAL PROPERTY AND A REAL						-1(3) 9(2)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		and the second	A A A A A A A A A A A A A A A A A A A				-3(2)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		83(4)	24(3)	38(3)	-7(3)		-19(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	And the second se	36(7)	33(7)	30(6)	-5(5)		-1(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					20(5)	-1(5)	1(5)
F(311)50(4)32(4)43(4)-9(3)10(3)14(3)F(312)49(4)28(3)51(4)23(3)16(3)8(3)C(118)26(6)30(6)36(6)8(5)7(5)0(5)			the second s			5(3)	3(3)
C(118) 26(6) 30(6) 36(6) 8(5) 7(5) 0(5)							
C(118) 26(6) 30(6) 36(6) 8(5) 7(5) 0(5)	F(312)	49(4)	28(3)	51(4)	23(3)	16(3)	8(3)
	C(118)					7(5)	0(5)
	F(316)	52(4)	34(4)	50(4)	13(3)	-10(3)	5(3)
F(317) 38(3) 21(3) 57(4) 13(3) 19(3) 3(2)							
F(318) 72(4) 31(4) 67(4) 9(3) 45(3) 21(3)						45(3)	21(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						5(5)	-/(5)
F(31) $62(4)$ $33(4)$ $84(5)$ $6(3)$ $46(4)$ $-10(3)$ $F(32)$ $45(4)$ $45(2)$ $45(2)$ $5(2)$ $5(2)$							-10(3)
F(32)45(4)17(3)42(3)10(3)6(3)-5(3) $F(23)$ 75(4)20(3)27(3)6(3)21(3)			and the second	the second s		the second s	-0(3)
F(33)75(4)30(3)37(3)-6(3)2(3)-31(3)C(115)38(7)27(6)35(6)0(5)16(5)3(5)		38(7)	27(6)			16(5)	-31(5)
F(37) $41(3)$ $28(3)$ $52(4)$ $-12(3)$ $15(3)$ $-10(2)$						and the second se	-10(2)
$\Gamma(37)$ $47(3)$ $20(3)$ $32(4)$ $-12(3)$ $13(3)$ $-13(3)$ $\Gamma(38)$ $45(3)$ $29(3)$ $47(3)$ $13(3)$ $12(3)$ $-13(3)$					13(3)		-13(3)
F(39) 26(3) 31(3) 45(3) 10(3) 7(3) 2(2)							2(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$							

Table 2.10 - Anisotropic displacement parameters (Å² x 10³) for Ar₂PH. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^2 U11 + 2h k a^* b^* U12]$

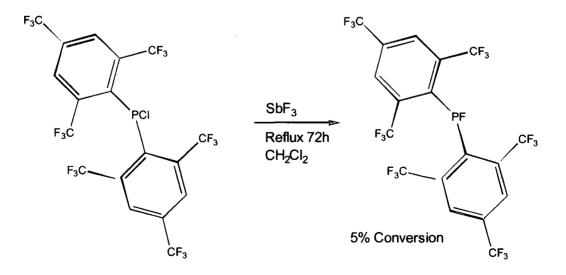
2.2.13 Attempted preparation of Ar₂PF

Synthesis of this compound was attempted because of the potentially useful complex it was expected to form with Pt(II), giving interesting NMR and potential anticancer applications as well (see Section 3.1).

Ar₂PCl was refluxed in CH_2Cl_2 with SbF_3 (analogous to the preparation of Ar'PF₂) for three days. Unfortunately the compound was only formed in very small quantities. This is probably due to the steric hindrance around the P-Cl bond which makes substitution (either S_N1 or S_N2) difficult.

The ¹⁹F NMR spectrum of the solution obtained at the end of the reaction showed a small doublet of doublets, the chemical shift of which is $\delta = -56.3$ ppm (⁴J_{P-F} = 16.3Hz) (⁵J_{P-F} = 6.1 Hz). This pattern is what would be expected for the six fluorine atoms of the *ortho* CF₃ groups, the larger coupling constant being ⁴J_{P-F} and the smaller one being ⁵J_{F-F}. The coupling pattern which would be expected for the fluorine atoms attached to the phosphorus would be a doublet of septets, and unfortunately due to the very small amount of the product synthesised, these peaks were not distinguishable from the background. There are a number of particularly small peaks, any one of which could be assigned to the *para* CF₃ group fluorines.

There is enough evidence to speculate that the compound was formed in small quantities, although not enough to characterise it fully.



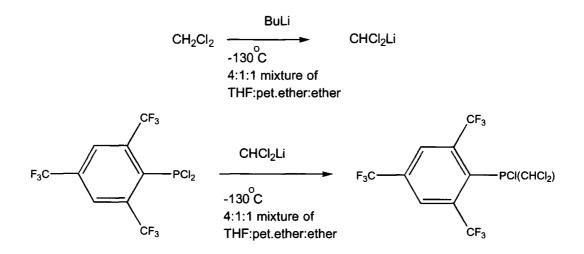
Equation 2.15- Synthesis of Ar₂PF

2.2.14 ArP(CI)CHCI₂

In the analogous reaction to the preparation of $Ar'P(Cl)CHCl_2$, lithiated dichloromethane was added to a solution of $ArPCl_2$ at $-130^{\circ}C$ in a mixed solvent, with vigorous stirring. Upon warming, the solution went a deep red colour. The solvent was removed in *vacuo* and the remaining colourless oil was purified by distillation.

The ³¹P NMR spectrum of a solution of the compound in dichloromethane showed the formation of a new septet with chemical shift $\delta = 62.0$ ppm (⁴J_{P-F} = 50.6 Hz). The ¹⁹F NMR spectrum showed a doublet and a singlet, $\delta = -54.7$ ppm (⁴J_{P-F} = 49.8 Hz) and $\delta = -64.8$ Hz.

These results as with those of the starting material ArPCl₂ agree with those reported by Goodwin [³¹P (CDCl₃) δ : 63.6ppm, ⁴J_{P-F} = 49.8 Hz]



Equation 2.16– Synthesis of ArPCl(CHCl₂)

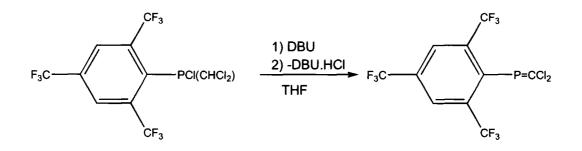
2.2.15 ArP=CCl₂

DBU was added to a solution of $ArP(Cl)CHCl_2$ in THF at $-78^{\circ}C$. A voluminous bright orange precipitate was formed as the solution was allowed to warm to room temperature. The solution was filtered and the solvent removed by distillation at room temperature. The product was purified by distillation, yielding an air stable colourless oil.

The ³¹P NMR spectrum of a solution of the compound in CH₂Cl₂ showed a septet with a chemical shift $\delta = 202.9$ ppm (⁴J_{P-F} = 21.4 Hz). The ¹⁹F NMR spectrum showed a doublet and a singlet, $\delta = -61.0$ ppm (⁴J_{P-F} = 21.4 Hz) and $\delta = -65.2$ ppm. Compared with Goodwin's results these coupling constants differ by less than 0.2 Hz.

It is worthy of note that the coupling constant ${}^{4}J_{P-F}$ in both cases of the phosphaalkenes, Ar'P=CCl₂ and ArP=CCl₂, is significantly smaller than other phosphanes described in this chapter. It should also be noted that the ${}^{19}F$ chemical shifts of the CF₃ groups in these two compounds are at lower frequency as well, thus implying more shielding and electron density on the CF₃ groups.

This change may be due in part to the formation of the P=C π double bond. The withdrawal of electrons from the phosphorus atom by the aryl group is more easily facilitated through the π system. The formation of the P=C double bond decreases the p character of the electrons on the phosphorus (sp³ goes to sp²), and thus enables more electron density to be delocalised into the ring. This in turn increases the electron density on the CF₃ groups, moving them to a lower frequency in the chemical shift range.



Equation 2.17- Synthesis of ArP=CCl₂

2.3 The resistance of Ar'PH₂ and ArPH₂ to reaction

In the formation of RP=CClH (R = Supermes) (see Section 2.1.2) RPH₂ is reacted with KOH and CHCl₃. The crystal structure of the salt RPH[-]K[+] has been published, demonstrating the acidity of the protons bonded to phosphorus in RPH₂.⁵

The Supermes ligand, whilst bulky, effectively donates electron density onto the phosphorus atom, thus making the P-H bonds comparatively stronger and the hydrogens less acidic. They are still, however, acidic enough to react with KOH and are easily lithiated by BuLi (in preference to any other hydrogen in the molecule).

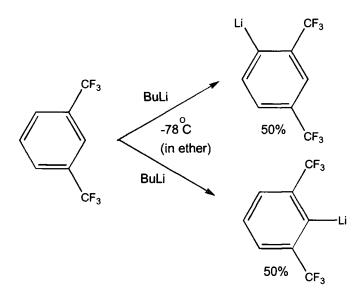
Fluoromes and Fluoroxyl are comparatively more electron withdrawing than Supermes, and this would infer that there would be more electron density withdrawn from the P-H bond, thus making the protons more acidic.

There is no reaction of either $ArPH_2$ or $Ar'PH_2$ with KOH or BuLi, which implies that the protons are much less acidic. The reasons for the apparent lack of reaction could be linked to an interaction, such as H-bonding, between the CF₃ groups and the hydrogens. There may be some close intramolecular contacts in the molecule which prevents cleavage of the P-H bond. The X-ray structure of $ArPH_2$ -PtCl₂(PEt₃) gives some insight into this possible interaction. The distances between the fluorine and hydrogen atoms in this structure (2.50/2.56 Å) are within distances which are accepted as those for H-bonds (see Section 3.2.3.1).

2.4 Experimental

2.4.1 Synthesis of Ar'Li and Ar"Li

BuLi (91.2 mmol, 57ml, 1.6M in hexanes) was added dropwise over 10 minutes to a solution of Ar'H (20.03g, 94 mmol) in ether (200ml) at -78° C. The solution was allowed to warm to room temperature and left to stir for four hours. A dark brown solution (Ar'Li + Ar''Li) was formed. The ¹⁹F NMR spectrum clearly showed the formation of two separate species. The spectrum showed three singlets in the ratio 2:1:1.



2.4.2 Synthesis of Ar'PCl₂/Ar''PCl₂

(Ar'Li, 71mmol) was added dropwise to a solution of PCl₃ (16ml, 25.2g, 162mmol) in ether (100ml) slowly over 10 minutes. The solution was allowed to warm to room temperature and a precipitate of LiCl was slowly formed. The solution was then filtered and the solvent and excess PCl₃ were removed *in vacuo*, leaving a brown intractable oil. The products were distilled from this oil under vacuum. Yield (based on Ar'H) 9.46g (42%); Bp 45°C (0.01 mmHg); ³¹P (CH₂Cl₂) δ = 148.0 ppm (septet), ⁴J_{P-F} = 65.2 Hz; ¹⁹F δ = -53.0 ppm (doublet), ⁴J_{P-F} =65.2 Hz. Ar''PCl₂, ³¹P: δ = 151.1 ppm (⁴J_{P-F} = 84.5 Hz).

Ar'Li
$$\xrightarrow{\text{PCl}_3}$$
 Ar'PCl₂ + LiCl ether, -78°C

2.4.3 Synthesis of Ar'Ar''PCI

In the synthesis described previously for Ar'PCl₂, a large by-product is Ar'Ar''PCl. Using the same synthesis, this product was purified by distillation under vacuum and then by recrystallisation from hexanes. Yield (based on Ar'H) 7.45g (26%); Bp 93°C (0.01mm Hg); ³¹P (CH₂Cl₂) δ = 67.3 ppm (complex multiplet), ⁴J_{P-F} = 67.1 Hz; ¹⁹F (room temperature) δ = -59.3 ppm (doublet), ⁴J_{P-F} =67.1 Hz, δ = -64.1 (singlet) δ = -55.4 (singlet – broad). Analysis found: %C, 38.94; %H, 1.24; Required for C₁₆F₁₂H₆PCl; %C, 41.85; %H, 1.17.

2.4.4 Synthesis of Ar'PH₂

Bu₃SnH (9.0ml, 9.2g, 31.6mmol) was added dropwise to a stirred solution of Ar'PCl₂ (5.0g, 15.8mmol) in ether (150ml) at room temperature, and the solution was allowed to stir for 30 minutes. The solvent was then removed by distillation at room temperature. The product was purified from the resulting oil by distillation under reduced pressure. Yield 2.81g (71.9%), Bp 46°C (10mm Hg); ³¹P{¹H} (CH₂Cl₂) $\delta = -140.3$ ppm (septet), ⁴J_{P-F} = 29.4 Hz; ¹⁹F $\delta = -61.5$ ppm (doublet of triplets); ¹H $\delta = 3.9$ (doublet) ¹J_{PH} = 216.7 Hz.

2Bu₃SnH Ar'PCl₂ → Ar'PH₂ + 2Bu₃SnCl ether

2.4.5 Synthesis of Ar'PF₂

SbF₃ (1.5g, 8.45mmol) was added to a solution of Ar'PCl₂ (2.1g, 6.65mmol) in (CHCl₂)₂ and the resulting mixture was refluxed over three days. The solution was then filtered and the solvent removed by distillation at room temperature. The product was purified by vacuum transfer at room temperature. Yield 1.22g (65%); Bp 63°C (0.03mm Hg); ³¹P (CH₂Cl₂) δ = 193.3 ppm (triplet of septets), ¹J_{P-F} = 1123.8 Hz, ⁴J_{P-F} = 48.3 Hz; ¹⁹F δ = -55.5 ppm (doublet of triplets) ⁴J_{P-F} = 48.4 Hz; δ = -91.85 ppm, (doublet of septets), ¹J_{P-F} = 1123.8 Hz, ⁵J_{F-F} = 14.1 Hz.

2.4.6 Synthesis of Ar'PBr₂ and Ar"PBr₂

BuLi (78.5ml, 2.5M, 196mmol) was added slowly over 10 minutes to a solution of Ar'H (42g, 196mmol) in ether (250ml) at -78°C. The solution was allowed to warm to room temperature and left to stir for four hours. The solution was then cooled to 0°C and added to a solution of PBr₃ (53g, 18ml, 196mmol) in ether (100ml) dropwise over twenty minutes. A precipitate was immediately formed and the solution was allowed to warm to room temperature and stirred for two hours. The solvent was then removed *in vacuo*. The product was isolated from the remaining brown oil by distillation under vacuum as a yellow oil. Yield 18.7g (29.0%) (mixed Ar''PBr₂ and Ar'PBr₂); Bp = 70°C (0.05mm Hg), ³¹P (CH₂Cl₂) δ = 135.8 ppm (septet), (⁴J_{P-F} = 62.8 Hz), δ = 143.9 ppm (quartet) (⁴J_{P-F} = 77.0 Hz); ¹⁹F δ = -50.70 ppm (doublet) ⁴J_{P-F} = 62.7 Hz , δ = -61.9 ppm (singlet), δ = -54.9 ppm, (doublet) ⁴J_{P-F} = 76.9 Hz.

2.4.7 Synthesis of Ar'P(CI)CHCl₂

BuLi (17.1ml, 1.6M in hexanes,27.3mmol) was added dropwise to a solution of CH₂Cl₂ (2.0 ml, 2.66g, 31 mmol) in a 4:1:1 mixture of pentane : THF : diethylether, at -130°C with vigorous stirring. This was allowed to stir for five minutes and was then added rapidly through pre-cooled cannulars to a solution of Ar'PCl₂ (6.64g, 27.3mmol) in ether (100ml) also at -130°C. The solution was then allowed to warm up to room temperature and left to stir for two hours. As the solution warmed up it produced a deep red colour and a precipitate of LiCl was formed. The solution was filtered and the solvent was removed *in vacuo*. The product was purified by distillation from the resulting oil to yield a colourless oil. Yield 5.3g (53.3%) Bp 60°C (0.09mm Hg); ³¹P (CH₂Cl₂) δ = 65.6 ppm (septet), ⁴J_{P-F} = 48.6Hz; ¹⁹F δ = -53.6 ppm (doublet) ⁴J_{P-F} = 48.6 Hz.

2.4.8 Synthesis of Ar'P=CCl₂

DBU (3.57g, 23mmol) was added dropwise to a solution of Ar'P(Cl)CHCl₂ (6.61g, 23mmol) in THF at -78°C. The reaction was very vigorous and a gelatinous precipitate was formed. The solution was allowed to warm to room temperature and left to stir for two hours. This produced a deep orange colour to the solution. The solvent was removed by distillation at room temperature and the product was purified by distillation under reduced pressure. Yield 5.12g (68%) Bp = 57°C (0.2mm Hg); ³¹P (CH₂Cl₂) δ = 206.8 ppm (septet), ⁴J_{P-F} = 21.5 Hz; ¹⁹F δ = -59.9 ppm (doublet) ⁴J_{P-F} = 21.6Hz.

2.4.9 Synthesis of Ar'Ar"PH

Bu₃SnH (2.4ml, 8.4mmol) was added dropwise to a solution of Ar'Ar''PCl (4.01g, 8.13mmol) in ether (100ml) and the solution was allowed to stir for two hours. The solvent was removed *in vacuo* leaving a colourless solution. The product was purified by distillation, producing a clear viscous oil, which solidified on standing. Yield 2.89g (77%) Bp = 48° C (0.01mm Hg); ³¹P (CH₂Cl₂) δ = -45.6 ppm (complex multiplet), ¹J_{PH} = 232.9 Hz, ⁴J_{P-F} = 39.4 Hz.



2.4.10 Synthesis of ArPCI₂

BuLi (31.2ml, 2.5M in hexanes, 78mmol) was added dropwise over five minutes to a solution of ArH (20.0g, 78mmol) in ether (250ml) at -78°C. The reaction was then allowed to warm to room temperature and stirred for four hours; a gelatinous brown solution was formed. This reaction mixture was then added to a solution of PCl₃ (7ml, 80mmol) in ether (100ml) slowly over ten minutes. A precipitate was formed of LiCl and the reaction was left to stir for two hours. The solution was then filtered and the solvent was removed *in vacuo* leaving an intractable brown oil. The product was purified by distillation yielding a colourless oil. Yield 20.8g (71%) Bp 47°C (0.2mm Hg); ³¹P (Et₂O) δ = 144.5 ppm (septet), ⁴J_{P-F} = 61.5 Hz; ¹⁹F δ = -53.3 ppm (doublet), ⁴J_{P-F} = 61.4Hz, δ = -64.5 ppm (singlet)

ArLi
$$\xrightarrow{\text{PCl}_3}$$
 ArPCl₂ + LiCl ether, -78°C

2.4.11 Synthesis of ArP(CI)CHCl₂

BuLi (18.95ml, 2.48M in hexanes, 47.0mmol) was added dropwise to a solution of CH₂Cl₂ (3.5ml, 4.7g, 54mmol) in a 4:1:1 mixture of pentane : THF : diethylether, at -130°C with vigorous stirring. This was allowed to stir for five minutes and was then added rapidly through a pre-cooled cannular to a solution of ArPCl₂ (17.75g, 47 mmol) in ether (100ml) also at -130°C. The solution was then allowed to warm up to room temperature and left to stir for two hours. As the solution warmed up it produced a deep red colouration and a precipitate was formed of LiCl. The solution was filtered and the solvent was removed *in vacuo*. The product was purified by distillation from the resulting oil to yield a colourless oil. Yield 13.1g (69%) Bp 67°C (0.07mm Hg); ³¹P (CH₂Cl₂) $\delta = 62.0$ ppm (septet), ⁴J_{P-F} = 50.6 Hz; ¹⁹F $\delta = -54.7$ ppm (doublet) ⁴J_{P-F} = 50.6 Hz, $\delta = -64.8$ ppm (singlet).

$$\begin{array}{c} \text{BuLi} & \text{ArPCl}_2 \\ \hline \text{CH}_2\text{Cl}_2 & \xrightarrow{-130^\circ\text{C}} & \text{CHCl}_2\text{Li} & \xrightarrow{\text{ArPCl}_2} & \text{ArP(Cl)CHCl}_2 \\ \hline \text{ether, -130^\circ\text{C}} & \text{ether, -130^\circ\text{C}} \end{array}$$

2.4.12 Synthesis of ArP=CCl₂

DBU (4.67g, 30.8mmol) was added dropwise to a solution of ArP(Cl)CHCl₂ (13.0g, 30.8mmols) in THF at -78°C. The reaction was very vigorous and a gelatinous precipitate was formed. The solution was allowed to warm to room temperature and left to stir for two hours. This produced a deep orange colour to the solution. The solvent was removed by distillation at room temperature and the product was purified by distillation under reduced pressure. Yield 5.0g (49%) Bp = 55°C (0.1mm Hg); ³¹P (CH₂Cl₂) δ = 202.6 ppm (septet), ⁴J_{P-F} = 21.4 Hz;¹⁹F δ = -61.2 ppm (doublet), ⁴J_{P-F} = 21.4 Hz, δ = -65.2 ppm (singlet).

2.4.13 Synthesis of Ar₂PCI

BuLi (12.8ml, 2.5M in hexanes, 32mmol) was added dropwise over five minutes to a solution of ArH (10.0g, 34mmol) in ether (250ml) at -78° C. The solution was then allowed to warm to room temperature and stirred for four hours; a gelatinous brown solution was formed. This reaction mixture was then added to a solution of ArPCl₂ (14.6g, 39mmol) in ether (100ml) at room temperature in 5 aliquots of 50ml. The reaction was allowed to stir for twenty minutes after the addition of each aliquot. A precipitate of LiCl was slowly formed. The solution was then filtered and the solvent removed *in vacuo* leaving a brown intractable oil.

The product was purified by distillation to yield a colourless oil, which on standing solidified to give a pale yellow solid. This was then recrystallised from hexanes forming a white crystalline solid. Yield 16.5g (56%) Bp = 95°C (0.05mm Hg); ³¹P (CH₂Cl₂) δ = 75.5 ppm (septet), ⁴J_{P-F} = 41.2Hz; ¹⁹F δ = -55.6 ppm (doublet), ⁴J_{P-F} = 41.2Hz, δ = -65.2 ppm (singlet).

2.4.14 Synthesis of Ar₂PH

Bu₃SnH (2.0ml, 7.0mmol) was added to a solution of Ar₂PCl (4.31g, 6.9mmol) in ether (100ml) at room temperature, and the solution was allowed to stir for two hours. The solution was then removed *in vacuo* leaving a colourless solution. The product was then recrystallised from a solution of hexane and then by sublimation. Yield 3.3g (80%) Bp(sublimes) = 62° C (0.08mm Hg); ³¹P (CH₂Cl₂) δ = -65.7 ppm (doublet of multiplets), ¹J_{P-F} = 251.5 Hz ⁴J_{P-F} = 21.2 Hz; ¹⁹F δ = -60.8 ppm (doublet of doublets), (⁴J_{P-F} = 21.21 Hz) (⁵J_{FH} = 7.14 Hz) and δ = -64.7 ppm (singlet); ¹H δ = 6.22 ppm, ¹J_{PH} = 249.4 Hz. Analysis found: %C, 36.25; %H, 0.81; Required for C₁₈F₁₈H₅P; %C, 36.38; %H, 0.85.

$$\begin{array}{r} & \text{Bu}_3\text{SnH} \\ \text{Ar}_2\text{PCI} & \longrightarrow & \text{Ar}_2\text{PH} + \text{Bu}_3\text{SnCI} \\ & \text{ether, } 297\text{K} \end{array}$$

¹ G. M. Kosolapoff., L. Maier., "Organic phosphorus Compounds", Wiley-Interscience. 1972, 4, 75.
² H. P. Goodwin., Ph.D. Thesis, Durham, 1990.
³ G. R. Desiraju., "Crystal Engineering – The design of organic solids", Material Science Monographs, Elsiever Science Publishers. B. V., 1989
⁴ H. Bonditi., J. Phys. Chem., 1964, 68, 441
⁵ G. W. Pache, G. P. A. Van, A. L. Pheirgeld, Incorport Chamistry, 1997, 10, 1990

⁵G. W. Rabe., G. P. A. Yap., A. L. Rheingold., *Inorganic Chemistry*, 1997, **10**, 1990.

Chapter 3

Synthesis and X-ray characterisation of some platinum-phosphane compounds

3.1 Introduction

When considering characterisation of compounds using NMR, bonding any phosphorus containing species directly to platinum has one immediate advantage. Both Pt(0) and Pt(II) in their normal complexes, are diamagnetic, and thus do not broaden the spectrum due to unpaired electrons (Pt (0) = d^{10} and Pt (II) = d^8). The effect is shown in Pt(II) because the complexes are square planar and not tetrahedral.

The diagram below (see Figure 3.1) shows the change in energy of the d orbitals on the metal, as the axial ligands are removed from an octahedral complex. Any orbital containing "z" character (d_{z2} and d_{xz} , d_{yz}) lowers in energy, and the other orbitals rise in energy accordingly. This effect causes the crystal field splitting pattern of the d-orbitals to change dramatically, thus causing the pairing of the eight d electrons.

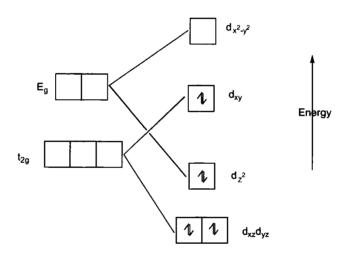


Figure 3.1 – Electron pairing in a square planar complex.

Platinum has an isotope which is NMR active (195 Pt, spin = $^{1}/_{2}$, abundance = 33.7%), thus in a 31 P NMR spectrum there will be two platinum satellites coupled to the phosphorus peak. This makes interpreting the spectrum much easier, as it can be established with certainty which peak is assignable to a phosphorus atom bonded to platinum.

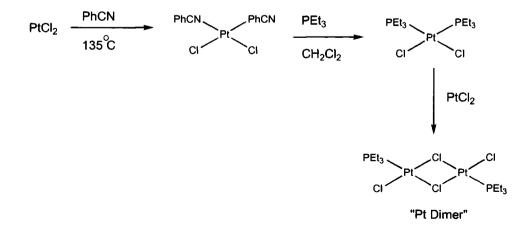
Some of the low coordinate phosphorus species (in which we are interested as a group), when bonded to platinum in the form $PtCl_2(PEt_3)(RP=PR)$ (R=Fluoromes), have shown anti-carcinogenic properties when tested against a range of cancers¹. The anti-carcinogenic properties of platinum(II) complexes have been known for years (e.g. Cis-platin, $PtCl_2(NH_3)_2)^2$. There has, however, been limited success in the replacement of the nitrogen atoms with phosphorus donors. This has been attributed to a strong *trans* effect exerted in dichloro-Pt(II) compounds. Fluorophosphanes in particular may overcome this effect due to their strong σ -donor and strong π -acceptor properties. We have to thank Johnson Matthey for their loan of platinum and palladium salts.

3.1.1 The "Pt dimer"

The platinum(II) dimer, the formation of which is shown below (see Equation 3.1), was used initially in previous work on these systems³ because the diphosphene ArP=PAr did not react with similar Pt(II) compounds, (e.g. $PtCl_2$, $PtCl_2(PhCN)_2$). The dimer is easily prepared⁴ using a three step method shown below.

 $PtCl_2$ was dissolved in a solution of PhCN at 70°C forming a yellow solution. As the solution cooled yellow crystals were formed and then isolated, washed, and dried. The product $[PtCl_2(PhCN)_2]$ was then dissolved in ether and added to a solution of PEt₃ in CH_2Cl_2 . The resulting white product was isolated, washed and dried.

It was then dissolved at high temperature in a solution of $PtCl_2$ in $(CHCl_2)_2$ to form the desired product. On cooling the yellow crystalline precipitate was formed and this was isolated, washed and dried.



Equation 3.1 – Synthesis of [(PtCl₂)PEt₃]₂

3.2 New phosphorus analogues of *cis*-platin

3.2.1 Reaction between the "Pt dimer" and low coordinate phosphorus species

There are two possible isomers formed in this series of reactions, between phosphanes and the dimer, *cis* and *trans*. The actual mechanism for the reaction is likely to be analogous to the normal substitution in a square planar complex². This is by the formation of an initial five coordinate species which then loses one of the original substituents to leave the square planar product.

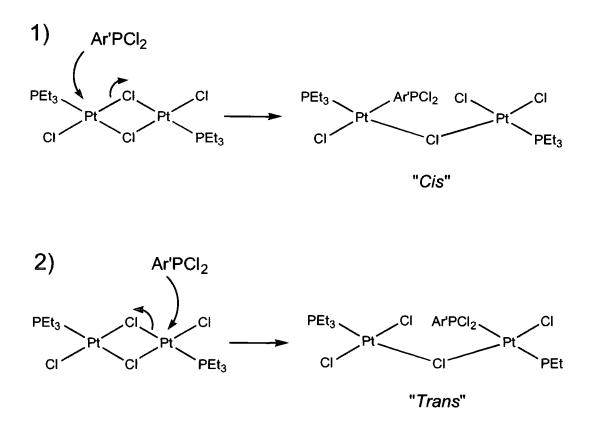


Figure 3.2 - Formation of two possible isomers upon initial reaction between Ar'PCl₂ and the dimer

The initial product upon the reaction of the dimer with the phosphane $\operatorname{Ar'_xPY_z}(X = 1, Y = H, F, Cl, Z = 2)$ (X = 2, Y = Cl, Z = 1) (X = 1, Y = [=CCl_2], Z = 1) is the kinetic product, the *trans*-isomer. This product then rearranges to give the thermodynamically more favourable product, the *cis*-isomer. The time taken for rearrangement varies with phosphane from a few seconds to days, and in the case of Ar'Ar''PCl the *trans*-isomer is stable over a period of weeks. Evidence for the *cis*-isomer is only visible upon prolonged heating.

The trans-influence is defined as "the extent to which that ligand weakens the bond trans to itself in the equilibrium state of the substrate"⁵.

The trans influence exerted by a phosphane is much greater than that of a halide and thus the effect is apparent in these types of systems.

This raises the question as to why the *trans*-isomer is the initial product. The answer comes from studying the Pt dimer. The "*trans* effect" is often seen in reaction of phosphanes with platinum complexes⁵, and this trend affects the reaction of the complex in question and the nature of the isomeric products.

Another factor may be that, as can be seen from the diagrams previously shown, if the phosphane approaches on the opposite side of the molecule to the PEt₃ group, it is sterically more favourable, thus forming the *trans* product first.

Because the initial product is the *trans*-isomer, it can be inferred that the initial platinum-chlorine bond which is cleaved is the bond which is *trans* to the PEt₃ group. This ties in with the "*trans* effect" described above.

The time taken to rearrange from the *trans*-isomer to give the thermodynamically more stable product (*cis* isomer) varies with each phosphane. This means that there must be an overriding energy barrier which must be overcome for rearrangement to occur. This could be due to more than one reason:

- During the rearrangement, the steric bulk of the phosphane may influence the approach of the detached PEt₃ group. The larger the steric bulk of the phosphane, the more likely the PEt₃ group is to coordinate in the *trans* position. (see Figure 3.3).
- 2) The strength of the Pt-P bond may directly influence the formation of the necessary intermediate. The relative strength of the Pt-P bond is related to the length of the Pt-P bond and thus to the size of the coupling constant ${}^{1}J_{P-Pt}$ (see Section 3.4).
- 3) There may well be a balance between factors 1 and 2 above.

The intermediate species formed in these types of re-arrangements have been shown to be three-coordinate species². This is formed by the loss of the weakest ligand on the platinum centre. The Pt-Cl bonds are stronger than the Pt-P bonds and X-ray crystallographic studies on the compounds have shown that the PEt₃ groups bonded to the platinum are more loosely bound than the phosphanes(phosphaalkene). This would imply that the weakest bond in the complex is the Pt-PEt₃ bond. (The average bond length of the PEt₃ groups bonded to platinum is 2.31 Å, and in the case of the other phosphane groups in the compounds studied, the average bond length is 2.18 Å).

Once the PEt₃ bond has cleaved, the PEt₃ group is then free to couple with the intermediate to form either a *cis* or *trans* isomer. The *cis* isomer is the thermodynamically more stable compound as there is no P-Pt-P interaction caused by the *trans* influence. The *cis* compound is therefore less likely to lose a PEt₃ group and form the three-coordinate species. This in turn eventually realises the total rearrangement from the *trans* to the *cis* isomer.

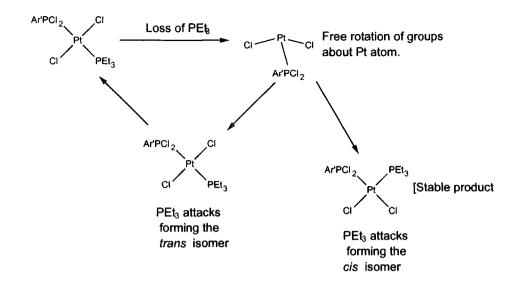


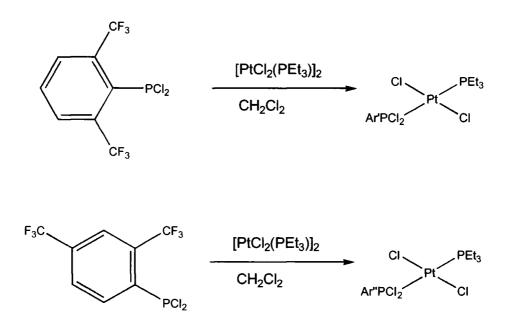
Figure 3.3 – Rearrangement of the initial trans product to give the kinetically more stable cis product

3.2.2 Reaction between [PtCl₂(PEt₃)]₂ and (C₈H₃F₆)PCl₂

During the formation of the starting material (Ar'PCl₂), the formation of the undesired phosphane Ar''PCl₂ is unavoidable (see Section 2.2.1). Purification of these materials proved impossible and thus upon addition of this mixture to the "platinum dimer" a mixture of products is to be expected. Both phosphane groups are similar in nature and will form similar products with the platinum species. This is apparent from the ³¹P and the ¹⁹F NMR spectra of the reaction mixture. Due to the similarities in the two compounds (again isolation of the pure products was impossible), crystals were obtained from the mixture using a layering technique (see Appendix 1) and submitted for X-ray analysis (see Section 3.2.2.1).

Ar'PCl₂ (Ar''PCl₂) was added to a solution of [PtCl₂(PEt₃)]₂ in (CCl₂H)₂ and allowed to stir for a period of a few days. Over this time there was a visible change in the ³¹P NMR spectrum. Initially there were two sets of peaks in the spectrum, the signals corresponding to the dimer itself and the phosphanes. After a number of days, the formation of a number of new peaks at a lower frequency to that of the starting phosphorus halides became apparent. These can be assigned to the new compounds formed between the phosphanes and the platinum complex. The peaks corresponding to the new species formed had distinctive satellites, due to the coupling to active platinum atoms. The reaction between a phosphane and the "Pt dimer" has two possible isomeric products (*cis* and *trans*). The initial isomer formed was the *trans* isomer (${}^{31}P \delta = 142.7$ ppm ${}^{2}J_{P-P} = 678.4$ Hz). There are of course two possible *trans* isomers; however, the greater concentration of the Ar'PCl₂ as compared to Ar''PCl₂ was such that it was assumed that the visible product was that due to the Ar'PCl₂. Unfortunately, the resonances associated with the *trans* isomer was so small they were indistiguishable from the backgroud and it was impossible to determine the coupling constant (${}^{1}J_{P-Pt}$). Values for the chemical shift and coupling constant assignable to the PEt₃ group in the compound were unobtainable due to the large number of peaks and low concentrations.

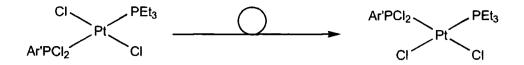
This value concurs with the value for the analogous $ArPCl_2$ compound recorded by H. Goodwin (${}^{2}J_{P-P} = 694 \text{ Hz}$)³.



Equation 3.2 - Synthesis of trans Ar'PCl₂ and Ar''PCl₂ derivatives of the dimer

These resonances were then superseded by the formation of new resonances assignable to the *cis*-isomers. The reaction was complete after 72 hours with only the *cis*-isomers present (${}^{31}P \ \delta = 97.9 \text{ ppm} {}^{1}J_{P-Pt} = 5488.1 \text{ Hz}$, singlet with Pt satellites, $\delta = 19.54$ ppm

 ${}^{1}J_{P-Pt} = 3444.7$ Hz, singlet with Pt satellites) for (Ar'PCl₂) and ($\delta = 94.5$ ppm, ${}^{1}J_{P-Pt} = 5260$ Hz, singlet with Pt satellites, $\delta = 20.14$ ppm ${}^{1}J_{P-Pt} = 2916.1$ Hz, singlet with Pt satellites) for (Ar'PCl₂).



Equation 3.3 - Re-arrangement of trans (Ar'PCl₂)PtCl₂(PEt₃)

This drawing is equally applicable to the rearrangement of the *trans* Ar''PCl₂-Pt compound.

The product was isolated as an impure white powder which was recrystallised using a layering technique (see Appendix 1). The crystals were submitted for X-ray crystallographic studies and the crystal structure partially solved (see Section 3.2.2.1). The crystal structure ascertained from these crystals was not as accurate as one would expect. This may be due to some impurities in the crystal caused by the Ar''PCl₂-Pt compound also formed in this reaction.

3.2.2.1 Molecular structure of $[PtCl_2(PEt_3)(C_8H_3F_6)PCl_2]$

Crystals submitted for X-ray characterisation were mounted on a glass fibre, introduced onto the diffractometer and diffraction data collected. The structure was subsequently solved and refined; the molecular structure is shown below in Figure 3.4.

Data were collected on a Siemens 3-circle diffractometer with a CCD area detector, ω scan mode $2\theta \le 60.2^{\circ}$. The structure was solved by direct methods and refined by full-matrix least squares against F². Lists of crystal data and refinement parameters, anisotropic displacement parameters, bond lengths and angles, and atomic coordinates are given in Table 3.1 through Table 3.5.

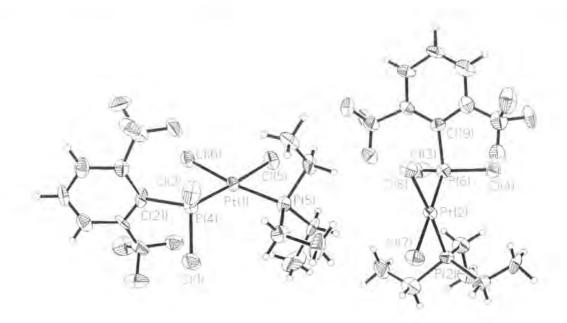


Figure 3.4 - Thermal ellipsoid diagram at 150K (50% Probability) for [PtCl₂(PEt₃)(Ar'PCl₂)]

The ESDs for the bond lengths not including platinum are only accurate to two decimal places. This inaccuracy may be caused by a large quantity of unassigned electron density in the difference map of the crystal structure. Residual unassigned electron density may be caused by a number of factors, including crystal degradation in the beam, twinning of the crystal, impurities in the crystal, or the incorrect space group.

Although the structure has been included, none of the data has been used in comparisons with other structures due to the inaccuracy of the data. Time did not allow for the structure to be further resolved or for data to be collected again.

Crystal data and structure refinement	
Identification code	Ar'PCl ₂
Empirical formula	C14 Hig C14 Fe P2 Pt
Formula weight	699.11
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Moneclinic
Space group	P21/c
Unit cell dimensions	a = 26.8126(1) Å α = 90 °.
Contraction of the second second	$b = 7.7868(1) \text{ Å}$ $\beta = 115.276(1)$ ".
transfer to the test of the second	c = 23.5307(3) Å x = 90 °.
Volume	4442.49(8) Å ³
Z	8
Number of reflections used	Calculation of cell = 512
	Total = 19445
	Unique = 7573
	Obs [I>2o(I)] = 6242
Crystal description	needle
Crystal colour	pale orange
Density (calculated)	2.091 g/cm ³
Absorption coefficient	69.89 cm ⁻¹
F(000)	2656
Crystal size	0.2 x 0.1 x 0.4 mm
Theta range for data collection	0.84 to 25.67 ".
Index ranges	_28<=h<=30, _9<=k<=4, _27<=l<=24
Experiment device	Siemens SMART
Experiment methods	ω scans
Reflections collected	18715
Independent reflections	7573 [R(int) = 0.1236]
Refinement method	Full_matrix least-squares on F ²
Data / restraints / parameters	7463 / 0 / 493
Goodness-of-fit on F ²	1.2/5
Final R indices [I>2o(I)]	$R_1 = 0.1027, wR_2 = 0.2559$
R indices (all data)	$R_1 = 0.1190, wR_2 = 0.3038$
Largest diff. peak and hole	3.584 and -4.282 e.Å-3

Table 3.1 - Crystal data and structure refinement for [PtCl₂(PEt₃)(Ar'PCl₂)]

	X	у	Z	U(eq)
Pt(2)	1554(1)	4272(1)	3995(1)	27(1)
Pt(1)	3423(1)	5150(1)	7449(1)	28(1)
P(3)	972(3)	2283(9)	3975(3)	31(1)
P(2)	3008(3)	6408(10)	6481(3)	
CI(1)	3747(3)	3638(9)	8405(3)	37(2)
CI(5)	1292(3)	5863(9)	4678(3)	37(2)
P(1)	4007(3)	7201(9)	7955(3)	32(2)
CI(6)	2144(3)	6538(9)	4045(4)	43(2)
P(4)	1890(3)	2974(9)	3360(3)	31(2)
CI(8)	395(3)	1537(11)	3113(3)	46(2)
CI(2)	2829(3)	2839(8)	6985(3)	40(2)
CI(4)	3699(3)	9566(9)	7950(3)	48(2)
CI(7)	1264(3)	-86(9)	4289(4)	46(2)
CI(3)	4553(3)	7863(11)	7596(4)	51(2)
C(13)	3262(12)	8508(39)	6361(14)	41(7)
C(27)	1749(12)	4274(37)	2678(13)	40(7)
C(9)	3010(13)	5028(43)	5866(12)	44(7)
C(28)	1144(12)	4667(41)	2285(12)	42(7)
C(14)	2971(15)	9268(41)	5716(13)	56(9)
C(25)	2637(12)	2821(44)	3759(15)	49(8)
C(23)	1649(11)	824(39)	3093(15)	43(7)
C(12)	2214(11)	8075(40)	6763(15)	46(8)
C(26)	2831(13)	1648(60)	4326(16)	71(12)
C(11)	2296(10)	6802(40)	6317(13)	41(7)
C(24)	1935(14)	-28(38)	2710(16)	47(8)
C(10)	3607(17)	4638(54)	5948(18)	71(12)
F(6)	4798(7)	4502(23)	8089(8)	46(4)
F(5)	1657(6)	2223(21)	5329(8)	42(4)
F(4)	1334(6)	39(21)	5617(9)	51(5)
F(3)	5548(8)	5897(25)	8431(9)	67(5)
F(2)	1361(7)	2473(33)	6031(8)	68(6)
C(16)	681(10)	2152(34)	5012(12)	30(6)
C(7)	5206(12)	5159(39)	8620(14)	41(7)
C(1)	4470(11)	6948(32)	8802(11)	31(6)
C(2)	5018(9)	6249(35)	9006(13)	33(6)
C(15)	522(11)	2664(37)	4390(12)	35(6)
C(22)	1291(11)	1779(42)	5510(14)	43(7)
C(20)	-29(11)	3424(40)	4068(13)	43(7)
C(6)	4336(11)	7502(37)	9269(12)	35(6)
C(4)	5285(11)	7347(39)	10054(13)	41(7)
C(5)	4734(12)	7825(37)	9889(13)	42(7)
C(3)	5425(12)	6515(41)	9618(13)	44(7)
F(12)	181(7)	5059(22)	3324(7)	45(4)
F(11)	3350(6)	7341(24)	8669(8)	47(4)
F(10)	3678(6)	9571(24)	9256(9)	52(5)
F(9)	_480(9)	5861(25)	3545(9)	66(6)
F(8)	-578(6)	3639(25)	2972(8)	54(5)
F(7)	3684(7)	7164(28)	9683(9)	59(5)
F(1)	5493(8)	3760(26)	8953(9)	61(5)

	X	у	Z	U(eq)
C(17)	294(11)	2024(35)	5270(15)	38(7)
C(8)	3759(12)	7895(35)	9211(16)	44(8)
C(21)	_194(13)	4465(41)	3488(14)	46(7)
C(18)	-255(11)	2591(42)	4910(15)	43(7)
C(19)	_394(14)	3334(49)	4345(17)	57(9)

Table 3.2 – Atomic coordinates ($x \ 10^4$) and equivalent isotropic displacement parameters (Å² $x \ 10^3$) for[PtCl₂(PEt₃)(Ar'PCl₂)]. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Bond lengths [A] a	and angles [°]
Pt(2)-P(3)	2.186(7)
PH(2)_P(4)	2 282(7)
Pt(2)_Cl(6)	2.339(7)
Pt(2)-CI(5)	2.362(7)
Pt(1)_P(1)	2.198(7)
Pt(1)-P(2)	2.284(7)
Pt(1)_Cl(2)	2.342(6)
P1(1)_CI(1)	2,354(6)
P(3)-C(15)	1.87(3)
P(3)-CI(7)	2.017(10)
P(3)-CI(8)	2.041(10)
P(2)_C(9)	1.80(3)
P(2)-C(11)	1.81(3)
P(2)_C(13)	1.84(3)
P(1)-C(1)	1.85(2)
P(1)-CI(4)	2.016(10)
P(1)-Cl(3)	2.045(10)
P(4)_C(27)	1.80/3
P(4)-C(23)	1.81(3)
P(4) - C(25)	1.01(3)
C(13)-C(14)	1.50(4)
C(13)-C(14)	1.50(4)
C(2) C(10)	1.52(4)
C(9)-C(10)	1.56(5)
C(23)-C(24)	1.56(4)
C(23)-C(24)	1.56(4)
F(6)_C(7)	1.35(4)
F(6) = C(7)	1.36(3)
F(4)_C(22)	1 27(4)
F(4) = O(22)	1.37(4)
F(3)-C(22)	1 29(2)
F(2)-C(22)	1.28(3)
C(16)_C(15)	1.39(4)
C(16)-C(17)	1.41(4)
C(16)_C(22)	1.58(4)
C(7)-F(1)	1.37(4)
C(1) - C(2)	1.48(4)
C(1)_C(6)	1.37(4)
0(1)-0(2)	1.44(3)
C(2)-C(3)	1.40(4)
C(15)-C(20)	1.47(4)
C(20)-C(19)	1.39(4)
C(20)-C(21)	1.48(4)
C(6)-C(5)	1.41(4)
C(6)_C(8)	1.53(4)
C(4)-C(3)	1.39(4)
C(4)-C(5)	1.41(4)
F(12)-C(21)	1.31(4)
F(11)-C(8)	1.35(4)
F(10)-C(8)	1.33(3)

Bond lengths [A] and	angles [°]
F(8)-C(21)	1.37(3)
C(17)-C(18)	1.42(4)
C(18) C(19)	1,35(5)
P(3)-Pt(2)-P(4)	98.6(2)
P(3)-Pt(2) Cl(6)	175.8(3)
P(4)-Pt(2)-CI(6)	85.4(3)
P(3)-PI(2)-CI(5)	88.2(2)
P(4)-Pt(2)-Cl(5)	173.1(2)
CI(6) - P1(2) - CI(5)	00.2(2)
P(1)-Pt(1)-P(2)	99.2(3)
P(2)-Pt(1)-Cl(2)	85.4(3)
P(1) P(1) O(1)	87.8(2)
P(2)-Pt(1)-Cl(1)	172.7(2)
G(2) - Pt(1) - G(1)	87 8(2)
C(15)-P(3)-Cl(7)	100.9(10)
C(15)-P(3)-CI(8)	100.4(9)
CI(7)-P(3)-CI(8)	96.6(4)
C(15)-P(3)-P(2)	119.4(9)
CI(7)-P(3)-Pt(2)	118.6(4)
CI(8)-P(3)-Pt(2)	117.0(4)
C(9)-P(2)-C(11)	107.1(14)
C(9)_P(2)_C(13)	106.2(14)
C(11)-P(2)-C(13)	104.1(14)
G(9)-P(2)-Pt(1)	112.2(10)
C(11)-P(2)-Pt(1)	107.8(10)
C(13)-P(2)-Pt(1)	118.7(10)
C(1)_P(1)_CI(4)	100.9(9)
C(1)-P(1)-Cl(3)	101.6(9)
CI(4)-P(1)-CI(3)	97.5(5)
.C(1)_P(1)_Pt(1)	120.1(8)
CI(4) - P(1) - Pt(1)	117.7(4)
Cl(3)-P(1)-Pt(1)	115.4(4)
C(27)-P(4)-C(23)	107.7(14)
C(27)-P(4)-C(25)	105(2)
C(23)-P(4)-C(25)	105.7(14)
G(27) P(4) P1(2)	110.1(10)
C(23)-P(4)-Pt(2)	117.1(10)
C(25) - P(4) - Pt(2)	110.3(10)
C(14)-C(13)-P(2)	116(2)
C(28)-C(27)-P(4) C(10) C(0) P(2)	115(2)
C(10)-C(9)-P(2)	112(2)
C(26)-C(25)-P(4) C(24)-C(23)-P(4)	114(2)
C(24)-C(23)-P(4) C(12)-C(11)-P(2)	114(2)
C(15)-C(16)-C(17)	121(2)
C(15)-C(16)-C(22)	126(2)
C(17)-C(16)-C(22)	113(2)

Bond lengths [A] and and	gles [°]
F(3)-C(7)-F(6)	105(2)
F(3)-C(7)-F(1)	104(2)
F(6)-C(7)-F(1)	105(2)
F(3)-C(7)-C(2)	115(3)
F(6)-C(7)-C(2)	115(2)
F(1)_C(7)_C(2)	111(2)
C(6)-C(1)-C(2)	-116(2)
C(6)-C(1)-P(1)	123(2)
C(2)-C(1)-P(1)	121(2)
C(3)-C(2)-C(1)	121(3)
C(3)-C(2)-C(7)	113(2)
C(1)-C(2)-C(7)	125(2)
C(16)-C(15)-C(20)	117(2)
C(16)-C(15)-P(3)	122(2)
C(20)-C(15)-P(3)	122(2)
F(5)-C(22)-F(2)	113(3)
F(5)-C(22)-F(4)	108(2)
F(2)-C(22)-F(4)	106(3)
F(5)-C(22)-C(16)	114(3)
F(2)-C(22)-C(16)	109(2)
F(4)-C(22)-C(16)	107(2)
C(19)-C(20)-C(15)	120(3)
C(19)-C(20)-C(21)	118(3)
C(15)-C(20)-C(21)	122(3)
C(1)-C(6)-C(5)	123(3)
C(1)-C(6)-C(8)	127(3)
C(5)-C(6)-C(8)	110(3)
C(3)-C(4)-C(5)	120(2)
C(4)-C(5)-C(6)	119(3)
C(4)-C(3)-C(2)	119(3)
C(16)-C(17)-C(18)	119(3)
F(10)-C(8)-F(7)	105(3)
F(10)-C(8)-F(11)	107(2)
F(7)_C(8)_F(11)	107(2)
F(10)-C(8)-C(6)	112(2)
F(7)-C(8)-C(6)	110(2)
F(11)-C(8)-C(6)	114(2)
F(12)-C(21)-F(9)	106(3)
F(12)-C(21)-F(8)	107(2)
F(9)-C(21)-F(8)	103(2)
F(12)-C(21)-C(20)	120(3)
F(9)-C(21)-C(20)	108(3)
F(8)-C(21)-C(20)	112(3)
C(19)-C(18)-C(17)	120(3)
C(18)-C(19)-C(20)	122(3)

 $\textit{Table 3.3}-Atomic Selected bond lengths [Å] and angles [^o] for [PtCl_2(PEt_3)(Ar'PCl_2)]$

-	U11	U22	U33	U23	U13	U12
Pt(2)	22(1)	27(1)	31(1)	-1(1)	9(1)	-1(1)
Pt(1)	20(1)	27(1)	30(1)	1(1)	5(1)	-1(1)
P(3)	30(3)	28(3)	33(3)	-3(3)	13(3)	-2(3)
P(2)	32(3)	35(4)	28(3)	-1(3)	8(3)	1(3)
CI(1)	26(3)	42(4)	35(3)	6(3)	4(3)	_4(3)
CI(5)	33(3)	34(4)	43(4)	-10(3)	16(3)	-3(3)
P(1)	28(3)	29(4)	32(3)	3(3)	6(3)	-3(3)
CI(6)	38(4)	36(4)	57(4)	-7(3)	22(3)	-12(3)
P(4)	25(3)	34(4)	34(3)	1(3)	13(3)	0(3)
CI(0)	35(3)	59(5)	40(4)	-16(3)	5(2)	-0(3)
CI(2)	35(3)	23(3)	47(4)	-3(3)	5(3)	-7(3)
CI(7)	56(4)	33(4)	63(5)	6(3)	37(4)	7(3)
CI(3)	34(4)	64(5)	48(4)	15(4)	13(3)	_8(4)
C(13)	39(15)	41(17)	46(16)	11(14)	20(13)	12(14)
C(27)	50(17)	32(15)	42(15)	6(13)	25(14)	4(13)
C(9)	53(18)	55(19)	17(12)	0(12)	10(12)	4(15)
C(28)	48(17)	48(18)	22(13)	10(12)	9(12)	11(14)
C(14)	71(23)	36(17)	33(16)	11(14)	-4(15)	-2(16)
C(25)	39(16)	53(20)	59(19)	-21(16)	26(15)	_2(15)
C(23)	28(14)	43(17)	55(18)	_4(14)	15(13)	5(13)
C(12)	23(13)	45(18)	63(19)	14(15)	12(13)	1(13)
C(26)	32(17)	110(34)	56(21)	7(22)	5(15)	21(20)
C(11)	23(13)	47(17)	35(14)	5(13)	4(11)	23(13)
C(24)	54(19)	28(15)	64(20)	-11(14)	28(16)	0(14)
C(10)	90(28)	79(28)	67(23)	-15(21)	55(22)	24(24)
F(6)	44(9)	48(10)	53(10)	-6(8)	27(8)	-11(8)
F(5)	25(8)	41(9)	55(10)	9(8)	13(7)	3(7)
F(4)	27(8)	34(9)	70(12)	21(9)	0(8)	8(7)
F(3)	53(11)	56(12)	80(13)	-2(10)	47(10)	6(12)
F(2) C(16)	40(10) 21(12)	123(19) 31(14)	30(9) 37(14)	-6(11) 1(11)	5(8)	-6(12)
C(7)	33(15)	38(16)	56(18)	-9(14)	22(14)	-9(13)
C(1)	35(14)	23(13)	24(12)	-12(10)	3(11)	-14(11)
C(2)	6(10)		49(16)	2(12)	4(10)	4(10)
C(15)	32(14)	40(16)	36(14)	-5(12)	17(12)	-5(12)
C(22)	23(13)	51(19)	47(17)	_6(15)	8(12)	2(13)
C(20)	32(14)	44(17)	40(15)	-15(13)	4(12)	-21(13)
C(6)	27(13)	37(15)	33(14)	-2(12)		2(12)
C(4)	24(14)	45(17)	33(14)	-3(13)	-8(11)	-5(12)
C(5)	45(17)	34(16)	33(14)	_3(12)	4(13)	-8(13)
C(3)	30(14)	48(18)	41(16)	16(14)	2(12)	-4(14)
F(12)	36(9)		42(9)	6(8)	4(7)	-11(8)
F(11)	14(7)	66(12)	51(10)	-15(9)	2(7)	3(8)
F(10)	25(8)	54(11)	77(13)	-11(10)	21(8)	2(8)
F(9)	75(13)	49(11)	54(11)	5(9)	8(10)	28(11)
F(8)	28(8)	61(12)	43(9)	-11(9)	-13(7)	-9(8)
F(7)	54(11)	84(15)	57(11)	0(10)	42(9)	7(11)
F(1)	50(11)	60(12)	78(13)	16(11)	32(10)	26(10)

	U11	U22	U33	U23	U13	U12
C(17)	27(13)	31(15)	62(18)	1(13)	24(13)	7(12)
C(8)	32(15)	22(14)	80(23)	-5(14)	26(16)	5(12)
C(21)	42(17)	45(18)	45(17)	-8(14)	13(14)	8(15)
C(18)	24(13)	52(19)	60(19)	1(15)	24(13)	0(13)
C(19)	46(18)	66(23)	64(21)	-1(19)	27(17)	-3(17)

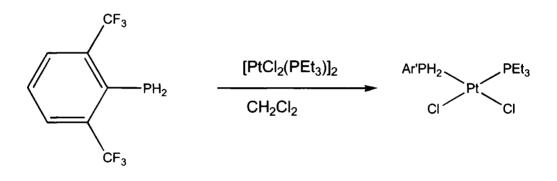
Table 3.4 – Anisotropic displacement parameters (Å² x 10³) for [PtCl₂(PEt₃)(Ar'PCl₂)]. The anisotropic displacement factor exponent takes the form: $-2 \pi^2$ [h² a^{*2} U11 + 2 h k a* b* U12]

	X	у	Z	U(eq)
H(12A)	3234(12)	9328(39)	6667(14)	49
H(12B)	3658(12)	8391(39)	6457(14)	49
H(11A)	1951(12)	5373(37)	2815(13)	47
H(11B)	1896(12)	3681(37)	2409(13)	47
H(10A)	2822(13)	3936(43)	5870(12)	52
H(10B)	2800(13)	5586(43)	5454(12)	52
H(9A)	1103(14)	5340(224)	1915(51)	62
H(9B)	999(24)	5325(226)	2536(33)	62.
H(9C)	938(18)	3589(41)	2148(79)	62
H(8A)	3120(73)	10414(139)	5711(34)	84
H(8B)	2576(21)	9357(295)	5606(49)	84
H(8C)	3026(86)	8531(173)	5411(21)	84
H(7A)	2778(12)	2386(44)	3460(15)	59
H(7B)	2793(12)	3982(44)	3896(15)	.59
H(6A)	1713(11)	97(39)	3463(15)	51
H(6B)	1246(11)	863(39)	2828(15)	51
H(5A)	1824(19)	8097(206)	6683(70)	69
H(5B)	2328(83)	9223(65)	6695(70)	69
H(5C)	2438(69)	7721(157)	7199(15)	69
H(4A)	3235(13)	1651(293)	4536(81)	106
H(4B)	2699(101)	478(96)	4190(22)	106
H(4C)	2684(99)	2055(224)	4618(65)	106
H(3A)	2102(10)	7242(40)	5882(13)	49
H(3B)	2122(10)	5697(40)	6338(13)	49
H(2A)	1819(71)	-1231(87)	2625(90)	71
H(2B)	2336(14)	27(253)	2953(47)	71
H(2C)	1829(73)	585(179)	2312(48)	71
H(1A)	3591(18)	3922(308)	5599(75)	107
H(1B)	3809(42)	4028(325)	6346(68)	107
H(1C)	3796(41)	5718(58)	5952(132)	107
H(15A)	5562(11)	7591(39)	10463(13)	49
H(14A)	4631(12)	8352(37)	10188(13)	50
H(13A)	5792(12)	6134(41)	9733(13)	53
H(28A)	400(11)	1564(35)	5679(15)	46
H(25A)	-525(11)	2448(42)	5068(15)	52
H(24A)	-753(14)	3810(49)	4129(17)	69

Table 3.5 – Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters (Å² $x \ 10^3$) for [PtCl₂(PEt₃)(Ar'PCl₂)]

3.2.3 Reaction between [PtCl₂(PEt₃)]₂ and (C₈H₃F₆)PH₂

Ar'PH₂ was added to a solution of $[PtCl_2(PEt_3)]_2$ in CH₂Cl₂ and allowed to stir. The ³¹P NMR spectrum shows no formation of the *trans* isomer and only the formation of the *cis*-isomer. The proton decoupled ³¹P NMR spectrum of the compound shows a new peak ($\delta = -79.9$ ppm) which is assignable to the *cis* isomer, due to the lack of distinct P-P coupling, which would be expected in the *trans* compound. The value for the P-Pt coupling constant confirms this as being significantly larger than the coupling expected from a *trans* compound. (¹J_{P-Pt} = 3834 Hz). Unfortunately due to an oversight these are the only values recorded for this compound.



Equation 3.4 - Synthesis of cis-[PtCl₂(PEt₃)(Ar'PH₂)]

This reaction is analogous to the previous one; the main difference between the two reactions is that in this case the shift of the signals associated with the Ar'PH₂ phosphorus atom in the complex is at higher frequency than that of the starting material (Ar'PH₂). This implies that there is an overall deshielding of the phosphane which accompanies the bonding to platinum. There will also be some back donation into the LUMO on the phosphorus, although this is not as significant in this case as compared with the Ar'PCl₂ bonded to platinum species. (see Section 3.5). This effect means that comparatively there is less electron density associated with the phosphorus atom after bonding to the platinum, rather than before.

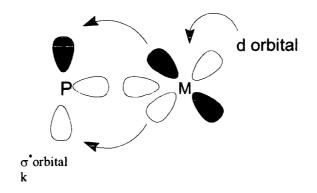


Figure 3.5 – Back donation of electron density from the metal centre to unoccupied π^{\dagger} orbitals on the phosphorus atom

Another explanation for this phenomenon could be that $Ar'PH_2$ is a unique case in itself because of the nature of the two P-H bonds. $Ar'PH_2$ and $ArPH_2$ are non-volatile liquids at room temperature and for mono-substituted phosphanes they are exceptionally stable. The shielding of the phosphane is due to the comparative lack of electron density in the P-H bonds.

The product was isolated as a white powder which was recrystallised using a layering technique (see Appendix 1). The crystals were submitted for X-ray crystallographic studies and the crystal structure solved.

3.2.3.1 The molecular structure of $[PtCl_2(PEt_3)(C_8H_3F_6)PH_2]$

Crystals submitted for X-ray characterisation were mounted on a glass fibre, introduced onto the diffractometer and diffraction Data were collected. The structure was subsequently solved; the molecular structure is shown below in Figure 3.6.

Data were collected on a Siemens 3-circle diffractometer with a CCD area detector, ω scan mode $2\theta \le 60.2^{\circ}$. The structure was solved by direct methods and refined by full-matrix least squares against F². Lists of crystal data and refinement parameters, anisotropic displacement parameters, bond lengths and angles, and atomic coordinates are given in Table 3.6 through Table 3.10.

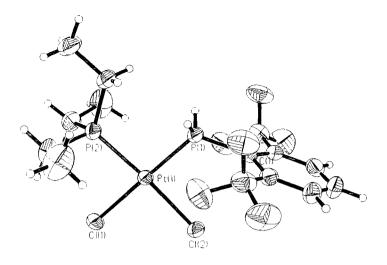


Figure 3.6 - Thermal ellipsoid diagram at 150K (50% Probability) for [PtCl₂(PEt₃)(Ar'PH₂)]

What is interesting to note from the structure is the lengthening of the P(1)-Pt bond and the decrease in coupling constant with respect to the Ar'PCl₂ case. This comparison is discussed in more detail later (see Section 3.4).

The distance between the hydrogen atoms attached to phosphorus(1) and the closest fluorine atoms on the CF₃ groups is within the range of distances that would signify an interaction and probable intramolecular hydrogen bond (H(1A)-(F4) = 2.56 Å, H(1B)-F(3) = 2.50 Å)⁶.

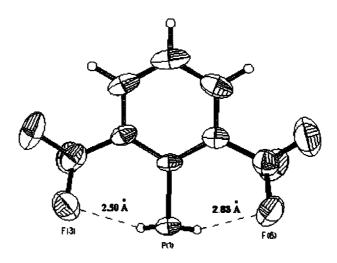


Figure 3.7 – Thermal ellipsoid diagram at 150K (50% Probability) showing the interactions between hydrogen and fluorine atoms in the molecule

These results confirm one of the hypotheses put forward regarding the lack of reaction between $Ar'PH_2$ and bases (see Section 2.3). The interactions between the hydrogens and fluorines will cause them to be less acidic and also potentially more sterically protected from attack by a nucleophile or base.

Crystal data a	nd structural refinment
Identification code	Ar'PH ₂ -Dimer
Empirical formula	CH4 H20 Cl2 F6 P2 Pt
Formula weight	630.23
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 14.069(3) Å a = 90 °.
	b = 12.676(3) Å β = 117.20(3) °.
A second the second	$c = 13.620(3) \text{ Å} \chi = 90^{\circ}$
Volume	2160.4(7) Å ³
Z	4
Number of reflections used	Calculation of cell = 512
	Total = 9226
	Unique = 3595
In Taking a state of the second	Obs [l>2σ(l)] = 3097
Crystal description	needle
Crystal colour	colourless
Density (calculated)	1.938 g/cm ³
Absorption coefficient	69.36 cm-1
F(000)	1200
Crystal size	0.2 x 0.1 x 0.4 mm
Theta range for data collection	1.63 to 25.39 °.
Index ranges	_12<=h<=16, _15<=k<=15, _
	16<= <=15
Experiment device	Siemens SMART
Experiment methods	o scans
Reflections collected	8977
Independent reflections	3595 [R(int) = 0.0417]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3577 / 0 / 229
Goodness-of-fit on F2	1.088
Final R indices [I>2o(I)]	$R_1 = 0.0287, wR_2 = 0.0670$
R indices (all data)	$R_1 = 0.0373, wR_2 = 0.0878$
Largest diff. peak and hole	.679 and _1.368 e.Å_ ³

Table 3.6 – Crystal data and structure refinement for $[PtCl_2(PEt_3)(Ar'PH_2)]$

	x	у	Z	U(eq)
Pt(1)	2220(1)	7077(1)	1688(1)	27(1)
CI(2)	3381(1)	7912(1)	1112(1)	36(1)
P(1)	2973(1)	7963(1)	3263(1)	33(1)
CI(1)	1434(1)	6137(1)	16(1)	37(1)
P(2)	1106(1)	6185(1)	2155(1)	37(1)
F(1)	5438(4)	7224(4)	5340(3)	63(1)
F(2)	6419(4)	7119(4)	4517(4)	78(2)
F(6)	2066(3)	9776(4)	1845(3)	62(1)
C(1)	4071(4)	8855(5)	3474(4)	30(1)
F(4)	2427(4)	10607(4)	3335(4)	69(1)
F(5)	2773(5)	11309(4)	2118(5)	88(2)
C(2)	5139(5)	8495(6)	3957(5)	37(2)
C(4)	5770(6)	10200(8)	3812(6)	61(2)
C(5)	4741(6)	10578(6)	3325(6)	49(2)
F(3)	4775(4)	6655(4)	3683(4)	64(1)
C(14)	456(8)	5844(9)	3827(7)	87(3)
C(11)	-282(5)	6442(6)	1187(6)	47(2)
C(6)	3888(5)	9916(5)	3140(5)	36(2)
C(9)	1279(6)	4767(5)	2110(6)	48(2)
C(8)	2796(6)	10389(6)	2615(6)	49(2)
C(3)	5969(5)	9163(7)	4119(6)	49(2)
C(7)	5432(6)	-7378(7)	4372(5)	48(2)
C(13)	1236(7)	6435(7)	3522(6)	64(2)
C(12)	598(7)	7596(7)	1184(11)	90(3)
C(10)	2381(7)	4379(8)	2889(9)	87(3)

Table 3.7 – Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for [PtCl₂(PEt₃)(Ar'PH₂)]. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

Bond lengths [Å] and	angles [0]
Pt(1)_P(1)	2.215(2)
Pt(1)_P(2)	2.248(2)
Pt(1)-Cl(1)	2.351(2)
Pt(1)-CI(2)	2.361(2)
P(1)-C(1)	1.828(6)
P(2)-C(13)	1.812(7)
P(2)-C(11)	1.818(7)
P(2)-C(9)	1.819(7)
F(1)-C(7)	1.329(8)
F(2)_C(7)	1.350(8)
F(6)-C(8)	1.332(8)
C(1)-C(6) -	1.405(9)
C(1)-C(2)	1.413(9)
F(4)-C(8)	1.331(8)
F(5)-C(8)	1.342(9)
C(2)-C(3)	1.376(9)
C(2)-C(7)	1.510(11)
C(4)_C(3)	1.368(12)
C(4)-C(5)	1.374(11)
C(5)-C(6)	1.389(9)
F(3)-C(7)	1.335(9)
C(14)-C(13)	1.535(10)
C(11)-C(12)	1.528(11)
C(6) C(8)	1.493(10)
C(9)-C(10)	1.506(11)
P(1)-Pt(1)-P(2)	93.87(6)
P(1)-Pt(1)-Cl(1)	179.54(5)
P(2)-Pt(1)-Cl(1)	86.52(6)
P(1)-Pt(1)-Cl(2)	89.85(6)
P(2)-Pt(1)-Cl(2)	175.87(6)
CI(1)-Pt(1)-CI(2)	89.76(6)
C(1)-P(1)-Pt(1)	117.5(2)
C(13)-P(2)-C(11)	106.6(4)
C(13)-P(2)-C(9)	104.8(4)
C(11)-P(2)-C(9)	105.6(3)
C(13)_P(2)_Pt(1)	116.5(2)
C(11)-P(2)-Pt(1)	111.1(3)
C(9)-P(2)-PI(1)	111.5(2)
C(6)-C(1)-C(2)	117.2(6)
C(6)-C(1)-P(1)	121.7(5)
C(2)-C(1)-P(1)	121.1(5)
C(3)-C(2)-C(1)	121.3(7)
C(3)-C(2)-C(7)	116.8(6)
C(1)-C(2)-C(7)	121.8(6)
C(3)-C(4)-C(5)	120.3(7)
C(4)_C(5)_C(6)	120.6(7)
C(12)-C(11)-P(2)	112.9(6)
C(5)-C(6)-C(1)	120,3(6)
C(5)-C(6)-C(8)	117.3(6)

	Bond lengths [Å]	and angles [°]
	C(1) C(6) C(8)	122.4(6)
	C(10)-C(9)-P(2)	114.2(6)
	F(4)-C(8)-F(6)	106.3(6)
	F(4)-C(8)-F(5)	105.3(6)
	F(6)C(8)-F(5)	106.2(6)
1.0	F(4)-C(8)-C(6)	113.2(6)
	F(6)-C(8)-C(6)	113.4(6)
	F(5)_C(8)_C(6)	111.9(6)
	C(4)-C(3)-C(2)	120.2(7)
	F(1)_C(7)_F(3)	106.6(6)
	F(1)-C(7)-F(2)	106.2(6)
	F(3)-C(7)-F(2)	105.7(6)
	F(1)-C(7)-C(2)	112.7(6)
	F(3)-C(7)-C(2)	113.5(5)
	F(2)-C(7)-C(2)	111.7(6)
	C(14)-C(13)-P(2)	116.3(5)

Table 3.8 – Atomic Selected bond lengths [Å] and angles [°] for [PtCl₂(PEt₃)(Ar'PH₂)]

	U11	U22	U33	U23	U13	U12
Pt(1)	26(1)	32(1)	24(1)	-3(1)	12(1)	-4(1)
CI(2)	37(1)	46(1)	31(1)	4(1)	20(1)	9(1)
P(1)	32(1)	44(1)	28(1)	-7(1)	17(1)	-12(1)
CI(1)	39(1)	44(1)	30(1)	-12(1)	16(1)	-7(1)
P(2)	36(1)	43(1)	32(1)	-9(1)	17(1)	-13(1)
F(1)	71(3)	76(3)	36(2)	10(2)	21(2)	15(2)
F(2)	52(3)	98(4)	83(3)	4(3)	29(3)	31(3)
F(6)	47(3)	70(3)	53(2)	-13(2)	9(2)	14(2)
C(1)	30(3)	39(4)	25(3)	-12(3)	16(2)	-13(3)
E(4)	58(3)	93(4)	61(3)	-20(3)	31(2)	17(3)
F(5)	95(4)	62(3)	104(4)	30(3)	44(3)	22(3)
C(2)	29(3)	51(4)	31(3)	-10(3)	13(3)	-7(3)
C(4)	47(5)	83(7)	58(5)	-24(5)	29(4)	-34(4)
C(5)	70(5)	41(4)	49(4)	-15(3)	38(4)	-19(4)
F(3)	74(3)	47(3)	50(3)	-2(2)	12(2)	6(2)
C(14)	104(7)	124(9)	61(5)	-36(5)	62(5)	-68(7)
C(11)	34(4)	54(5)	57(4)	-8(4)	23(3)	-5(3)
C(6)	40(4)	42(4)	34(3)	-9(3)	23(3)	8(3)
C(9)	45(4)	38(4)	58(4)	7(3)	21(3)	-7(3)
C(8)	56(5)	44(4)	48(4)	-8(4)	25(4)	1(4)
C(3)	30(4)	73(6)	39(4)	-13(4)	12(3)	-14(3)
C(7)	40(4)	68(5)	33(4)	-3(3)	13(3)	6(4)
C(13)	76(6)	81(6)	52(4)	-25(4)	45(4)	-45(5)
G(12)	54(5)	.59(6)	165(11)	-13(7)	56(6)	8(5)
C(10)	70(6)	75(7)	104(7)	39(6)	29(6)	18(5)

Table 3.9 – Anisotropic displacement parameters (Å² x 10³) for [PtCl₂(PEt₃)(Ar'PH₂)]. The anisotropic displacement factor exponent takes the form: -2 π² [h² a*² U11 + 2 h k a* b* U12]

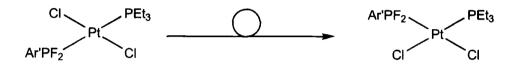


	X	у	Z	U(eq)
H(1A)	2420(1)	8373(1)	3325(1)	40
H(1B)	3236(1)	7455(1)	3862(1)	
H(4)	6335(6)	10651(8)	3934(6)	73
H(5)	4614(6)	11283(6)	3118(6)	59
H(14A)	647(40)	5968(52)	4590(19)	130
H(14B)	492(45)	5102(10)	3707(61)	130
H(14C)	-257(12)	6093(43)	3375(46)	130
H(11A)	-401(5)	6250(6)	450(6)	57.
H(11B)	-738(5)	6001(6)	1374(6)	57
H(9A)	764(6)	4414(5)	2286(6)	57
H(9B)	1122(6)	4569(5)	1363(6)	57
H(3)	6666(5)	8910(7)	4438(6)	59
H(13A)	1959(7)	6253(7)	4058(6)	- 77
H(13B)	1146(7)	7185(7)	3589(6)	77.
H(12A)	-1292(30)	7715(17)	576(40)	135
H(12B)	-84(37)	8043(8)	1110(69)	135
H(12C)	-618(62)	7753(19)	1864(29)	135
H(10A)	2412(19)	3628(11)	2820(44)	130
H(10B)	2537(24)	4554(51)	3633(10)	130
H(10C)	2896(10)	4709(44)	2709(39)	130

Table 3.10 – Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters (Å² $x \ 10^3$) for[PtCl₂(PEt₃)(Ar'PH₂)]

3.2.4 Reaction between $[PtCl_2(PEt_3)]_2$ and $(C_8H_3F_6)PF_2$

Ar'PF₂ was added to a solution of $[PtCl_2(PEt_3)]_2$ in $(CHCl_2)_2$ and the solution was allowed to stir. The ³¹P NMR spectrum of this product is more complex than some of the other products due to the P–F couplings as well as P–Pt. It is interesting to note that in the ¹⁹F NMR spectrum it is possible to observe F–Pt coupling as well as the F–P coupling for the two fluorine atoms bonded to the phosphorus atom.



Equation 3.5 - Rearrangement of trans-[PtCl₂(PEt₃)(Ar'PF₂)]

In this case the *trans* isomer was comparatively stable for a number of hours and was characterised. The ³¹P NMR spectrum of the compound shows the initial formation of the *trans* isomer. The peaks associated with this species form a doublet of triplets, each with its corresponding platinum satellite. The spectrum shows the species to have chemical shift values $\delta = 163.1$ ppm (${}^{1}J_{P-Pt} = 2723$ Hz, ${}^{1}J_{P-F} = 1207.5$ Hz, ${}^{2}J_{P-P} = 692$ Hz doublet of triplets with Pt satellites) and $\delta = 18.75$ ppm (${}^{1}J_{P-Pt} = 1091.0$ Hz, ${}^{2}J_{P-P} = 690.6$ Hz, doublet with Pt satellites).

What is interesting to note from these results is that the coupling constant $({}^{1}J_{P-Pt} = 2723 \text{ Hz})$ is at the upper end of expected values for *trans* complexes (2200-2800 Hz). This high value implies that the distance between the phosphorus atom and the platinum atom is significantly shorter than in other species discussed in this chapter. This result is confirmed by the coupling constant for the *cis* compound and the associated P-Pt bond length ascertained from X-ray crystallographic analysis.

The ³¹P NMR spectrum of the resulting *cis* compound shows a triplet, with each of the peaks having the corresponding Pt satellites, giving the impression of a triplet of triplets. The coupling constant for this compound, as with the *trans* compound, is higher than normally observed for a *cis* compound. The signals associated with the PEt₃ groups shows a singlet with Pt satellites. The compound has chemical shift values $\delta = 135.6$ ppm (¹J_{P-Pt} = 6194.8 Hz, ¹J_{P-F} = 1140 Hz, ²J_{P-P} = 42.6Hz) and $\delta = 20.51$ ppm (¹J_{P-Pt} = 2916.2 Hz, ²J_{P-P} = 42.8 Hz).

The ¹⁹F NMR spectrum shows a number of peaks corresponding to the different fluorine species in the compound, the CF₃ groups on the aryl group producing a singlet ($\delta = -55.8$ ppm). The signal assignable to the fluorine atoms bonded directly to the phosphorus atom gives a number of peaks due to coupling to the phosphorus atom, the platinum atom and a very small coupling to the CF₃ groups. The chemical shift of the fluorine is $\delta = -75.7$ ppm (¹J_{P-F} = 1207.4 Hz) (²J_{F-Pt} = 150.6 Hz) (⁵J_{F-F} = 19.77 Hz).

The product was isolated as a white powder which was recrystallised using a layering technique (see Appendix 1). The crystals were submitted for X-ray crystallographic studies and the crystal structure solved.

3.2.4.1 The molecular structure of $[PtCl_2(PEt_3)(C_8H_3F_6)PF_2]$

Crystals submitted for X-ray characterisation were mounted on a glass fibre, introduced onto the diffractometer, and Data were collected. The structure was subsequently solved and refined; the molecular structure is shown below with a table of significant bond length within the structure.

Data were collected on a Siemens 3-circle diffractometer with a CCD area detector, ω scan mode $2\theta \le 60.2^{\circ}$. The structure was solved by direct methods and refined by full-matrix least squares against F^2 . Lists of crystal data and refinement parameters, anisotropic displacement parameters, bond lengths and angles, and atomic coordinates are given in Table 3.11 through Table 3.15.

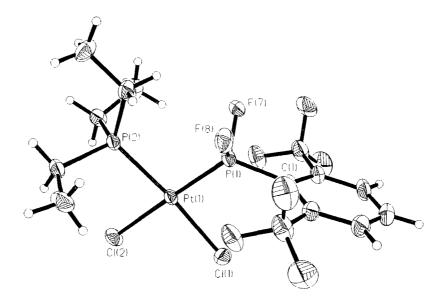


Figure 3.8 – Thermal ellipsoid diagram at 150K (50% probability) for [PtCl₂(PEt₃)(Ar'PF₂)]

	nd structural refinement
Identification code	Ar'PF ₂ -dimer
Empirical formula	Cita Hite Cl2 Fe P2 Pt (CH2Cl2)
Formula weight	751.14
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	P212121
Space group	Orthogonal
Unit cell dimensions	a = 7.3197(3) Å α = 90 °.
	b = 14.2513(5) Å β = 90 °.
A DESCRIPTION OF A DESC	$c = 23.2656(8) \text{ Å} \chi = 90^{\circ}.$
Volume	2427.0(2) Å ³
Z	4
Number of reflections used	Calculation of cell = 512
	Total = 17182
A DATE OF THE PARTY OF THE PARTY	Unique = 6540
	Obs [l>2σ(l)] = 6160
Crystal description	needie
Crystal colour	colourless
Density (calculated)	2,056 g/cm ³
Absorption coefficient	64.16 cm_1
F(000)	1432
Crystal size	0.2 x 0.1 x 0.4 mm
Theta range for data collection	1.68 to 30.31 °.
Index ranges	_10<=h<=9, _11<=k<=19, _28<=l<=33
Experiment device	Siemens SMART
Experiment methods	ω scans
Reflections collected	17125
Independent reflections	6540 [R(int) = 0.0547]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters Goodness-of-fit on F ²	6528 / 0 / 265
	$R_1 = 0.0363$, w $R_2 = 0.0780$
Final R indices [I>2o(I)] R indices (all data)	$R_1 = 0.0363$, $WR_2 = 0.0780$ $R_1 = 0.0419$, $WR_2 = 0.0835$
Absolute structure parameter	-0.007(7)
Largest diff. peak and hole	1.671 and -1.729 e.Å-3
Largest unit, peak and note	1.01 1 dilu -1.120 0.A-0

Table 3.11 – Crystal data and structure refinement for [PtCl₂(PEt₃)(Ar'PF₂)]

	X	у	Z	U(eq)
Pt(1)	-16130(1)	4602(1)	-3975(1)	19(1)
CI(1)	13633(2)	4871(1)	3354(1)	28(1)
P(2)	-18451(2)	4195(1)	_4575(1)	21(1)
P(1)	-17044(2)	-6019(1)-	-3824(1)	23(1)
F(8)	-19020(6)	6149(3)	-3593(2)	35(1)
F(7)	_17270(7)	6638(3)	-4372(2)	33(1)
C(1)	-15766(10)	6818(4)	-3352(3)	25(1)
C(9)	-20363(9)	4993(5)	-4637(3)	26(1)
C(11)	-17585(11)	4028(5)	-5306(3)	28(2)
F(6)	-13754(8)	6482(3)	_4417(2)	40(1)
F(5)	-14575(8)	7922(3)	-4529(2)	45(1)
C(6) -	-16180(13)-	6896(5)	-2768(3)	31(1)
C(7)	-13631(13)	7341(5)	_4186(3)	38(2)
C(2)	-14339(10)	7381(5)	-3571(3)	27(1)
F(4)	-11884(8)	7595(4)	_4215(2)	54(1)
C(13)	-19447(11)	3071(5)	_4370(3)	29(2)
C(10)	-21815(10)	4710(6)	-5076(3)	38(2)
C(5)	-15332(13)	7561(6)	-2428(3)	39(2)
C(4)	-13992(14)	8137(5)	-2646(3)	42(2)
C(3)	-13475(12)	8034(5)	_3218(3)	37(2)
C(12)	-17022(12)	4940(6)	-5602(3)	36(2)
F(3)	-17668(7)	5410(3)	-2672(2)	42(1)
F(2)	-19280(7)	6655(4)	-2489(2)	51(1)
F(1)	_17189(9)	6210(4)	-1904(2)-	57(2)
C(8)	-17610(13)	6300(6)	-2468(4)	40(2)
GI(2)	-14990(3)	3093(1)	_4142(1)	32(1)
C(14)	-19983(12)	3018(6)	-3741(4)	39(2)
C(15)	-12178(25)	4835(12)	-1956(7)	110(5)
CI(3)	-11572(6)	3883(3)	-1473(2)	60
CI(3')	-11241(20)	3956(8)	-1713(7)	60
CI(4)	-12499(6)	5904(3)	-1592(2)	60
CI(4')	_13249(20)	5631(10)	_1719(6)_	60

Table 3.12 – Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for [PtCl₂(PEt₃)(Ar'PF₂)].U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Bond lengths [Å] and	angles [°]
Pt(1)_P(1)	2.157(2)
PI(1)-P(2)	2.275(2)
Pt(1)-Cl(2)	2.339(2)
PI(1)-CI(1)	2.360(2)
P(2)-C(9)	1.809(7)
P(2)-C(13)	1.824(7)
P(2)-C(11)	1.830(7)
P(1)-F(8)	1.554(5)
P(1)-F(7)	1.558(4)
P(1)-C(1)	1.838(6)
C(1)-C(6)	1.396(9)
C(1)-C(2)	1.413(10)
C(9)-C(10)	1.529(9)
C(11)-C(12)	1.528(10)
F(6)-C(7)	1.339(8)
F(5)-C(7)	1.341(9)
C(6)-C(5)	1.382(11)
C(6)-C(8)	1.518(12)
C(7)-F(4)	1.331(10)
C(7)-C(2)	1.523(10)
C(2)-C(3)	1.394(10)
C(13)-C(14)	1.518(11)
C(5)-C(4)	1.376(13)
C(4)-C(3)	1.390(11)
F(3)-C(8)	1.356(9)
F(2)-C(8)	1.324(11)
F(1)_C(8)	1.353(10)
C(15)-CI(4')-	1.49(2)
C(15)-CI(3')	1.54(2)
C(15)-Cl(4)	1,76(2)
C(15)-CI(3)	1.82(2)
P(1)-Pt(1)-P(2)	96,11(6)
P(1)-Pt(1)-Cl(2)	177.13(7)
P(2)-Pt(1)-Cl(2)	86.00(6)
P(1)-Pt(1)-CI(1)	89.35(6)
P(2)-Pt(1)-CI(1)	174.51(6)
CI(2)-Pt(1)-CI(1)	88.57(6)
C(9)-P(2)-C(13)	105.3(3)
C(9)-P(2)-C(11)	106.0(3)
C(13)-P(2)-C(11)	105.5(3)
C(9)-P(2)-Pt(1)	117.8(2)
C(13)-P(2)-Pt(1)	111.2(2)
C(11)-P(2)-Pt(1)	110.2(3)
F(8)-P(1)-F(7)	96.7(3)
F(8)-P(1)-C(1)	101.2(3)
F(7)_P(1)_C(1)	101.1(3)
F(8)-P(1)-Pt(1)	117.1(2)
F(7)-P(1) Pt(1)	115.5(2)
C(1)_P(1)_Pt(1)	121.3(2)
	.=(=/

Bond lengths [Å] and	angles [°]
C(6)-C(1)-C(2)	117.8(6)
C(6)-C(1)-P(1)	121.4(6)
C(2)-C(1)-P(1)	120.8(5)
C(10)-C(9)-P(2)	115.1(5)
C(12)-C(11)-P(2)	113.7(5)
C(5)-C(6)-C(1)	120.9(8)
C(5)-C(6)-C(8)	115.5(7)
C(1)-C(6)-C(8)	123.6(7)
F(4)-G(7)-F(6)	107.0(7)
F(4)_C(7)_F(5)	107.3(6)
F(6)-C(7)-F(5)	106,9(6)
F(4)-C(7)-C(2)	111.3(7)
F(6)_C(7)_C(2)	112.9(6)
F(5)-C(7)-C(2)	111.1(7)
C(3)-C(2)-C(1)	120.2(7)
C(3)-C(2)-C(7)	115.1(6)
C(1)-C(2)-C(7)	124.7(6)
C(14)-C(13)-P(2)	113.5(6)
C(4)-C(5)-C(6)	121.3(7)
C(5)-C(4)-C(3)	118.9(7)
C(4)-C(3)-C(2)	120.7(8)
F(2)-C(8)-F(1)	106.5(7)
F(2)-C(8)-F(3)	108.4(7)
F(1)-C(8)-F(3)	105.0(7)
F(2)-C(8)-C(6)	113.9(7)
F(1)-C(8)-C(6)	110.0(7)
F(3)-C(8)-C(6)	112.5(6)
CI(4')-C(15)-CI(3')	136.0(2)
CI(4)-C(15)-CI(3)	112.4(9)

Table 3.13 – Atomic Selected bond lengths [Å] and angles $[^{o}]$ for $[PtCl_2(PEt_3)(Ar'PF_2)]$

	ALC: NOT THE OWNER OF THE OWNER OWNER OF THE OWNER OWNER OF THE OWNER OWNE OWNER OWNE	1		_		
	U11	U22	U33	U23	U13	U12
Pt(1)	26(1)	14(1)	18(1)	-1(1)	1(1)	1(1)
CI(1)	31(1)	27(1)	27(1)	-2(1)	-3(1)	3(1)
P(2)	29(1)	15(1)	18(1)	-1(1)	0(1)	-2(1)
P(1)	29(1)	16(1)	23(1)	-3(1)	-1(1)	-2(1)
F(8)	31(2)	31(2)	43(2)	-15(2)	2(2)	3(2)
F(7)	53(3)	18(2)	27(2)	2(2)	-12(2)	1(2)
C(1)	39(4)	13(3)	23(3)	-2(2)	-6(3)	-2(3)
C(9)	27(3)	26(3)	26(3)	8(3)	0(3)	-1(3)
C(11)	43(4)	22(3)	19(3)	-3(3)	3(3)	4(3)
F(6)	62(3)	25(2)	33(2)	-3(2)	15(2)	-2(2)
F(5)	74(4)	26(2)	35(2)	15(2)	2(2)	-5(2)
C(6)	42(4)	25(3)	25(3)	-5(2)	-2(3)	3(3)
C(7)	50(5)	24(3)	39(4)	1(3)	5(4)	-5(3)
C(2)	31(4)	20(3)	31(3)	-1(3)	-3(3)	-4(3)
F(4)	51(3)	54(3)	57(3)	2(3)	16(3)	-15(3)
C(13)	40(4)	19(3)	30(3)	3(3)	-2(3)	-7(3)
C(10)	36(4)	46(5)	32(3)	-15(4)	-10(3)	1(4)
C(5)	58(5)	33(4)	25(4)	-7(3)	0(3)	3(4)
C(4)	61(5)	27(3)	37(4)	-7(3)	-9(4)	-6(4)
C(3)	56(5)	19(3)	37(4)	-2(3)	-3(3)	-11(3)
C(12)	46(5)	34(4)	27(3)	-2(3)	4(3)	-9(3)
F(3)	61(3)	25(2)	41(2)	1(2)	18(2)	-4(2)
F(2)	52(3)	49(3)	52(3)	-16(2)	22(2)	7(2)
F(1)	85(4)	56(3)	29(2)	6(2)	17(3)	-2(3)
C(8)	56(5)	29(4)	35(4)	-3(3)	16(4)	-2(4)
CI(2)	45(1)	18(1)	32(1)	-3(1)	-1(1)	9(1)
C(14)	40(5)	35(4)	43(4)	18(4)	2(4)	_4(4)

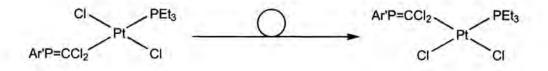
Table 3.14 – Anisotropic displacement parameters (Å² x 10³) for [PtCl₂(PEt₃)(Ar'PF₂)]. The anisotropic displacement factor exponent takes the form: $-2 \pi^2$ [h² a^{*2} U11 + 2 h k a^{*} b^{*} U12]

	X	у	Z	U(eq)
H(9A)	-20942(9)	5047(5)	-4263(3)	31
H(SB)	-19900(9)	5608(5)	4739(3)	31
H(11A)	-16538(11)	3612(5)	-5292(3)	34
H(11B)	-18522(11)	3725(5)	_5535(3)	34
H(13A)	-20521(11)	2957(5)	_4604(3)	35
H(13B)	-18573(11)	2577(5)	_4452(3)	35
H(10A)	-22705(49)	5202(21)	-5110(20)	57
H(10B)	-22405(61)	4143(26)	-4952(14)	57
H(10C)	-21246(16)	4607(44)	-5443(7)	57
H(5)	-15675(13)	7621(6)	-2045(3)	47
H(4)	-13440(14)	8588(5)	-2415(3)	50
H(3)	-12542(12)	8406(5)	_3366(3)	45
H(12A)	-16447(70)	4799(6)	-5963(12)	54
H(12B)	_16181(61)	5276(20)	-5362(11)	54
H(12C)	-18085(15)	5320(18)	-5669(22)	54
H(14A)	-18905(13)	3041(44)	-3507(4)	59
H(14B)	-20623(76)	2442(21)	-3670(7)	59
H(14C)	-20762(71)	3539(25)	-3648(8)	59
H(15A)	-11219(25)	4911(12)	-2239(7)	132
H(15B)	-13294(25)	4673(12)	-2158(7)	132

Table 3.15 – Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters (Å² $x \ 10^3$) for[PtCl₂(PEt₃)(Ar'PF₂)]

3.2.5 Reaction between [PtCl₂(PEt₃)]₂ and (C₈H₃F₆)P=CCl₂

Ar'P=CCl₂ was added to a solution of [PtCl₂(PEt₃)]₂ in (CHCl₂)₂ and the solution was allowed to stir. The time period over which the *trans* isomer is visible in this reaction is fairly short and rearrangement is complete within five minutes. This was visible in the ³¹P NMR spectrum only by performing an NMR scale reaction and then running a spectrum immediately. The phosphaalkene and platinum starting material are both consumed within 30 minutes and the *cis* isomer is the sole product visible in the NMR spectrum.



Equation 3.6 - Re-arrangement of trans-[PtCl2(PEt3)(Ar'P=CCl2)]

The ³¹P NMR spectrum of this product shows a doublet with Pt satellites, which signifies the formation of the *trans* isomer. This is not present in large yields and at the time it was not possible to determine an accurate value for the P-Pt coupling constant. It is possible to ascertain an approximate value from the spectrum. The *trans* species has a chemical shift value $\delta = 184.5$ ppm (¹J_{P-Pt} ≈ 2400 Hz) (²J_{P-P} = 580.2 Hz).

The ³¹P NMR spectrum also shows a number of peaks assignable to the PEt₃ groups *trans* to the phosphane in question. Again, unfortunately these peaks are small and the coupling constants are impossible to determine accurately. Approximate values for the coupling constants were, however, determined manually $\delta = 18.3$ ppm (¹J_{P-Pt} ≈ 2900 Hz) (²J_{P-P} = 579.9 Hz).

After a short period of time, the ³¹P NMR spectrum shows two singlets with associated Pt satellites, assigned to the *cis* species. There is a small amount of coupling visible between the *cis* phosphorus species although it is very small as compared with the *trans* isomer. The chemical shift values for the *cis* compound are $\delta = 155.3$ ppm (¹J_{P-Pt} = 3143 Hz, ²J_{P-P} = 19.2 Hz) (doublet with Pt satellites) and $\delta = 12.9$ Hz (¹J_{P-Pt} = 3030 Hz, ²J_{P-P} = 19.8 Hz) (doublet with Pt satellites). The ¹⁹F spectrum shows a singlet with chemical shift value $\delta = -57.1$ ppm.

The product was isolated as a white powder which was recrystallised using a layering technique (see Appendix 1). The crystals were submitted for X-ray crystallographic studies and the crystal structure solved.

3.2.5.1 The molecular structure of $[PtCl_2(PEt_3)(C_8H_3F_6)P=CCl_2]$

Crystals submitted for X-ray characterisation were mounted on a glass fibre, introduced onto the diffractometer, and Data were collected. The structure was subsequently solved and refined; the molecular structure is shown below in Figure 3.9.

Data were collected on a Siemens 3-circle diffractometer with a CCD area detector, ω scan mode $2\theta \le 60.2^{\circ}$. The structure was solved by direct methods and refined by full-matrix least squares against F². Lists of crystal data and refinement parameters, anisotropic displacement parameters, bond lengths and angles, and atomic coordinates are given in Table 3.16 through Table 3.21.

The solid state X-ray crystal structure of this compound reveals that the angle between the P=C bond and the aryl ring is 68.7° . This is far from ideal, and the most significant factor may be the steric interactions with the CF₃ groups *cis* to the phosphorus. The angle between the square planar platinum (PtCl₂(PEt₃)) and the plane of the aryl ring is only 13.1°.

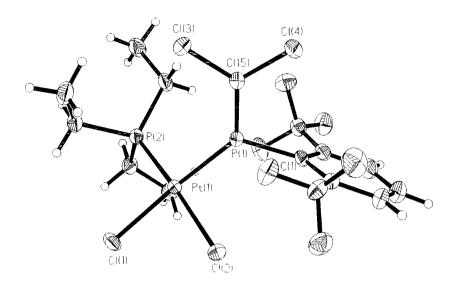


Figure 3.9 – Thermal ellipsoid diagram at 150K (50% probability) for [PtCl₂(PEt₃)(Ar'P=CCl₂)]

Crystals data	and structure refinement
Identification code	Ar'P=CCl2-dimer
Empirical formula	G15 H18 Cl4 F8 P2 Pt
Formula weight	711.12
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	$a = 8.0329(1) \text{ Å} \alpha = 90 ^{\circ}$
TRACE AND ADDRESS OF ADDRESS ADDRESS OF ADDRESS OF ADDR	b = 20.2638(3) Å β = 94.728(2) ".
	c = 13.7371(2) Å x = 90 °.
Volume	2228.48(5) Å ³
Z	4
Number of reflections used	Calculation of cell = 512
	Total = 13434
Stratt the at the little is setting	Unique = 4235
And a colour the	Obs [l>2σ(l)] = 3760
Crystal description	needle
Crystal colour	pale
Density (calculated)	2.120 g/cm ³
Absorption coefficient	69.69 cm_1
F(000)	1352
Crystal size	0.28 x 0.09 x 0.09 mm
Theta range for data collection	1.80 to 27.98 °.
Index ranges	_9<=h<=9, _23<=k<=22, _15<=l<=17
Experiment device	Siemens SMART
Experiment methods	o scans
Reflections collected	13167
Independent reflections	4235 [R(int) = 0.0449]
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	4227 / 0 / 256
Goodness-of-fit on F2	1.074
Final R indices [I>2o(I)]	$R_1 = 0.0271$, w $R_2 = 0.0567$
R indices (all data)	R ₁ = 0.0343, wR ₂ = 0.0621
Largest diff. peak and hole	.692 and -1.025 e.Å-3

Table 3.16 - Crystal data and structure refinement for [PtCl₂(PEt₃)(Ar'P=CCl₂)]

	Х	У	Z	U(eq)
Pt(1)	5303(1)	3031(1)	7739(1)	18(1)
CI(1)	4459(2)	1973(1)	7264(1)	31(1)
P(1)	6334(1)	4025(1)	8056(1)	18(1)
CI(3)	8538(2)	3761(1)	9856(1)	27(1)
CI(2)	6151(2)	3219(1)	6155(1)	27(1)
CI(4)	8526(2)	5068(1)	8994(1)	30(1)
P(2)	4151(2)	2805(1)	9158(1)	20(1)
F(1)	9176(4)	4115(2)	6947(2)	33(1)
F(5)	2140(4)	5464(2)	8109(2)	36(1)
F(6)	2656(4)	4422(2)	8074(2)	35(1)
F(4)	4203(4)	5068(2)	9019(2)	33(1)
F(3)	8710(4)	4376(2)	- 5429(2)	37(1)
F(2)	9886(4)	5073(2)	6449(2)	43(1)
C(1)	5956(6)	4741(2)	7239(3)	19(1)
C(2)	7004(6)	4913(2)	6518(3)	22(1)
C(8)	8673(6)	4609(3)	6347(3)	28(1)
C(3)	6590(7)	5434(3)	5876(4)	32(1)
C(4)	5138(7)	5795(3)	5947(4)	36(1)
C(5)	4116(7)	5646(3)	6673(4)	32(1)
C(6)	4505(6)	5129(2)	7321(3)	23(1)
C(7)	3375(6)	5022(2)	8123(3)	24(1)
C(9)	5056(6)	2084(2)	9792(4)	27(1)
C(10)	6912(7)	2133(3)	10129(4)	35(1)
G(11)	1974(6)	2567(3)	8904(3)	26(1)
C(12)	947(7)	2986(3)	8140(4)	31(1)
C(13)	4130(6)	3480(2)	10029(3)	26(1)
C(14)	3687(8)	3298(3)	11058(4)	38(1)
C(15)	7749(6)	4275(2)	8942(3)	21(1)

Table 3.17 – Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2 x 103) for $[PtCl_2(PEt_3)(Ar'P=CCl_2)].U(eq)$ is defined as one third of the trace of the orthogonalized Uij tensor.

Selected Bond ler	
Pt(1)-P(1)	2.2082(12)
Pt(1)-P(2)	2.2735(11)
Pt(1)_Cl(1)	2.3257(12)
Pt(1)-Cl(2)	2.3632(11)
P(1)-C(15)	1.673(5)
P(1) C(1)	1.844(5)
CI(3)-C(15)	1.712(5)
CI(4)-C(15)	1.723(5)
P(1)-Pt(1)-P(2) P(1)-Pt(1)-Cl(1)	100.76(4)
P(2)-Pt(1)-Cl(1)	85.69(4)
P(1)-Pt(1)-Cl(2)	84.43(4)
P(2)-Pt(1)-Cl(2)	172.22(4)
CI(1)-PI(1)-CI(2)	89.44(4)
C(15)-P(1)-C(1)	105.8(2)
C(15)-P(1)-Pt(1)	129.9(2)
C(1)_P(1)_Pt(1)	123.9(2)

Table 3.18 – Atomic Selected bond lengths [Å] and angles [°] for [PtCl₂(PEt₃)(Ar'P=CCl₂)]

Bond lengths [Å] a	and angles [9]
Pt(1)-P(1)	2,2082(12)
$P_{1}(1) = P(1)$	2.2002(12)
Pt(1)_Cl(1)	2.3257(12)
Pt(1) = Ot(1)	2.3632(11)
P(1) = O(2)	1.672/5)
P(1)-C(15)	1.673(5)
P(1)-U(1)	1.044(0)
CI(3)-C(15)	1.712(5)
CI(4)-C(15)	1.723(3)
P(2)-C(13)	1.818(5)
P(2)-G(11)	1.820(5)
P(2)-C(9)	1.821(5)
F(1)-C(8)	1.33/(6)
F(5)_C(7)	1.335(5)
F(6)-C(7)	1.346(6)
F(4)-C(7)	1.353(5)
F(3)-C(8)	1.349(6)
F(2)-C(8)	1.353(6)
C(1)-C(2)	1.396(6)
C(1)-C(6)	1.418(7)
C(2)-C(3)	1.398(7)
C(2)-C(8)	1.512(7)
C(3)-C(4)	1.386(8)
C(3)-H(3)	.93
C(4)-C(5)	1.377(8)
C(4)_H(4)	.93
C(5)-C(6)	1.393(7)
C(5)-H(5)	.93
C(6) - C(7)	1.501(7)
C(9)_C(10)	1.527(7)
C(9)-H(9A)	97
C(9)-H(9B)	.97
C(10)-H(10A)	96
C(10)-H(10B)	.96
MARINE CONTRACTOR	.50
C(10)-H(10C)	1.537(7)
C(11) - C(12)	1.557(1)
C(11)-H(11A)	,97
C(11)-H(11B)	.97
Q(12)-H(12A)	.90
C(12)-H(12B)	.96
G(12)-H(12C)	.96
C(13)-C(14)	1.532(6)
C(13)-H(13A)	.97
C(13)-H(13B)	.97
C(14)-H(14A)	.96
C(14)-H(14B)	.96
C(14)-H(14C)	.96
P(1)-Pt(1)-P(2)	100.76(4)
P(1)-Pt(1)-CI(1)	172.98(4)
P(2)-Pt(1)-Cl(1)	85.69(4)

Bond lengths [Å] and	angles [°]
P(1)-Pt(1)-Cl(2)	84.43(4)
P(2)-Pt(1)-Cl(2)	172.22(4)
CI(1)-Pt(1)-CI(2)	89.44(4)
C(15)-P(1)-C(1)	105.8(2)
C(15)-P(1)-Pt(1)	129.9(2)
C(1)_P(1)_Pt(1)	123.9(2)
C(13)-P(2)-C(11)	105.4(2)
C(13)-P(2)-C(9)	108.3(2)
C(11)-P(2)-C(9)	102.6(2)
C(13)-P(2)-Pt(1)	116.1(2)
C(11)-P(2)-Pt(1)	110.0(2)
C(9)-P(2)-Pt(1)	113.4(2)
C(2)-C(1)-C(6)	117.7(4)
C(2)-C(1)-P(1)	123.3(4)
C(6)-C(1)-P(1)	118.9(3)
C(1)-C(2)-C(3)	120.7(4)
C(1)-C(2)-C(8)	127.1(4)
C(3)-C(2)-C(8)	112.2(4)
F(1)-C(8)-F(3)	106.6(4)
F(1)-C(8)-F(2)	106.1(4)
F(3)-C(8)-F(2)	105.6(4)
F(1)-C(8)-C(2)	115.9(4)
F(3)-C(8)-C(2)	112.1(4)
F(2)-C(8)-C(2)	109.9(4)
C(4)-C(3)-C(2)	120.7(5)
C(4)-C(3)-H(3)	119.6(3)
C(2)-C(3)-H(3)	119.6(3)
C(5)-C(4)-C(3)	119.4(5)
C(5)-C(4)-H(4)	120.3(3)
C(3)-C(4)-H(4)	120.3(3)
C(4)-C(5)-C(6)	120.8(5)
C(4)-C(5)-H(5)	119.6(3)
C(6)-C(5)-H(5)	119.6(3)
C(5)-C(6)-C(1)	120.6(4)
C(5)-C(6)-C(7)	117.5(4)
C(1)-C(6)-C(7)	121.9(4)
F(5)-C(7)-F(6)	106.9(4)
F(5)-C(7)-F(4)	106.0(4)
F(6)-C(7) F(4)	106.6(4)
F(5)-C(7)-C(6)	112.7(4)
F(6)-C(7)-C(6)	112.1(4)
F(4)_C(7)_C(6)	112.1(4)
C(10)-C(9)-P(2)	115.8(4)
C(10)-C(9)-H(9A)	108.3(3)
P(2)-C(9)-H(9A)	108.3(2)
C(10)-C(9)-H(9B)	108.3(3)
P(2)-C(9)-H(9B)	108.3(2)
H(9A)_C(9)_H(9B)	107.4
C(9)-C(10)-H(10A)	109.5(3)
C(9)-C(10)-H(10B)	109.5(3)

Bond lengths [Å] and angles [°]	
H(10A) C(10) H(10B)	109.5
C(9)-C(10)-H(10C)	109.5(3)
H(10A)_C(10)_H(10C)	109.5
H(10B)_C(10)_H(10C)	109.5
C(12)-C(11)-P(2)	115.9(3)
C(12)-C(11)-H(11A)	108.3(3)
P(2)_C(11)_H(11A)	108.3(2)
C(12)-C(11)-H(11B)	108.3(3)
P(2)-C(11)-H(11B)	108.3(2)
H(11A)_C(11)_H(11B)	107.4
C(11)_C(12)_H(12A)	109.5(3)
C(11)-C(12)-H(12B)	109.5(3)
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5(3)
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)_C(13)_P(2)	116.2(4)
C(14)-C(13)-H(13A)	108.2(3)
P(2)-C(13)-H(13A)	108.2(2)
C(14)-C(13)-H(13B)	108.2(3)
P(2)-C(13)-H(13B)	108.2(2)
H(13A)_C(13)_H(13B)	107.4
C(13)-C(14)-H(14A)	109.5(3)
C(13)-C(14)-H(14B)	109.5(3)
H(14A)-C(14)-H(14B)	109.5
C(13)_C(14)_H(14C)	109.5(3)
H(14A)_C(14)_H(14C)	109.5
H(14B)_C(14)_H(14C)	109.5
P(1)-C(15)-Cl(3)	122.5(3)
P(1)-C(15)-CI(4)	122.3(3)
CI(3)-C(15)-CI(4)	115.2(3)

 $\textit{Table 3.19}-\text{Bond lengths [Å] and angles [}^o\text{] for [PtCl_2(PEt_3)(Ar'P=CCl_2)]}$

	U11	U22	U33	U23	U13	U12
Pt(1)	22(1)	15(1)	16(1)	-1(1)	1(1)	0(1)
CI(1)	46(1)	18(1)	30(1)	-6(1)	6(1)	-7(1)
P(1)	21(1)	15(1)	18(1)	2(1)	0(1)	-1(1)
CI(3)	31(1)	26(1)	22(1)	3(1)	-5(1)	2(1)
CI(2)	37(1)	25(1)	18(1)	0(1)	6(1)	0(1)
C1(4)	34(1)	22(1)	31(1)	-0(1)	-6(1)	-9(1)
P(2)	24(1)	17(1)	20(1)	1(1)	3(1)	-1(1)
F(1)	30(2)	37(2)	33(2)	11(1)	8(1)	
F(5)	32(2)	32(2)	43(2)	4(1)	7(1)	10(1)
F(6)	33(2)	23(2)	50(2)	1(1)	8(1)	-7(1)
F(4)	33(2)	41(2)	26(1)	-3(1)	2(1)	3(1)
F(3)	46(2)	40(2)	27(2)	1(1)	11(1)	7(2)
F(2)	31(2)	46(2)	53(2)	5(2)	7(1)	-14(2)
C(1)	21(2)	14(2)	22(2)	0(2)	0(2)	-5(2)
C(2)	28(3)	19(3)	18(2)	0(2)	2(2)	0(2)
C(8)	29(3)	34(3) -	21(2)	6(2)	4(2)	-1(2)
C(3)	42(3)	27(3)	26(2)	7(2)	3(2)	-3(2)
C(4)	44(3)	29(3)	33(3)	9(2)	-1(2)	2(3)
C(5)	33(3)	26(3)	36(3)	2(2)	-6(2)	3(2)
C(6)	26(3)	19(3)	25(2)	-2(2)	3(2)	-2(2)
C(7)	20(2)	21(3)	31(2)	0(2)	-2(2)	2(2)
C(9)	33(3)	21(3)	28(2)	2(2)	3(2)	5(2)
C(10)	39(3)	28(3)	38(3)	9(2)	-4(2)	4(2)
C(11)	27(3)	25(3)	28(2)	4(2)	2(2)	-6(2)
C(12)	28(3)	34(3)	30(2)	2(2)	3(2)	0(2)
C(13)	33(3)	17(3)	28(2)	0(2)	8(2)	-4(2)
C(14)	67(4)	24(3)	26(3)	-5(2)	16(3)	-1(3)
C(15)	25(2)	18(3)	21(2)	1(2)	0(2)	1(2)

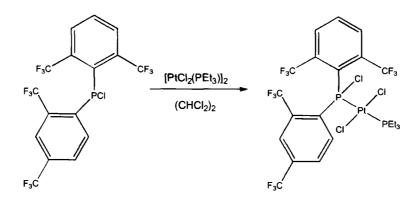
Table 3.20 – Anisotropic displacement parameters (Å² x 10³) for [PtCl₂(PEt₃)(Ar'P=CCl₂)]. The anisotropic displacement factor exponent takes the form: $-2 \pi^2$ [h² a^{*2} U11 + 2 h k a^{*} b^{*} U12]

	X	у	Z	U(eq)
H(3)	7297(7)	5541(3)	5396(4)	38
H(4)	4857(7)	6134(3)	5507(4)	43
H(5)	3154(7)	5893(3)	6731(4)	38
H(9A)	4444(6)	2001(2)	10360(4)	32
H(9B)	4893(6)	1706(2)	9363(4)	32
H(10A)	7273(13)	1729(7)	10446(25)	53
H(10B)	7090(9)	2493(12)	10579(21)	53
H(10C)	7540(8)	2206(19)	9574(5)	53
H(11A)	1939(6)	2112(3)	8686(3)	32
H(118)	1436(6)	2585(3)	9511(3)	-32
H(12A)	-189(12)	2834(11)	8080(19)	46
H(12B)	1412(28)	2947(14)	7521(7)	- 46
H(12C)	976(37)	3440(4)	8341(13)	46
H(13A)	5225(6)	3685(2)	10081(3)	31
H(13B)	3336(6)	3808(2)	9766(3)	31
H(14A)	3700(48)	3689(4)	11455(9)	57
H(14B)	4490(28)	2988(15)	11342(11)	57
H(14C)	2594(21)	3104(18)	11024(5)	57

Table 3.21 – Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters (Å² $x \ 10^3$) for[PtCl₂(PEt₃)(Ar'P=CCl₂)]

3.2.6 Reaction between [PtCl₂(PEt₃)]₂ and (C₈H₃F₆)₂PCl

Ar'Ar''PCl was added to a solution of $[PtCl_2(PEt_3)]_2$ in $(CHCl_2)_2$ and the solution was allowed to stir. This reaction shows a distinct difference to the previous ones in that the *trans* isomer did not rearrange over time. This is probably due to the steric bulk of the phosphane itself which inhibits the formation of the *cis* isomer, due to interaction with the PEt₃ group.



Equation 3.7 - Synthesis of trans-[PtCl₂(PEt₃)(Ar'Ar''PCl)]

The ³¹P NMR spectrum shows a doublet and the associated Pt satellites for both the phosphane in question (Ar'Ar''PCl) and the PEt₃ group, signifying the formation of the *trans* compound. The chemical shifts of the species has values $\delta = 94.5$ ppm (¹J_{P-Pt} = 2531.4 Hz, ²J_{P-P} = 562.0 Hz) and $\delta = 21.19$ ppm (¹J_{P-Pt} = 2765.3 Hz, ²J_{P-P} = 561.8 Hz).

The ¹⁹F NMR spectrum is more interesting in that it shows a distinct difference in the coupling from the CF₃ groups on the Ar' group and the *cis* CF₃ group on the Ar'' group. The spectrum shows two doublets and two singlets. This result confirms the interesting NMR results for the Ar'Ar''PCl phosphane itself (see Section 2.2.8.2). All the CF₃ groups are unique on the NMR time scale and the coupling constants are significantly different from one CF₃ group to the next.

The expected signals would be three doublets and one singlet, but as in the case of the free phosphane, one CF_3 group is reasonably far away from the phosphorus atom to reduce the coupling significantly enough, that it only appears as a singlet in the spectrum.

The chemical shift values for the species are $\delta = -52.8$ ppm (singlet), $\delta = -53.4$ ppm (doublet) (${}^{4}J_{P-F} = 12.7$ Hz), $\delta = -55.1$ ppm (singlet) and $\delta = -56.4$ ppm (doublet) (${}^{4}J_{P-F} = 61.19$ Hz).

In the X-ray structure of the ligand Ar'Ar''PCl, it is apparent that one of the CF_3 groups in the Ar' aryl group is significantly further away from the phosphorus atom than the other, and this causes there to be no P-F coupling due to that interaction. In this case, not only is this observation confirmed, but also the P-F coupling constant between the phosphorus and the *cis* CF₃ group on the Ar'' group is significantly smaller than that of the Ar'(CF₃)-P interaction. This implies that the fluorine atoms on this CF₃ group are also on average further away from the phosphorus. Unfortunately the crystals grown of this compound were not suitable for X-ray analysis so it is impossible to confirm this deduction at present.

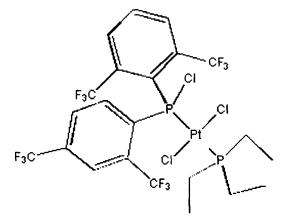


Figure 3.10 - Trans-[PtCl₂(PEt₃)(Ar'Ar''PCl)]

This result does, however, show that there must be significant steric hindrance around the P-Pt bond which would help to explain the apparent lack of rearrangement from the *trans* to the *cis* complex in this case.

The *trans* compound was heated for four days at 45°C and a small quantity was observed to rearrange to the *cis* compound. The formation of a number of other products was also apparent from the ³¹P NMR spectrum and although the species was identified from the ³¹P NMR spectrum, the ¹⁹F NMR spectrum was too complex to determine exactly which peaks were significant. This formation of a number of products is probably due to the decomposition of the Ar'Ar''PCl species and the subsequent formation of platinum compounds of the by-products.

The ³¹P NMR spectrum of the *cis* compound shows the formation of a singlet with the corresponding platinum satellites and the decrease in size of the doublet of triplets associated with the *trans* isomer. The chemical shift of the *cis* isomer has a value $\delta = 69.3$ ppm (¹J_{P-Pt} = 4783.3 Hz).

Isolation and purification of the *cis* compound could not be achieved and crystals of the compound were not obtained.

3.2.7 Attempted reaction between [PtCl₂(PEt₃)]₂ and Ar'Ar''PH

Ar'Ar''PH was added to a solution of $[PtCl_2(PEt_3)]_2$ in $(CHCl_2)_2$ and allowed to stir. No reaction was apparent from the ³¹P NMR spectrum even after extended refluxing over a number of days.

3.2.8 Attempted reaction between [PtCl₂(PEt₃)]₂ and Ar₂PH

Ar₂PH was added to a solution of $[PtCl_2(PEt_3)]_2$ in $(CHCl_2)_2$ and allowed to stir. No reaction was apparent from the ³¹P NMR spectrum even after extended refluxing over a number of days.

3.3 Results

3.3.1 A comparison of coupling constants

Complexes were prepared by reaction of the "Pt dimer" and the following compounds, Ar'PH₂, Ar'PF₂, Ar'PCl₂, Ar'P=CCl₂, and Ar'Ar''PCl. The results are shown in Table 3.22.

Species reacted with Pt dimer	Isomer	Coupling constant ^I J _{P-Pt} [Hz]	Bond length Pt–P(1) [Å]
Ar'PH ₂	cis	3809	2.215(2)
	trans		
Ar'PCl ₂	cis	5511	2.186(7)
	trans	678.4	
Ar'PF ₂	cis	6252	2.157(2)
	trans	2723.3	
Ar'P=CCl ₂	cis	3143	2.2082(12)
	trans	2340	
Ar'Ar''PCl	cis	4783.3	
	trans	2531.6	

Table 3.22 – Coupling constants and P-Pt bond lengths for a series of synthesised platinum phosphane complexes

As can be seen from Table 3.22 the largest coupling constants are formed in the compounds where there is the greatest electron withdrawal from the groups attached to the phosphorus. The coupling constants for the *cis* compounds range from 3100 Hz to over 6100 Hz. This increase is due to the amount of back donation occurring from the platinum to the phosphorus atom. This in turn shortens the P–Pt bond length (see Section 3.4).

3.4 Comparison between coupling constants and Pt-P bond length

Many studies⁷ have been carried out which show conclusively that the coupling constant ${}^{1}J_{Pt-P}$ is directly comparable to the Pt-P bond length. This trend is indicative of the factors which determine the magnitude of the coupling constant.

In NMR studies, the electrons which give rise to this effect are the s electrons. It is the s electrons and the amount of s character in the bonding orbital which gives rise to the coupling constants. Interaction between s-electrons from two different atoms give rise to the coupling. As the s electrons on the platinum and the s electrons on the phosphorus become closer, the coupling constant increases⁸.

We must now consider what actually causes the bond length to be shorter and thus the coupling constant to be greater. An average coupling constant for ${}^{1}J_{Pt-P}$ for an η^{1} complex is in the region of 2000–4000Hz; however, some of the values for the compounds discussed in Table 3.22 are relatively larger than this.

As discussed in the introduction, there are two main interactions in phosphane bonding, σ -bond donation from the phosphane to the metal and π -back-donation from the metal to the phosphane. The greater the back donation then the stronger the bond and thus the greater the coupling constant. In this comparison the extent of back donation is wholly dependent on the phosphane, as in all cases the PtCl₂(PEt₃) moiety remains constant. The greater the π -electron withdrawing capacity of the ligand the greater the back donation. The phosphanes concerned all have the Fluoroxyl group, which as discussed earlier (Chapter 2) is electron withdrawing, and the varying factor is the other substituents on phosphorus. In the series Ar'PH₂ < Ar'PCl₂ < Ar'PF₂ the coupling constant increases while the bond length decreases. This can be attributed to the electronegativity of the attached X group.

In the other cases, however, $(Ar'Ar''PCl, Ar'P=CCl_2)$ there may be further factors involved, such as steric hindrance which may affect the bond length.

3.5 Changes in the chemical shifts upon bonding

When discussing bonding in phosphane-platinum (II) complexes there are two factors to consider; firstly the contribution to bonding from the σ bond, and secondly the contribution of the back donation from the platinum atom into the LUMO on the phosphorus atom.

With the exception of Ar'PH₂, the chemical shift moves to a lower frequency on bonding to Pt(II). This implies that there is an increase in electron density at the phosphorus centre. It can therefore be reasonably assumed that the back donation of electrons from the platinum contributes more to the shielding than the electrons from the phosphorus in the σ bond.

In the case of the compound formed with $Ar'PH_2$, however, the shift is to a higher frequency thus implying that the dominant factor in bonding is the σ bond, comparative to the back donation from the platinum atom.

This can be explained by looking at the substituents on the phosphorus atom. Halogen atoms bonded to phosphorus cause an overall effect of electron withdrawal from the s and more importantly p orbitals on the phosphorus atom itself. This increases the capacity for the phosphorus to accept electron density from the platinum in the form of back donation to the LUMO (π^*).

Hydrogen, however, has approximately the same electronegativity as phosphorus⁵ and as such does not aid back donation from the platinum atom. The aryl group will withdraw some electrons but this is an equal factor when looking at the series of compounds.

This feature of back donation also ties in with the fact that the bond lengths become shorter $Ar'PF_2 < Ar'PCl_2 < Ar'PH_2$ and the coupling constants decrease.

Phosphane	Chemical shift (δ) prior to bonding (ppm)	Chemical shift (δ) of the <i>cis</i> platinum compound (ppm)	Change in Chemical shift upon bonding (ppm)
Ar'PH ₂	-140.3	-79.9	+ 60.4
Ar'PCl ₂	148.0	142.7	- 5.3
Ar'PF ₂	193.3	163.1	- 30.2

3.5.1 Change in chemical shift upon bonding to platinum

Table 3.23 - Changes in chemical shift upon bonding to platinum

As can be seen from Table 3.23, there would seem to be no correlation between the change in chemical shift of the phosphane, upon bonding to the platinum and the strength of the bond formed. What it does demonstrate is the vast change in electron density around the phosphorus atom upon bonding in certain cases. In the case of $Ar'PH_2$ the electron density is reduced on the phosphorus and in the case of the $Ar'PF_2$ phosphane electron density is greatly increased upon bonding.

3.6 Variations in the delocalisation of electrons in the aryl ring

Table 3.24 shows the variation in carbon–carbon bond lengths within each of the aryl rings once bonded to the platinum atom. The information given in the table reveals that the electronic distribution is far from uniform.

The carbon atoms connected to the CF_3 group are most affected by the electron withdrawal. The expected pattern is that the bond lengths around atoms C(2) and C(6) would be shortest and the bonds around C(4) would be longest.

If the results for the Ar'PCl₂ compound are not included in the comparisons (they are only accurate to two decimal places and not three like the others), it is clear that the shortest bond lengths in the compounds are those between C(4)–C(5) and C(3)–C(4) and that the longest bond lengths in the compounds are those between C(1)–C(6) and C(1)–C(2).

There are other influences on the carbon C(1) as it is bonded to phosphorus directly; however, this shows that the stronger bonds (shorter C–C bond lengths) are between those atoms furthest away from the CF₃ groups in the ring.

Compound	C(1)-C(2)	C(1)-C(6)	C(2)-C(3)	C(5)-C(6)	C(3)-C(4)	C(4)-C(5)
	1.396(6)	1.418(7)	1.398(7)	1.393(7)	1.386(8)	1.377(8)
Ave. C–C bond length = 1.395						
Figure (Ca) Figure (Ca) Figur	1.44(3)	1.37(4)	1.40(4)	1.41(4)	1.39(4)	1.41(4)
Ave. C–C bond length = 1.40						·
F140 F161 F161 F161 F161 F161 F161 F161 F16	1.413(5)	1.405(9)	1.376(9)	1.389(9)	1.368(12)	1.374(11)
Ave. C–C bond length = 1.388						
F(3) F(4) F(4) F(4) F(4) F(4) F(4) F(4) F(4	1.413(10)	1.396(9)	1.394(10)	1.382(11)	1.390(11)	1.376(13)
Ave. C-C bond length = 1.391						

Table 3.24 - Comparison between carbon-carbon bond lengths in the aryl rings

3.7 Experimental

3.7.1 The "Platinum dimer" *trans*–[PtCl₂(PEt₃)]₂

3.7.1.1 Synthesis of cis-[PtCl₂(PhCN)₂]

 $PtCl_2$ (2.0g, 7.5mmol) was added to PhCN (20ml) and was heated to 100°C for ten minutes, yielding a bright yellow solution which upon cooling gave a bright yellow precipitate. The solution was filtered and the crystals were washed with petroleum ether and dried *in vacuo*. Yield 2.5g (90%).

PtCl₂ xs PhCN PtCl₂(PhCN)₂

3.7.1.2 Synthesis of cis-[PtCl₂(PEt₃)₂]

PEt₃ (1.3ml, 4.2mmol) was added to a solution of cis-[PtCl₂(PhCN)₂] (1.0g, 2.1mmol) dissolved CH₂Cl₂ (5ml) and the reaction was stirred for three hours at room temperature. The solvent was removed *in vacuo* and the resulting white crystals were washed with hexane and dried *in vacuo*. Yield 0.8g (97%)

$$PtCl_{2}(PhCN)_{2} \xrightarrow{2 PEt_{3}} PtCl_{2}(PEt_{3})_{2}$$

$$- 2 PhCN$$

3.7.1.3 Synthesis of trans-[PtCl₂(PEt₃)]₂

cis-[PtCl₂(PEt₃)₂] (2.2g, 4.4mmol) was added to a solution of PtCl₂ (1.6g, 6.02 mmol) in (CHCl₂)₂ (5ml) and heated to 150°C for 1 hour. The solution turned bright orange. Upon cooling pale yellow crystals were formed. The solvent was removed carefully *in vacuo* and the product was purified by recrystallisation from CH₂Cl₂. Yield 3.5g (80%).

$$\begin{array}{c} \mathsf{PtCl}_2\\ \mathsf{PtCl}_2(\mathsf{PEt}_3)_2 & \longrightarrow & trans - [\mathsf{PtCl}_2(\mathsf{PEt}_3)]_2 \end{array}$$

3.7.2 Synthesis of *cis*-[PtCl₂(PEt₃)(Ar'PCl₂)]

A mixture of Ar''PCl₂ and Ar'PCl₂ (0.40g) and [PtCl₂(PEt₃)]₂ (0.49g, 0.7mmol) was dissolved in CH₂Cl₂ (25ml) and left to react for three days. A white precipitate was formed and the solution was filtered and washed with hexanes. Crystals of the resulting product were grown by layering hexanes above a solution of the product in (CHCl₂)₂. Yield 0.7 g; ³¹P δ = 97.9 ppm ¹J_{P-Pt} = 5488.1 Hz, singlet with Pt satellites, δ = 19.54 ppm ¹J_{P-Pt} = 3444.7 Hz, singlet with Pt satellites) for (Ar''PCl₂) and (δ = 94.5 ppm, ¹J_{P-Pt} = 5260 Hz, singlet with Pt satellites, δ = 20.14 ppm ¹J_{P-Pt} = 2916.1 Hz, singlet with Pt satellites) for (Ar'PCl₂). Analysis found: %C, 22.97; %H, 2.93; Required for C₁₄F₆H₁₈P₂PtCl₄; %C, 24.05; %H, 2.60.

$$\begin{array}{rl} trans - [PtCl_2(PEt_3)]_2 \\ Ar'PCl_2 & & \longrightarrow & PtCl_2(PEt_3)(Ar'PCl_2) \end{array}$$

3.7.3 Synthesis of *cis*–[PtCl₂(PEt₃)(Ar'PH₂)]

Ar'PH₂ (0.30g, 1.2mmol) and [PtCl₂(PEt₃)]₂ (0.46g, 0.6mmol) were dissolved in CH₂Cl₂ (25ml) and left to react for three days. A white precipitate was formed and the solution was filtered and washed with hexanes. Yield 0.5g; ³¹P {¹H} (CH₂Cl₂) $\delta = -79.9$ ppm

 $(^{1}J_{P-Pt} = 3834 \text{ Hz}).$

$$\begin{array}{rl} trans - [PtCl_2(PEt_3)]_2 \\ Ar'PH_2 & \longrightarrow & PtCl_2(PEt_3)(Ar'PH_2) \end{array}$$

3.7.4 Synthesis of *cis*–[PtCl₂(PEt₃)(Ar'PF₂)]

Ar'PF₂ (0.35g, 1.2mmol) and [PtCl₂(PEt₃)]₂ (0.46g, 0.6mmol) were dissolved in CH₂Cl₂ (25ml) and left to react for three days. A white precipitate was formed and the solution was filtered and washed with hexanes. Crystals of the resulting product were grown by layering hexanes above a solution of the product in (CHCl₂)₂. ³¹P (CHCl₂)₂ δ = 135.6 ppm (¹J_{P-Pt} = 6194.8 Hz, ¹J_{P-F} = 1140 Hz, ²J_{P-P} = 4.26Hz) (triplet with Pt satellites),

 $\delta = 20.51 \text{ ppm} ({}^{1}J_{P-Pt} = 2916.2 \text{ Hz}, {}^{2}J_{P-P} = 42.8 \text{ Hz})$ (singlet with Pt satellites). ${}^{19}F$: (CH₂Cl₂) $\delta = -75.7 \text{ ppm}$ (doublet and Pt satellites, ${}^{1}J_{P-F} = 1207.4 \text{ Hz}, {}^{2}J_{F-Pt} = 150.6 \text{ Hz},$ ${}^{5}J_{F-F} = 19.77 \text{ Hz}$).

$$\begin{array}{rl} trans - [PtCl_2(PEt_3)]_2 \\ \hline \\ Ar'PF_2 & \longrightarrow & PtCl_2(PEt_3)(Ar'PF_2) \end{array}$$

3.7.5 Synthesis of *cis*-[PtCl₂(PEt₃)(Ar'P=CCl₂)]

Ar'P=CCl₂ (0.46g, 1.4mmol) and [PtCl₂(PEt₃)]₂ (0.4g, 0.52mmol) were dissolved in a solution of CH₂Cl₂ and left to react for three days. An orange precipitate formed and the solution was filtered and washed with hexanes. Crystals of the resulting product were grown by layering hexanes above a solution of the product in (CHCl₂)₂. ³¹P (CH₂Cl₂) $\delta = 155.3$ ppm (¹J_{P-Pt} = 3143.8 Hz, ²J_{P-P} = 19.24 Hz) (doublet with Pt satellites). ¹⁹F (CH₂Cl₂) $\delta = -57.1$ ppm (singlet).

 $trans - [PtCl_2(PEt_3)]_2$ $Ar'P=CCl_2 \longrightarrow PtCl_2(PEt_3)(Ar'P=CCl_2)$

3.7.6 Synthesis of trans-[PtCl₂(PEt₃)(Ar'Ar"PCl)]

Ar'Ar''PCl (0.50g, 0.1mmol) was added to a solution of $[PtCl_2(PEt_3)]_2$ (0.39g, 0.05mmol) in $(CHCl_2)_2$. The solution was allowed to stir for ten days. Attempts to grow crystals suitable for X-ray analysis were unsuccessful. ³¹P (CH₂Cl₂) δ = 94.5 ppm (¹J_{P-Pt} = 1265.7 Hz) (²J_{P-P} = 562.0 Hz) (doublet with Pt satellites), δ = 21.19 ppm (¹J_{P-Pt} = 2765.3 Hz, ²J_{P-P} = 561.8 Hz). ¹⁹F (CH₂Cl₂) δ = -52.8 ppm (singlet), δ = -53.4 ppm (doublet) (⁴J_{P-F} = 12.7 Hz), δ = -55.1 ppm (singlet) and δ = -56.4 ppm (doublet) (⁴J_{P-F} = 61.19 Hz).

3.7.7 Synthesis of *cis*-[PtCl₂(PEt₃)(Ar'Ar''PCl)]

A solution of *trans*-PtCl₂(PEt₃)(Ar'Ar''PCl) in (CHCl₂)₂ was heated to 45°C for four days. Attempts to grow crystals suitable for X-ray analysis were not successful. ³¹P [CHCl₂)₂] $\delta = 69.3$ ppm (¹J_{P-Pt} = 4783.3 Hz).

trans - PtCl₂(PEt₃)(Ar'Ar"PCl) for 3 days

⁸ Unidentate Phosphorus Ligands", P. S. Pregosin, in Phosphorus-31 NMR Spectroscopy in

¹ H. P. Goodwin., K. B. Dillon., B. Murrer, Unpublished Work.

² N. N. Greenwood., A. Earnshaw., *Chemistry of the Elements*, Pergamon Press, Oxford, 1989.

³ H. P. Goodwin., Ph.D thesis., 1990.

⁴ J. Chatt., L. M. Venanzi., J. Am. Chem. Soc., 1955, 2787.

⁵ J. E. Huheey., "Inorganic Chemistry (third edition)"., Harper and Row 1983.

⁶ G. R. Desiraju., "Crystal Engineering – The design of organic solids", Material Science Monographs, Elsiever Science Publishers. B. V., 1989

⁷ J. G. Verkade., L. D. Quin., "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis of Organic Compounds and Metal Complexes", VCH Publishers, 1987

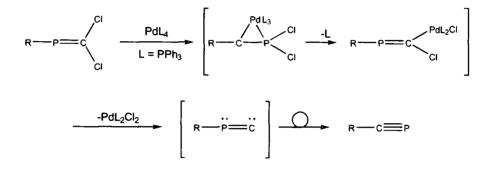
Stereochemical Analysis Organic Compounds and Metal Complexes", J. G. Verkade and L. D. Quin (eds), VCH Publishers, 1987, 509 – 511

Chapter 4

Synthesis of novel vinyl platinum complexes

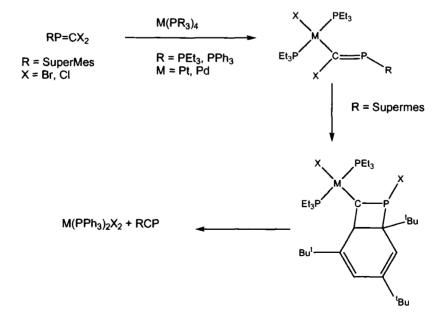
4.1 Introduction

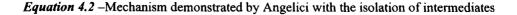
The synthesis of the phosphaalkyne R-CP (where R = Supermes), by the reaction of the phosphaalkene RP=CCl₂ with Pd(PPh₃)₄, was reported by Sanchez *et al*¹, with a proposed mechanism involving the rearrangement of the intermediate species [RP=C:].



Equation 4.1 – Proposed mechanism for the synthesis of a phosphaalkyne using PdL_4 and $RP=CCl_2$

A more detailed literature search revealed that this reaction was identical to work published subsequently by Angelici *et al* in 1994². The major difference is that Angelici had X-ray structures for the intermediates in the reaction with Pd(0) and Pt(0) which shows the formation of a four-membered ring between a C=C bond in the aryl ring and the P=C phosphaalkene bond.





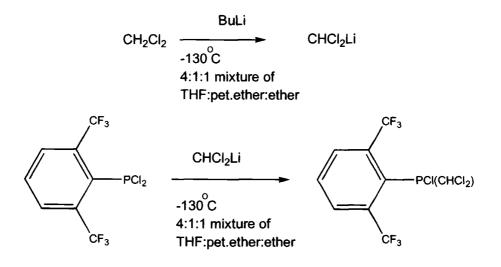
The phosphaalkene ArP=CCl₂ was first prepared by Goodwin³ by the removal of HCl from a substituted phosphane [ArP(Cl)CHCl₂]. It was proposed that the reaction between this phosphaalkene and Pd(0) and Pt(0) compounds would potentially facilitate a simple synthesis of a new phosphaalkene Ar-CP. There was also the possibility for the formation of η^2 complexes as well of the type Pt(L₂)(η^2 -ArP=CCl₂).

4.2 Phosphaalkenes

4.2.1 Synthesis of Ar'P=CCl₂

4.2.1.1 Ar'P(CI)CHCI₂

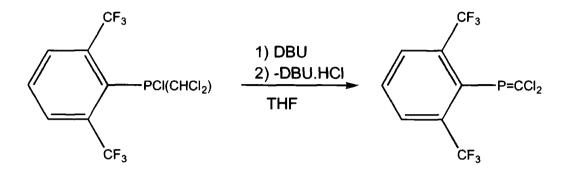
The synthesis and characterisation of the compound is described in Section 2.2.6.



Equation 4.3 – Preparation of Ar'PCl(CHCl₂)

4.2.1.2 Reaction between Ar'P(CI)CHCl₂ and DBU

The formation of this phosphaalkene is described in Section 2.2.7.



Equation 4.4 – Preparation of Ar'P=CCl₂

As described in Section 2.2.7 this low coordinate phosphorus species is stabilised by the steric bulk of the Fluoroxyl group and the electron withdrawing effects of that group.

The analogous compounds $RP=CCl_2$ (R = 2,4,6-tris(tritertiarybutyl)phenyl and $R=^tBu$) are well known ⁴ and their chemistry has been extensively studied. The reactions described in this chapter were performed to see if the perfluorinated aryl species would react in an analogous fashion to their non-fluorinated partners.

4.2.2 Formation of ArP=CCl₂

The analogous phosphaalkene was prepared by the same method described above, using Fluoromes as the aryl group instead of Fluoroxyl. This compound was synthesised because the extra CF_3 group on the aryl group would not only produce a more electronically stable compound but there would also be less chance of side reactions in the *para* position.

4.3 Attempted synthesis of η^2 -bonded phosphaalkene complexes

This section concerns the reaction of $Ar'P=CCl_2$ and $ArP=CCl_2$ with a number of different Pt(0) and Pd(0) compounds, in the attempt to make η^2 – bonded species. It was also expected that if the synthesis followed the same mechanism as Angelici's reaction, that it may in turn provide a method of synthesis for phosphaalkynes.

4.3.1 Reaction between Ar'P=CCl₂ and Pt(PPh₃)₄

 $Ar'P=CCl_2$ was added to a solution of $Pt(PPh_3)_4$ in toluene, which produced an orange colour to the solution. Orange crystals were formed over a few days and these were isolated and submitted for X-ray crystallographic characterisation.

This reaction was an attempt to form an η^2 -complex of the phosphaalkene. It did not, however, yield this product. The novel vinyl platinum species, *trans* PtCl(CCl=PAr')(PPh₃)₂ was formed. The reaction is analogous to a reaction performed using the Supermes R group described in Section 4.1.

The ³¹P NMR spectrum showed the formation of a number of new peaks; a septet with platinum satellites ($\delta = 201.93 \text{ ppm}^{-1}J_{P-Pt} = 413.1 \text{ Hz}$). (⁴J_{P-F} = 19.7 Hz) which is assignable to the phosphaalkene ligand, and two peaks associated with the PPh₃ groups still bonded to the platinum. The first PPh₃ ligand shows no P-P coupling ($\delta = 13.63 \text{ ppm}^{-1}J_{P-Pt} = 4019.8 \text{ Hz}$) (singlet and platinum satellites). The second PPh₃ ligand does show some P-P interaction ($\delta = 16.12 \text{ ppm}^{-1}J_{P-Pt} = 1846.9 \text{ Hz}$, ³J_{P-P} = 44.4 Hz) (doublet with platinum satellites). There is also a signal for free PPh₃ ($\delta = -2.75 \text{ ppm}$).

It is interesting to note the difference in the coupling constant between the two PPh₃ groups and the platinum. Both the ligands are *cis* to the phosphaalkene derivative and yet one of the species clearly shows P-P coupling and a significantly smaller P-Pt coupling constant. The P-P interaction must therefore be a through space interaction similar to that seen between the phosphorus atoms and the CF_3 groups on the aryl species.

The size of the coupling constant is directly related to the bond length P-Pt. The crystal structure shown in Section 4.3.1.1 demonstrates that the difference in P-Pt bond lengths is negligible (2.32Å and 2.33Å). This implies that there is significant interaction between one of the PPh₃ groups and the phosphaalkene derivative. The P-P distances in the molecule are P(1)-P(2) = 3.76Å and P(1)-P(3) = 4.48Å.

If we consider the sizes of the coupling constants, the interaction of 4019 Hz is typical of a *cis* complex and the interaction of 1846 Hz is typical of a *trans* complex.

In Angelici's paper² he describes the formation of both the *cis* and *trans* isomers upon initial addition of the two reactants. Taking that into consideration in this case, it would suggest that we have formed the two separate isomers. There is no evidence, however, for two signals assignable to the phosphaalkene derivative and there would also be more peaks assignable to inequivalent PPh₃ groups.

Assuming that we have only formed the *trans* isomer, as the NMR and X-ray structure suggest, we have to consider the difference in the signals assignable to the PPh₃ groups. If we consider the PPh₃ group closest to P(1) to be comparable to being *cis* and the PPh₃ group containing P(3) to be comparable to a *trans* complex this would go some way to describe the spectrum. The P-P coupling constant for a *trans* complex is normally of the order of 5-600 Hz and negligible for *cis* complexes. The coupling constant in this case is only of the order of 50 Hz.

We believe that the signal with ${}^{1}J_{P-Pt} = 1846$ Hz and ${}^{3}J_{P-P}$ to be assignable to the PPh₃ group containing P(3) and the signal with ${}^{1}J_{P-Pt} = 4019$ Hz to be assignable to the PPh₃ groups containing P(2) and being closer to the phosphorus atom in the phosphaalkene derivative.

The crystal structure also shows that there is no rotation of the phosphaalkene derivative about the Pt-C bond due to steric interactions. The distance between P(1) and P(2) is much smaller than that between P(1) and P(3)

The ¹⁹F spectrum showed a large number of indistinguishable peaks possibly due to decomposition and side reactions involving the product. Unfortunately none of the peaks could be identified accurately as those relating to the peaks in the ³¹P NMR spectrum.

Orange plate-like crystals were grown from toluene using the layering technique described in Appendix 1. The crystals were submitted for X-ray structural characterisation.

$$Ar'P=CCl_2 \xrightarrow{Pt(PPh_3)_4} PtCl(CCl=PAr')(PPh_3)_2$$

Equation 4.5 – Preparation of trans-[PtCl(CCl=PAr')(PPh_3)2]

4.3.1.1 The molecular structure of $[PtCl(CCl=PAr')(PPh_3)_2]$

Crystals submitted for X-ray characterisation were mounted on a glass fibre, introduced onto the diffractometer, and diffraction data were collected. The structure was subsequently solved and refined; the molecular structure is shown in Figure 4.1.

Data were collected on a Siemens 3-circle diffractometer with a CCD area detector, ω scan mode $2\theta \le 60.2^{\circ}$. The structure was solved by direct methods and refined by full-matrix least squares against F^2 . Lists of crystal data and refinement parameters, anisotropic displacement parameters, bond lengths and angles, and atomic coordinates are given in tables 4.1 through 4.5.

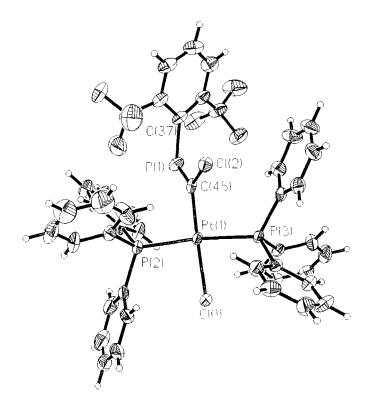
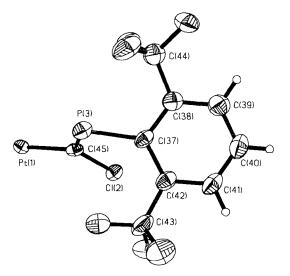
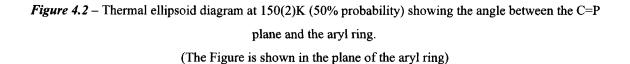


Figure 4.1 – Thermal ellipsoid diagram 150(2)K (50% probability) showing trans-[PtCl(CCl=PAr')(PPh₃)₂]

A significant factor in the structure of this compound is the steric hindrance. There is a large interaction is between the CF_3 groups on the aryl ring and the chlorine atom bonded to the phosphaalkene fragment [Cl(2)]. To minimise interaction the plane of the aryl ring is orthogonal to the plane of the Pt-C-Cl bonds.

This is not the case as can be seen from Figure 4.2, which is shown in the plane of the six carbons of the aryl ring.





The electronic effects in the structure would be at a maximum if the ring interacts with the lone pair on the phosphorus atom [P(1)] which would also mean that the plane of the aryl ring would be orthogonal to the Pt-C-Cl bonds.

The actual angle between the plane of the aryl ring and the plane of the Pt-C-Cl bonds is 76.1° . This suggests that there is also an interaction between the CF₃ groups and the PPh₃ groups.

It is worth noting from the structure that the two PPh₃ groups adopt a "*trans*" conformation which minimises any steric interaction between these two groups. This implies that the structure is based more around the steric positioning of the Fluoroxyl group than the PPh₃ groups.

Crystal data and structure refinement				
Identification code	Ar'P=C(CI)Pt(PPh ₃) ₂ CI			
Empirical formula	C45 H33 Cl2 F6 P3 Pt			
Formula weight	1046.61			
Temperature	150(2) K			
Wavelength	0.71073 Å			
Crystal system	Triclinic			
Space group	P-1			
Unit-cell dimensions	$a = 9.4710(2)$ Å $\alpha = 104.76^{\circ}$.			
	b = 11.6532(1) Å β = 91.851(1) °.			
	$c = 21.3936(3) \text{ Å}$ $\chi = 105.36^{\circ}$.			
Volume	2188.95(6) Å ³			
Z	2			
Number of reflections used	Calculation of cell = 512			
	Total = 16114			
	Unique = 11479			
	Obs [l>2σ(l)] = 8413			
Crystal description	needle			
Crystal colour	orange			
Density (calculated)	1.588 g/cm ³			
Absorption coefficient	34.93 cm ⁻¹			
F(000)	1028			
Crystal size	0.2 x 0.2 x 0.4 mm			
Theta range for data collection	0.99 to 30.49 °			
Index ranges	-12<=h<=10 -16<=k<=15 -29<=l<=28			
Experiment device	Siemens SMART			
Experiment methods	ω scans			
Reflections collected	16114			
Independent reflections	11497 [R(int) = 0.0288]			
Refinement method	Full-matrix least-squares on F ²			
Data / restraints / parameters	11488 / 0 / 512			
Goodness-of-fit on F ²	0.990			
Final R indices [I>2o(I)]	$R_1 = 0.0417$, w $R_2 = 0.0832$			
R indices (all data)	$R_1 = 0.0679$, $wR_2 = 0.0965$			
Largest diff. peak and hole	1.879 and -1.499 e.Å ⁻³			

Table 4.1 - Crystal data and structure refinement for [PtCl(CCl=PAr')(PPh_3)_2]

1 march 1 m	and and a state of the state of	and the second	in monstable a	Lacen I Lovel
	Х	У	Z	U(eq)
Pt(1)	10957(1)	2138(1)	13075(1)	22(1)
P(3)	10825(1)	127(1)	13111(1)	22(1)
P(2)	11247(1)	4214(1)	13156(1)	23(1)
C(30)	12894(6)	6072(5)	12644(3)	41(2)
C(7)	12648(5)	32(5)	13340(2)	26(1)
C(45)	9883(5)	1588(4)	12166(2)	23(1)
C(1)	9615(5)	-395(5)	13690(2)	24(1)
C(2)	9231(5)	463(5)	14187(2)	29(1)
C(8)	12872(6)	-778(5)	13693(3)	33(1)
C(13)	10217(6)	-1150(5)	12365(2)	27(1)
C(32)	9145(6)	5123(5)	12602(3)	31(1)
C(19)	12166(6)	5304(5)	13931(3)	31(1)
C(24)	13646(6)	5431(5)	14077(3)	38(1)
C(25)	12413(5)	4815(5)	12579(3)	30(1)
C(31)	9478(6)	4524(5)	13054(3)	30(1)
C(4)	7854(6)	-1165(6)	14616(3)	36(1)
C(3)	8353(6)	68(6)	14644(3)	36(1)
C(26)	12886(7)	4026(6)	12097(3)	54(2)
C(12)	13846(6)	710(5)	13107(3)	34(1)
C(23)	14417(8)	6231(6)	14654(3)	53(2)
C(9)	14265(6)	-905(6)	13798(3)	46(2)
C(6)	9094(6)	-1647(5)	13663(3)	37(1)
C(5)	8234(7)	-2017(6)	14127(3)	45(2)
CI(1)	12253(2)	2709(1)	14123(1)	38(1)
C(18)	8747(6)	-1506(5)	12103(3)	35(1)
C(14)	11183(6)	-1722(5)	12019(3)	35(1)
C(11)	15244(6)	580(6)	13210(3)	42(2)
C(16)	9276(7)	-2969(6)	11185(3)	48(2)
C(15)	10703(7)	-2629(5)	11439(3)	44(2)
C(17)	8280(7)	-2398(6)	11515(3)	47(2)
C(33)	7729(6)	5246(6)	12531(3)	42(2)
C(36)	8406(6)	4081(6)	13428(3)	44(2)
C(34)	6689(7)	4832(6)	12916(3)	52(2)
C(35)	7015(7)	4242(7)	13365(3)	57(2)
CI(2)	10851(1)	879(1)	11563(1)	31(1)
P(3)	8220(2)	1773(1)	11993(1)	31(1)
F(3)	6002(4)	-785(3)	11832(2)	52(1)
F(2)	4855(4)	461(4)	11628(2)	56(1)
F(1)	4297(4)	-1420(4)	11040(2)	71(1)
C(37)	7730(6)	1003(5)	11094(2)	30(1)
C(29)	13830(7)	6523(7)	12214(4)	55(2)
C(20)	11471(8)	5982(6)	14378(3)	52(2)
C(42)	8482(6)	1409(6)	10595(3)	35(1)
C(44)	5438(7)	-457(6)	11339(3)	45(2)
C(22)	13719(11)	6903(6)	15090(3)	71(2)
C(38)	6526(6)	-72(5)	10884(3)	35(1)
F(6)	9805(5)	3411(4)	11275(2)	71(1)
F(5)	9220(5)	3240(4)	10279(2)	73(1)
F(4)	10944(4)	2547(4)	10545(2)	72(1)
	10011(1)	2011(1)	10010(2)	12(1)

-	X	у	z	U(eq)
C(39)	6225(6)	-764(6)	10242(3)	44(2)
C(28)	14269(8)	5744(7)	11734(4)	64(2)
C(40)	- 7081(7)	-406(6)	9779(3)	46(2)
C(41)	8173(7)	704(6)	9958(3)	44(2)
C(43)	9596(8)	2649(6)	10690(3)	48(2)
C(21)	12261(10)	6784(7)	14961(3)	68(2)
C(27)	13823(9)	4497(8)	11666(4)	74(2)
C(10)	15429(7)	-245(6)	13551(3)	47(2)
CI(3)	16004(6)	4366(5)	10175(3)	230(2)
C(46)	14049(25)	4218(23)	10033(11)	126(8)

Table 4.2 - Atomic coordinates ($x \ 10^4$) and equivalent isotropic displacement parameters (Å² $x \ 10^3$) for [PtCl(CCl=PAr')(PPh_3)_2]. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

Bond lengths [Å]	and Angles [°]
Pt(1)-C(45)	2.030(5)
PI(1)-P(2)	2.3219(13)
Pt(1)-P(3)	2.3341(12)
Pt(1)-Cl(1)	2.3674(13)
P(3)-C(7)	1.819(5)
P(1)-C(1)	1.824(5)
P(3)-C(13)	1.836(5)
P(2)-G(31)	1.823(5)
P(2)-C(25)	1.830(5)
P(2)-C(19)	1.834(6)
C(30)-C(25)	1.382(7)
C(30)-C(29)	1.402(8)
C(7)-C(12)	1.387(7)
C(7)-C(8)	1.401(7)
C(45)-P(1)	1.688(5)
C(45)-CI(2)	1,767(5)
C(1)-C(2)	1.392(7)
C(1)-C(6)	1.395(7)
C(2)-C(3)	1.392(7)
C(8)-C(9)	1.384(7)
C(13)-C(14)	1.394(7)
C(13)-C(18)	1.397(7)
C(32)-C(33)	1.393(7)
C(32)-C(31)	1.401(7)
C(19)-C(20)	1.380(8)
C(19)-C(24)	1.387(8)
C(24)-C(23)	1.386(8)
C(25)-C(26)	1.370(8)
C(31)-C(36)	1.386(7)
C(4)-C(3)	1.373(8)
C(4)-C(5)	1.375(8)
C(26)-C(27)	1.410(9)
C(12)-C(11)	1.388(7)
C(23)-C(22)	1.364(10)
C(9)-C(10)	1.372(8)
C(6)-C(5)	1.386(7)
C(18)-C(17)	1.384(8)
C(14)-C(15)	1.379(8)
C(11)-C(10)	1.389(8)
C(16)-C(15)	1.356(8)
C(16)-C(17)	1.403(9)
C(33)-C(34)	1.373(8)
C(36)-C(35)	1.386(8)
C(34)-C(35)	1.385(8)
P(1)-C(37)	1.886(5)
F(3)-C(44)	1.350(6)
F(2)-C(44)	1.353(7)
F(1)-C(44)	1.335(7)
C(37)-C(38)	1.412(8)

Bond lengths [Å] and	Angles [°]
C(37)-C(42)	1.414(7)
C(29)-C(28)	1.343(10)
C(20)-C(21)	1.402(10)
C(42)-C(41)	1.377(8)
C(42)-C(43)	1.507(9)
C(44)-C(38)	1.501(8)
C(22)-C(21)	1.363(11)
C(38)-C(39)	1.379(8)
F(6)-C(43)	1.309(7)
F(5)-C(43)	1.339(6)
F(4)-C(43)	1.352(7)
C(39)-C(40)	1.378(8)
C(28)-C(27)	1.370(10)
C(40)-C(41)	1.379(9)
CI(3)-C(46)	1.82(2)
CI(3)-C(46)	1.83(2)
C(46)-CI(3)	1.83(2)
C(45)-Pt(1)-P(2)	92.66(13)
C(45)-Pt(1)-P(3)	93,93(13)
P(2)-Pt(1)-P(3)	173.39(5)
C(45)-Pt(1)-Cl(1)	177 59(13)
P(2)-Pt(1)-Cl(1)	89.34(5)
$P(3)_{P(1)_{-}Cl(1)}$	84.05(4)
C(7)-P(3)-C(1)	107.5(2)
O(7) P(3) O(13)	102.2(2)
C(1) P(3) C(13)	103.3(2)
C(1)-P(3)-C(13)	109.9(2)
C(1) P(2) P(1)	100.0[2]
C(1)-P(3)-Pt(1)	113.4(2)
C(13)-F(3)-F(1)	109.0(2)
C(31)-P(2)-C(25)	108.0(2)
C(31)-P(2)-C(19)	105.0(3)
C(25)-P(2)-C(19)	101.1(3)
C(31)-P(2)-P((1)	111.5(2)
C(25)-P(2)-Pt(1)	114.5(2)
C(19)-P(2)-Pt(1)	115.8(2)
C(25)-C(30)-C(29)	120.2(6)
C(12)-C(7)-C(8)	118.9(5)
C(12)-C(7)-P(3)	118.3(4)
C(8)-C(7)-P(3)	122.6(4)
P(3)-C(45)-Cl(2)	122.5(3)
P(3)-C(45)-Pt(1)	123.9(3)
CI(2)-C(45)-Pt(1)	113.6(2)
C(2)-C(1)-C(6)	118.4(5)
C(2)-C(1)-P(3)	120.1(4)
C(6)-C(1)-P(3)	121.5(4)
C(1)-C(2)-C(3)	120.1(5)
C(9)-C(8)-C(7)	120.2(5)
C(14)-C(13)-C(18)	118.1(5)
C(14)-C(13)-P(3)	122.8(4)
C(18)-C(13)-P(3)	118.8(4)

Bond lengths [Å] and A	Angles [°]
C(33)-C(32)-C(31)	119.1(5)
C(20)-C(19)-C(24)	118.4(6)
C(20)-C(19)-P(2)	124.1(5)
C(24)-C(19)-P(2)	117.5(4)
C(23)-C(24)-C(19)	121.0(6)
C(26)-C(25)-C(30)	119.0(5)
C(26)-C(25)-P(2)	120.2(4)
C(30)-C(25)-P(2)	120.7(4)
C(36)-C(31)-C(32)	119.7(5)
C(36)-C(31)-P(2)	116.9(4)
C(32)-C(31)-P(2)	123.4(4)
C(3)-C(4)-C(5)	119.1(5)
C(4)-C(3)-C(2)	121.1(5)
C(25)-C(26)-C(27)	120.0(6)
C(7)-C(12)-C(11)	121.0(5)
C(22)-C(23)-C(24)	120.0(7)
C(10)-C(9)-C(8)	120.0(5)
C(5)-C(6)-C(1)	120.4(5)
C(4)-C(5)-C(6)	120.9(6)
C(17)-C(18)-C(13)	120.3(5)
C(15)-C(14)-C(13)	121.2(5)
C(12)-C(11)-C(10)	118.9(5)
C(15)-C(16)-C(17)	119.7(6)
C(16)-C(15)-C(14)	120.5(6)
C(18)-C(17)-C(16)	120.1(6)
C(34)-C(33)-C(32)	120.6(5)
C(35)-C(36)-C(31)	120.5(5)
C(33)-C(34)-C(35)	120.5(5)
C(34)-C(35)-C(36)	119.6(5)
C(45)-P(3)-C(37)	104.9(2)
C(38)-C(37)-C(42)	115.5(5)
C(38)-C(37)-P(3)	119.2(4)
C(42)-C(37)-P(3)	125.3(4)
C(28)-C(29)-C(30)	120.6(6)
C(19)-C(20)-C(21)	120.0(0)
C(41)-C(42)-C(37)	121.4(6)
C(41)-C(42)-C(43)	113.9(5)
C(37)-C(42)-C(43)	124.7(5)
E(1)-C(44)-E(3)	105.7(5)
F(1)-C(44)-F(2)	105.9(5)
F(3)-C(44)-F(2)	105.3(5)
F(1)-C(44)-C(38)	112.8(5)
F(3)-C(44)-C(38)	112.0(5)
and the second	112.0(5)
F(2)-C(44)-C(38)	120.1(7)
C(21)-C(22)-C(23)	
C(39)-C(38)-C(37)	121.9(5)
C(39)-C(38)-C(44)	116.6(5)
C(37)-C(38)-C(44)	121.3(5)
C(40)-C(39)-C(38)	120.6(6)
C(29)-C(28)-C(27)	120.2(6)

Bond lengths [Å] and	Angles [°]
C(39)-C(40)-C(41)	118.8(6)
C(42)-C(41)-C(40)	121.2(5)
F(6)-C(43)-F(5)	107.0(6)
F(6)-C(43)-F(4)	105.6(6)
F(5)-C(43)-F(4)	104.3(5)
F(6)-C(43)-C(42)	116.3(5)
F(5)-C(43)-C(42)	110.4(5)
F(4)-C(43)-C(42)	112.4(6)
C(22)-C(21)-C(20)	120.4(7)
C(28)-C(27)-C(26)	120.0(8)
C(9)-C(10)-C(11)	121.0(6)
C(46)-Cl(3)-C(46)#1	75.5(12)
Cl(3)-C(46)-Cl(3)#1	104.5(12)

Table 4.3 - Bond lengths [Å] and angles [°] for [PtCl(CCl=PAr')(PPh₃)₂]

	U11	U22	U33	U23	U13	U12
Pt(1)	24(1)	20(1)	27(1)	10(1)	0(1)	7(1)
P(3)	23(1)	20(1)	26(1)	10(1)	1(1)	7(1)
P(2)	26(1)	21(1)	28(1)	12(1)	7(1)	10(1)
C(30)	36(3)	35(3)	63(4)	31(3)	16(3)	14(3)
C(7)	29(3)	30(3)	21(3)	8(2)	3(2)	11(2)
C(45)	25(3)	21(3)	31(3)	15(2)	9(2)	11(2)
C(1)	17(2)	31(3)	28(3)	14(2)	3(2)	8(2)
C(8)	35(3)	40(3)	32(3)	17(3)	4(2)	16(3)
C(13)	32(3)	21(3)	29(3)	13(2)	4(2)	10(3)
C(32)	33(3)	29(3)	39(3)	15(3)	7(2)	14(2)
C(19)	48(4)	19(3)	28(3)	- 8(2)	6(2)	12(2)
C(24)	47(4)	26(3)	33(3)	8(2)	-1(3)	-1(3)
C(25)	25(3)	35(3)	34(3)	18(3)	8(2)	8(2)
C(31)	32(3)	30(3)	40(3)	18(3)	14(2)	18(2)
C(4)	28(3)	49(4)	34(3)	19(3)	2(2)	8(3)
C(3)	30(3)	52(4)	27(3)	10(3)	3(2)	15(3)
C(26)	53(4)	38(4)	57(4)	3(3)	31(3)	-7(3)
C(12)	28(3)	32(3)	42(3)	15(3)	-1(2)	3(2)
C(23)	74(5)	31(3)	44(4)	16(3)	-7(3)	-9(3)
C(9)	48(4)	66(5)	37(4)	25(3)	0(3)	29(3)
C(5)	40(4)	20(3)	41(4)	28(2)	12(3)	TU(3)
C(5)	47(4)	37(4)	57(4)	28(3)	10(3)	5(3)
C(18)	33(3)	34(3)	36(3)	11(3)	9(3)	4(3)
C(14)	34(3)	33(3)	41(4)	10(3)	6(3)	15(3)
C(11)	26(3)	53(4)	41(4)	9(3)	1(3)	7(3)
C(16)	61(4)	41(4)	29(3)	1(3)	5(3)	- 0(3)
C(15)	54(4)	33(3)	41(4)	2(3)	7(3)	13(3)
C(17)	35(3)	52(4)	36(4)	4(3)	-3(3)	-9(3)
C(33)	39(4)	48(4)	56(4)	27(3)	9(3)	27(3)
C(36)	42(4)	53(4)	63(4)	42(4)	26(3)	29(3)
C(34)	37(4)				22(3)	36(3)
C(35)	46(4)	74(5)	80(5)		39(4)	37(4)
CI(2)	34(1)	32(1)			9(1)	
P(3)	27(1)	41(1)	and the second se	and the second se	4(1)	13(1)
F(3)	52(2)					
F(1)	43(2)			35(2) 21(2)		-29(2) -21(2)
C(37)	30(3)	44(3)	24(3)	17(3)	5(2)	15/3)
C(29)	38(4)	61(5)	83(6)		11(3)	9(3)
C(20)					14(3)	41(4)
C(42)				19(3)	4(2)	15(3)
C(44)	34(3)	64(5)	37(4)	22(3)	-6(3)	
C(22)	136(8)	35(4)		11(3)	-16(5)	
C(38)	29(3)	45(4)	35(3)	20(3)	-1(2)	11(3)
F(6)	102(3)	48(2)	49(3)			-6(2)
F(5)	106(3)	60(3)	61(3)	41(2)	-4(2)	17(2)
F(4)	57(3)	71(3)	91(3)	38(3)	26(2)	5(2)

	U11	U22	U33	U23	U13	U12
C(39)	35(3)	52(4)	44(4)	16(3)	2(3)	10(3)
C(28)	56(5)	76(6)	58(5)	28(4)	32(4)	0(4)
C(40)	45(4)	65(5)	29(3)	8(3)	2(3)	20(3)
C(41)	45(4)	65(4)	29(3)	21(3)	8(3)	20(3)
C(43)	67(5)	55(4)	29(4)	22(3)	13(3)	19(4)
C(21)	142(8)	50(5)	31(4)	12(3)	18(4)	59(5)

Table 4.4 - Anisotropic displacement parameters ($Å^2 \ge 10^3$) for [PtCl(CCl=PAr')(PPh_3)_2]. The anisotropic displacement factor exponent takes the form: -2 pi² [$h^2 a^2 U11 + ... + 2 h k a^* b^* U12$]

condition restor	x	V	Z	U(eq)
H(30A)	12595(6)	6619(5)	12975(3)	49
H(2A)	9561(5)	1302(5)	14213(2)	35
H(8A)	12081(6)	-1231(5)	13858(3)	40
H(32A)	9859(6)	5435(5)	12354(3)	-38
H(24A)	14129(6)	4973(5)	13784(3)	45
H(4A)	7267(6)	-1421(6)	14923(3)	43
H(3A)	8101(6)	648(6)	14973(3)	43
H(26A)	12589(7)	3179(6)	12053(3)	65
H(12A)	13712(6)	1260(5)	12879(3)	41
H(23A)	15410(8)	6310(6)	14744(3)	64
H(9A)	14412(6)	-1437(6)	14036(3)	55
H(6A)	9324(6)	-2236(5)	13331(3)	44
H(5A)	7910(7)	-2852(6)	14109(3)	54
H(18A)	8079(6)	-1142(5)	12325(3)	42
H(14A)	12170(6)	-1488(5)	12182(3)	42
H(11A)	16042(6)	1038(6)	13052(3)	50
H(16A)	8959(7)	-3579(6)	10793(3)	58
H(15A)	11362(7)	-3010(5)	11222(3)	53
H(17A)	7304(7)	-2620(6)	11337(3)	56
H(33A)	7486(6)	5611(6)	12219(3)	51
H(36A)	8622(6)	3673(6)	13724(3)	53
H(34A)	5760(7)	4948(6)	12875(3)	63
H(35A)	6305(7)	3956(7)	13622(3)	68
H(29A)	14150(7)	7370(7)	12261(4)	66
H(20A)	10477(8)	5907(6)	14292(3)	62
H(22A)	14239(11)	7443(6)	15475(3)	85
H(39A)	5438(6)	-1479(6)	10122(3)	52
H(28A)	14877(8)	6052(7)	11446(4)	77
H(40A)	6925(7)	-904(6)	9353(3)	56
H(41A)	8710(7)	981(6)	9642(3)	52
H(21A)	11787(10)	7237(7)	15261(3)	81
H(27A)	14138(9)	3960(8)	11337(4)	89
H(10A)	16357(7)	-353(6)	13613(3)	56

Table 4.5 - Hydrogen coordinates (x 104) and isotropic displacement parameters ($Å^2$ x 103) for[PtCl(CCl=PAr')(PPh_3)_2]

4.3.2 Reaction between ArP=CCl₂ and Pt(PPh₃)₄

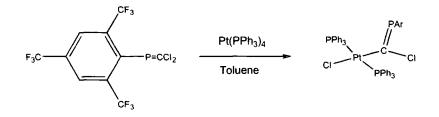
In an analogous reaction to the previous one the Fluoromes phosphaalkene was added to a solution of $Pt(PPh_3)_4$ in toluene and the solution was allowed to stir. The solution became dark orange in colour.

The ³¹P NMR spectrum showed the formation of a number of new peaks; a septet with platinum satellites ($\delta = 197.8$ ppm ²J_{P-Pt} = 404.2 Hz) which can be assigned to the phosphaalkene ligand (⁴J_{P-F} = 18.9 Hz), and two peaks associated with the PPh₃ groups still bonded to the platinum. The first PPh₃ group shows no P-P coupling ($\delta = 15.67$ ppm ¹J_{P-Pt} = 4015.0 Hz) (singlet and platinum satellites), but the second PPh₃ ligand does show some P-P interaction ($\delta = 18.22$ ppm ¹J_{P-Pt} = 1923.8 Hz, ²J_{P-P} = 44.6 Hz) (doublet with platinum satellites). There is also a signal for free PPh₃ ($\delta = -2.67$ ppm).

This reaction is analogous to that of the compound containing Ar' (see Section 4.3.1). The same effect of differing coupling constants for the two PPh₃ groups can clearly be seen. Unfortunately, no crystallographic data were obtained due to a poor crystal structure solution. A number of crystals were submitted for structure solution and none of them gave a satisfactory solution. In one case the solution appeared to be a compound with the PPh₃ ligands *cis* to each other, which is inconsistent with the NMR studies which indicated a compound with the PPh₃ groups *trans* to each other at all times.

The ¹⁹F NMR spectrum shows the formation of a new doublet ($\delta = -58.0$ ppm, ⁴J_{P-F} = 18.9 Hz). Over a period of time, however, a number of new peaks appeared. Unfortunately these were not assignable to anything indicating the formation of a single new product.

It is worth noting that although there is a difference in chemical shift for the compounds, the coupling constants between the phosphorus atom and the platinum are almost identical. This would imply that the *para* CF_3 group on the compound has little or no influence over bonding or the coupling constant.



Equation 4.6 – Preparation of trans-[PtCl(CCl=PAr)(PPh₃)₂]

4.3.2.1 Molecular structure of trans-[PtCl(CCl=PAr)(PPh₃)₂]

Orange plate-like crystals were grown from toluene using the layering technique described in Appendix 1. The crystals were submitted for X-ray structural characterisation.

The data collection and structure solution was performed by Miss C. Broder.

Unfortunately the structure solution of this compound is not complete and cannot be included. A preliminary ORTEP diagram is shown below. The R value for the structural refinement is 4.7% although the residual electron density peaks in the density map are of the order of two electrons which is too great to be ignored.

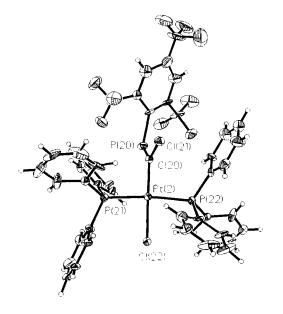
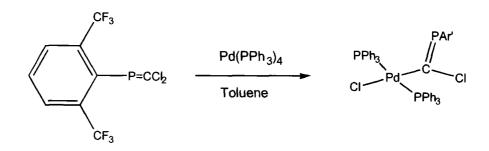


Figure 4.3 – Thermal ellipsoid diagram 150(2)K (50% probability) showing trans-[PtCl(CCl=PAr)(PPh₃)₂]

4.3.3 Reaction between Ar'P=CCl₂ and Pd(PPh₃)₄

Ar'P=CCl₂ was added to a solution of Pd(PPh₃)₄ in toluene and the reaction was allowed to stir. The solution changed colour from bright yellow to dark orange. The ³¹P NMR spectrum showed the formation of a new septet in the spectrum. The chemical shift value for this compound is $\delta = 199.5$ ppm (⁴J_{P-F} = 24.8 Hz). The ¹⁹F NMR spectrum show the formation of a new doublet, $\delta = -59.6$ ppm (⁴J_{P-F} = 24.7Hz).



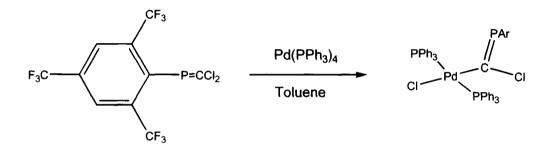
Equation 4.7 – Preparation of trans-[PdCl(PPh₃)₂(CCl=PAr')]

From the ³¹P NMR spectrum it is apparent that a similar type of reaction has occurred to that in the Platinum reaction see Section 4.3.1. This palladium compound appears to be comparatively more unstable than the analogous Platinum compound, and after only a few hours the NMR spectrum becomes more complex as other species are formed.

Unfortunately the crystals grown of this product were not suitable for X-ray crystallographic studies.

4.3.4 Reaction between ArP=CCl₂ and Pd(PPh₃)₄

ArP=CCl₂ was added to a solution of Pd(PPh₃)₄ in toluene and the reaction was allowed to stir. The solution changed colour from bright yellow to dark orange. The ³¹P NMR spectrum showed the formation of a new septet in the spectrum which correlates to the formation of a similar type of compound to those described in Section 4.3.3. The chemical shift value for the new compound is $\delta = 195.3$ ppm (⁴J_{P-F} = 22.4 Hz). The ¹⁹F NMR spectrum shows the formation of a new doublet and singlet, corresponding to the new compound. The chemical shift values are $\delta = -54.0$ ppm (⁴J_{P-F} = 22.2Hz) (doublet) and $\delta = -63.8$ ppm (singlet).



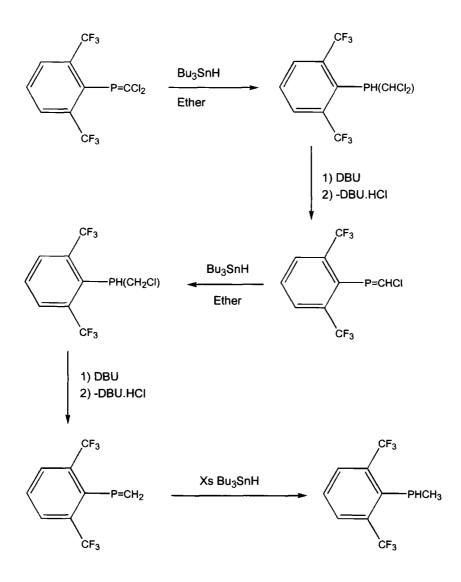
Equation 4.8 – Preparation of trans-[PdCl(PPh₃)₂(CCl=PAr)]

After a short period of time a doublet formed in the spectrum at a higher frequency to that of the new septet. This new compound was unstable and after only a matter of minutes the signal was lost from the spectrum and the formation of a number of new peaks was visible, all of which were unassignable.

4.4 Synthesis of other phosphaalkenes

4.4.1 Reaction between Ar'P=CCl₂, Bu₃SnH and DBU

An NMR scale reaction was carried out to try and determine whether or not it was possible to create the two phosphaalkenes Ar'P=C(H)Cl and $Ar'P=CH_2$. The standard synthesis of these two compounds is the reaction between RPH₂, base and CH_2Cl_2 ⁵. This works for other large aryl groups such as supermesitylene and mesitylene, but not for Fluoroxyl or Fluoromes.



Equation 4.9 - Preparation of a number of phosphaalkenes

It has been shown that the phosphaalkene RP=C(H)Cl can lose HCl when irradiated with UV. With this in mind, an attempt to prepare Ar'P=C(H)Cl via this route was made.

Bu₃SnH was added dropwise into a solution containing Ar'P=CCl₂ and DBU in ether, reducing the P=C bond and forming the compound Ar'PH-CHCl₂ (δ = 38.6ppm). It then reacted with the DBU in solution to form the phosphaalkene Ar'P=C(H)Cl. (δ = 252.3ppm).

This compound then in turn was reduced again by the Bu₃SnH to form Ar'PH-CH₂Cl (δ = -56.6ppm). It then reacted with DBU to form the phosphaalkene Ar'P=CH₂ (δ = 288.0 ppm). If an excess of Bu₃SnH had been added, the final product would have been Ar'PH-CH₃ because without chlorine atoms remaining on the phosphorus or carbon atoms, it wouldn't react with DBU.

Going from Ar'P=CCl₂ to Ar'P=C(H)Cl and Ar'P=CH₂ there is a shift to higher frequency in the ³¹P NMR spectrum.

Due to the yields in the formation of the initial phosphaalkene (Ar'P=CCl₂) these reactions were not performed on a larger scale due to the quantity of available starting material.

4.5 Experimental

4.5.1 Preparation of [PtCl(CCl=PAr')(PPh₃)₂]

A solution of Ar'P=CCl₂ (0.5g 1.5mmol) in toluene (50ml) was added to a solution of Pt(PPh₃)₄ (1.89g 1.5mmol) in toluene (50ml) and the solution was allowed to stir. The solution turned dark orange in colour and an orange precipitate was formed. The product was then recrystallised from a solution of toluene.. Yield 1.2g (73%) ³¹P (CH₂Cl₂) δ = 201.9 ppm (²J_{P-Pt} = 406 Hz) (Septet with Pt satellites)

$$Ar'P=CCl_2 \xrightarrow{Pt(PPh_3)_4} PtCl(CCl=PAr')(PPh_3)_2$$

4.5.2 Preparation of [PtCl(CCl=PAr)(PPh₃)₂]

A solution of ArP=CCl₂ (0.5g 1.2mmol) in toluene (50ml) was added to a solution of Pt(PPh₃)₄ (1.49g 1.2mmol) in toluene (50ml) and the solution was allowed to stir. The solution turned dark orange in colour and an orange precipitate was formed. The product was then recrystallised from a solution of toluene. ³¹P: δ = 197.8ppm ¹J_{P-Pt} = 202 Hz (⁴J_{P-F} = 23.8 Hz) (Singlet with Pt Satellites).¹⁹F δ = 55.9 ppm (23.7 Hz) (doublet), δ = -61.1ppm (singlet). Yield 0.6g (57%).

ArP=CCl₂ $\xrightarrow{Pt(PPh_3)_4}$ PtCl(CCl=PAr)(PPh_3)₂

4.5.3 Preparation of [PdCl(CCl=PAr')(PPh₃)₂]

A solution of Ar'P=CCl₂ (0.5g 1.5mmol) in toluene (50ml) was added to a solution of Pd(PPh₃)₄ (1.73g 1.5mmol) in toluene (50ml) and the solution was allowed to stir. The solution turned dark orange in colour. ³¹P: δ = 199.5 ppm (⁴J_{P-F} = 24.8 Hz) (multiplet), ¹⁹F: δ = -59.6 ppm (⁴J_{P-F} = 24.7Hz) (doublet).

Ar'P=CCl₂ $\xrightarrow{Pd(PPh_3)_4}$ PdCl(CCl=PAr')(PPh_3)₂

4.5.4 Preparation of [PdCl(CCl=PAr)(PPh₃)₂]

A solution of ArP=CCl₂ (0.5g 1.2mmol) in toluene (50ml) was added to a solution of Pd(PPh₃)₄ (1.73g 1.5mmol) in toluene (50ml) and the solution was allowed to stir. The solution turned dark orange in colour. ³¹P: δ = 195.3 ppm (⁴J_{P-F} = 22.4 Hz) (singlet), ¹⁹F: δ = -54.0 ppm (⁴J_{P-F} = 22.2 Hz) (doublet) and δ = -63.8 ppm (singlet).

 $ArP=CCl_2 \xrightarrow{Pd(PPh_3)_4} PdCl(CCl=PAr)(PPh_3)_2$

¹ V. D. Romanenko., M. Sanchez., T. V. Sarina., M-R. Mazieres., R. Wolf., *Tetrahedron Lett.*, **33**, 2981, 1992.

² R. J. Angelici., H. Jun., V. G. Young., Organometallics, 1994, 13, 2444.

³ H. P. Goodwin., Ph.D. Thesis., Durham, 1990.

⁴ J. F. Nixon., *Chem. Rev.*, 1988, **88**, 1327.

⁵ R. Appel., C. Casser., M. Immelkeppel., F. Knoch., Angew. Chem. Ed. Engl., 1984, 23, 895.

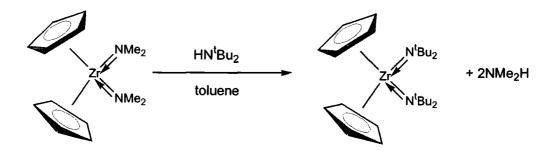
Chapter 5

-

Synthesis and characterisation of novel P(I) compounds

5.1 Introduction

Metal phosphides have been known in the literature for some time now¹. There have been a number of synthetic strategies employed, although none are analogous to a substitution reaction commonly used in metal-amide chemistry. In metal-amide chemistry, substitution of the amide ligand is possible by the reaction with an amine which is more acidic than the amine formed upon protonation of the amide ligand ($HN^{t}Bu_{2}$ is more acidic than $HNMe_{2}$).



Equation 5.1 – Substitution of amines in metal-amide chemistry

No reaction between PPh_2H and a metal amide has been reported as far as we are aware. This is probably due to the weakly acidic proton on PPh_2H , rather than availability of the reagent.

The most commonly used reagent in P(I) chemistry is LiPPh₂ which is formed by the reaction of BuLi with PPh₂H. This reagent is then used in reaction with metal chloride bonds in an analogous way to lithiated amides, releasing LiCl and forming the desired metal phosphide.

5.2 Starting materials

5.2.1 Fluoroxyl disubstituted phosphanes

Ar'Ar''PCl and Ar'Ar''PH were both prepared as described in sections 2.2.8 and 2.2.9, where both compounds were used in the attempt to make P(I) compounds. Ar' has the major disadvantage over Ar in that it has a potential reaction site easily accessible by both electrophiles and nucleophiles. All attempts to make stable P(I) complexes have resulted in a large mixture of products, probably due to reaction of the P(I) species with other components of the reaction mixture.

5.2.2 Fluoromes disubstituted phosphanes

 Ar_2PCl and Ar_2PH were both prepared as described before in sections 2.2.11 and 2.2.12. Both Ar_2PCl and Ar_2PH can be used to produce relatively stable P(I) complexes although the stability of some of the products is solvent dependent (see section 5.4). The stability of these compounds is much greater than that of the Fluoroxyl derivative, and they can be isolated and characterised. Ar_2PLi has not been isolable, however, due to the reasons discussed later (see sections 5.4.1 through 5.4.3).

5.3 The anionic P(I) species Ar₂P⁽⁻⁾

The phosphorus (I) species $Ar_2P^{(-)}$ is very intensely coloured. It is dichroic, appearing dark blue ($\lambda_{max} = 583$ nm , 599nm, 615nm) in concentrated solutions and red ($\lambda_{max} = 383$ nm) in weaker concentrations. The intense blue colour is an indication of the formation of the species and it has been used qualitatively to see if the species has been produced. The species can be prepared by two basic methods:

- 1) Deprotonation of the disubstituted phosphane Ar_2PH . This can be observed with a reasonably weak base (e.g. pyrrolidine $pK_b = 11.3$). With weaker bases such as NEt₃ ($pK_b = 9.81$) the blue colour indicating the existence of the species can be facilitated if the solution is cooled in liquid nitrogen (see section 5.3.1).
- Removal of the chlorine from the disubstituted phosphane Ar₂PCl in a redox reaction with a number of different low oxidation state metals compounds [e.g. Pt(0), Pd(0)]

UV studies on some of the blue solutions formed in these reactions (bases used NEt₃, NⁱPr₃, DBU) showed that the blue colours were not identical. The maximum absorbance for the three solutions tested varied from 583nm to 615nm. This change implies that the anion and solvent may have some bearing on the colour.

The colour may be due to internal electron delocalisation in the $Ar_2P^{(-)}$ anion, possibly between π and π^* orbitals, though no modelling of the anion was performed.

In the literature² the standard preparation of a P(I) species is the lithiation of diphenyl phosphane, which forms the stable, yellow crystalline product LiPPh₂.

$$Ph_2PH \xrightarrow{BuLi} \left[Ph_2P^{(-)}Li^{(+)} \right]$$

Stable yellow solid

Equation 5.2 – Synthesis of $PPh_2^{(-)}Li^{(+)}$

The lithiation of Ar₂PH, however, presents a problem not encountered in the above example (equation 5.2). As seen in the lithiation of Fluoromes (see section 1.4) care must be taken to ensure that there is not an excess of BuLi otherwise there is the explosive risk of the formation of LiF. In the formation of $Ar_2P^{(-)}$ an extreme canonical form can be drawn which implies that some of the electron density associated with the negative charge of the P⁽⁻⁾ species is delocalised on to the CF₃ groups. It then makes them even more susceptible to attack by the electrophilic Li⁽⁺⁾. In the formation of Ar_2PLi a species is being formed which is very reactive towards itself, leading to the formation of coupling products and LiF.

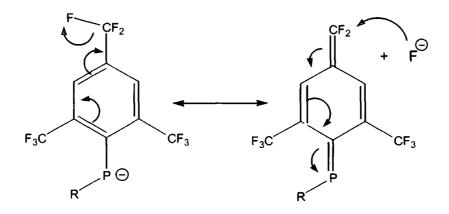


Figure 5.1 – A canonical form of RP⁽⁻⁾Fmes

The stability of the Ar_2PLi species is solvent dependent, and it has proved to be impossible to isolate. Due to the instability of this compound and its potentially explosive nature, characterising NMR data were not recorded.

5.3.1 The appearance of the blue colour at low temperature

Equilibrium constants for acids and bases in solution determine the protondonating (or accepting) ability at equilibrium. In a situation where the dissociation constant for the acid is much greater than that for the base, there will be little or no reaction (see equation 5.2).

Ar₂PH + NEt₃
$$\xrightarrow{k_a}$$
 HNEt₃⁽⁺⁾ + Ar₂P⁽⁻⁾

Equation 5.3 – Equilibrium in the reaction between Ar_2PH and NEt_3

In the reaction between Ar_2PH and NEt_3 at room temperature there is no sign of any blue colour, so it is reasonable to assume that NEt_3 is not a strong enough base to remove a proton from Ar_2PH in the solution (toluene). The equilibrium constants for the reaction K_a and K_b are defined in Figure 5.2.

Figure 5.2 – Equilibrium constants for the reaction between Ar₂PH and NEt₃

The concentration of the Ar_2PH and NEt_3 is much greater than that of the anions and thus there is no colour visible. When the solution is cooled, however, a blue colour is observed. The temperature at which this colour is apparent depends on the solvent, and the base involved (not always NEt_3). The colder the temperature the more intense the colour.

The blue colour is very intense and if, as predicted, the $Ar_2P^{(\cdot)}$ anion is coloured due to charge transfer, then only a very small amount need be present in the solution to produce a visible colour.

At room temperature there will be "some" of the anions present as is required if we assume an equilibrium. The concentration is so small and the length of time of their existence is so short that the blue colour is not visible. As the solution is cooled, the rate of exchange is lowered. This means that the length of time in which the very small concentration of these anions is present, becomes longer.

As the solution is cooled, there comes a point where enough of the $Ar_2P^{(-)}$ anion is present that it can be detected. To prove the existence of anions in the solution, if a conductimetry experiment were to be conducted, as the solution cooled, the conductance of the solution should be seen to rise. This type of experiment was not possible in the time frame of the experimental for this thesis.

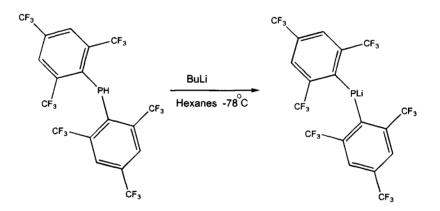
This effect shows the existence of an equilibrium even when a strong acid and weak base are mixed together.

5.4 Reactions between Ar₂PH and selected bases

5.4.1 Attempted preparation of Ar₂PLi (in hexanes)

BuLi was added to a solution of Ar_2PH in hexanes at room temperature with the reaction vessel open to the mercury bubbler at all times. The solution became a very intense purple colour which almost instantly dissipated. The resulting solution showed no signs of any new phosphorus species according to the solution ³¹P NMR spectrum.

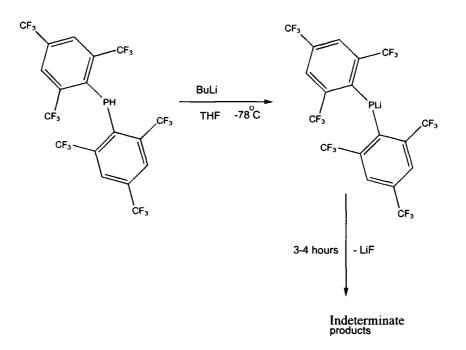
BuLi was added to a solution of Ar_2PH in hexane at -78°C. The solution turned a very pale pink colour and over time did not darken. Upon warming the pink colour dissipated at approximately -30°C and the ³¹P NMR spectrum showed no products other than the starting material present in the final solution.



Equation 5.4 – Possible product formed by the lithiation in hexanes of Ar_2PH at $-78^{\circ}C$

5.4.2 Preparation of Ar₂PLi (in THF)

BuLi was added to Ar₂PH in a solution of THF at -78°C. The solution turned a deep blue colour and was allowed to warm to room temperature, the solution remaining deep blue in colour. After approximately two hours, the solution turned dark brown in colour and there were no tangible products distinguishable in the ³¹P NMR spectrum (other than the starting material). The ¹⁹F NMR spectrum of the final solution showed the formation of a number of new species, none of which were distinguishable. Due to inherent instability of the compound, it was decided not to perform an NMR experiment on the blue solutions and so there are no characterising data on this compound.



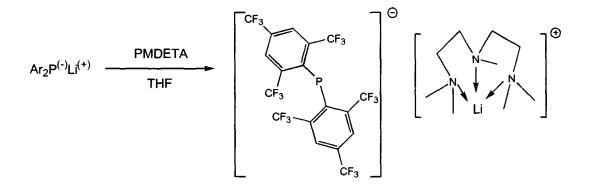
Equation 5.5 – Lithiation in THF of Ar₂PH at -78°C

5.4.3 Attempted stabilisation of Ar₂Li using PMDETA

PMDETA (pentamethyldiethylenetriamine) has been reported in the literature to stabilise the species $\text{Li}(\text{PPh}_3)_2$,³ and has also been used extensively by Davidson *et al* ⁴to stabilise lithiated species in solution.

BuLi was added to a solution containing an equimolar ratio of Ar_2PH and PMDETA in toluene at -78°C. The solution turned a dark blue colour and was allowed to warm to room temperature. The solution was allowed to stir for 30 minutes and then was placed in the freezer at -30°C in an attempt to freeze out the product. After eight hours the blue colour had dissipated from the solution and a brown slurry was left.

Again, due to the instability it was decided not to perform an NMR experiment on the blue solution so there are no NMR data on this compound.



Equation 5.6 – Predicted products formed in the lithiation Ar_2PH using PMDETA to stabilise the lithium ion

The use of PMDETA was an attempt to coordinate the lithium ion in the product, and thus prevent it from attacking the CF_3 groups on a neighbouring molecule. This appears to slow down the process but does not prevent coupling and loss of LiF.

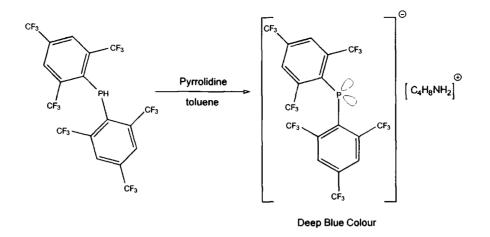
Again the ³¹P NMR spectrum of the resulting final solution (not blue) showed no new species, whilst the ¹⁹F NMR spectrum showed the formation of a number of indeterminate new fluorine species.

5.4.4 Reaction between Ar₂PH and pyrrolidine

Equimolar quantities of Ar_2PH and pyrrolidine were reacted together in toluene and a pale blue colour was observed. Upon being heated to $80^{\circ}C$ the colour was almost entirely removed. The colour returned to the solution when cooled. The reaction was cooled in the freezer which resulted in the solution becoming more intensely coloured and resulted in the formation of crystals.

Upon warming to room temperature, the crystals turned from dark blue to a pale red colour and degenerated into a non-crystalline material before redesolving.

On examination under the microscope, under cooled conditions the blue crystals were not suitable for X-ray crystallography analysis.

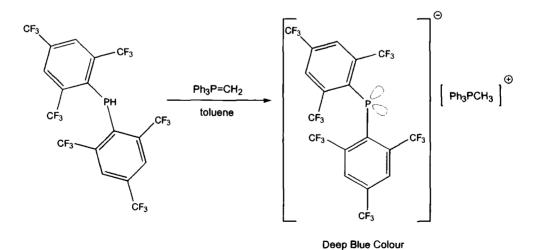


Equation 5.7 – Speculated products formed in the synthesis of $Ar_2P^{(-)}$ [pyrrolidineH]⁽⁺⁾

5.4.5 Reaction between Ar₂PH and Ph₃P=CH₂

A solution of Ar_2PH in toluene was added to an equimolar solution of the unstabilised ylide ($Ph_3P=CH_2$) in toluene. The solution produced a deep blue colour. From this reaction, very deep red crystals were formed and the compound was characterised by X-ray analysis. This reaction was performed by Miss S. Lamb.

The ³¹P NMR solution spectrum shows the formation of $Ar_2P^{(-)} \delta = 21.0$ ppm (multiplet, ⁴J_{P-F} = 32.6 Hz) and the phosphonium salt $[Ph_3PCH_3]^{(+)} \delta = 21.6$ ppm. The ¹⁹F NMR spectrum shows a doublet and a singlet $\delta = -61.2$ ppm (⁴J_{P-F} = 32.6 Hz) and $\delta = -63.3$ ppm, respectively.



Equation 5.8 – Synthesis of $Ar_2P^{(-)}[PPh_3CCH_3]^{(+)}$

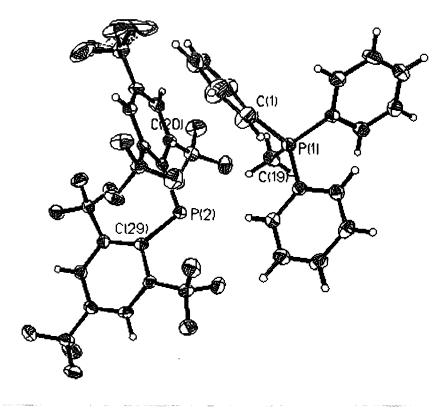


Figure 5.3 – Thermal Ellipsoid diagram for Ar₂P⁽⁻⁾[PPh₃CCH₃]⁽⁺⁾

Data were collected on a Siemens 3-circle diffractometer with a CCD area detector, ω scan mode $2\theta \le 60.2^{\circ}$. The structure was solved by direct methods and refined by full-matrix least squares against F^2 . Lists of crystal data and refinement parameters, anisotropic displacement parameters, bond lengths and angles, and atomic coordinates are given in tables 5.1 to 5.5.

Crystal data and	structure refinement
Identification code	Ar ₂ P-PPh ₃ CH ₃
Empirical formula	G37 H20 F18 P2
Formula weight	868.47
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 11.532(2) Å, a = 110.21(3) °.
and the second states of the second	b = 12.625(3) Å, β = 102.85(3) °.
	$c = 13.579(3) Å$, $\gamma = 96.96(3)$ °.
Volume	1765.7(6) Å ³
Z	2
Number of reflections used	Calculation of cell = 512
	Total = 12640
	Unique = 9504
	Obs [l>2σ] = 4709
the state of the second second second	000[120] 1100
Crystal description	cube shaped
Crystal colour	dark red
Density (calculated)	1.633 g/cm ³
Absorption coefficient	2.47 cm ⁻¹
F(000)	868
Crystal size	0.1 x 0.2. x 0.1 mm
Theta range for data collection	1.67 to 30.09 °.
Index ranges	-14<=h<=16, -17<=k<=12, -10<=l<=18
Experiment device	Siemens SMART
Experiment methods	ω scans
Reflections collected	12640
Independent reflections	9054 [R(int) = 0.0290]
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	9044 / 0 / 537
Goodness-of-fit on F2	0.929
Final R indices [I>2o(I)]	$R_1 = 0.0461$, $wR_2 = 0.0758$
R indices (all data)	R ₁ = 0.1182, wR ₂ = 0.0999
Largest diff. peak and hole	0.374 and -0.319 e.(Å-3)

Table 5.1 - Crystal data and structure refinement for $(Ar_2P)(PPh_3CH_3)$

	x	y	Z	U(eq)
P(1)	7796(1)	7494(1)	2572(1)	24(1)
C(1)	6834(2)	6318(2)	2654(2)	26(1)
C(2)	7325(3)	5587(2)	3118(2)	34(1)
P(2)	6594(2)	9427(1)	2104(2)	24(1)
C(3)	6584(3)	4633(2)	3104(2)	40(1)
C(5)	4841(3)	5115(3)	2175(3)	54(1)
C(6)	5580(3)	- 6074(2)	2180(2)	43(1)
C(7)	8391(2)	6931(2)	1424(2)	22(1)
C(8)	7930(2)	5807(2)	656(2)	33(1)
C(9)	8391(3)	5402(2)	-229(2)	39(1)
C(10)	9308(2)	6116(2)	-350(2)	33(1)
C(11)	9768(2)	7230(2)	406(2)	30(1)
C(12) C(13)	6937(2)	2525(2)	2206(2)	28(1)
C(14)	6584(2)	8535(2)	2386(2)	22(1)
C(15)	5962(2)	9459(2)	1251(2)	30(1)
C(16)	5683(2)	10212(2)	2148(2)	32(1)
C(17)	6015(2)	10123(2)	3153(2)	32(1)
C(18)	6650(2)	9289(2)	3282(2)	29(1)
C(19)	9028(2)	8190(2)	3791(2)	31(1)
C(20)	8466(2)	7916(2)	6448(2)	19(1)
C(21)	9561(2)	7506(2)	6568(2)	23(1)
F(101)	11696(1)	7718(1)	6865(1)	43(1)
F(102)	11097(1)	9177(1)	7807(1)	40(1)
F(103)	10834(1)	8749(1)	6083(1)	36(1)
C(22)	9569(2)	6367(2) 5581(2)	6452(2)	27(1)
C(24)	7395(2)	5918(2)	5972(2)	24(1)
C(25)	7369(2)	7048(2)	6068(2)	20(1)
F(107)	6041(1)	7709(1)	4921(1)	39(1)
F(108)	5240(1)	6325(1)	5293(1)	39(1)
F(109)	5796(1)	8044(1)	6518(1)	36(1)
C(26)	10783(2)	8286(2)	6837(2)	28(1)
C(28)	6133(2)	7294(2)	5705(2)	28(1)
C(29)	7798(2)	10091(2)	7666(2)	21(1)
C(30)	7831(2)	9940(2)	8682(2) 9527(2)	22(1)
C(31) C(32)	7114(2)	10730(2) 11692(2)	9440(2)	24(1) 24(1)
C(33)	6991(2)	11843(2)	8463(2)	23(1)
C(34)	7294(2)	11070(2)	7596(2)	21(1)
C(35)	8278(2)	8970(2)	8939(2)	26(1)
F(118)	7510(1)	7924(1)	8335(1)	36(1)
F(117)	8387(1)	9103(1)	9985(1)	36(1)
F(116)	9372(1)	8849(1)	8788(1)	35(1)
C(36)	6882(3)	12563(2)	10401(2)	31(1)
F(113)	7916(1)	13301(1)	11125(1)	44(1)

	x	у	Z	U(eq)
F(114)	6343(2)	12083(1)	10974(1)	43(1)
F(115)	6160(1)	13237(1)	10117(1)	39(1)
C(37)	7019(2)	11234(2)	6552(2)	29(1)
F(112)	8030(1)	11563(1)	6259(1)	37(1)
F(111)	6283(1)	10372(1)	5691(1)	38(1)
F(110)	6452(2)	12171(1)	6627(1)	43(1)
C(27)	8507(3)	4371(3)	6110(3)	38(1)
F(104)	9421(3)	3970(3)	5697(6)	64(2)
F(105)	8663(8)	4251(3)	7031(3)	-83(2)-
F(106)	7513(3)	3603(4)	5418(4)	51(1)
F(202)	9584(9)	4291(13)	6668(26)	93(8)
F(201)	7873(20)	4192(14)	6829(18)	97(7)
F(200)	8066(39)	3622(15)	5257(12)	185(14)

Table 5.2 - Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for (Ar₂P)(PPh₃CH₃). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

Bond lengths [Å] a	nd angles [°]
P(1)-C(19)	1.782(3)
P(1)-C(13)	1.791(2)
P(1)-C(1)	1.793(3)
P(1)-C(7)	1.799(2)
C(1)-C(6)	1.393(4)
G(1)-G(2)	1.394(3)
C(2)-C(3)	1.380(4)
P(2)-C(29)	1.802(2)
P(2)-C(20)	1.841(2)
C(3)-C(4)	1.373(4)
C(4)-C(5)	1.378(4)
C(5)-C(6)	1.391(4)
C(7)-C(8)	1.390(3)
C(7)-C(12)	1.393(3)
C(8)-C(9)	1.383(3)
C(9)-C(10)	1.381(4)
C(10)-C(11)	1.376(3)
C(11)-C(12)	1.385(3)
C(13)-C(14)	1.391(3)
C(13)-C(18)	1.397(3)
C(14)-C(15)	1.382(3)
C(15)-C(16)	1.393(3)
C(16)-C(17)	1.380(3)
C(17)-C(18)	1.390(3)
C(20)-C(21)	1.419(3)
C(20)-C(25)	1.433(3)
C(21)-C(22)	1.393(3)
C(21)-C(26)	1.508(3)
F(101)-C(26)	1.344(3)
F(102)-C(26)	1.341(3)
F(103)-C(26)	1.351(3)
C(22)-C(23)	1.381(3)
C(23)-C(24)	1.387(3)
C(23)-C(27)	1.497(4)
C(24)-C(25)	1.391(3)
C(25)-C(28)	1.508(3)
F(107)-C(28)	1.329(3)
F(108)-C(28)	1.356(3)
F(109)-C(28)	1.350(3)
C(29)-C(30)	1.448(3)
C(29)-C(34)	1.451(3)
C(30)-C(31)	1.389(3)
C(30)-C(35)	1.503(3)
C(31)-C(32)	1.383(3)
C(32)-C(33)	1.383(3)
C(32)-C(36)	1.491(3)
C(33)-C(34)	1.391(3)
C(34)-C(37)	1.506(3)
C(35)-F(116)	1.341(3)

Bond lengths [Å] and	angles [°]
G(35)-F(117)	1.345(3)
C(35)-F(118)	1.358(3)
C(36)-F(114)	1,344(3)
C(36)-F(115)	1.350(3)
C(36)-F(113)	1.354(3)
C(37)-F(111)	1.344(3)
C(37)-F(110)	1.348(3)
C(37)-F(112)	1.358(3)
C(27)-F(200)	1.17(2)
C(27)-F(105)	1.287(4)
C(27)-F(106)	1.326(5)
C(27)-F(202)	1.339(13)
C(27)-F(104)	1.371(4)
C(27)-F(201)	1.403(14)
F(104)-F(202)	1.20(3)
F(104)-F(200)	1.49(4)
F(105)-F(201)	.88(2)
F(105)-F(202)	1.268(14)
F(106)-F(200)	.72(4)
F(106)-F(201)	1.73(2)
C(19)-P(1)-C(13)	108.70(12)
C(19)-P(1)-C(1)	110.81(13)
C(13)-P(1)-C(1)	110.01(12)
C(19)-P(1)-C(7)	109.33(12)
C(13)-P(1)-C(7)	109.45(11)
C(1)-P(1)-C(7)	108.53(11)
C(6)-C(1)-C(2)	118.8(2)
C(6)-C(1)-P(1)	120.0(2)
C(2)-C(1)-P(1)	121.1(2)
C(3)-C(2)-C(1)	120.7(3)
C(29) - P(2) - C(20)	109.09(11)
C(4)-C(3)-C(2)	120.0(3)
C(3)-C(4)-C(5)	120.5(3)
C(4)-C(5)-C(6)	119.9(3)
C(5)-C(6)-C(1)	120.1(3)
C(8)-C(7)-C(12)	119.7(2)
C(8)-C(7)-P(1)	121.3(2)
C(12)-C(7)-P(1)	119.1(2)
C(3)-C(0)-C(1)	120.1(2)
C(10)-C(9)-C(8)	119.9(2)
C(11)-C(10)-C(9)	120.3(2)
C(10)-C(11)-C(12)	120.3(2)
C(11)-C(12)-C(7) C(14)-C(13)-C(18)	119.9(2)
C(14)-C(13)-C(10)	121.0(2)
C(18)-C(13)-P(1)	119.1(2)
C(15)-C(13)-P(1)	120.4(2)
C(14)-C(15)-C(16)	119.5(3)
C(17)-C(16)-C(15)	120.5(2)
C(16)-C(17)-C(18)	120.2(2)
	120.2(2)

Bond lengths [Å] and an	ngles [º]
C(17)-C(18)-C(13)	119.5(2)
C(21)-C(20)-C(25) C(21)-C(20)-P(2)	115.2(2)
C(25)-C(20)-P(2)	123.4(2)
C(22)-C(21)-C(20)	122.0(2)
C(22)-C(21)-C(26)	116.4(2)
C(20)-C(21)-C(26)	121.6(2)
C(23)-C(22)-C(21)	120.7(2)
C(22)-C(23)-C(24)	119.3(2)
C(22)-C(23)-C(27)	120.7(2)
C(24)-C(23)-C(27)	120.0(2)
C(23)-C(24)-C(25)	120.7(2)
C(24)-C(25)-C(20)	121.5(2)
C(24)-C(25)-C(28)	116.5(2)
C(20)-C(25)-C(28)	121.9(2)
F(102)-C(26)-F(101)	105.7(2)
F(102)-C(26)-F(103)	106.3(2)
F(101)-C(26)-F(103)	105.6(2)
F(102)-C(26)-C(21)	114.2(2)
F(101)-C(26)-C(21)	112.2(2)
F(103)-C(26)-C(21)	112.1(2)
F(107)-C(28)-F(109)	106.9(2)
F(107)-C(28)-F(108)	105.9(2)
F(109)-C(28)-F(108) F(107)-C(28)-C(25)	104.6(2)
	113.2(2)
F(109)-C(28)-C(25) F(108)-C(28)-C(25)	114.1(2)
	113.1(2)
C(30)-C(29)-C(34) C(30)-C(29)-P(2)	130.7(2)
C(34)-C(29)-P(2)	115.3(2)
C(31)-C(30)-C(29)	122.1(2)
C(31)-C(30)-C(35)	114.4(2)
C(29)-C(30)-C(35)	123.4(2)
C(32)-C(31)-C(30)	122.1(2)
C(31)-C(32)-C(33)	118.4(2)
C(31)-C(32)-C(36)	120.0(2)
C(33)-C(32)-C(36)	121.5(2)
C(32)-C(33)-C(34)	121.2(2)
C(33)-C(34)-C(29)	122.8(2)
C(33)-C(34)-C(37)	115.5(2)
C(29)-C(34)-C(37)	121.6(2)
F(116)-C(35)-F(117)	105.7(2)
F(116)-C(35)-F(118)	106.2(2)
F(117)-C(35)-F(118)	104.6(2)
F(116)-C(35)-C(30)	113.9(2)
F(117)-C(35)-C(30)	112.5(2)
F(118)-C(35)-C(30)	113.1(2)
F(114)-C(36)-F(115)	106.5(2)
F(114)-C(36)-F(113)	105.9(2)
F(115)-C(36)-F(113)	105.5(2)

Bond lengths [Å] and a	ngles [°]
F(114)-C(36)-C(32)	113.0(2)
F(115)-C(36)-C(32)	112.7(2)
F(113)-C(36)-C(32)	112.7(2)
F(111)-C(37)-F(110)	105.6(2)
F(111)-C(37)-F(112)	106.5(2)
F(110)-C(37)-F(112)	105.3(2)
F(111)-C(37)-C(34)	113.1(2)
F(110)-C(37)-C(34)	112.3(2)
F(112)-C(37)-C(34)	113.4(2)
F(200)-C(27)-F(105)	124.5(12)
F(200)-C(27)-F(106)	33(2)
F(105)-C(27)-F(106)	107.3(4)
F(200)-C(27)-F(202)	115.2(12)
F(105)-C(27)-F(202)	57.7(9)
F(106)-C(27)-F(202)	133.9(7)
F(200)-C(27)-F(104)	72(2)
F(105)-C(27)-F(104)	106.0(4)
F(106)-C(27)-F(104)	103.1(3)
F(202)-C(27)-F(104)	52.6(11)
F(200)-C(27)-F(201)	108(2)
F(105)-G(27)-F(201)	37.7(7)
F(106)-C(27)-F(201)	78.5(10)
F(202)-C(27)-F(201)	95.2(9)
F(104)-C(27)-F(201)	137.3(6)
F(200)-C(27)-C(23)	117.8(9)
F(105)-C(27)-C(23)	114.3(3)
F(106)-C(27)-C(23)	113.7(3)
F(202)-C(27)-C(23)	111.9(6)
F(104)-C(27)-C(23)	111.6(3)
F(201)-C(27)-C(23)	106.2(6)
F(202)-F(104)-C(27)	62.3(5)
F(202)-F(104)-F(200)	103.1(11)
C(27)-F(104)-F(200)	47.8(8)
F(201)-F(105)-F(202)	141(2)
F(201)-F(105)-C(27)	78.3(12)
F(202)-F(105)-C(27)	63.2(9)
F(200)-F(106)-C(27)	61(2)
F(200)-F(106)-F(201)	109(2)
C(27)-F(106)-F(201)	52.8(6)
F(104)-F(202)-F(105)	118.6(13)
F(104)-F(202)-C(27)	65.1(11)
F(105)-F(202)-C(27)	59.1(4)
F(105)-F(201)-C(27)	63.9(9)
F(105)-F(201)-F(106)	102.9(13)
C(27)-F(201)-F(106)	48.8(6)
F(106)-F(200)-C(27)	86(2)
F(106)-F(200)-F(104)	143(2)
C(27)-F(200)-F(104)	60.6(14)

Table 5.3 - Bond lengths [Å] and angles [°] for (Ar₂P)(PPh₃CH₃)

	U11	U22	U33	U23	U13	U12
P(1)	24(1)	23(1)	24(1)	9(1)	8(1)	7(1)
C(1)	27(2)	28(1)	26(1)	12(1)	12(1)	8(1)
C(2)	36(2)	34(2)	35(2)	16(1)	11(1)	10(1)
C(3)	30(1) 59(2)	18(1) 32(2)	38(2)	6(1) 19(1)	11(1) 21(2)	14(2)
C(4)	56(2)	36(2)	42(2)	12(2)	25(2)	-2(2)
C(5)	34(2)	54(2)	76(2)	34(2)	12(2)	-1(2)
C(6)	34(2)	44(2)	58(2)	30(2)	10(2)	7(2)
C(7)	20(1)	21(1)	23(1)	9(1)	5(1)	7(1)
C(8) C(9)	46(2)	26(2) 26(2)	35(2)	-2(1)	15(1)	5(1)
C(10)	31(2)	39(2)	28(2)	-2(1)	14(2)	5(1)
C(11)	23(2)	36(2)	33(2)	15(1)	10(1)	6(1)
C(12)	28(2)	25(1)	27(2)	6(1)	7(1)	4(1)
C(13)	21(1)	22(1)	25(1)	10(1)	7(1)	6(1)
C(14)	25(2)	27(1)	27(2)	11(1)	10(1)	6(1)
C(15)	25(2)	35(2)	36(2)	20(1)	7(1)	6(1)
C(17)	32(2)	30(2)	36(2)	12(1)	15(1)	13(1)
C(18)	35(2)	28(2)	29(2)	14(1)	13(1)	10(1)
C(19)	29(2)	35(2)	25(2)	7(1)	5(1)	8(1)
C(20)	20(1)	20(1)	14(1)	4(1)	5(1)	4(1)
C(21)	22(1)	24(1)	18(1)	5(1)	3(1)	6(1)
F(101)	21(1) 33(1)	44(1)	63(1)	20(1)	2(1)	9(1)
F(102) F(103)	30(1)	38(1) 43(1)	28(1)	-2(1)	2(1) 10(1)	-9(1)
C(22)	22(2)	28(2)	30(2)	9(1)	7(1)	11(1)
C(23)	30(2)	19(1)	31(2)	8(1)	9(1)	9(1)
C(24)	28(2)	18(1)	25(1)	5(1)	8(1)	2(1)
C(25)	22(1)	21(1)	19(1)	6(1)	8(1)	7(1)
F(107) F(108)	32(1) 21(1)	49(1)	40(1)	25(1)	3(1)	12(1)
F(109)	29(1)	26(1) 33(1)	56(1) 42(1)	8(1) 4(1)	1(1) 12(1)	0(1) 15(1)
C(26)	24(2)	29(2)	28(2)	8(1)	5(1)	5(1)
C(28)	27(2)		31(2)	7(1)	7(1)	4(1)
C(29)	19(1)	17(1)	21(1)	3(1)	2(1)	1(1)
C(30)	22(1)	21(1)	19(1)	6(1)	5(1)	1(1)
C(31)	26(2)	23(1)	21(1)	6(1)	7(1)	2(1)
C(32) C(33)	24(2)	21(1)	24(1) 30(2)	5(1)	9(1)	5(1)
C(34)	20(1)	19(1)	25(1)	10(1)	7(1)	2(1)
C(35)	35(2)	25(2)	20(1)	8(1)	11(1)	8(1)
F(118)	50(1)	20(1)	35(1)	9(1)	10(1)	5(1)
F(117)	58(1)	38(1)	22(1)	15(1)	16(1)	23(1)
F(116)	35(1)	47(1)	34(1)	21(1)	14(1)	22(1)

	U11	U22	U33	U23	U13	U12
C(36)	36(2)	24(2)	33(2)	7(1)	14(1)	9(1)
F(113)	41(1)	36(1)	34(1)	-6(1)	7(1)	4(1)
F(114)	63(1)	34(1)	42(1)	12(1)	34(1)	14(1)
F(115)	46(1)	30(1)	42(1)	8(1)	19(1)	20(1)
C(37)	32(2)	27(2)	34(2)	15(1)	12(1)	12(1)
F(112)	43(1)	40(1)	45(1)	28(1)	24(1)	15(1)
F(111)	40(1)	45(1)	26(1)	12(1)	3(1)	11(1)
F(110)	57(1)	47(1)	44(1)	28(1)	22(1)	33(1)
F(104)	63(2)	36(2)	106(4)	20(2)	34(2)	24(2)
F(105)	178(6)	31(2)	31(2)	14(1)	8(3)	26(3)
F(106)	41(2)	18(2)	78(4)	13(2)	-1(2)	-1(1)
F(202)	37(6)	66(8)	208(25)	90(13)	28(9)	32(5)
F(201)	125(14)	60(7)	177(18)	80(10)	103(13)	58(9)
F(200)	456(41)	52(11)	14(6)	-11(6)	9(18)	115(20)

Table 5.4 - Anisotropic displacement parameters (Å² x 10³) for (Ar₂P)(PPh₃CH₃). The anisotropic displacement factor exponent takes the form: -2 π² [h² a² U11 + ... + 2 h k a* b* U12]

	X	у	Z	U(eq)
H(2A)	8160(3)	5742(2)	3442(2)	41
H(3A)	6921(3)	4150(2)	3415(2)	47
H(4A)	4856(3)	3751(3)	2614(2)	53
H(5A)	4003(3)	4958(3)	1865(3)	64
H(6A)	5237(3)	6554(2)	1866(2)	52
H(8A)	7310(2)	5327(2)	736(2)	40
H(9A)	8085(3)	4649(2)	-741(2)	47
H(10A)	9615(2)	5842(2)	-946(2)	40
H(11A)	10382(2)	7707(2)	317(2)	35
H(12A)	9641(2)	8395(2)	1815(2)	34
H(14A)	6769(2)	8115(2)	775(2)	31
H(15A)	5731(2)	9518(2)	574(2)	36
H(16A)	5270(2)	10780(2)	2070(2)	38
H(17A)	5814(2)	10622(2)	3745(2)	38
H(18A)	6881(2)	9233(2)	3960(2)	34
H(19A)	9496(2)	7640(2)	3900(2)	47
H(19B)	8713(2)	8498(2)	4404(2)	47
H(19C)	9539(2)	8807(2)	3726(2)	- 47
H(22A)	10306(2)	6133(2)	6554(2)	32
H(24A)	6667(2)	5382(2)	5761(2)	29
H(31A)	7573(2)	10608(2)	10172(2)	29
H(33A)	6701(2)	12474(2)	8385(2)	28

Table 5.5 - Hydrogen coordinates ($x~10^4$) and isotropic displacement parameters (Å² x 10³) for $(Ar_2P)(PPh_3CH_3)$

There are some very interesting things to note concerning the anion in the molecular structure of $[CH_3PPh_3]^{(+)}Ar_2P^{(-)}$. The structure of the phosphonium cation shows no interesting variations from other compounds containing this species. There are, however, a number of notable points in the structure of the anion as compared with the $(PPh_2)^{(+)}$ anion.

The geometry of the anion is influenced by the steric bulk of the aryl groups. The structural orientation of the molecule is such that the interaction between neighbouring *ortho* CF_3 groups on the two aryl groups is at a minimum. The angle between the planes of the two aryl rings is 86.4°

This factor in itself causes two phenomena: the angle (C-P-C) between the two aryl groups is larger than in equivalent compounds recorded in the CSD⁵, and the angle between the two planes containing the aryl groups is significantly larger.

The twisting of the aryl groups would also appear to have some electronic consequences. There is a distinct difference in the length of the two P-C bonds [1.802(2) and 1.841(2)Å], and both aryl groups are inequivalent. The aryl group associated with the longer P-C bond is not in the same plane as this bond and the ring itself is not planar. This would suggest that there is significantly more delocalisation of the negative charge onto this aryl group, rather than equal delocalisation onto both groups.

Figure 5.4 shows the deviation of one of the aryl rings from planarity. The diagram was composed by superimposing one aryl ring on the top of the other one, so comparing the planarity of each ring.

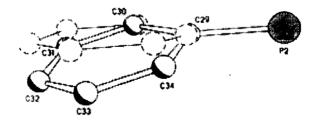
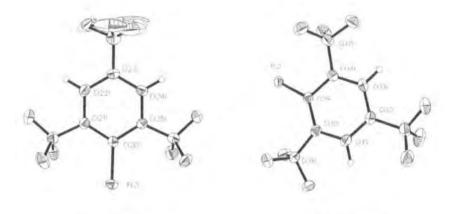


Figure 5.4 - Superimposition of the two aryl rings, highlighting the distortion from planarity

Delocalisation of electron density from the lone pair into the aryl groups is shown in the irregularity of the carbon-carbon bond lengths in the two aryl groups. The carbon-carbon bonds which are adjacent to the phosphorus atom are significantly longer than other bonds in the aryl ring (see Table 5.6).

C-C bonds in aryl group 1	C-C Bond length (Å)	C-C bonds in aryl group 2	C-C Bond length (Å)
C(20)-C(21)	1.419(3)	C(29)-C(30)	1.448(3)
C(25)-C(20)	1.433(3)	C(29)-C(34)	1.451(3)
C(21)-C(22)	1.393(3)	C(30)-C(31)	1.389(3)
C(22)-C(23)	1.381(3)	C(31)-C(32)	1.383(3)
C(23)-C(24)	1.387(3)	C(32)-C(33)	1.383(3)
C(24)-C(25)	1.391(3)	C(33)-C(34)	1.391(3)

Table 5.6 - Comparisons of carbon-carbon bond lengths in the aryl rings



Aryl ring (1)

Aryl ring (2)

Figure 5.5 – The two aryl rings in the compound $Ar_2P^{(-)}$

The angle (C-P-C) between the two aryl groups in Ar_2PH is 107.5°, and this increases slightly to 109.1° upon deprotonation. This is probably due to an electronic effect and allows a greater interaction between the lone pair of electrons on the phosphorus and the aryl rings.

If we consider the plane of the aryl ring (1), which is the non-deformed ring, and assume the other ring (2) is twisted away from that one, it is possible to draw some conclusions about the electronic properties of the system.

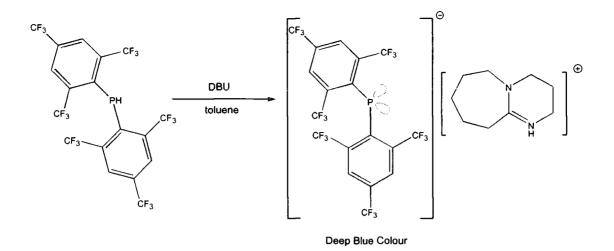
The aryl ring (2) is not in the same plane as the C-P-C bonds, and the ring itself is also slightly buckled, which would imply a greater change in hybridisation of C(29) than C(20). Because the ring is twisted almost 90° away from the lone pairs, there is very little direct delocalisation arising from the π - π interactions between the lone pair and the ring. If we infer that the oxidation state of the phosphorus in Ar₂P⁽⁻⁾ is P(I) then it may be regarded as sp³ hybridised. Due to the twisting of the rings significantly away from the planar system from an expected sp³ hybrid phosphorus atom, it is possible to infer that the terms hybridisation and oxidation are not the best ways to describe the electronic effects inherent in the system. Although the removal of hydrogen is intrinsically known as oxidation, calling the oxidation state of the phosphorus atom in Ar₂P⁽⁻⁾ "P(I)" does not tell the whole story.

The formation of this compound illustrates the possibility for the formation of a number of stable $Ar_2P^{(-)}$ species and comparisons thereof. The phosphonium ion is bulky and there are a number of hydrogen bonded interactions between the anion and cation which also contribute to stability. Thus far, this is the only successful X-ray structure of the anion despite numerous attempts to grow crystals of other materials.

5.4.6 Reaction between Ar₂PH and DBU

DBU was added to a solution of Ar₂PH in toluene, resulting in a deep blue colour. The ³¹P NMR spectrum of this solution showed the complete reaction of the Ar₂PH and the formation of a new resonance which was shifted significantly to a higher frequency ($\delta = 30.2 \text{ ppm}$) (⁴J_{P-F} = 36.7 Hz) (complex multiplet). The ¹⁹F Spectrum shows the formation of two new sets of peaks, a doublet ($\delta = -59.4 \text{ ppm}$) (⁴J_{P-F} = 37.5 Hz) and a singlet ($\delta = -60.7 \text{ppm}$).

This species appeared to be more stable than the secondary amine derivative formed using pyrrolidine. The species is relatively stable in solution over a number of days. Unfortunately, during any attempt to isolate the material it decomposes rapidly, producing a large number of peaks in both the ³¹P and the ¹⁹F NMR spectra.



Equation 5.9 – Synthesis of $Ar_2P^{(-)}[DBUH]^{(+)}$

5.5 Results of substitution reactions between Ar₂PH and metal amides

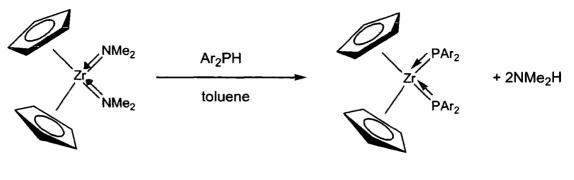
5.5.1 Reaction between Ar₂PH and Cp₂Zr(NMe₂)₂

Ar₂PH and Cp₂Zr(NMe₂)₂ were added together under an inert atmosphere of N₂ in a glove box; toluene was then added to the solution and the solution turned deep purple in colour. There appeared to be no new products in the ³¹P NMR spectrum. The reaction was warmed to 60°C, but after a period of hours the purple colour was lost. This was assigned to the instability of the starting materials and products to heat.

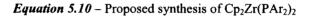
As with the formation of $Ar_2P^{(-)}$ the colour is probably due to electron delocalisation within the aryl species. Even a small amount of this compound formed would produce an intense colour.

Attempts to isolate the species resulted in decomposition and the formation of a large number of new species in the ³¹P and ¹⁹F NMR spectra. It is unclear as to whether or not di-substitution was achieved in this reaction. Equation 5.10 highlights the potential products should di-substitution occur.

(In the reaction between Cp_2ZrCl_2 and $2LiPPh_2$, the reaction goes to completion and the formation of the di-phosphide $Cp_2Zr(PPh_2)_2$ may be possible.)



Deep Purple Colour



5.5.1.1 Mechanism for the substitution of Ar₂PH for NMe₂H

For substitution of this nature to occur, the proton on the phosphane must be more acidic than the proton on the equivalent amine (NMe₂H). Metal phosphides have been prepared by a number of methods⁶ and this particular method has not been apparent. This implies that the normal precursor for metal phosphides (Ph₂PH) is not as acidic as the disubstituted amines normally associated with this type of system.

Ar₂PH is comparatively more acidic than Ph_2PH because of the electron withdrawing capacities of the Fluoromes groups compared to the phenyl rings. The electrons are delocalised through the π system of the rings, thus weakening any phosphorus bonds with p character (the P-H bond is formally sp³).

The mechanism for the reaction⁷ involves the coordination of the phosphane ligand to the metal centre and then transfer of the proton from the phosphane to the amide, liberating the amine.

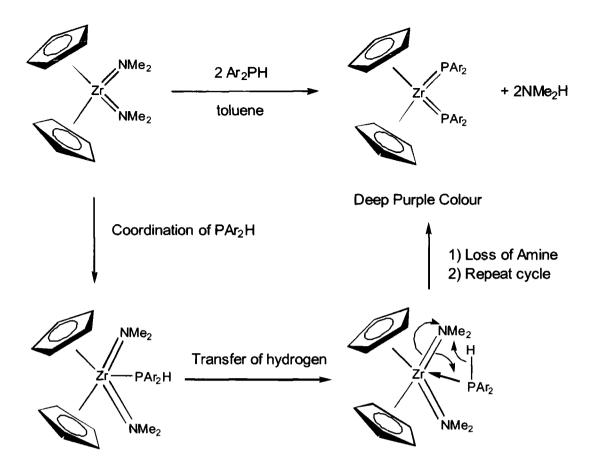


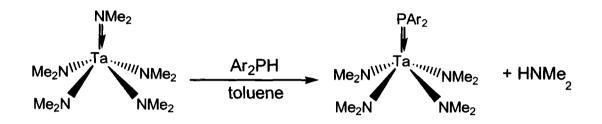
Figure 5.6 – Proposed mechanism for the proton transfer in a reaction between $Cp_2Zr(NMe_2)_2$ and $2Ar_2PH$

5.5.2 Reaction between Ar₂PH and Ta(NMe₂)₅

Equimolar quantities of Ar_2PH and the yellow crystalline $Ta(NMe_2)_5$ were dissolved in toluene at room temperature and a dark purple solution was produced. Even before the solvent was added to the reaction it was apparent that there was some reaction between the two solids because there was a faint purple colour to the mixture.

The ³¹P NMR spectrum of the reaction showed one broad singlet ($\delta = 112.6$ ppm) and the complete removal of the starting material Ar₂PH. This indicates that there is only mono-substitution of the phosphane for the amine. If there were more than one product there would be more than one signal in the phosphorus NMR spectrum.

Unfortunately, the ¹⁹F NMR spectrum showed the formation of a large number of new species. Like the phosphide formed with zirconium, this appears to be a very unstable species. What is apparent from the ³¹P NMR spectrum is the large change in chemical shift, indicating a large decrease in shielding. The fact that there is only mono-substitution of the amine is due to the steric bulk of the phosphide ligand. For substitution to occur, the phosphane must first bind to the metal before losing the hydrogen (see Equation 5.11). The phosphide is sterically bulkier than the amide ligands and is less likely to facilitate coordination of another phosphane ligand. The structure of $Ta(NMe_2)_5$ is a square based pyramid. One of the NMe₂ groups is more likely to be substituted because of the steric positioning of the other groups around the tantalum atom.



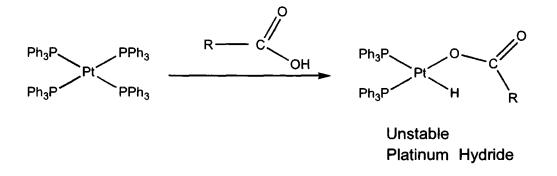
Equation 5.11 – Proposed synthesis of Ta(NMe₂)₄(PAr₂)

Attempts were made to isolate the species and record NMR spectra and UV data. The species decomposed almost immediately when these attempts were made. The ³¹P NMR spectrum of the resulting solution showed the formation of a number of new phosphorus species in the solution. Some of the peaks are close enough together to suggest that they may be coupled. This decomposition may be analogous to the decomposition of unstable metal amide species which results in coupled N-N amine species and the formation of P-P bonds in metal phosphide chemistry⁶.

5.6 Reaction of Ar₂PH with low oxidation state transition metals

5.6.1 Reaction of Ar₂PH with Pt(PPh₃)₄

Ar₂PH was reacted with $Pt(PPh_3)_4$ in benzene on an NMR scale and a dark orange solution was formed. $Pt(PPh_3)_4$ is known to react with acidic protons⁸ to form highly unstable Pt-H species.



Equation 5.12 – Synthesis of a platinum hydride⁸

The ³¹P NMR spectrum showed the complete consumption of the Pt(0) species and the formation of a broad peak ($\delta \approx 35-40$ ppm). This broad peak is probably due to rapid exchange from the platinum of the phosphorus species bonded to it.

The ¹⁹F NMR spectrum showed a new doublet and singlet in the spectrum. Although these were very small in comparison to those of the starting material (Ar₂PH), they are distinct. The chemical shift values were $\delta = -55.7$ ppm (⁴J_{P-F} = 39.3 Hz) (doublet) and $\delta = -63.7$ ppm. ¹⁹F NMR is a more sensitive tool than ³¹P and the appearance of these new peaks is an indication of the formation of a new species.

The ¹H NMR spectrum of the solution was attempted, but addition of deuterated solvent to a mixture of the starting material resulted in instant effervescence and there was no peak in the spectrum which could be attributed to having platinum satellites and thus be indicative of a Pt-H species.

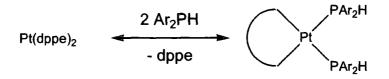
Attempts were made to grow crystals from the reaction. When attempts were made to isolate the crystals, the solution effervesced vigorously and became green in appearance. The rapid evolution of gas would suggest the decomposition of a compound which is intrinsically a platinum hydrido complex, although this is only one possibility. This effect may be caused by localised heating or dissolved gases coming out of the solution. Only approximately 0.5cm³ of gas would be expected if H₂ was formed by the complete decomposition of the expected product.

5.6.2 Reaction of Ar₂PH with Pd(PPh₃)₄

Toluene was added to a mixture of Ar₂PH and Pd(PPh₃)₄ in a Schlenk tube. The initial solution formed was dark orange, but effervesced instantaneously and became dark green in colour. The ³¹P NMR spectrum showed the formation of two new peaks, $\delta = 25.1$ ppm, and $\delta = -4.8$ ppm (free PPh₃). The peak at $\delta = 25.1$ ppm is typical of Pd(II) species such as Pd(PPh₃)₂X₂ where X is a halide or organic species. The ¹⁹F showed the formation of a number of new species although none of them are high in yield.

5.6.3 Reaction of Ar₂PH with Pt(dppe)₂

Toluene was added to a mixture of Ar_2PH and $Pt(dppe)_2$ in a Schlenk tube. The solution became a slightly darker orange colour. The ³¹P NMR spectrum showed the formation of a broad peak ($\delta = 41.8$ ppm). This again is typical of Pt(0) species in solution, and shows the rapid dissociation and exchange of ligands at the platinum centre. This reaction showed no evidence of effervescence, although when attempts were made to isolate the product, the solution became bright green. This initial spectrum suggests that the Ar₂PH ligands may be exchanging with dppe ligands at the platinum centre, rather than oxidising the Pt(0) to Pt(II).



Equation 5.13 - Possible substitution of dppe ligands in the attempted formation of a platinum hydride

5.7 Attempted reaction of Ar₂PH and Ar₂PCI with Pt(II) compounds.

5.7.1 Reaction between Ar₂PH and the "Pt Dimer"

Ar₂PH was refluxed in CH_2Cl_2 in a 2:1 ratio with the platinum dimer $[PtCl_2(PEt_3)]_2$. No reaction was observed even after a few days of heating.

5.7.2 Reaction between Ar₂PH and PtCl₂(PhCN)₂

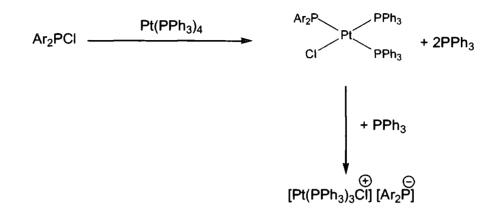
In the second step of the preparation of the "Pt Dimer" (see section 3.7.1), PtCl₂(PhCN)₂ is reacted with PEt₃ to form PtCl₂(PEt₃)₂. Ar₂PH was refluxed with PtCl₂(PhCN)₂ in CH₂Cl₂ for 48 hours. The only species present in the reaction after this time were the starting materials.

5.7.3 Reaction between Ar₂PCI and Pt(PPh₃)₄

Under an inert atmosphere of N₂, Ar₂PCl and Pt(PPh₃)₄ were added together. The mixture of solids became pale green in colour. Toluene was added to this mixture and the solution immediately became deep blue-green in colour. The initial ³¹P NMR spectrum showed formation of a new phosphorus peak ($\delta = 23.7$ ppm), although there was no obvious fluorine coupling visible in any of the peaks. After 24 hours, the formation of Ar₂PH was observed in the spectrum ($\delta = -67$ ppm) and the ¹⁹F spectrum became very complex with a large number of fluorine peaks being observed.

The predicted products for this reaction come from oxidative insertion of platinum into the phosphorus chlorine bonds, analogous to the reaction with Ar_2PH (see section 5.6.1) and the insertion reaction observed upon reaction with $Ar'P=CCl_2$ (see section 4.3).

From the ³¹P and ¹⁹F spectra it is apparent that the species formed is unstable with respect to further reaction and can remove a proton from either solvent or one of the other reactants.



Equation 5.15 – Possible reaction between $Pt(PPh_3)_4$ and Ar_2PH

The deep blue colour of the solution indicates the formation of the $Ar_2P^{(-)}$ anion. This is an indication that the phosphide is not bound to the platinum, (in the case of other reactions the solution is dark orange and not blue). A possible mechanism for the reaction is shown in Equation 5.15.

5.7.4 Reaction between Ar₂PCI and Pt(dppe)₂

Toluene was added to a mixture of Ar_2PCl and $Pt(dppe)_2$ in a Schlenk tube. There was no initial reaction. Over a period of three hours the solution became colourless and a very fine dark blue particulate solid was formed. This solid was isolated by filtration. The remaining solution showed only one main peak in the ³¹P NMR spectrum ($\delta = 20.6$ ppm), which can be attributed to free dppe. The ¹⁹F NMR spectrum shows the formation of a large number of new species. Again a number of side reactions appear to have taken place.

The dark blue solid which was formed in this reaction was not soluble in any solvent tried (hexanes, toluene, THF, ether) which implies that it is potentially some form of polymeric species. Due to time constraints, this compound was not characterised further.

From the ³¹P and ¹⁹F spectra it is apparent that the species formed is unstable with respect to further reaction and can remove a proton from either solvent or one of the other reactants.

The deep blue colour of the solution indicates the formation of the $Ar_2P^{(-)}$ anion. This is an indication that the phosphide is not bound to the platinum, (in the case of other reactions the solution is dark orange and not blue).

5.7.4 Reaction between Ar₂PCI and Pt(dppe)₂

Toluene was added to a mixture of Ar_2PCl and $Pt(dppe)_2$ in a Schlenk tube. There was no initial reaction. Over a period of three hours the solution became colourless and a very fine dark blue particulate solid was formed. This solid was isolated by filtration. The remaining solution showed only one main peak in the ³¹P NMR spectrum ($\delta = 20.6$ ppm), which can be attributed to free dppe. The ¹⁹F NMR spectrum shows the formation of a large number of new species. Again a number of side reactions appear to have taken place.

The dark blue solid which was formed in this reaction was not soluble in any solvent tried (hexanes, toluene, THF, ether) which implies that it is potentially some form of polymeric species. Due to time constraints, this compound was not characterised further.

5.8 Experimental

5.8.1 Attempted synthesis of $[Ar_2P]^{(-)}[Li]^{(+)}$ in Hexanes

BuLi (0.97ml, 2.41M, 0.23mmol) was added slowly to a solution of Ar_2PH (0.15g, 0.2mmol) in hexanes at $-78^{\circ}C$. The solution became very pale pink in colour. Upon warming to room temperature, the pink colour dissipated leaving a colourless solution. The ³¹P NMR spectrum showed only the starting material and no new species. The ¹⁹F NMR spectrum showed the formation of a large number of indeterminate species.

5.8.2 Attempted synthesis of $[Ar_2P]^{(-)}[Li]^{(+)}$ in THF

BuLi (0.97ml, 2.41M, 0.23mmol) was added to a solution of Ar_2PH (0.15g, 0.2mmol) in THF. The solution became an intense dark blue colour and was allowed to warm to room temperature. After two hours the solution became colourless and a brown precipitate was formed. Again, the NMR spectra showed the formation of a large number of indeterminate species.

5.8.3 Attempted synthesis of $[Ar_2P]^{(-)}[Li]^{(+)}(PMDETA)$

BuLi (0.97ml, 2.41M, 0.23mmol) was added to a solution of Ar₂PH (0.15g, 0.2mmol) and a large excess of PMDETA in THF. The solution became dark blue in colour and was allowed to warm to room temperature. After four hours at room temperature, the solution was placed in a fridge at -20° C. After another four hours, the solution became colourless and a brown solid was precipitated. The NMR spectra showed the formation of a number of new indistinguishable peaks.

5.8.4 Attempted synthesis of [DBUH]⁽⁺⁾[Ar₂P]⁽⁻⁾

DBU (0.5ml, 0.3mmol) was added to a solution of Ar₂PH (0.2g, 0.3mmol) in toluene. The solution became dark blue in colour, which appeared stable over a number of hours. The product was not isolated. ³¹P (toluene) δ = 30.2 ppm (13 line multiplet), ⁴J_{PF} = 36.7 Hz; ¹⁹F δ = -59.4 ppm (doublet) (⁴J_{PF} = 37.5 Hz), δ = -60.7 ppm (singlet).

5.8.5 Attempted synthesis of $[Ar_2P]^{(-)}[(C_4H_8NH)H]^{(+)}$

Pyrrolidine (0.02g, 0.3mmol) was added to a solution of Ar_2PH (0.2g, 0.3mmol) in toluene. The solution became a pale blue colour, which darkened when cooled in the fridge. A crystalline material was formed although the crystals were not stable enough to be submitted for X-ray crystallographic analysis. Numerous attempts were made to collect NMR data on the compound, but at room temperature the only signal in the ³¹P NMR spectrum was from the starting material. Facilities for low temperature NMR were not available at the time of the experiment.

5.8.6 Synthesis of $[Ar_2P]^{(-)}[Ph_3PCH_3]^{(+)}$

Toluene (10ml) was added to a Schlenk tube containing Ph₃P=CH₂ (0.14g, 0.5mmol) and Ar₂PH (0.3g, 0.5mmol). The resulting deep blue coloured solution was stirred at room temperature for 15 minutes, during which time a red precipitate was formed. Upon the addition of more toluene (15ml) and gentle warming, the solid redissolved. Upon standing for three hours deep red crystals were formed. Yield 0.24g, (55%). m. p. 129-130°C. ³¹P (toluene) δ = (21.0 ppm) (multiplet), ⁴J_{PF} = 32.6 Hz; ¹⁹F δ = -61.2 ppm (doublet), (⁴J_{PF} = 32.6 Hz) δ = - 62.3 ppm (singlet).

$$Ar_2PH \xrightarrow{Ph_3P=CH_2} (Ar_2P)^{(-)}(Ph_3PCH_3)^{(+)}$$

5.8.7 Attempted synthesis of ZrCp₂(PAr₂)₂

Toluene was added to a mixture of $Cp_2Zr(NMe_2)_2$ (0.093g, 0.3mmol) and Ar_2PH (0.36g, 0.6mmol). The solution became a deep purple colour and was allowed to stir. The mixture was placed in the fridge overnight and crystals grew. When attempts to isolate these crystals were made the solution became pale green and the crystals disintegrated. No NMR spectra were recorded on the purple species in solution.

5.8.8 Attempted synthesis of $Ta(NMe_3)_4(PAr_2)$

Toluene was added to a solution of $Ta(NMe_2)_5$ (0.14 g, 0.35mmol) and Ar₂PH (0.42g, 0.7mmol). The resulting solution was deep purple in colour and the solution was allowed to stir. Attempts to isolate the product resulted in both the loss of the purple colour and the formation of a large numbers of peaks in the ¹⁹F NMR spectrum.

The purple solution did yield useful NMR data; ³¹P (toluene) $\delta = 112.6$ ppm (broad singlet). ¹⁹F showed a large number of indistinguishable products.

5.8.9 Attempted synthesis of [HPt(PPh₃)₂(Ar₂P)]

Toluene (20ml) was added to a mixture of Ar₂PH (0.10g, 0.17mmol) and Pt(PPh₃)₄ (0.20g, 0.17mmol) in a Schlenk tube under an atmosphere of N₂. The solution became dark orange in colour and was stable over time. ¹⁹F; δ = -55.7 ppm (⁴J_{P-F} = 39.3 Hz) (doublet) and δ = -63.7 ppm (singlet).

Any attempt to isolate the product resulted in the formation of a dark green solution with rapid effervescence. The resulting solution showed a large number of peaks in the ¹⁹F NMR spectrum, although none were assignable.

5.8.10 Attempted synthesis of [PtH(dppe)(Ar₂P)]

Toluene (20ml) was added to a mixture of Ar₂PH (0.10g, 0.17mmol) and Pt(dppe)₂ (0.17g, 0.17mmol) in a Schlenk tube under an atmosphere of N₂. The resulting ³¹P NMR showed the formation of a broad peak ($\delta = 41.8$ ppm). The ¹⁹F NMR spectrum showed a large number of non-assignable peaks.

5.8.11 Attempted synthesis of [PdH(PPh₃)₂(Ar₂P)]

Toluene (20ml) was added to a mixture of Ar₂PH (0.10g, 0.17mmol) and Pd(PPh₃)₄ (0.18g, 0.17mmol) in a Schlenk tube under an atmosphere of N₂. The solution became dark orange in colour and was stable over time. ³¹P, 25.1 ppm, (singlet) $\delta = -4.8$ ppm (singlet). ¹⁹F and ¹H NMR showed the formation of a large number of new peaks which were non-assignable. Any attempt to isolate the product resulted in the formation of a dark green solution with rapid effervescence. The resulting solution showed a large number of peaks in the ¹⁹F NMR spectrum, although none were assignable.

5.8.12 Attempted synthesis of [PtCl(PPh₃)₂(Ar₂P)]

Under an inert atmosphere of N₂, Ar₂PCl (0.1g, 0.16mmol) and Pt(PPh₃)₄ (2.0g, 0.16mmol) were added together. The mixture of solids became pale green. Toluene was added to this mixture and the solution immediately became a deep blue-green colour. ³¹P : $\delta = 23.7$ ppm (singlet); ¹⁹F: Many complex non-assignable peaks.

5.8.13 Attempted synthesis of [PtCl(dppe)(Ar₂P)]

Toluene was added to a mixture of Ar₂PCl and Pt(dppe)₂ in a Schlenk tube. There was no initial reaction. Over a period of three hours the solution became colourless and a very fine dark blue particulate solid was formed. ³¹P: $\delta = 20.6$ ppm (singlet = dppe).

¹S. R. Wade., M. G. H. Wallbridge., G. R. Willey., J. Chem. Soc. Dalton. Trans., 1983, 2555.

² K. Issleib., H. Hackert., Z. Naturforsch., 1966, 21, 519.

³ K. Wade, W. Clegg., R. Snaith., G. T. Walker., D. R. Armstrong., R. E. Mulvey., *Polyhedron.*, 1987, 7, 698.

⁴ M. G. Davidson., Private Communication.

⁵ F. H. Allen., O. Kennard., Chemical Design Automation News., 1993, 8, 31.

⁶Z. Hou., T. L. Breen., D. Stephenson., Organometallics, 1993, 12, 3158.

⁷ D. J. Cardin., S. A. Keppie., M. F. Lappert., J. Chem. Soc(A), 1970, 2594.

⁸ J. E. Huheey., *Inorganic Chemistry* (third edition)., Harper and Row, London, 1983.

Appendix 1

.

Crystal growth and crystallographic methods

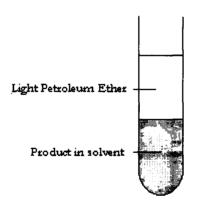
A.1 Crystal growth and crystallographic methods

A.1.1 Growing Crystals

A.1.1.1 The layering technique

This method of crystallisation was used to grow most of the crystals used for Xray structural determination described in this thesis. The method employed here is commonly referred to as the "layering technique".

A pure solution of the desired compound in a suitable solvent was introduced into a small capillary tube, diameter of 5-8mm. On top of this, some low boiling petrol was carefully poured so that a distinct interface was visible between the two solvents. The tube was then covered and allowed to stand for a number of days. The two solutions slowly diffused into one another which causes the solute to come out of solutions into a crystalline form.



A.1.1.1.1 Pt dimer complexes

In the case of the platinum dimer complexes (see Chapter 3) the solvent used was either CH_2Cl_2 or $(CHCl_2)_2$. The solutions were bright yellow and upon addition of the petrol a small amount of white precipitate was visible on the boundary of the two solvents. After diffusion of the petrol a colourless solution was left and colourless needle like crystals were formed.

A.1.1.1.2 Phosphaalkene-platinum complex

To attain crystals of the complex formed in the reaction between the phosphaalkene $ArP=CCl_2$ and $Pt(PPh_3)_4$ (see Chapter 4) the solid product was dissolved in toluene and placed in the capillary tube as before. The solution was a bright orange colour. Petrol was slowly poured onto the top of this and no precipitate was visible.

After a few days, long flat plate-like orange crystals were produced and these were used for X-ray structural determination of the compound.

A.1.1.2 Vacuum sublimation

This method involved the slow growth of crystals in a sealed glass container under vacuum.

A small quantity of solid was placed at the bottom of a glass tube and the system was evacuated. It was then sealed and allowed to warm to room temperature in a shielded area. The tube was then placed in bright sunlight and allowed to stand for a few days. Crystals of the desired product were then formed and used for X-ray characterisation. It was found that better quality crystals were obtained when the heat was less direct and the growth of crystals slower.

This method is only viable if the sublimation temperature of the compound (under vacuum) is not much higher than room temperature. The slower the crystals form the better.

This method was used for growing crystals of Ar₂PH.

A.1.1.3 Recrystallisation

Where laying and vacuum sublimation were not successful or not possible, crystals were grown from a saturated solution in a freezer at -30° C.

A.1.2 Crystallographic methods

All the crystallographic experiments carried out were performed on the Siemens SMART 3-circle diffractometer. The air sensitive crystals were removed from the reaction vessel under a suspension of perfluoropolyether oil which protected the crystals from solvent evaporation and from air or moisture oxidation/hydrolysis.

The crystals were then checked for quality and singularity by rotating them through polarised light using a light microscope. A pure single crystal under a specific orientation will allow all the polarised light to pass through it, giving the appearance under the microscope that the crystal has disappeared.

The X-rays are generated by accelerating electrons (generated from a heated filament) towards a metal target (in this case molybdenum). These are then monochromated to a specific wavelength ($K_{\alpha} = 0.71073$ Å) and collimated. This collimation produces X-rays of this specific wavelength in a beam approximately 0.5mm in diameter.

After a crystal of a suitable size has been selected (all side lengths <0.5mm) the crystals were then mounted on a glass fibre, on a goniometer head, and placed on the goniometer (see figure A.1). The maximum size of the crystal is determined by the size of the collimated beam. The crystal must remain wholly in the beam under all orientations and thus a crystal of no more than 0.4mm in any one width is preferable.



Figure A.1 – A Goniometer

The goniometer was then placed immediately onto the SMART and the crystal rests in a stream of dry nitrogen produced by an Oxford Cryosystems " N_2 open flow cryostat cooler" (cryostream)¹ at 150K and was allowed to cool.

An initial search for diffracted intensities usually yields at least 20 reflections in the case of a good crystal. Using these intensities, the software calculated the unit cell dimensions. Once it had been established that these were within acceptable parameters, data collection commenced.

Once crystallinity and quality have been established, a "hemisphere" of Data were collected over a period of time using ω scans of an interval of 0.3°. Once the data collection was complete, the Data were integrated, solved, and then refined.

The Data were processed using the SAINT² program and after that the space group was determined from the integrated intensities, by the XPREP³ program. The structure solution was then provided by using the XS^4 package and refined using SHELXL-93⁵.

- ¹ J. Cozier., A. M. Glazier., J. Appl. Cryst., 19, 1986, 105
- ² Siemens SAINT Version 4.050 (Siemens Analytical X-ray Instruments), 1995.
- ³ SHELXTL Sheldrick, G, M., 1994.
- ⁴ SHELXS-86 Acta., Crystallographica., A46, 1990, 467.
- ⁵ SHELXL-93 Sheldrick, G, M., 1993.

Appendix 2

Crystal structure of compounds completed during the period 1994-1997, not included in the main body of the thesis

A.2 Other crystals structures 1994-1997

A.2.1 1,2,bisdiphenylphosphoniumethylene hydroxide bromide

This compound was synthesised by Miss Jennifer Boon and is a hydrolysis product formed in the reaction between PCl₃ and dppe.

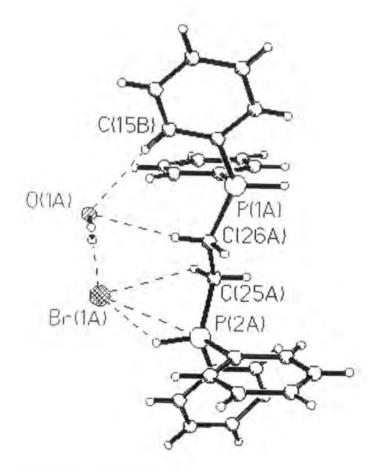


Figure A2.1 - A Diagrammatical representation of the product formed in the reaction between PCl₃ and dppe.

Crystal data	and structure refinement.
Identification code	Jenny Boon
Empirical formula	Con Hos Bro O Po
Formula weight	578.24
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 11.4590(5) Å α = 90 °.
	b = 14.3115(5) Å. β = 100.4620(10) °.
	$c = 15.5895(6) \text{ Å} \ \chi = 90^{\circ}$
Volume	2514.1(2) Å ³
7	4
Number of reflexions used	507
Crystal description	needle
Crystal colour	colourless
Density (calculated)	1.528 g/cm ³
Absorption coefficient	33.68 cm ⁻¹
F(000)	1168
Crystal size	0.2 x 0.2 x 0.4 mm
Theta range for data collection	1.95 to 25.67 °.
Index ranges	-13<=h<=13, -17<=k<=7, -16<=l<=18
Experiment device	Siemens Smart
Experiment methods	ω scans
Reflections collected	10581
Independent reflections	4266 [R(int) = 0.0429]
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	4220 / 0 / 315
Goodness-of-fit on F2	1.179
Final R indices [I>2o(I)]	$R_1 = 0.0431, wR_2 = 0.0792$
R indices (all data)	R1 = 0.0624, wR2 = 0.1083
Largest diff. peak and hole	.414 and383 e.Å· ³

Table 1 Crystal data and structural refinement

	X	у	z	U(eq)
P(1)	8639(1)	7214(1)	1451(1)	24(1)
P(2)	8562(1)	6711(1)	4239(1)	23(1)
C(4)	12506(4)	8124(4)	1870(3)	37(1)
C(13]	9291(4)	7435(3)	5110(3)	23(1)
C(19)	6976(4)	6763(3)	4137(3)	24(1)
C(12)	7399(4).	- 6861(3)	- 193(3)	28(1)
C(23)	5151(4)	7634(4)	3882(3)	34(1)
C(24)	6370(4)	7612(3)		31(1)
C(15)	10442(4)	7578(4)	6555(3)	32(1)
C(15)	8610(4)	5585(3)	477(3)	30(1)
C(6)	10437(4)	8494(4)	1497(3)	35(1)
C(1)	10164(4)	7560(3)	1585(3)	26(1)
C(17)	9726(4)	8955(4)	5745(3)	33(1)
C(14)	9930(4)	7021(3)	5862(3)	27(1)
C(7)	8175(4)	6487(3)	521(3)	23(1)
G(18)	9200(4)	8408(3)	5052(3)	30(1)
C(11)	7089(4)	6340(4)	-946(3)	33(1)
C(20)	6356(4)	5955(3)	4256(3)	29(1)
C(26)	8411(4)	6630(3)	2430(3)	27(1)
C(21)	6128(4)	5989(3)	4185(3)	30(1)
C(22)	4532(4)	6828(3)	4002(3)	29(1)
C(5)	11615(5)	8771(4)	1633(3)	40(1)
C(9)	8302(4)	5071(3)	-278(3)	32(1)
G(10)	7553(4)	5457(4)	-992(3)	35(1)
C(16)	10320(4)	8540(4)	6500(3)	33(1)
C(2)	11061(4)	6899(3)	1819(3)	34(1)
C(3)	12240(4)	7188(4)	1964(4)	41(1)
C(25)	9022(4)	7126(3)	3264(3)	25(1)
Br(1)	11455(1)	5610(1)	4270(1)	34(1)
Br(2)	7741(1)	9344(1)	2518(1)	-36(1)
0(1)	10149(4)	4654(3)	2390(3)	43(1)

Table 2 Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for C₂₆H₂₈Br₂OP₂. U(eq) is defined as one third of the trace of the *ortho*gonalized Uij tensor

Bond lengths [Å] an	d angles [°]
P(1)-C(7)	1.785(4)
P(1)-C(1)	1.791(4)
P(1)-C(26)	1.801(5)
P(2)-C(13)	1.789(5)
P(2)-C(19)	1.797(4)
P(2)-C(25)	1./9/(5)
C(4)-C(5)	1.378(7)
C(13)-C(14)	1.396(6)
C(13)-C(18)	1.399(6)
C(19)-C(20)	1.386(6)
C(19)-C(24)	1.404(6)
C(12)-C(11)	1.382(7)
- C(12)-C(7)	1.398(6)
C(23)-C(24)	1.382(6)
C(15)-C(14)	1.384(7) 1.385(6)
C(15)-C(16)	1385(7)
C(15)-C(9)	1.379(6)
C(15)-C(7)	1.390(6)
C(6)-C(5)	1.385(7)
C(6)-C(1)	1.386(7)
C(1)-C(2)	1.396(6)
C(17)-C(18)	1.381(7)
C(17)-C(16)	1.383(7)
C(20)-C(21)	1.392(6)
C(26)-C(25)	1.534(6)
C(21)-C(22)	1.385(7)
C(9)-C(10)	1.391(7)
C(2)-C(3)	1.391(7)
O(7)-P(1)-C(1)	113.3(2)
C(7)-P(1)-C(26)	110.5(2)
C(1)-P(1)-C(26)	108.5(2)
C(13)-P(2)-C(19)	111.6(2)
C(19)-P(2)-C(25)	106.4(2)
C(5)-C(4)-C(3)	120.6(5)
C(14)-C(13)-C(18)	119.9(4)
C(14)-C(13)-P(2)	119.5(3)
C(18)-C(13)-P(2)	120.5(4)
C(20)-C(19)-C(24)	120.2(4)
C(20)-C(19)-P(2)	119.3(3)
C(24)-C(19)-P(2) C(11)-C(12)-C(7)	120.5(3)
C(24) C(23) C(22)	119.8(4)
C(23)-C(24)-C(19)	119.4(4)
C(14)-C(15)-C(16)	120,1(5)
C(9)-C(15)-C(7)	119.9(4)
C(5)-C(6)-C(1)	119.5(5)
C(6)-C(1)-C(2)	120.7(4)
C(B)-C(1)-P(1)	119.2(4)
C(2)-C(1)-P(1)	120.0(4)
C(18)-C(17)-C(16)	120.0(0)

Bond lengths [Å] and angles [°]				
C(15)-C(14)-C(13)	119.6(4)			
C(15)-C(7)-C(12)	119.9(4)			
C(15)-C(7)-P(1)	121.6(3)			
C(12)-C(7)-P(1)	118.4(3)			
C(17)-C(18)-C(13)	119.8(5)			
C(10)-C(11)-C(12)	119.8(5)			
C(19)-C(20)-C(21)	119.7(4)			
C(25)-C(26) P(1)	112.9(3)			
C(22)-C(21)-C(20)	120.0(5)			
C(23)-C(22)-C(21)	120.3(4)			
C(4)-C(5)-C(6)	120.3(5)			
C(15)-C(9)-C(10)	119.8(5)			
C(11)-C(10)-C(9)	120.7(5)			
C(17)-C(16)-C(15)	120.5(5)			
C(3)-C(2)-C(1)	119.2(5)			
C(4)-C(3)-C(2)	119.7(5)			
C(26)-C(25)-P(2)	113.9(3)			

Table 3 - Bond lengths [Å] and angles [°] for $C_{26}H_{28}Br_2OP_2$

	U11	U22	U33	U23	U13	U12
P(1)	22(1)	22(1)	28(1)	-2(1)	4(1)	-2(1)
P(2)	20(1)	23(1)	25(1)	2(1)	4(1)	2(1)
C(4)	29(3)	52(3)	34(3)	-11(3)	16(2)	-13(3)
C(13)	20(2)	20(2)	27(2)	2(2)	7(2)	2(2)
C(19)	21(2)	28(2)	23(3)	-2(2)	4(2)	2(2)
G(12)	27(2)	27(3)	33(3)	4(2)	9(2)	1/21
C(23)	27(3)	32(3)	44(3)	0(2)	9(2)	7(2)
C(24)	25(2)	29(3)	41(3)	5(2)	9(2)	0(2)
C(15)	25(2)	43(3)	26(3)	4(2)	0(2)	1(2)
C(15)	31(3)	29(3)	28(3)	2(2)	1(2)	-1(2)
C(6)	25(3)	37(3)	39(3)	7(2)	-2(2)	-4(2)
C(1)	19(2)	29(3)	30(3)	-4(2)	5(2)	-3(2)
C(17)	23(2)	32(3)	44(3)	-2(2)	4(2)	4(2)
C(14)	25(2)	25(3)	30(3)	1(2)	6(2)	-1(2)
C(7)	22(2)	25(2)	23(2)	-1(2)	8(2)	-2(2)
C(18)	27(3)	31(3)	31(3)	0(2)	0(2)	5(2)
C(11)	28(3)	44(3)	25(3)	1(2)	4(2)	-3(2)
C(20)	31(3)	25(2)	- 29(3)	1(2)	4(2)	3(2)
C(26)	26(2)	30(3)	27(3)	-3(2)	7(2)	-6(2)
C(21)	23(2)	32(3)	35(3)	-4(2)	2(2)	-7(2)
C(22)	20(2)	36(3)	31(3)	-3(2)	4(2)	-1(2)
C(5)	41(3)	40(3)	39(3)	8(3)	9(3)	-14(3)
C(9)	36(3)	24(3)	35(3)	-7(2)	7(2)	0(2)
G(10)	36(3)	40(3)	29(3)	-11(2)	5(2)	-10(2)
C(16)	25(3)	38(3)	35(3)	-12(2)	4(2)	-1(2)
C(2)	31(3)	30(3)	41(3)	-7(2)	10(2)	-2(2)
C(3)	24(3)	49(3)	50(4)	-15(3)	6(2)	2(2)
G(25)	18(2)	30(3)	28(3)	3(2)	3(2)	0(2)
Br(1)	29(1)	28(1)	46(1)	-1(1)	7(1)	4(1)
Br(2)	- 39(1)	22(1)	48(1)	-2(1)	12(1)	2(1)

Table 4 Anisotropic displacement parameters (Å² x 10³) for C₂₆H₂₈Br₂OP₂. The anisotropic displacement factor exponent takes the form: -2 π² [h² a² U11 + 2 h k a* b* U12]

EI/40A)	X	y y	Z	U(eq)
H(18A)	13294(4)	8317(4)	1967(3)	46(16)
H(99A)	7093(4)	7459(3)	-160(3)	16(11)
H(11A)	4743(4)	8193(4)	3753(3)	34(14)
H(12A)	6786(4)	6156(3)	3876(3)	54(17)
H(14A)	10869(4)	7306(4)	7057(3)	25(12)
H(16A)	9108(4)	5328(3)	957(3)	- 22(12)
H(17A)	9835(4)	8932(4)	1348(3)	35(14)
H(21A)	9662(4)	9603(4)	5703(3)	50(17)
H(25A)	10011(4)	6375(3)	5897(3)	10(10)
H(28A)	8787(4)	8686(3)	4548(3)	37(14)
H(29A)	6568(4)	6585(4)	-1420(3)	41(15)
H(2A)	6759(4)	5394(3)	4382(3)	25(12)
H(3A)	7566(4)	6593(3)	2432(3)	55(17)
H(3B)	8713(4)	5997(3)	2429(3)	50(16)
H(4A)	4708(4)	5448(3)	4260(3)	57(18)
H(5A)	3713(4)	6850(3)	3960(3)	33(18)
H(6A)	11804(5)	9395(4)	1565(3)	57(18)
H(7A)	8594(4)	4468(3)	-310(3)	35(14)
H(8A)	7363(4)	5115(4)	-1507(3)	37(14)
H(9A)	10640(4)	8910(4)	6975(3)	36(14)
H(10A)	10873(4)	6272(3)	1877(3)	38(15)
H(12B)	12847(4)	6756(4)	2123(4)	43(15)
H(20A)	8857(4)	7790(3)	3205(3)	40(14)
H(20B)	9873(4)	7044(3)	3324(3)	
H(3P)	8020(31)	8020(25)	1293(23)	
HAP	8856(34)	5870(27)	4418(25)	8(10)
H(2W)	9519(60)	AA69(AE)	I LINKENY	76(10)
H(1)40	The second se	4468(45)	2478(42)	76(22)
IN INVI	10608(67)	4304(04)	2980(01)	114(27)

Table 2.5 Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters (Å² $x \ 10^3$) for C₂₆H₂₈Br₂OP₂.

A.2.2 cis-dibromo(triethylphosphane)(1,1-dihydroxy-2,6bis(trifluoromethyl)phenyl)platinum(ll)

This compound is formed by the hydrolysis of the product, formed in the reaction between $Ar'PBr_2/Ar''PBr_2$ and $[PtCl_2(PEt_3)]_2$. The expected product from this reaction would be $RPBr_2[PtCl_2(PEt_3)]$.

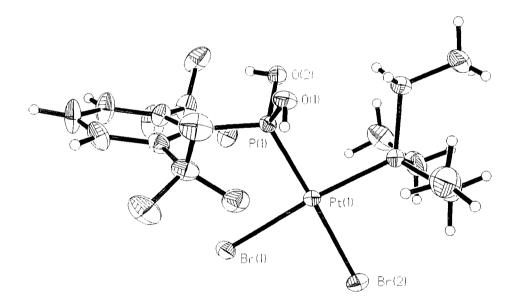


Figure A2.2 - Thermal ellipsoid diagram at 150K (50% Probability) for Ar'P(OH)₂[PtBr₂(PEt₃)]

Crystal d	ata and structure refinement
Identification code	-PIBr2
Empirical formula	C14 H20 Br2 F6 O2 P2 P1
Formula weight	751.15
Temperature	150(2) K
Wavelength	0.71073 Å
Grystal system	Orthorhomble
Space group	P212121
Unit cell dimensions	e = 19.332(3) Å a = 90 °.
	b = 19.332(3) Å,b = 90 °.
	$c = 12.856(3) \text{ Å} = 90^{\circ}$
Volume	4804.4(14) Å ³
Z-	8
Number of reflections used	15711
Crystal description	cube
Crystal colour	colourless
Density (calculated)	2.077 g/cm ³
Absorption coefficient	93.53 cm ⁻¹
F(000)	2816
Crystal size	0.2 x 0.2 x 0.2 mm
Theta range for data collection	1.49 to 27.48 °.
Index ranges	-25<=h<=23, -25<=k<=24, -12<=l<=16
Experiment device	Siemens SMART
Experiment methods	ω scans
Reflections collected	15711
Independent reflections	5487 [R(int) = 0.0517]
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	5475/0/249
Goodness-of-fit on F ²	1.196
Final R indices [I>2o(I)]	$R_1 = 0.0316$, w $R_2 = 0.0669$
R indices (all data)	$R_1 = 0.0386$, w $R_2 = 0.0727$
Absolute structure parameter	019(8)
Largest diff. peak and hole	.937 and699 e.A.3

Table 6 Crystal data and structural refinement

	X	y	z	U(eq)
Pt(1)	3048(1)	3044(1)	4956(1)	21(1)
Br(2)	3533(1)	3640(1)	6506(1)	30(1)
Br(1)	3292(1)	1943(1)	5904(1)	27(1)
F(3)	1602(2)	2101(2)	5324(3)	33(1)
F(2)	846(2)	1679(3)	4255(4)	38(1)
C(6)	1966(4)	1176(4)	4196(6)	25(2)
F(1)	1179(3)	1095(3)	5578(4)	45(1)
G(8)	1405(4)	1529(4)	4830(6)	29(2)
C(1)	2539(4)	1529(3)	3760(5)	20(1)
C(2)	3058(4)	1109(4)	3313(6)	26(2)
P(2)	2961(1)	4099(1)	4194(2)	28(1)
C(4)	2377(5)	81(4)	3563(8)	43(2)
F(6)	3969(2)	1941(2)	3440(4)	31(1)
F(5)	4240(2)	903(3)	3069(5)	51(1)
F(4)	3753(3)	1537(3)	1918(4)	44(1)
C(7)	3740(4)	1389(4)	2923(7)	32(2)
C(3)	2963(4)	403(4)	3206(7)	38(2)
C(13)	2464(5)	4709(4)	4952(8)	43(2)
C(9)	2595(5)	4151(4)	2896(6)	36(2)
C(14)	1712(5)	4538(5)	4978(11)	57(2)
C(12)	4305(5)	4057(5)	3379(8)	52(3)
C(11)	3835(5)	4466(5)	4072(8)	44(2)
C(10)	2535(7)	4884(5)	2449(8)	58(3)
C(5)	1888(4)	469(4)	4084(7)	34(2)
P(1)	2568(1)	2482(1)	3651(1)	20(1)
0(1)	1781(3)	2684(3)	3461(4)	26(1)
O(2)	2932(3)	2603(3)	2565(4)	26(1)

Table 7 Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for C₁₄H₂₀Br₂F₆O₂P₂Pt. U(eq) is defined as one third of the trace of the *ortho*gonalized Uij tensor

Bond lengths [Å] and	angles [°]
Pt(1)-P(1)	2.203(2)
Pt(1)-P(2)	2,269(2)
Pt(1)-Br(2)	2.4859(8)
PI(1)-Br(1)	2.4979(8)
F(3)-C(8)	1.330(9)
F(2)-C(8)	1,343(9)
C(6)-C(5)	1.384(11)
G(6)-G(1)	1.417(10)
C(6)-C(8)	1.518(10)
C(1)-C(2)	1.449(8)
C(1)-C(2)	1.412(10)
C(2)-C(3)	1.384(11)
C(2)-C(7)	1.512(10)
P(2)-C(13)	1.808(9)
P(2)-C(9)	1.815(8)
P(2)-C(11)	1.839(9)
C(4)-C(3)	1.371(12)
C(4)-C(5)	1.380(12)
F(6)-C(7)	1.333(9)
F(5)-C(7)	1.361(9)
F(4)-C(7)	1.324(10)
C(13)-C(14)	1.492(13)
C(9)-C(10)	1.532(11)
C(12)-C(11)	1.498(14)
P(1)-O(2)	1.580(5)
P(1)-O(1)	1.589(5)
P(1)-P(1)-P(2)	84.79(7) 170.00(E)
P(1)-Pt(1)-Br(2)	176.20(5)
P(1)-Pt(1)-Br(1)	91.80(5)
P(2)-Pt(1)-Br(1)	172 16(6)
Br(2)-Pt(1)-Br(1)	86.11(3)
C(5)-C(6)-C(1)	121.3(7)
C(5)-C(6)-C(8)	114.9(7)
C(1)-C(6)-C(8)	123.7(7)
F(3)-C(8)-F(2)	108.3(6)
F(3)-C(8)-F(1)	105.6(6)
F(2)-C(8)-F(1)	105.4(6)
F(3)-C(8)-C(6)	115.2(6)
F(2)-C(8)-C(6)	112.1(6)
F(1)-C(8)-C(6)	109.6(6)
C(2)-C(1)-C(6)	116.0(6)
C(2)-C(1)-P(1)	121.4(5)
C(6)-C(1)-P(1)	122.2(5)
C(3)-C(2)-C(7)	120.9(7) 115.8(7)
C(1)-C(2)-C(7)	123.2(7)
C(13)-P(2)-C(9)	104.6(4)
C(13)-P(2)-C(11)	106.4(4)
C(9)-P(2)-C(11)	105.0(4)
C(13)-P(2)-PI(1)	113.1(3)
C(9)-P(2)-Pt(1)	118.4(3)
C(11)-P(2)-Pi(1)	108.4(3)

Bond lengths [Å] and	d angles [°]
C(3)-C(4)-C(5)	118.9(8)
F(4)-C(7)-F(6)	107.9(6)
F(4)-C(7)-F(5)	105.7(6)
F(6)-C(7)-F(5)-	104.4(6)
F(4)-C(7)-C(2)	114.6(7)
F(6)-C(7)-C(2)	114.3(6)
F(5)-C(7)-C(2)	109.1(6)
C(4)-C(3)-C(2)	- 121.5(8)
C(14)-C(13)-P(2)	112.7(7)
C(10)-C(9)-P(2)	115.2(6)
C(12)-C(11)-P(2)	113.8(7)
C(6)-C(5)-C(4)	120.8(7)
O(2)-P(1)-O(1)	104.7(3)
O(2)-P(1)-C(1)	103.2(3)
O(1)-P(1)-C(1)	103.1(3)
O(2)-P(1)-Pt(1)	114.3(2)
O(1)-P(1)-Pt(1)	113.5(2)
C(1)-P(1)-Pt(1)	116.5(2)

Table 8 - Bond lengths [Å] and angles [°] for C14H20Br2F6O2P2Pt

- DUGL	U11	U22	U33	U23	U13	U12
Pt(1)	27(1)	19(1)	16(1)	- 0(1)	0(1)	1(1)
87(2)	37(1)	33(1)	22(1)	-5(1)	-5(1)	-2(1)
Br(1)	33(1)	25(1)	22(1)	4(1)	0(1)	4(1)
F(3)	33(2)		26(2)	-2(2)	8(2)	8(73)
F(2)	18(2)	55(3)	41(3)	2(2)	-2(2)	7(2)
C(6)	23(4)	28(4)	23(3)	6(3)	2(3)	F(2)
F(1)	42(3)	55(3)	36(3)	16(2)	19(2)	-2(2)
C(8)	23(3)	41(4)	22(4)	5(3)	5(3)	-2(2)
C(1)	24(4)	17(3)	18(3)	-1(3)	0(3)	-4/3)
C(2)	21(4)	25(4)	32(4)	-5(3)	5(3)	-4(3)
P(2)	42(1)	20(1)	22(1)	0(1)	-3(1)	-1(1)
C(4)	45(5)	17(4)	66(6)	-2(4)	14(5)	-1(1)
F(6)	25(2)	30(2)	38(3)	-5(2)	3(2)	2(2)
F(5)		40(3)	86(4)	-5(3)	10/2	-3(2)
F(4)	46(3)	52(3)	34(3)	-15(2)	22(2)	10(2)
C(7).	18(4)	31(4)	46(5)	-5(3)	11(2)	-18(2)
C(3)	30(4)	24(4)	59(6)	-8(4)	16(4)	-3(3)
C(13)	66(6)	34(4)	30(4) -	0(4)	-6(5)	0(3)
C(9)	59(6)	27(4)	22(4)	3(3)	-	2(4)
C(14)	63(6)	58(6)	51(5)	-1(6)	-9(4)	-6(4)
C(12)	46(6)	58(6)	53(6)	16(5)	2(5)	19(5)
C(11)	52(6)	32(5)	49(5)	12(4)	-3(5)	6(5)
C(10)	108(10)	29(5)	36(5)	A CONTRACTOR OF THE OWNER	17(0)	-12(4)
C(5)	30(4)	30(4)	13(5)	14(4)	-17(6)	-11(5)
P(1)	23(1)	18(1)	17(1)	13(4)	0(4)	-3(3)
0(1)	28(3)	32(3)	18(2)	1(1)	2(1)	2(1)
O(2)	35(3)	23(3)	20(2)	0(2)	1(2)	2(2)
	0010/	20(0)	20(2)	0(2)	5(2)	-1(2)

Table 9 Anisotropic displacement parameters (Å² x 10³) for C₁₄H₂₀Br₂F₆O₂P₂Pt. The anisotropic displacement factor exponent takes the form: -2 π² [h² a² U11 + 2 h k a* b* U12]

	X	V	z	U(eq)
H(4)	2310(5)	-390(4)	3456(8)	51
H(3)	3305(4)	140(4)	2884(7)	45
H(13A)	2641(5)	4716(4)	5658(8)	52
H(138)	2523(5)	5168(4)	4662(8)	-52
H(9A)	2879(5)	3877(4)	2430(6)	44
H(8B)	2138(5)	3945(4)	2909(6)	44
H(14A)	1518(9)	4600(36)	4297(16)	86
H(146)	1481(8)	4837(26)	5462(43)	66
H(14C)	1653(5)	4065(12)	5190(56)	86
H(12A)	4729(16)	4306(18)	3279(47)	78
H(12B)	4084(17)	3986(34)	2718(22)	78
H(12C)	4402(32)	3618(16)	3695(28)	78
H(11A)	3798(5)	4933(5)	3801(8)	53
H(11B)	4041(5)	4495(5)	4758(8)	53
H(10A)	2214(33)	5147(14)	2860(39)	87
H(10B)	2371(41)	4859(5)	-1745(22)	87
H(10C)	2980(11)	5104(16)	2463(59)	87
H(5)	1501(4)	252(4)	4364(7)	-41
H(1)	1571(11)	2670(45)	4015(12)	39
H(2)	3145(40)	2254(17)	2398(35)	39

Table 2.10 Hydrogen coordinates ($x~10^4$) and isotropic displacement parameters (Å $^2~x~10^3$) for $C_{14}H_{20}Br_2F_6O_2P_2Pt$

A.2.3 1,1-dihydroxy-2,6-bis(trifluoromethyl)phenylphosphane

This crystal structure represents the product formed by the slow air oxidation of $Ar'PH_2$. It is interesting to note that the hydrogen atoms on the OH groups attached to phosphorus, are both directed towards the electron rich CF₃ groups. This factor may explain the stability of the compound. Hydrolysis of a P(III) compound normally results in the formation of a P(V) compound via the rearrangement of a P-OH bond into a P=O bond and a P-H bond.

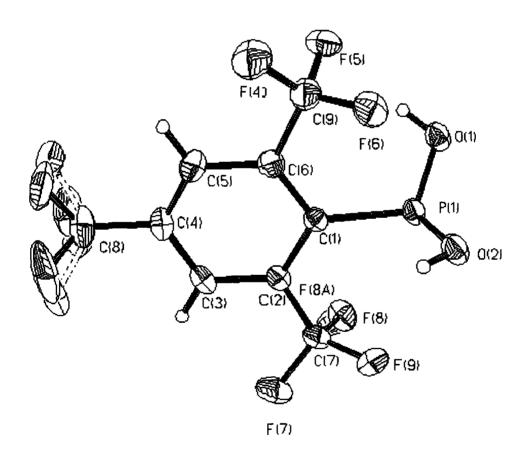


Figure A2.3 - Thermal ellipsoid diagram at 150K (50% Probability) for ArP(OH₂)

Crystal data and	structure refinement
Identification code	Ar'P(OH)2
Empirical formula	Co He Fo O2 P
Formula weight	346.09
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 8.397(2) Å. cc = 90 °.
	b = 6,4175(13) Å β = 96.08(3).°
	c = 11.150(2) Å x = 90 °.
Volume	597.4(2) Å ³
Z	2
Number of reflexions used	4286
Crystal description	cube
Crystal colour	colourless
Density (calculated)	1.924 g/cm ³
Absorption coefficient	3.50 cm ⁻¹
F(000)	340
Crystal size	0.2 x 0.2 x 0.2 mm
Theta range for data collection	1.84 to 30.07 °.
Index ranges	-11<=h<=11, -8<=k<=7, -14<=l<=15
Experiment device	Siemens SMART
Experiment methods	w scans
Reflections collected	4286
Independent reflections	2528 [R(int) = 0.0187]
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	2528 / 1 / 236
Goodness-of-fit on F ²	1.018
Final R indices [I>2o(I)]	$R_1 = 0.0349, wR_2 = 0.0866$
R indices (all data)	$R_1 = 0.0442$, w $R_2 = 0.0901$
Absolute structure parameter	.43(13)
Largest diff. peak and hole	0.502 and -0.354 e.Å-3

Table 11 Crystal data and structural refinement

	x	y	z	U(eq)
P(1)	-39(1)	1618(1)	1093(1)	23(1)
0(1)	220(2)	1554(2)	-208(1)	28(1)
O(2)	80(2)	-530(2)	1712(1)	30(1)
C(1)		3361(3)	1986(2)	- 20(1)
C(2)	840(2)	4585(3)	2932(2)	22(1)
G(3)	1810(2)	6116(3)	3505(2)	28(1)
C(4)	3333(2)	6446(3)	3161(2)	27(1)
Q(5)	3914(2)	5216(3)	2296(2)	28(1)
C(6)	2940(2)	3661(3)	1718(2)	23(1)
C(7)	-818(2)	4354(3)	3340(2)	31(1)
F(4)	5322(1)	2346(2)	1038(1)	50(1)
F(5)	3392(2)	3048(2)	-329(1)	43(1)
F(6)	3254(1)	343(2)	812(1)	37(1)
C(8)	4324(3)	8197(4)	3772(2)	42(1)
F(1)	5642(4)	8631(6)	3105(4)	73(1)
F(1A)	5836(4)	7983(6)	3706(4)	-75(1)
F(2)	4238(3)	8064(5)	5043(2)	50(1)
F(2A)	4807(5)	7949(6)	4824(3)	79(1)
F(3)	3646(4)	10035(6)	3531(3)	22(1)
F(3A)	3385(6)	9974(9)	3733(5)	43(1)
F(3B)	3975(8)	10008(10)	3401(6)	67(2)
C(9)	3705(2)	2346(4)	795(2)	33(1)
F(7)	-906(2)	5238(2)	4421(1)	50(1)
F(8)	-1933(3)	5365(5)	2642(3)	44(1)
F(8A)	-1958(3)	5222(6)	2519(3)	36(1)
F(9)	-1246(1)	2361(2)	3441(1)	40(1)

Table 12 Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for Ar'P(OH)₂. U(eq) is defined as one third of the trace of the *ortho*gonalized Uij tensor

Bond lengths [Å] an	d angles (°)
P(1)-O(1)	1.4901(12)
P(1)-O(2)	1 5309(14)
P(1)-C(1)	1.832(2)
G(1)-C(6)	1.406(2)
C(1)-C(2)	1.423(2)
C(2)-C(7)	1.517(3)
C(3)-C(4)	1.389(3)
C(4)-C(5)	1.375(3)
C(4)-C(8)	1.516(3)
C(5)-C(6)	1.403(3)
C(7)-F(8)	1.322(4)
C(7)-F(9)	1.337(3)
C(7)-F(7)	1.342(2)
C(7)-F(8A)	1.370(4)
F(4)-C(9)	1.356(2)
F(5)-C(9)	1.331(2)
F(6)-C(9)	1.341(3)
G(8)-F(2A)	-1.211(4)
C(8)-F(3B)	1.258(7)
C(0)-F(1A)	1.324(5)
C(8)-F(3)	1.324(5)
C(8)-F(1)	1.424(4)
C(8)-F(2)	1.429(4)
F(1)-F(1A)	.791(5)
F(1)-F(3B)	1.716(8)
F(1A)-F(2A)	1.591(6)
F(2)-F(2A) F(2A) F(2D)	.004(b)
F(3A)-F(3B)	.649(9)
O(1)-P(1)-C(1)	113.25(8)
O(2)-P(1)-O(1)	106.98(8)
C(6)-C(1)-C(2)	116.6(2)
C(6)-C(1)-P(1)	122.39(13)
C(2)-C(1)-P(1)	120.79(13)
C(3)-C(2)-C(1)	121.7(2)
C(3)-C(2)-C(7)	116.3(2)
C(2)-C(3)-C(4)	119.5(2)
C(5)-C(4)-C(3)	120.8(2)
C(5)-C(4)-C(8)	121.4(2)
C(3)-C(4)-C(8)	117.8(2)
C(4)-C(5)-C(6)	119.8(2)
C(5)-C(6)-C(1)	121.4(2)
C(5)-C(6)-C(9)	115.9(2)
C(1)-C(6)-C(9)	122.7(2)
F(8)-C(7)-F(9)	109.9(2)
F(9)-C(7)-F(7)	102.0(2)
F(8)-C(7)-F(8A)	67(2)
F(9)-C(7)-F(8A)	105.7(2)
F(7)-C(7)-F(8A)	109.1(2)

Bond lengths [Å] and a	angles [°]
F(8)-C(7)-C(2)	113.0(2)
F(9)-C(7)-C(2)	112.5(2)
F(7)-C(7)-C(2)	111.6(2)
F(2A)-C(8)-F(3B)	111.0(2)
F(2A)-C(8)-F(1A)	79.0(3)
F(3B)-C(8)-F(1A)	106.1(4)
F(2A)-C(8)-F(3)	114.0(3)
F(3B)-C(8)-F(3)	14.2(4)
F(1A)-C(8)-F(3)	119.2(3)
F(2A)-C(8)-F(3A) F(3B)-C(8)-F(3A)	105.7(3)
F(1A)-C(8)-F(3A)	130.4(3)
F(3)-C(8)-F(3A)	13.9(3)
F(2A)-C(8)-F(1)	109.4(3)
F(3B)-C(8)-F(1)	79.3(4)
F(1A)-C(8)-F(1)	33.4(2)
F(3A)-C(8)-F(1)	107.1(3)
F(2A)-C(8)-F(1)	22.8(3)
F(3B)-C(8)-F(2)	110.3(4)
F(1A)-C(8)-F(2)	101.8(3)
F(3)-C(8)-F(2)	100.9(3)
F(3A)-C(8)-F(2)	89.5(3)
F(1)-C(8)-F(2)	130.7(2)
F(2A)-0(8)-0(4)	110.7(3)
F(3B)-C(8)-C(4)	116.1(3)
F(3)-C(8)-C(4)	111.4(2)
F(3A)-C(8)-C(4)	108.2(3)
F(1)-C(8)-C(4)	109.3(2)
F(2)-C(8)-C(4)	108.5(2)
F(1A)-F(1)-C(8)	63.7(4)
C(8)-F(1)-F(3B)	46.1(2)
E(1)-E(1A)-C(B)	40.1(2)
F(1)-F(1A)-F(2A)	126.2(5)
C(8)-F(1A)-F(2A)	48.4(2)
F(2A)-F(2)-C(8)	56.3(5)
F(2)-F(2A)-C(8)	100.9(6)
F(2)-F(2A)-F(1A)	153.2(6)
F(3B)-F(3A)-C(8)	65.1(8)
F(3A)-F(3B)-C(8)	87 0(9)
F(3A)-F(3B)-F(1)	141.2(10)
C(8)-F(3B)-F(1)	54.6(3)
F(5)-C(9)-F(6)	108.0(2)
F(5)-C(9)-F(4)	106.4(2)
F(6)-C(9)-F(4)	106.0(2)
F(5)-C(9)-C(6)	113,1(2)
F(6)-C(9)-C(6)	112.4(2)
F(4)-C(9)-C(6)	110.3[2]

Table 13 - Bond lengths [Å] and angles [°] for Ar'P(OH)_2

	U11	U22	U33	U23	U13	U12
P(1)	27(1)	20(1)	20(1)	-2(1)	-1(1)	-2(1)
0(1)	42(1)	20(1)	21(1)	0(1)	1(1)	-3(1)
0(2)	45(1)	24(1)	20(1)	0(1)	-2(1)	-4(1)
6(1)	23(1)	19(1)	18(1)	1(1)	1(1)	- 2(1)
C(2)	26(1)	20(1)	20(1)	0(1)	1(1)	2(1)
G(3)	34(1)	26(1)	22(1)	-6(1)	-2(1)	4/11
C(4)	27(1)	22(1)	31(1)	-2(1)	-6(1)	-1(1)
C(5)	23(1)	25(1)	37(1)	1(1)	0(1)	-1(i)
C(6)	25(1)	20(1)	25(1)	-2(1)	2(1)	1(1)
C(7)	34(1)	37(1)	25(1)	-7(1)	9(1)	-1(1)-
F(4)	26(1)	55(1)	71(1)	-21(1)	14(1)	3(1)
F(5)	53(1)	47(1)	30(1)	-4(1)	18(1)	-6(1)
F(6)	38(1)	28(1)	45(1)	-9(1)	9(1)	7(1)
C(8)	37(1)	29(1)	56(1)	-12(1)	-8(1)	-2(1)
F(1)	46(2)	67(2)	108(3)	-37(2)	20(2)	-29(2)
F(1A)	29(1)	91(2)	106(3)	-65(2)	17(2)	-28(2)
F(2)	50(2)	62(2)	34(1)	-16(1)	-8(1)	-11(2)
F(2A)	123(3)	41(2)	59(2)	16(2)	-65(2)	-25(2)
F(3)	24(2)	19(2)	21(2)	1(2)	-2(1)	0(1)
F(3A)	49(3)	25(2)	57(3)	-6(2)	12(2)	-10(2)
F(3B)	94(5)	32(3)	69(4)	9(3)	-25(3)	-27(3)
0(9)	27(1)	33(1)	40(1)	-7(1)	7(1)	1(1)
F(7)	51(1)	66(1)	35(1)	-19(1)	21(1)	-7(1)
F(8)	29(1)	50(2)	56(2)	11(2)	and the second second	9(1)
F(8A)	21(1)	49(2)	37(2)	-9(2)	-3(1)	6(1)
F(9)	43(1)	40(1)	38(1)	3(1)	13(1)	-11(1)

Table 14 Anisotropic displacement parameters (Ų x 10³) for Ar'P(OH)2. The anisotropic displacement
factor exponent takes the form: $-2 \pi^2 [h^2 a^2 U11 + 2 h k a^* b^* U12]$

A.2-22

Appendix 3

Courses attended

A.3 Courses Attended

A.3.1 First Year Induction Courses : October 1993

The course consists of a series of one hour lecture on the services available in the department.

- 1. Departmental Safety
- 2. Safety Matters
- 3. Electrical Appliances and Infrared Spectroscopy
- 4. Chromatography and Elemental Analysis
- 5. Atomic Absorption and Inorganic Analysis
- 6. Library Facilities
- 7. Mass Spectroscopy
- 8. Nuclear Magnetic Resonance
- 9. Glassblowing Techniques

A.3.2 Examined Lecture Courses : October 1993 – April 1994

Three courses were attended consisting of 6 one hour lectures followed by a written examination in each.

"Diffraction and Scattering Methods" 6 lectures by Prof. Judith Howard

"Synthetic Methodology in Organometallic Chemistry and Coordination Chemistry", 3 lectures by Prof. V. C. Gibson and 3 lectures by Prof. D. Parker.

"Practical NMR" 6 lectures by Alan Kenwright

Appendix 4

Colloquia, Lectures and Seminars organised by the Department of Chemistry 1994-1997

A.4 COLLOQUIA, LECTURES AND SEMINARS FROM INVITED SPEAKERS

A.4.1 1994 - 1995 (August 1 - July 31)

<u>1994</u>

October 5	Prof. N. L. Owen, Brigham Young University, Utah, USA Determining Molecular Structure - the INADEQUATE NMR way
October 19	Prof. N. Bartlett, University of California Some Aspects of Ag(II) and Ag(III) Chemistry
November 2	Dr P. G. Edwards, University of Wales, Cardiff The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands
November 3	Prof. B. F. G. Johnson, Edinburgh University Arene-metal Clusters
November 9	Dr G. Hogarth, University College, London New Vistas in Metal-imido Chemistry
November 10	Dr M. Block, Zeneca Pharmaceuticals, Macclesfield Large-scale Manufacture of ZD 1542, a Thromboxane Antagonist Synthase Inhibitor
November 16	Prof. M. Page, University of Huddersfield Four-membered Rings and β -Lactamase
November 23	Dr J. M. J. Williams, University of Loughborough New Approaches to Asymmetric Catalysis
December 7	Prof. D. Briggs, ICI and University of Durham Surface Mass Spectrometry
<u>1995</u>	
January 11	Prof. P. Parsons, University of Reading Applications of Tandem Reactions in Organic Synthesis
January 18	Dr G. Rumbles, Imperial College, London Real or Imaginary Third Order Non-linear Optical Materials
January 25	Dr D. A. Roberts, Zeneca Pharmaceuticals The Design and Synthesis of Inhibitors of the Renin-angiotensin System

February 1	Dr T. Cosgrove, Bristol University Polymers do it at Interfaces
February 8	Dr D. O'Hare, Oxford University Synthesis and Solid-state Properties of Poly-, Oligo- and Multidecker Metallocenes
February 22	Prof. E. Schaumann, University of Clausthal Silicon- and Sulphur-mediated Ring-opening Reactions of Epoxide
March 1	Dr M. Rosseinsky, Oxford University Fullerene Intercalation Chemistry
March 22	Dr M. Taylor, University of Auckland, New Zealand Structural Methods in Main-group Chemistry
April 26	Dr M. Schroder, University of Edinburgh Redox-active Macrocyclic Complexes : Rings, Stacks and Liquid Crystals
May 4	Prof. A. J. Kresge, University of Toronto <i>The Ingold Lecture</i> Reactive Intermediates : Carboxylic-acid Enols and Other Unstable Species

A.4.2 1995 - 1996 (August 1 - July 31)

<u>1995</u>

October 11	Prof. P. Lugar, Frei Univ Berlin, FRG Low Temperature Crystallography
October 13	Prof. R. Schmutzler, Univ Braunschweig, FRG. Calixarene-Phosphorus Chemistry: A New Dimension in Phosphorus Chemistry
October 18	Prof. A. Alexakis, Univ. Pierre et Marie Curie, Paris, Synthetic and Analytical Uses of Chiral Diamines
October 25	Dr. D.M Davies, University of Northumbria Chemical reactions in organised systems.
November 1	Prof. W. Motherwell, UCL London New Reactions for Organic Synthesis
November 3	Dr B. Langlois, University Claude Bernard-Lyon Radical Anionic and Psuedo Cationic Trifluoromethylation
November 8	Dr. D. Craig, Imperial College, London New Stategies for the Assembly of Heterocyclic Systems

November 15	Dr A. Sella, UCL, London Chemistry of Lanthanides with Polypyrazoylborate Ligands
November 17	Prof. D. Bergbreiter, Texas A&M, USA Design of Smart Catalysts, Substrates and Surfaces from Simple Polymers
November 22	Prof. I Soutar, Lancaster University A Water of Glass? Luminescence Studies of Water-Soluble Polymers.
November 29	Prof. D. Tuck, University of Windsor, Ontario, Canada New Indium Coordination Chemistry
December 8	Professor M.T. Reetz, Max Planck Institut, Mulheim Perkin Regional Meeting
<u>1996</u>	
January 10	Dr B. Henderson, Waikato University, NZ Electrospray Mass Spectrometry - a new sporting technique
January 17	Prof. J. W. Emsley, Southampton University Liquid Crystals: More than Meets the Eye
January 24	Dr A. Armstrong, Nottingham Univesity Alkene Oxidation and Natural Product Synthesis
January 31	Dr J. Penfold, Rutherford Appleton Laboratory, Soft Soap and Surfaces
February 7	Dr R.B. Moody, Exeter University Nitrosations, Nitrations and Oxidations with Nitrous Acid
February 12	Dr P. Pringle, University of Bristol Catalytic Self-Replication of Phosphines on Platinum(O)
February 14	Dr J. Rohr, Univ Gottingen, FRG Goals and Aspects of Biosynthetic Studies on Low Molecular Weight Natural Products
February 21	Dr C R Pulham, University. Edinburgh Heavy Metal Hydrides - an exploration of the chemistry of stannanes and plumbanes
February 28	Prof. E. W. Randall, Queen Mary & Westfield College New Perspectives in NMR Imaging

March 6	Dr R. Whitby, University of Southampton New approaches to chiral catalysts: Induction of planar and metal centred asymmetry
March 7	Dr D. S. Wright, University of Cambridge Synthetic Applications of Me ₂ N-p-Block Metal Reagents
March 12	RSC Endowed Lecture - Prof. V. Balzani, Univ of Bologna Supramolecular Photochemistry
March 13	Prof. D. Garner, Manchester University Mushrooming in Chemistry
April 30	Dr L. D.Pettit, Chairman, IUPAC Commission of Equilibrium Data pH-metric studies using very small quantities of uncertain purity

A.4.3 1996 - 1997 (August 1 - July 31)

<u>1996</u>

Professor G. Bowmaker, University Aukland, NZ Coordination and Materials Chemistry of the Group 11 and Group 12 Metals : Some Recent Vibrational and Solid State NMR Studies
Professor A. R. Katritzky, University of Gainesville, University of Florida, USA Recent Advances in Benzotriazole Mediated Synthetic Methodology
Professor Ojima, Guggenheim Fellow, State University of New York at Stony Brook Silylformylation and Silylcarbocyclisations in Organic Synthesis
Professor L. Gade, University Wurzburg, Germany Organic transformations with Early-Late Heterobimetallics: Synergism and Selectivity
Professor B. J. Tighe, Department of Molecular Sciences and Chemistry, University of Aston Making Polymers for Biomedical Application - can we meet Nature's Challenge? Joint lecture with the Institute of Materials
Professor H. Ringsdorf (Perkin Centenary Lecture), Johannes Gutenberg-Universitat, Mainz, Germany Function Based on Organisation

October 29	Professor D. M. Knight, Department of Philosophy, University of Durham. The Purpose of Experiment - A Look at Davy and Faraday
	The Fulpose of Experiment - A Look at Davy and Faraday
October 30	Dr P. Mountford, Nottingham University Recent Developments in Group IV Imido Chemistry
November 6	Dr M. Duer, Chemistry Department, Cambridge Solid-state NMR Studies of Organic Solid to Liquid-crystalline Phase Transitions
November 12	Professor R. J. Young, Manchester Materials Centre, UMIST New Materials - Fact or Fantasy? Joint Lecture with Zeneca & RSC
November 13	Dr G. Resnati, Milan Perfluorinated Oxaziridines: Mild Yet Powerful Oxidising Agents
November 18	Professor G. A. Olah, University of Southern California, USA Crossing Conventional Lines in my Chemistry of the Elements
November 19	Professor R. E. Grigg, University of Leeds Assembly of Complex Molecules by Palladium-Catalysed Queueing Processes
November 20	Professor J. Earnshaw, Deptartment of Physics, Belfast Surface Light Scattering: Ripples and Relaxation
November 27	Dr R. Templer, Imperial College, London Molecular Tubes and Sponges
December 3	Professor D. Phillips, Imperial College, London "A Little Light Relief" -
December 4	Professor K. Muller-Dethlefs, York University Chemical Applications of Very High Resolution ZEKE Photoelectron Spectroscopy
December 11	Dr C. Richards, Cardiff University Sterochemical Games with Metallocenes
<u>1997</u>	
January 15	Dr V. K. Aggarwal, University of Sheffield Sulfur Mediated Asymmetric Synthesis
January 16	Dr S. Brooker, University of Otago, NZ Macrocycles: Exciting yet Controlled Thiolate Coordination Chemistry

January 21	Mr D. Rudge, Zeneca Pharmaceuticals High Speed Automation of Chemical Reactions
January 22	Dr N. Cooley, BP Chemicals, Sunbury Synthesis and Properties of Alternating Polyketones
January 29	Dr J. Clarke, UMIST What can we learn about polymers and biopolymers from computer- generated nanosecond movie-clips?
February 4	Dr A. J. Banister, University of Durham From Runways to Non-metallic Metals - A New Chemistry Based on Sulphur
February 5	Dr A. Haynes, University of Sheffield Mechanism in Homogeneous Catalytic Carbonylation
February 12	Dr GJan Boons, University of Birmingham New Developments in Carbohydrate Chemistry
February 18	Professor Sir James Black, Foundation/King's College London My Dialogues with Medicinal Chemists
February 19	Professor B. Hayden, University of Southampton The Dynamics of Dissociation at Surfaces and Fuel Cell Catalysts
February 25	Professor A. G. Sykes, University of Newcastle The Synthesis, Structures and Properties of Blue Copper Proteins
February 26	Dr T. Ryan, UMIST Making Hairpins from Rings and Chains
March 4	Professor C. W. Rees, Imperial College Some Very Heterocyclic Chemistry
March 5	Dr J. Staunton FRS, Cambridge University Tinkering with biosynthesis: towards a new generation of antibiotics
March 11	Dr A. D. Taylor, ISIS Facility, Rutherford Appleton Laboratory Expanding the Frontiers of Neutron Scattering
March 19	Dr K. Reid, University of Nottingham Probing Dynamical Processes with Photoelectrons

