



National Library
of Canada

Bibliothèque nationale
du Canada

Canadian Theses Service

Service des thèses canadiennes

Ottawa, Canada
K1A 0N4

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Tetra- and Tri- Coordinate Phosphoryl Systems

by

Rupert Edward von Haken Spence

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

at

Dalhousie University

Halifax, Nova Scotia

February, 1991

© Copyright by Rupert Edward von Haken Spence



National Library
of Canada

Bibliothèque nationale
du Canada

Canadian Theses Service Service des thèses canadiennes

Ottawa, Canada
K1A 0N4

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-315-64449-4

Canada

To Mum, Dad, Steve, Gloria, my brothers and to Rosie.

TABLE OF CONTENTS

	Page
Table of Contents	v
List of Tables	ix
List of Figures	xi
Abstract	xiii
List of Abbreviations Used in Text	xiv
Acknowledgements	xv
Section 1: Introduction	1
Introduction	2
Section 2: Results and Discussion	12
Chapter 1: The Coordinative Bonding Modes of Chalcogenophosphoryls.	13
2.0.1. N.m.r. Characterisation of Some Group 13 Trihalide Complexes of Ph_3PO , $(\text{Me}_2\text{N})_3\text{PO}$, $(\text{Me}_2\text{N})_3\text{PS}$ and Ph_3AsO .	14
2.0.2. X-Ray Crystal Structures of the Lewis Acid-base Complexes $\text{Ph}_3\text{PO} \cdot \text{BF}_3$, $\text{Ph}_3\text{AsO} \cdot \text{BF}_3$, $\text{Ph}_3\text{PO} \cdot \text{AlBr}_3$, $\text{Ph}_3\text{PO} \cdot \text{GaCl}_3$ and $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S} \cdot \text{AlCl}_3$.	19
2.0.3. The Phosphorus-Chalcogen-Acid Linkage.	28
Chapter 2: The Chemistry of the Bis(dialkylamino)phosphoryl Chlorides, $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{Ch}$ ($\text{R} = \text{Me}, \text{Et}$ or ^iPr; $\text{Ch} =$ $\text{NPh}, \text{O}, \text{S}$ and Se), with AlCl_3, AgSO_3CF_3 and Other Halide Ion Abstracting Reagents.	33

2.2.1.	N.m.r. and Structural Characterisation of the Diaminophosphoryl Chlorides, $(R_2N)_2P(Cl)Ch$ ($R = Me, Et, iPr$; $Ch = NPh, S, Se$) and $[(Me_3Si)_2N]_2P(Cl)S$.	33
2.2.2.	Reactions Between Bis(dialkylamino)chalcogenophosphoryl Chlorides, $(R_2N)_2P(Cl)Ch$ ($R = Me, Et$ or iPr ; $Ch = NPh, O, S$ and Se) and $AlCl_3$.	34
2.2.3.	Alternative Preparation of $(R_2N)_2P(Cl)NPh.AlCl_3$ ($R = Et, iPr$) Complexes. The Reactions of Phosphenium Cations with Phenyl Azide.	42
2.2.4.	Infra-red Spectroscopic Characterisation of Bis(dialkylamino)phosphoryl Chlorides, $(R_2N)_2P(Cl)Ch$ ($R = Me, Et$ and iPr ; $Ch = NPh, S$ and Se), and $R_4N_2PChAlCl_4$ Solids.	42
2.2.5.	Mass Spectra of the $R_4N_2PChAlCl_4$ Solids.	43
2.2.6.	Crystal Structures of $[(NEt_2)_2PS]_2[AlCl_4]_2$ and $[(NEt_2)_2PSe]_2[AlCl_4]_2$.	44
2.2.7.	X-Ray Crystal Structure of $(iPr_2N)_2P(Cl)NPh.AlCl_3$.	49
2.2.8.	Reaction between $(R_2N)_2P(Cl)S.AlCl_3$ and CH_2Cl_2 .	49
2.2.9.	Chalcogenophosphenium Cations $[(R_2N)_2PCh]_2^{2+}$ ($Ch = S, Se$) in Solution.	51
2.2.10.	The Iminophosphenium Cation and Hydrolysis of the $(R_2N)_2P(Cl)NPh.AlCl_3$ Complexes.	52
2.2.11.	The Monomeric Structure of $(iPr_2N)_2P(Cl)NPh$ and the Dimerisation Process of the Thiophosphoryl Chlorides.	53

2.2.12.	Alternative Halide Ion Abstracting Reagents with the Thiophosphoryl Chlorides, $(R_2N)_2P(Cl)S$.	55
2.2.13.	The Diaminophenyliminophosphoryl Chloride- Silver Triflate System.	55
2.2.14.	The Tricoordinate Phosponium Electronic Environment.	56
Chapter 3:	The Reactions and Cyclisation of the Novel Phosphoryls $[(Me_3Si)^tBuN]^tBuN)PS$ and $[(Me_3Si)_2N]_2P(Cl)S$ with Lewis Acids.	59
2.3.1.	Isolation and Characterisation of PNSiS Heterocycles from the Reactions of $[(Me_3Si)^tBuN]^tBuN)PS$, <u>I</u> , and $[(Me_3Si)_2N]_2P(Cl)S$, <u>II</u> with ECl_3 ($E = Al,$ Ga) and $H_2SO_3CF_3$.	60
2.3.2.	PNSiN Heterocycles <u>IV</u> . Thermolysis and Isomerisation of the PNSiS Heterocycles, <u>III</u> .	65
2.3.3.	Modes of Cyclisation for <u>I</u> and <u>II</u> : A Common Intermediate Tricoordinate Phosponium Cation?	68
Section 3:	Conclusions and Future Work	70
	Conclusions and Future Work	71
Section 4:	Experimental	73
4.0.1.	General Procedures.	74
4.0.2.	Preparation and Characterisation of the Compounds of Section 2, Chapter 1.	75

4.0.3.	Preparation and Characterisation of the Compounds of Section 2, Chapter 2.	76
4.0.4.	Preparation and Characterisation of the Compounds of Section 2, Chapter 3.	85
Section 5: Appendix of Crystallographic Data		92
Appendix of Crystallographic Data		93
Section 6: References		96
References		97

LIST OF TABLES

Table	Title	Page
2.1.1.	Carbon-13, ^{31}P , ^{11}B , ^{27}Al and ^{71}Ga n.m.r. data for derivatives of Y_3PnCh , $\text{Y}_3\text{PnCh}\cdot\text{EX}_3$ ($\text{Y} = \text{Ph}$, Me_2N ; $\text{Pn} = \text{P}$, As ; $\text{Ch} = \text{O}$, S ; $\text{E} = \text{B}$, Al , Ga ; $\text{X} = \text{F}$, Cl , Br) and related compounds.	15
2.1.2.	Selected bond lengths (\AA) and angles ($^\circ$) for $\text{Ph}_3\text{PnO}\cdot\text{BF}_3$ ($\text{Pn} = \text{P}$, As).	20
2.1.3.	Selected bond lengths (\AA) and angles ($^\circ$) for $\text{Ph}_3\text{PO}\cdot\text{AlBr}_3$.	21
2.1.4.	Selected bond lengths (\AA) and angles ($^\circ$) for $\text{Ph}_3\text{PO}\cdot\text{GaCl}_3$.	22
2.1.5.	Selected bond lengths (\AA) and angles ($^\circ$) for $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$.	23
2.1.6.	Comparison of Pn-O bond lengths (\AA) and Pn-O-E angles ($^\circ$) in some Lewis acid-base complexes with terminal oxophosphoryl and oxoarsonyl ligands.	25
2.1.7.	Comparison of Pn-Ch bond lengths (\AA) and Pn-Ch-E angles ($^\circ$) in some Lewis acid-base complexes with terminal thio and seleno phosphoryl and thioarsonyl ligands.	27
2.2.1.	Phosphorus-31 and ^{13}C n.m.r. data for derivatives of $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{S}$ and the products with AlCl_3 .	35
2.2.2.	Selected bond lengths (\AA) and angles ($^\circ$) for $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}$.	36
2.2.3.	Selected bond lengths (\AA) and angles ($^\circ$) for $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}$.	37
2.2.4.	Selected bond lengths (\AA) and angles ($^\circ$) for $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{Se}$.	38

2.2.5.	Selected bond lengths (Å) and angles (°) for [{(Et ₂ N) ₂ PS} ₂][AlCl ₄] ₂ .	45
2.2.6.	Selected bond lengths (Å) and angles (°) for [{(Et ₂ N) ₂ PSe} ₂][AlCl ₄] ₂ .	46
2.2.7.	Structural parameters and ³¹ P n.m.r. chemical shifts for dichalcogenodiphosphetanes (<u>15</u>).	48
2.2.8.	Selected bond lengths (Å) and angles (°) for (ⁱ Pr ₂ N) ₂ P(Cl)NPh.AlCl ₃ .	50
2.2.9.	Selected bond lengths (Å) and angles (°) for (ⁱ Pr ₂ N) ₂ P(O)N(Ph)(SO ₂ CF ₃).	57
2.3.1.	Selected bond lengths (Å) and angles (°) for (^t BuN)-(Me ₂ Si)-S-P(Me)[N(^t Bu)(.AlCl ₃)], <u>III</u> (a), {(^t BuN)-(Me ₂ Si)-S-P(Me)[N(^t Bu)(H)]}{SO ₃ CF ₃ }, <u>III</u> (c) and {(Me ₃ SiN)-(Me ₂ Si)-S-P(Me)[N(Me ₃ Si) ₂]}{GaCl ₄ }, <u>III</u> (e).	64
2.3.2.	1-Hydrogen, ¹³ C, and ³¹ P n.m.r. data the PNSiS and PNSiN heterocycles <u>II</u> and <u>IV</u> .	66
2.3.3.	Selected bond lengths (Å) and angles (°) for (Me ₃ Si)N-(Me ₂ Si)-(Me ₃ Si)N-P(Me)S.GaCl ₃ , <u>IV</u> (d).	67
5.0.1.	Structural parameters for derivatives of (ⁱ Pr ₂ N) ₂ P(Cl)Ch (Ch = NPh, S, and Se).	93
5.0.2.	Structural parameters for (ⁱ Pr ₂ N) ₂ P(Cl)NPh.AlCl ₃ and (ⁱ Pr ₂ N) ₂ P(O)N(Ph)(SO ₂ CF ₃).	94
5.0.3.	Structural parameters for {(^t BuN)-(Me ₂ Si)-S-P[N(^t Bu)(H)]}{CF ₃ SO ₃ }, <u>III</u> (c), and (Me ₃ SiN)-(Me ₂ Si)-(Me ₃ Si)N-P(Me)[S.GaCl ₃], <u>IV</u> (d).	95

List of Figures

Figure	Title	Page
1.0.1.	The Phosphoryl System: <u>A</u> , the classical tetracoordinate phosphoryl bonding environment; <u>B</u> , the neutral tricoordinate phosphoryl environment; <u>C</u> , the cationic tricoordinate phosphoryl (phosphonium) environment.	2
1.0.2.	Some templates of the classical phosphoryl system.	3
1.0.3.	The resonance structures of the chalcogenophosphoryls.	3
1.0.4.	Some crystallographically characterised derivatives of the neutral tricoordinate phosphoryl system.	8
1.0.5.	Some templates of the tricoordinate phosphonium centre.	8
2.1.1.	Aluminium-27 n.m.r. spectra for $(Me_2N)_3PS \cdot AlCl_3$. [(a) 0.1 M; (b) 0.02 M].	17
2.1.2.	Crystallographic view of $Ph_3PnO \cdot BF_3$ (Pn = P, As).	20
2.1.3.	Crystallographic view of $Ph_3PO \cdot AlBr_3$.	21
2.1.4.	Crystallographic view of $Ph_3PO \cdot GaCl_3$.	22
2.1.5.	Crystallographic view of $(^iPr_2N)_2P(Cl)S \cdot AlCl_3$.	23
2.2.1.	Crystallographic view of $(^iPr_2N)_2P(Cl)NPh$.	36
2.2.2.	Crystallographic view of $(^iPr_2N)_2P(Cl)S$.	37
2.2.3.	Crystallographic view of $(^iPr_2N)_2P(Cl)Se$.	38
2.2.4.	³¹ P-Phosphorus n.m.r. spectrum of the $(Et_2N)_2P(Cl)Se/AlCl_3$ system in CH_2Cl_2 .	41
2.2.5.	Crystallographic view of $\{[(Et_2N)_2PS]_2\}[AlCl_4]_2$.	45
2.2.6.	Crystallographic view of $\{[(Et_2N)_2PSe]_2\}[AlCl_4]_2$.	46
2.2.7.	Crystallographic view of $(^iPr_2N)_2P(Cl)NPh \cdot AlCl_3$.	50

2.2.8.	Crystallographic view of $(^i\text{Pr}_2\text{N})_2\text{P}(\text{O})\text{N}(\text{Ph})(\text{SO}_2\text{CF}_3)$.	57
2.3.1.	The reactants and products of Chapter 3.	61
2.3.2.	Crystallographic views of $(^t\text{BuN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\cdot\text{AlCl}_3)]$, <u>III(a)</u> , $\{(^t\text{BuN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\text{H})]\}\{\text{SO}_3\text{CF}_3\}$, <u>III(c)</u> and $\{(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(\text{Me}_3\text{Si})_2]\}\{\text{GaCl}_4\}$, <u>III(e)</u> .	63
2.3.3.	Crystallographic view of $(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-(\text{Me}_3\text{SiN})-\text{P}(\text{Me})[\text{S}\cdot\text{GaCl}_3]$, <u>IV(d)</u> .	67

ABSTRACT

The reactions and products of tetracoordinate phosphoryls and tricoordinate phosphoryls (phosphoranes) with various reagents, particularly the group 13 trihalides, are examined to gain a better understanding of the bonding within the phosphoryl systems and to explore their potential as precursors to the tricoordinate phosphonium (phosphoryl cation) centre.

The Lewis acid-base complexes $R_3PnCh.EX_3$ ($R = Ph$ or NMe_2 ; $Pn = P$ or As ; $Ch = O$ or S ; $E = B, Al$ or Ga ; $X = F, Cl$ or Br) have been comprehensively examined both in solution and the solid state. The oxophosphoryl derivatives are found to have novel linear $P-O-E$ ($E = Al$ and Ga) frameworks while the thio and seleno phosphoryl and arsenyl systems have "typical" bent geometries. Together with a literature review, the results permit the coordinative bonding modes of the chalcogenophosphoryls to be classified into two general categories.

Reaction of $(R_2N)_2P(Cl)Ch$ ($R = Me, Et$ or iPr ; $Ch = NPh, O, S$ or Se) with $AlCl_3$ is found to give Lewis acid-base complexes or ionic products dependent on R, Ch and whether the products are examined in solution or the solid state. The thermodynamically most stable ionic product is found to be a dicationic P_2Ch_2 heterocycle. There is no evidence, as previously suggested, for the involvement of a tricoordinate phosphonium centre in these systems. Addition of $AgSO_3CF_3$ to $(R_2N)_2P(Cl)NPh$ gives a oxophosphoryl centre, demonstrating a kinetic stabilisation for the recently prepared methylenephosphonium cation.

Finally, $[(Me_3Si)^tBuN](^tBuN)PS$ and $[(Me_3Si)_2N]_2P(Cl)S$ both give novel $PNSiS$ heterocycles on reaction with ECl_3 ($E = Al$ or Ga). The results are supportive of a common tricoordinate phosphonium intermediate and the $PNSiS$ heterocycles are found to be thermodynamically unstable with respect to alternative $PNSiN$ rings.

LIST OF ABBREVIATIONS USED IN TEXT

n.m.r.	nuclear magnetic resonance
ppm	parts per million
Hz	hertz
$\Delta\nu_{1/2}$	line width at half height
Å	Ångstrom unit, 10^{-10} metres
s.o.a.	sum of angles
m.p.	melting point
b.p.	boiling point
i.r.	infra-red
w	weak
m	medium
s	strong
v	very
sh	shoulder
br	broad
mmol	millimole
rel. int.	relative intensity
min	minute(s)
h	hour(s)
d	day(s)

ACKNOWLEDGEMENTS

Firstly, I must thank Neil Burford for his outstanding support, encouragement and guidance as my Ph.D. supervisor and friend during my time at Dalhousie. I wish him all the luck and success he definitely deserves for the future and hope that the expression 'We in the Burford group' lives on for a considerable number of years.

Very special thanks also go to Bruce Royan, a great friend and long time companion in the Burford group.

I would also like to acknowledge the following people who have been involved in the work discussed in this manuscript: Marc Whalen for his hard work on the preliminary investigations of $[(\text{Me}_3\text{Si})^t\text{BuN}](^t\text{BuN})\text{PS}$ with AlCl_3 ; Jurgen Mueller for his glass-blowing expertise and excellent ideas on equipment modification; Dr. Don Hooper, Bruce MacDonald and Maureen Yeats for running many of the solution n.m.r. spectra (all spectra were obtained at the Atlantic Regional Magnetic Resonance Centre, Dalhousie University); Drs. T. Stanley Cameron and Tony Linden and Ms. Bozena Borecka (Dalhousie University), Robin D. Rogers (Northern Illinois University) and John F. Richardson (University of Louisville) for the crystal structure determinations; Dr. Kim for obtaining the mass spectra; and Mel Schriver, Ann Dipchand, and Robin Hicks, my co-workers in the Burford group.

I also acknowledge the financial support of Dalhousie University in the form of a Dalhousie Fellowship and Teaching Assistantship.

Special thanks to Helene Burford for the many meals and excellent stories, and to my many friends at Dalhousie.

SECTION 1: INTRODUCTION

Introduction

The phosphoryl centre is one of the fundamental electronic environments of phosphorus. It is classically represented, Figure 1.0.1. **A**, as a tetracoordinated phosphorus (V), with three sigma bonds and one $d\pi-p\pi$ double bond. However, two other π bonded, oxidation state five phosphorus environments are known, Figure 1.0.1. **B** and **C**. Therefore, for the purposes of this thesis, these tricoordinate electronic structures may also be described as phosphoryl centres. This work examines the bonding and reactivity of derivatives of **A** and **B**, explores routes to new derivatives of **C**, and demonstrates some of the relationships between the three electronic environments. A brief discussion of the chemistry and stability of these systems is therefore presented.

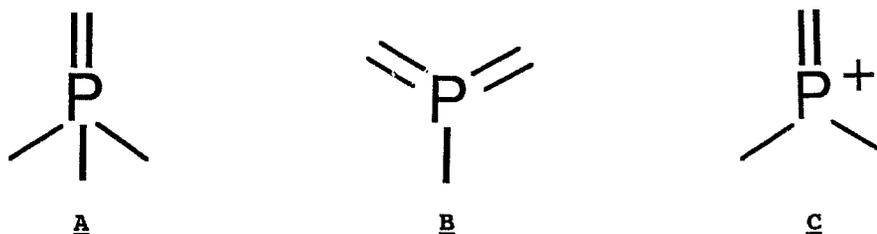
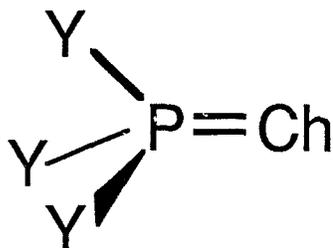


Figure 1.0.1.: The Phosphoryl System: **A**, the classical tetracoordinate phosphoryl bonding environment; **B**, the neutral tricoordinate phosphoryl environment; **C**, the cationic tricoordinate phosphoryl (phosphonium) environment.

The chemistry of the classical phosphoryl system, **A**, is dominated by the methylene [(a), $\text{Ch} = \text{CY}_2$], imine [(b), $\text{Ch} = \text{N-Y}$] and chalcogen [(c), $\text{Ch} = \text{O, S, Se, Te}$] derivatives, Figure 1.0.2. A multitude of examples are known for each of the three derivatives and the general preparative routes are given in ref 1. The methylenephosphoryls are commonly labelled as Wittig reagents, playing an important role in organic chemistry for carbonyl olefination.² The imino and chalcogeno



(a) Methylenephosphoryl, Ch = CY_2

(b) Iminophosphoryl, Ch = NY

(c) Chalcogenophosphoryl, Ch = O, S, Se, Te

Figure 1.0.2.: Some templates of the classical phosphoryl system.

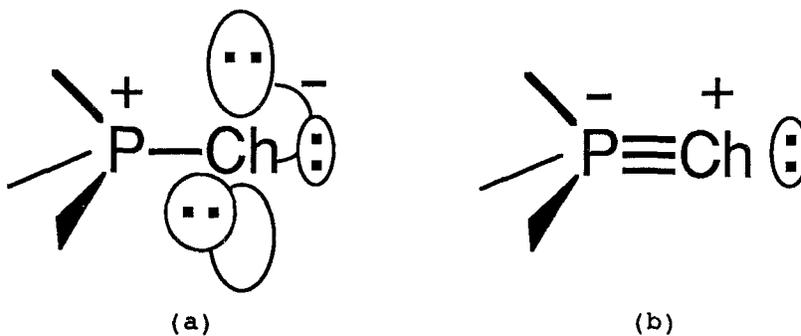


Figure 1.0.3.: The resonance structures of the chalcogenophosphoryls.

(The formal charges, introduced by the Lewis model, are not representative of the actual electronic distribution)

phosphoryls are frequently referred to in the reverse form i.e. as phosphoryl imines and phosphoryl chalcogenides, or alternatively as phosphine imines and phosphine chalcogenides.

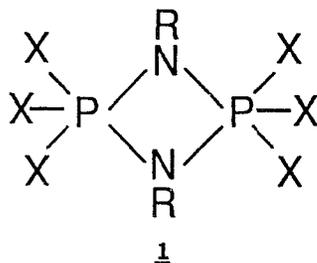
Examples of the classical phosphoryl systems have been structurally characterised and the P-Ch linkage is shown to be significantly shorter than the respective P-Ch single bond.³ To explain this additional bonding interaction, a full double bond is commonly drawn, e.g. Figure 1.0.1. A, to represent a π overlap between the d -orbital of phosphorus with a p -orbital of Ch. However, recent theoretical studies by Gordon⁴ and others⁵ have shown that the bonding within the phosphoryl unit is best described by a strong P-Ch single bond, reinforced by only "some"^{4c} π back-donation from the lone pairs of Ch. The results show that for the methylenephosphoryls the double bond representation, e.g. Figure 1.0.2. (a), may be used (the methylene carbon centres are generally planar)³ but the ylide structure, e.g. Figure 1.0.3. (a), is a better representation. For the chalcogenophosphoryls, however, the degeneracy of the chalcogen p -orbitals, imposed by the three-fold symmetry of the molecules, requires that the P-Ch bonding is best described by a combination of the two resonance structures (a) and (b) of Figure 1.0.3.. The P-N bond of the iminophosphoryls can be described in a similar manner.⁶ Interestingly, the triple bond structure, Figure 1.0.3. (b), was recognised on symmetry arguments for the oxophosphoryls as early as 1961,⁷ but the double bond depiction is used almost exclusively by chemists.

Gordon^{4c} suggests that the strong P-Ch single bond can be viewed as forming in an acid-base reaction, with the phosphine donating to the acid centre Ch. This bond is then comparable to that found for the boron-phosphine linkage in the adducts $R_3P.BR_3$. Trinquier⁸ explains that the initial attack of a carbene on a phosphine occurs by a similar bonding arrangement, with the phosphine lone pair of electrons being donated into the methylene's vacant p -orbital. Furthermore, the Lewis

acid-base model is also useful to describe the bonding found in derivatives of $R_3P=C=PR_3$, where the P-C-P angles range from 117 to 148°. ^{9a} Schmidbaur ^{9b} proposes that these compounds can be viewed as diphosphorus complexes of naked carbon.

For the triply bonded model of the chalcogeno and imino phosphoryls a non-bonding or σ (N-R) pair of electrons at the Ch centre must lie on the C_3 axis of the molecule. Therefore, it might be expected that some covalent iminophosphoryls and complexes of the chalcogenophosphoryls would adopt a linear P-Ch-Y (Ch = N, Y = R; Ch = chalcogen, Y = Lewis acid) framework. However, this is not observed either theoretically (H_3P-N-H , 120°) ⁶ or experimentally (e.g. $Ph_2FP-N-Me$, $119.1(2)^\circ$ ¹⁰, $Ph_3P-N-C_6H_4Br$, $124.2(5)^\circ$ ¹¹) for the imines and there is only limited experimental evidence for axial coordination at the chalcogenides. ^{12,13}

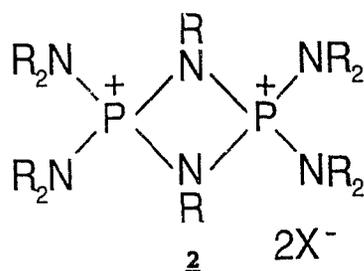
While the tetracoordinate methylene and chalcogeno phosphoryls are monomeric, many iminophosphoryl systems dimerise ¹⁴ to the cyclophosphazanes, 1.



These systems should not be confused with the unsaturated PN heterocycles, the cyclophosphazenes, which represent important examples of the phosphoryl unit. ¹⁵ The dimerisation of the iminophosphoryls is favoured by electron withdrawing substituents on phosphorus and electron donating substituents on the imino nitrogen. ¹⁴ In addition, dimerisation, which involves geometric rearrangement of the phosphorus from tetra- to pentacoordination, is enhanced by inclusion of the phosphorus centre into a four or five membered ring. ^{14a} The $F_3P=NR$ unit

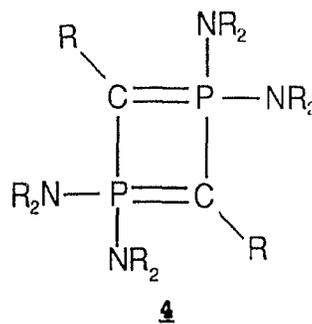
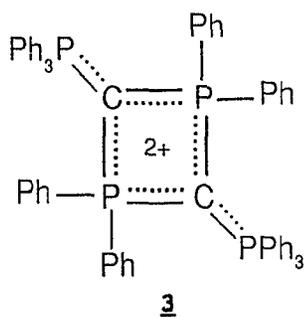
always dimerise and the $\text{Cl}_3\text{P}=\text{N}-\text{Ar}$ unit is either a monomer or dimer depending on the aryl substituents.¹⁴ The steric requirements of the substituents can prohibit dimerisation,¹⁴ eg. 2,4,6-tri-*tert*-butylbenzene- $\text{N}=\text{P}\text{Cl}_3$ is a monomer.¹⁶

Recently, Chernega et al¹⁷ have demonstrated an alternative dimerisation process for specific derivatives of the iminophosphoryls. They found the sterically unrestricted bis(dialkylamino)iminophosphoryl halides, $(\text{R}_2\text{N})_2\text{P}(\text{X})\text{NR}$ ($\text{R} = \text{Me}, \text{Et}; \text{X} = \text{Cl}, \text{Br}$) cyclise by way of auto-ionisation to give the novel 1,3,2,4-diazadiphosphetidin-2,4-ium dihalides, 2.

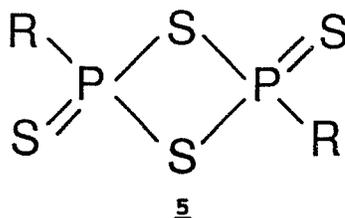


No explanation is available for the monomeric nature of the tetracoordinate methylene and chalcogeno phosphoryls. However, Haiduc¹⁸ suggests that the preferred geometry of phosphorus is tetrahedral rather than trigonal bi-pyramidal and, as such, the formation of the cyclophosphazane heterocycles from the iminophosphoryls should be considered "as an exception rather than a general rule in phosphorus chemistry."

Only a few $\text{P}(\text{V})_2\text{C}_2$ heterocycles are known, e.g. 3¹⁹ and 4 ($\text{R} = \text{H}, \text{Me}, \text{Et}, \text{Ph}$).²⁰



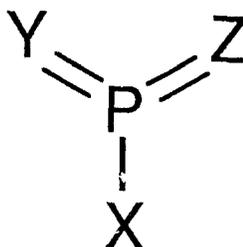
They may be considered dimers of $Y_2P\equiv CY$ and in 3 the charge has been shown¹⁹ to be delocalised over the ring and the exocyclic phosphorus centres. In contrast, there are numerous examples²¹ of $P(V)_2S_2$ rings and two examples²² of $P(V)_2Se_2$ rings in which the phosphorus centre is a tetracoordinate phosphoryl. The thiophosphetanes, 5 ($R = Me, Et, Ph, NMe_2$ etc.),



are generally synthesised by the reaction of thiophosphoryl dichlorides with H_2S .²¹ They may be viewed as dimers of the novel neutral tricoordinate phosphoryl centres, Figure 1.0.1. B.

The neutral tricoordinate phosphoryl systems are frequently postulated as reaction intermediates.²³ However, they have been successfully stabilised and isolated by employing sterically demanding substituents (e.g. *tert*-butyl, 1,3,5-tri-*tert*-butylbenzene) that prevent dimerisation. Steric protection is commonly referred to as a kinetic stabilisation. However, as Cowley²⁴ has pointed out for the disilenes ($R_2Si=SiR_2$) and the dipnictogenes ($R-Pn=Pn-R$, $Pn = P, As, Sb$), sterically stabilised compounds may also be thermodynamically stable relative to the alternative sterically strained oligomers. The bonding within the tricoordinate phosphoryl unit may be described in terms of one sigma bond, one $d\pi-p\pi$ bond and one $p\pi-p\pi$ bond. This view is simplistic and a contribution from both types of π interaction is anticipated in each of the two multiple bonds.

Numerous derivatives²⁵ of the neutral tricoordinate phosphoryls are now known and some examples are given in Figure 1.0.4.. They are frequently,²⁶ but not exclusively,²⁷ labelled tricoordinate phosphoranes,

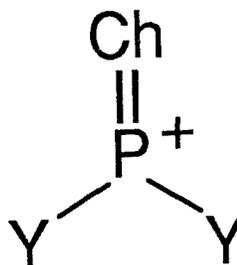


X	Y	Z	Ref
N(TMS) ₂	N(TMS)	N(TMS)	26a
Mes	S	S	26b
Mes	CPh(TMS)	O	26c
Mes	P(Mes)	S	27

TMS = trimethylsilyl

Mes = 2,4,6-tri-*tert*-butylbenzene.

Figure 1.0.4.: Some crystallographically characterised derivatives of the neutral tricoordinate phosphoryl system.



- (a) Ch = CY₂, methylenephosphoryl
- (b) Ch = NY, iminophosphoryl
- (c) Ch = O, oxophosphoryl
- (d) Ch = S, thiophosphoryl
- (e) Ch = Se, selenophosphoryl

Figure 1.0.5.: Some templates of the tricoordinate phosphonium centre.

classifying them as neutral phosphorus (V) centres. However, the phosphoryl nomenclature is preferable as it implies a degree of π bonding within the molecule. To differentiate between these neutral tricoordinate phosphoryl centres and the cationic tricoordinate phosphoryl systems, Figure 1.0.1. c, the latter systems will be referred to as tricoordinate phosphonium cations. The phosphonium nomenclature derives from the tetracoordinate cationic phosphorus environment and is consistent with the current name assigned to these centres.²⁸

The tricoordinate phosphonium cation, an isovalent analog of the alkenic environment ($R_2C=$), represents an important synthetic goal in phosphorus chemistry. Very recently (1989) the first crystallographically characterised example of this system was reported by Bertrand.²⁸ Addition of trimethylsilyl triflate across a novel phosphinocarbene, $(iPr_2N)_2P-\overset{\ominus}{C}-SiMe_3$, gave the salt $[(iPr_2N)_2P=C(SiMe_3)_2][SO_3CF_3]$. This methylene derivative of the tricoordinate phosphonium, Figure 1.0.5. (a), has a short P-C bond length (1.620 (3) Å), consistent with a π bonded arrangement, but the dihedral angle between the N_2P and Si_2C planes is unusually large at 60°. Unfortunately full discussion of the stability of this important molecule is not yet available. However, evidence for kinetic (steric) stabilisation is presented in Chapter 2.

Other examples of the tricoordinate phosphonium cation are incompletely characterised. Appel²⁹ reports that the bis(dialkylamino)methylenephosphoryl chlorides, $(R_2N)_2P(Cl)CR_2$, give the tricoordinate methylenephosphonium centre, Figure 1.0.5. (a), on reaction with both $AlCl_3$ and $AgBF_4$. However, the ^{31}P n.m.r. chemical shifts reported for the products are inconsistent with that reported for Bertrand's isolated cation.²⁸

Sanchez and Wolf^{30a} report the reaction of bis(dialkylamino)iminophosphoryl chlorides, $(R_2N)_2P(Cl)NR$, with $AlCl_3$ to give initially Lewis acid-base complexes which, on heating, yield the

iminophosphonium cation, Figure 1.0.5. (b). In support of their discovery, they also found the reaction of the phosphonium cations (two coordinate phosphorus (III) centres) with phenyl azide to yield the same species. However, the products were not isolated and spectroscopic evidence for the proposed structure is poor. Furthermore, the results are incongruent with Chernega's¹⁷ later reports on the auto-ionisation of bis(dialkylamino)iminophosphoryl chlorides and bromides mentioned above.

The oxophosphonium cation, Figure 1.0.5. (c), has been suggested³¹ as an auto-ionisation product of Cl_3PO and the thio centre, Figure 1.0.5. (d), was identified³² as a reaction species in Friedel-Craft arylation of thiophosphoryl chloride by Maier. The thio derivative has also been reported by Light and Paine³³ as the product of diaminothiophosphoryl fluoride with phosphorus pentafluoride. The absence of a P-F n.m.r. coupling in the product confirms fluoride ion abstraction and provides the only evidence for the tricoordinate phosphonium cation.

Gordon's⁴ results demonstrate that the bonding in the classical chalcogenophosphoryls is not fully characterised experimentally. To gain a better understanding of P-Ch linkage, Chapter 1 of the thesis examines the complexes of the simple chalcogenophosphoryls, Y_3PCh ($\text{Y} = \text{Ph}$ or NMe_2 ; $\text{Ch} = \text{O}$ or S) with the Group 13 trihalides, EX_3 ($\text{E} = \text{B}, \text{Al}$ or Ga ; $\text{X} = \text{F}, \text{Cl}$ or Br). The results, together with a review of other phosphoryl and arsenyl (Y_3AsCh) complexes, reveal the coordinative bonding modes of the chalcogenophosphoryls to be dependent on the chalcogen.

Clearly, the chemistry of the imino, oxo, thio and seleno bis(dialkylamino)phosphoryl chlorides, $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{Ch}$ [$\text{Ch} = \text{NPh}, \text{O}, \text{S}$ or Se ; $\text{R} = \text{Me}, \text{Et}$ or ^iPr] is incomplete. For example, their potential as precursors to the novel tricoordinate phosphonium centres, Figure 1.0.1. c, has not been fully realised, while Chernega¹⁷ has only revealed novel

behaviour (i.e. auto-ionisation) for the imino derivatives. Hence, in Chapter 2, the interactions of these derivatives with the Lewis acid AlCl_3 , and other halide ion abstracting reagents, have been comprehensively examined.

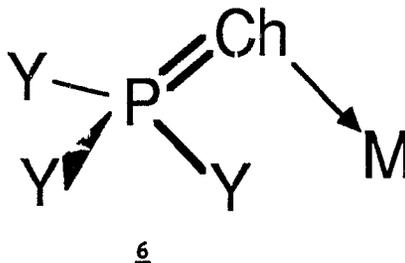
In Chapter 3, the reactions of the silylamino phosphoryls $[(\text{Me}_3\text{Si})^t\text{BuN}](^t\text{BuN})\text{PS}^{34}$ (tricoordinate) and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$ (tetracoordinate) with ECl_3 (E = Al or Ga) and triflic acid (HSO_3CF_3) are examined. Both phosphoryls give identical novel PNSiS heterocyclic products and a tricoordinate phosphonium (phosphoryl cation) centre is postulated as a transient intermediate to the rings.

SECTION 2: RESULTS AND DISCUSSION

Chapter 1

The Coordinative Bonding Modes of Chalcogenophosphoryls.

As mentioned in the introduction, the 3-fold symmetry of the chalcogenophosphoryls (Ch = O, S, Se) requires that the bonding is best described by a combination of singly bonded P-Ch and triply bonded P-Ch resonance structures (see Figure 1.0.3.).⁴ One early method by which the P-Ch bonding was investigated was to involve the chalcogenophosphoryl in a Lewis acid-base complex, 6, to a metal centre and to observe the effect on the P-Ch stretching frequency in the infra-red spectrum.



Numerous studies³⁵ showed that the P-Ch stretch of the free base generally moved to lower wavenumber upon complexation and it was concluded that significant $d\pi-p\pi$ bonding existed in the P-Ch linkage.

In comparison to the many infra-red studies, there are few comprehensive studies of the Lewis acid-base complexes of the phosphoryl unit that have applied both the modern analytical tools of n.m.r. spectroscopy and X-ray crystallography. In this chapter both techniques are employed to comprehensively examine complexes of Ph_3PO , $(\text{Me}_2\text{N})_3\text{PO}$, $(\text{Me}_2\text{N})_3\text{PS}$ and Ph_3AsO (an oxoarsenyl) and the group 13 trihalides. In general, the results confirm the conclusions of the infra-red spectroscopic studies on such complexes.³⁵ However, for the oxophosphoryl derivatives, novel linear P-O-E (E = Al and Ga) frameworks are observed in solution and the solid state. More typical bent

geometries are observed in related thio and seleno phosphoryl and arsenyl systems. Comparison of these adducts with other complexes prepared during the course of this thesis (Chapters 2 and 3), together with a literature review, allows for a classification of the bonding modes of the chalcogenophosphoryls, consistent with the current⁴ bonding description of the system.

This project was investigated in collaboration with Dr. Bruce W. Royan, formerly of this laboratory. His contributions are referenced and primarily relate to the derivatives of $\text{Ph}_3\text{PCh} \cdot \text{AlCl}_3$ (Ch = O,³⁶ S,³⁷ Se³⁷) mentioned within this chapter.

2.0.1. N.m.r. Characterisation of Some Group 13 Trihalide Complexes of Ph_3PO , $(\text{Me}_2\text{N})_3\text{PO}$, $(\text{Me}_2\text{N})_3\text{PS}$ and Ph_3AsO .

The Lewis acid-base complexes studied are given in Table 2.1.1., together with n.m.r. data and comparative data for related compounds.

Changes in ^{31}P chemical shifts of the free base on complex formation appear dependent on the chalcogenophosphoryl rather than the acid. The Ph_3PO adducts are deshielded from the free base by approximately the same extent (except Ph_3POH^+).³⁸ In contrast, no significant difference in chemical shifts is observed between $(\text{Me}_2\text{N})_3\text{PO} \cdot \text{AlCl}_3$ and its free base and the ^{31}P chemical shift of $(\text{Me}_2\text{N})_3\text{PS}$ is shielded on complex formation. Similar effects on the chemical shift are observed for other amine substituted oxo- and thiophosphoryl centres on adduct formation (Chapter 2).

The ipso carbons of Ph_3PO and Ph_3AsO experience shielding and the para positions show deshielding in the ^{13}C n.m.r. on adduct formation. Freeman³⁹ notes parallel features for phenyl substituted Wittig reagents (e.g. $\text{Ph}_3\text{P}=\text{CH}_2$) and iminophosphoryl centres (e.g. $\text{Ph}_3\text{P}=\text{NPh}$) and their corresponding cations ($\text{Ph}_3\text{P}-\text{Me}^+$, $\text{Ph}_3\text{P}-\text{NHPh}^+$) and they can be rationalised in terms of simple resonance considerations. They provide evidence for π -interaction between the phenyl groups and the phosphorus centre as

Table 2.1.1.: Carbon-13, ^{31}P , ^{11}B , ^{27}Al and ^{71}Ga n.m.r. data for derivatives of Y_3PnCh , $\text{Y}_3\text{PnCh.EX}_3$ ($\text{Y} = \text{Ph}$ or Me_2N ; $\text{Pn} = \text{P}$ or As ; $\text{Ch} = \text{O}$ or S ; $\text{E} = \text{B}$, Al or Ga ; $\text{X} = \text{F}$, Cl or Br) and related compounds.

Chemical Shifts in ppm.

Compound	$^{13}\text{C}^{\text{a}}$				^{31}P	$^{11}\text{B}/^{27}\text{Al}/^{71}\text{Ga}^{\text{b}}$	Ref
	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>			
$\text{Ph}_3\text{PO.BF}_3$	124.6 (112.1)	132.9 (11.4)	129.1 (13.4)	134.2 (1.9)	44	-0.9 (12.5)	
$\text{Ph}_3\text{PO.AlCl}_3$	124.6 (112.1)	132.6 (11.6)	129.4 (13.8)	134.6	45	90 (40)	36
$\text{Ph}_3\text{PO.AlBr}_3$	124.1 (109.8)	132.8 (11.8)	129.5 (13.6)	134.8	46	79 (31)	
$\text{Ph}_3\text{PO.GaCl}_3$	125.2 (109.3)	132.8 (11.4)	129.3 (13.2)	134.4	46	230 (5,100)	
Ph_3POH^+ (H_2SO_4)	120.0 (107.4)	131.1 (9.8)	129.0 (12.2)	132.8	57		38
$\text{Ph}_3\text{AsO.BF}_3$	126.1	132.1	130.1	134.0			
$\text{Ph}_3\text{PS.AlCl}_3$	124.4 (81.7)	133.2 (10.9)	129.4 (13.3)	134.1	43	107 (200)	37
$(\text{Me}_2\text{N})_3\text{PO.AlCl}_3$	36.4				24	88 (18)	
$(\text{Me}_2\text{N})_3\text{PS.AlCl}_3$	37.6				69	107 (80), 102 (<20)	
Ph_3PO	132.8 (103.5)	132.1 (9.8)	128.5 (17.7)	131.8 (2.4)	29		38
Ph_3AsO	132.4	131.3	129.2	132.0			
Ph_3PS	133.0 (85.0)	132.2 (10.6)	128.5 (12.7)	131.5 (2.8)	43		
$(\text{Me}_2\text{N})_3\text{PO}$					23		
$(\text{Me}_2\text{N})_3\text{PS}$					82		

^a Coupling constants J_{CP} /Hz in parentheses.

^b $\Delta\nu_{1/2}$ /Hz values in parentheses.

does the larger $^1J_{CP}$ in the adducts.³⁸

$\text{Ph}_3\text{PO} \cdot \text{AlBr}_3$ and $(\text{Me}_2\text{N})_3\text{PO} \cdot \text{AlCl}_3$ give only single signals (79 and 88 ppm respectively) in their ^{27}Al n.m.r. spectra. In contrast, solutions of $(\text{Me}_2\text{N})_3\text{PS} \cdot \text{AlCl}_3$ give a broad resonance at 107 ppm, assigned to the adduct, and a sharp signal ($\Delta\nu_{1/2} < 20$ Hz) at 102 ppm characteristic of AlCl_4^- .^{13,40} Similar spectral features are observed for other AlCl_3 adducts of thiophosphoryl³⁷ (See Chapter 2) and selenophosphoryl³⁷ centres and representative spectra are shown in Figure 2.1.1.. The ratio of the two signals is concentration dependent, the ratio of AlCl_4^- increasing with dilution, perhaps indicative of adduct dissociation. Consistent with dissociation, dilute solutions of $\text{Ph}_3\text{PS} \cdot \text{AlCl}_3$ reveal signals for the free base in the ^{31}P n.m.r..³⁷ The mechanism for the formation of AlCl_4^- is unclear. However, ^{27}Al n.m.r. is sensitive to tetrahedral environments^{13,40} and the amount of AlCl_4^- may be very small. The interaction of thiophosphoryl- AlCl_3 adducts with CH_2Cl_2 to give salts of AlCl_4^- is discussed in Chapter 2.

The line width of ^{27}Al n.m.r. resonances is indicative of the geometry about the aluminium centre.¹³ Frequently the quadrupolar nature of the nucleus leads to very broad lines.^{13,40} However, sharp signals are commonly observed for Al centres with substituents arranged in a pseudo-tetrahedral or octahedral array.¹³ For example, the perfectly tetrahedral AlCl_4^- has a signal with $\Delta\nu_{1/2} = 3$ Hz, while the adduct $\text{AlMe}_3 \cdot \text{OEt}_2$ has a significantly broader signal ($\Delta\nu_{1/2} = 2000$ Hz).⁴⁰ Thus, ^{27}Al line shapes may be generally used to establish the geometry about the aluminium centre, although other processes, such as chemical exchange, can occasionally play a role.^{13,40}

$\text{Ph}_3\text{PO} \cdot \text{AlBr}_3$ and $(\text{NMe}_2)_3\text{PO} \cdot \text{AlCl}_3$ both have narrow ($\Delta\nu_{1/2} = 31$ Hz and 18 Hz respectively) ^{27}Al signals, diagnostic of a highly symmetric environment for the aluminium centre in solution. A narrow signal (90 ppm, $\Delta\nu_{1/2} = 40$ Hz) is also observed for $\text{Ph}_3\text{PO} \cdot \text{AlCl}_3$.³⁶ The data implies a pseudotetrahedral environment at aluminium by virtue of a linear

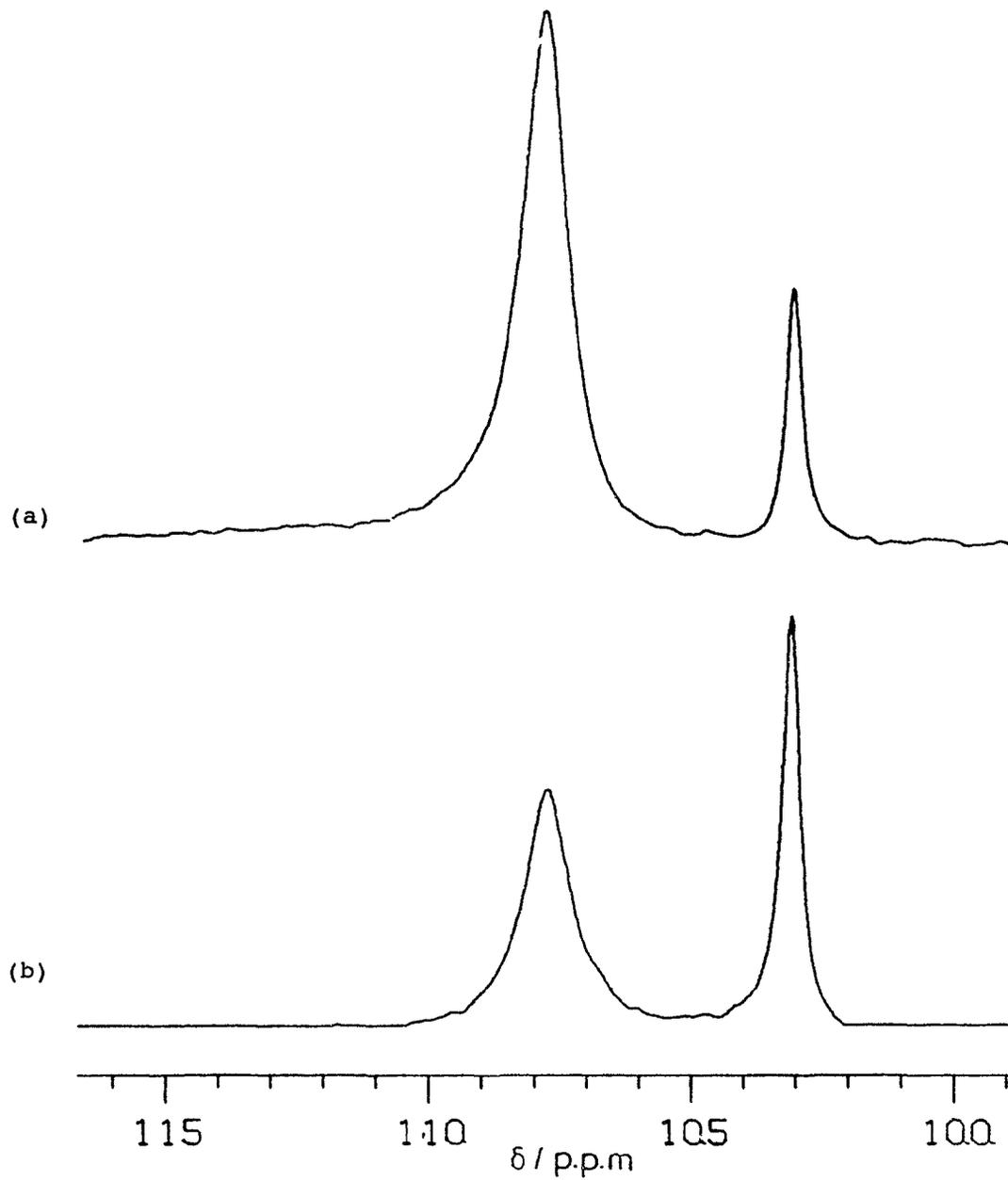


Figure 2.1.1.: Aluminium-27 n.m.r. spectra for $(\text{Me}_2\text{N})_3\text{PS}.\text{AlCl}_3$. [(a) 0.1 M; (b) 0.02 M].

P-O-Al backbone in solution, and is in agreement with the solid state structure of $\text{Ph}_3\text{PO}\cdot\text{AlBr}_3$ (see below) and $\text{Ph}_3\text{PO}\cdot\text{AlCl}_3$.³⁶ Interestingly, $\text{Al}[(\text{Me}_2\text{N})_3\text{PO}]_4^{3+}$ and $\text{Al}[(\text{Me}_2\text{N})_3\text{PO}]_6^{3+}$ also have narrow signals (3-5 Hz), which has been used to postulate linear P-O-Al frameworks.¹³ In contrast to the oxophosphoryl adducts, $(\text{Me}_2\text{N})_3\text{PS}\cdot\text{AlCl}_3$ ($\Delta\nu_{1/2} > 80$ Hz) and $\text{Ph}_3\text{PS}\cdot\text{AlCl}_3$ ($\Delta\nu_{1/2} = 200$ Hz)³⁷ have broad ^{27}Al lines, indicative of a non-linear P-S-Al framework in solution. Broad lines are also found for other thiophosphoryl adducts [see Chapter 2, e.g. $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$] and $\text{Ph}_3\text{PSe}\cdot\text{AlCl}_3$ ³⁷ and are consistent with the bent P-Ch-Al (Ch = S, Se) frameworks found in the solid state structures (see below).

^{71}Ga signals are intrinsically broader than the corresponding aluminium signals.⁴⁰ It is difficult to correlate the very broad single line (230 ppm, $\Delta\nu_{1/2} = 5100$ Hz) observed in the ^{71}Ga n.m.r. spectrum of $\text{Ph}_3\text{PO}\cdot\text{GaCl}_3$ with the linear P-O-Ga framework of the solid state structure (see below). Some spectra of $(\text{Me}_2\text{N})_3\text{PS}\cdot\text{GaCl}_3$ show a ^{71}Ga spectral pattern analogous to the AlCl_3 adduct, a broad ($\Delta\nu_{1/2} = 1130$ Hz) peak at 260 ppm with a sharp ($\Delta\nu_{1/2} = 215$ Hz) shoulder at 249 ppm (GaCl_4^-). The ^{11}B n.m.r. chemical shift of $\text{Ph}_3\text{PO}\cdot\text{BF}_3$ (-0.9 ppm) is slightly upfield from that of the free acid (9.4-11.6 ppm),⁴¹ as reported for other oxygen complexed BF_3 units.⁴¹

Heating of $\text{Ph}_3\text{PO}\cdot\text{AlBr}_3$ in CH_2Cl_2 at 80 °C for 15 h gives three ^{27}Al n.m.r. signals at 90.2, 87.5, and 83.6 ppm, of similar integral. These signals are assigned to $\text{Ph}_3\text{PO}\cdot\text{AlCl}_3$, $\text{Ph}_3\text{PO}\cdot\text{AlCl}_2\text{Br}$ and $\text{Ph}_3\text{PO}\cdot\text{AlClBr}_2$, respectively, by comparison with the data for $\text{Ph}_3\text{PO}\cdot\text{AlCl}_3$ and by analogy with the data for the series of corresponding mixed tetrahalo-aluminate anions, AlX_nY_m^- (X = Cl, Y = Br, $n = 4 - m$, $m = 4 - n$).⁴² The apparent exchange process, involving transfer of chlorine from the solvent, is similar to that observed for combined solutions of BF_3 and BCl_3 adducts of tetramethylurea which give mixed haloboron centres.⁴³

2.0.2. **X-Ray Crystal Structures of the Lewis Acid-base Complexes**
 $\text{Ph}_3\text{PO}\cdot\text{BF}_3$, $\text{Ph}_3\text{AsO}\cdot\text{BF}_3$, $\text{Ph}_3\text{PO}\cdot\text{AlBr}_3$, $\text{Ph}_3\text{PO}\cdot\text{GaCl}_3$ and
 $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$.

The crystal structures of $\text{Ph}_3\text{PO}\cdot\text{BF}_3$ ⁴⁴ and $\text{Ph}_3\text{AsO}\cdot\text{BF}_3$ ⁴⁴ were solved by Drs. Cameron and Linden at Dalhousie University and the structures of $\text{Ph}_3\text{PO}\cdot\text{AlBr}_3$,³⁶ $\text{Ph}_3\text{PO}\cdot\text{GaCl}_3$ ³⁶ and $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$ ⁴⁵ were determined by Dr. R. D. Rogers at N.I.U.. Views of the molecules are given in Figures 2.1.2.-2.1.5. (the BF_3 adducts are isostructural and only one view is given) and selected bond lengths and angles are presented in Tables 2.1.2.-2.1.5. The crystal structures all consist of discrete molecules, with the group 13 centre (E) coordinated via the chalcogen centre and distorted tetrahedral geometries about the phosphorus (arsenic) and E centres.

(a) The Oxophosphoryl (Oxoarsenyl) Complexes: The most notable feature of the structures is the Pn-O-E angle (Pn = pnictogen). The BF_3 adducts both adopt a bent geometry at the oxygen centre [P-O-B, 134.5 (2)°, As-O-B, 125.7 (2)°]. In contrast, $\text{Ph}_3\text{PO}\cdot\text{AlBr}_3$ and $\text{Ph}_3\text{PO}\cdot\text{GaCl}_3$ have a linear P-O-E backbone that lies on a crystallographic three-fold axis. $\text{Ph}_3\text{PO}\cdot\text{AlCl}_3$ also has a linear framework.³⁶ The oxygen centre of $\text{Ph}_3\text{PO}\cdot\text{GaCl}_3$ exhibits a large degree of off-axis motion, indicative of a bent geometry at oxygen. However, Dr. Rogers³⁶ was unable to model any possible disorder, although he calculated potential angles at oxygen ranging from 162 to 170°. Dr. Cameron³⁶ has likewise modeled the $\text{Ph}_3\text{P-O-AlCl}_3$ system and calculated a minimum angle at oxygen of 175.8°.

The Pn-O bond lengths of the AlBr_3 and BF_3 complexes [P, AlBr_3 1.513 (7), BF_3 1.522 (3); As, BF_3 1.690 (3) Å] are significantly longer than in the free base Ph_3PnO [P, 1.483 (2),^{46a} 1.46 (1) Å;^{46b} As, 1.644 (7) Å ($\text{Ph}_3\text{AsO}\cdot\text{H}_2\text{O}$)⁴⁷] while for the GaCl_3 complex (1.487 (11) Å) no significant lengthening is observed. All the Pn-O bond lengths of the adducts are significantly shorter than Pn-O single bonds [e.g. P-O,

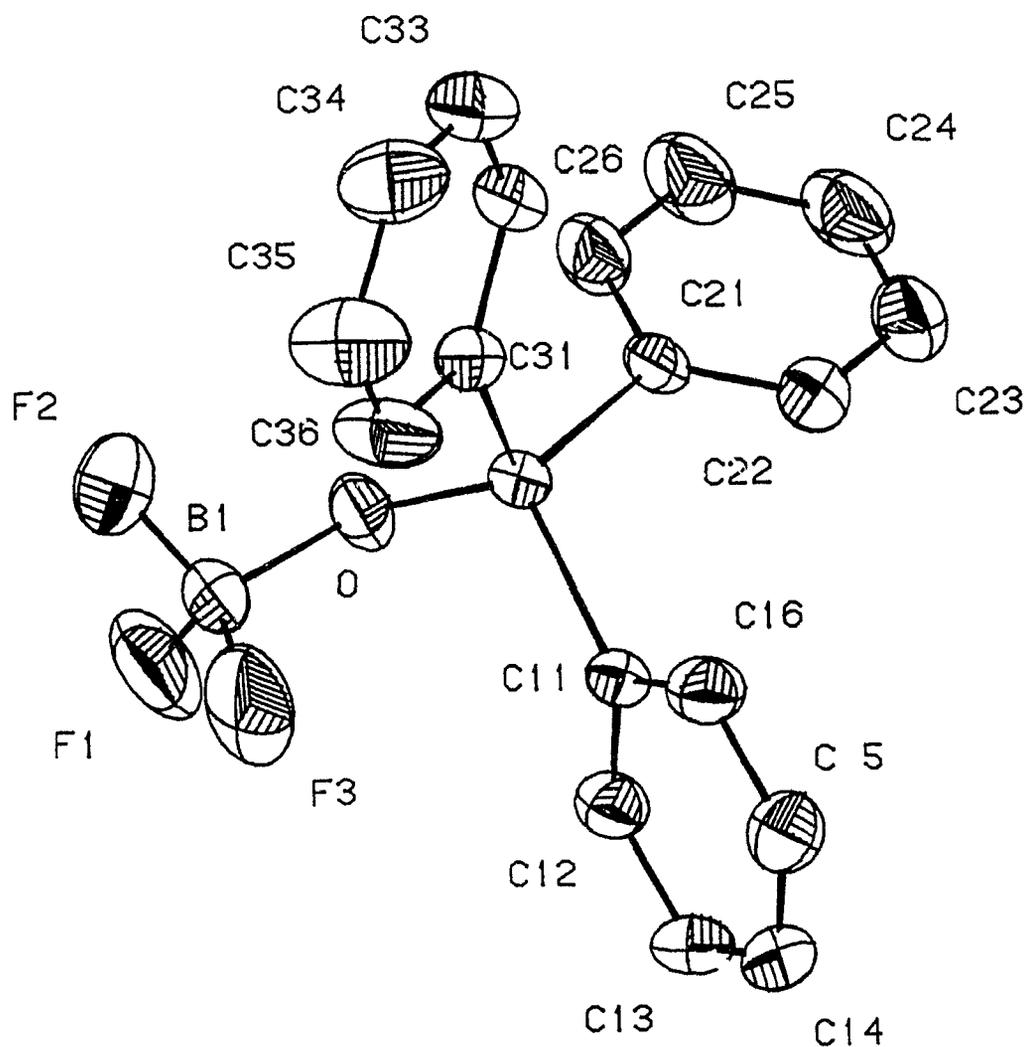


Figure 2.1.2.: Crystallographic view of $\text{Ph}_3\text{PnO} \cdot \text{BF}_3$ (Pn = P, As).

Table 2.1.2.: Selected bond lengths (Å) and angles (°) for $\text{Ph}_3\text{PnO} \cdot \text{BF}_3$ (Pn = P, As).

	$\text{Ph}_3\text{PO} \cdot \text{BF}_3$	$\text{Ph}_3\text{AsO} \cdot \text{BF}_3$
Pn-O	1.522 (3)	1.690 (3)
O-B	1.516 (6)	1.486 (5)
B-F(1)	1.357 (5)	1.354 (5)
Pn-C(11)	1.784 (4)	1.900 (3)
Pn-O-B	134.5 (2)	125.7 (2)
O-B-F(1)	105.7 (3)	106.4 (3)
F(1)-B-F(2)	109.3 (4)	109.0 (4)
O-P-C(11)	111.6 (2)	110.8 (1)
C(11)-P-C(21)	107.7 (2)	108.1 (1)

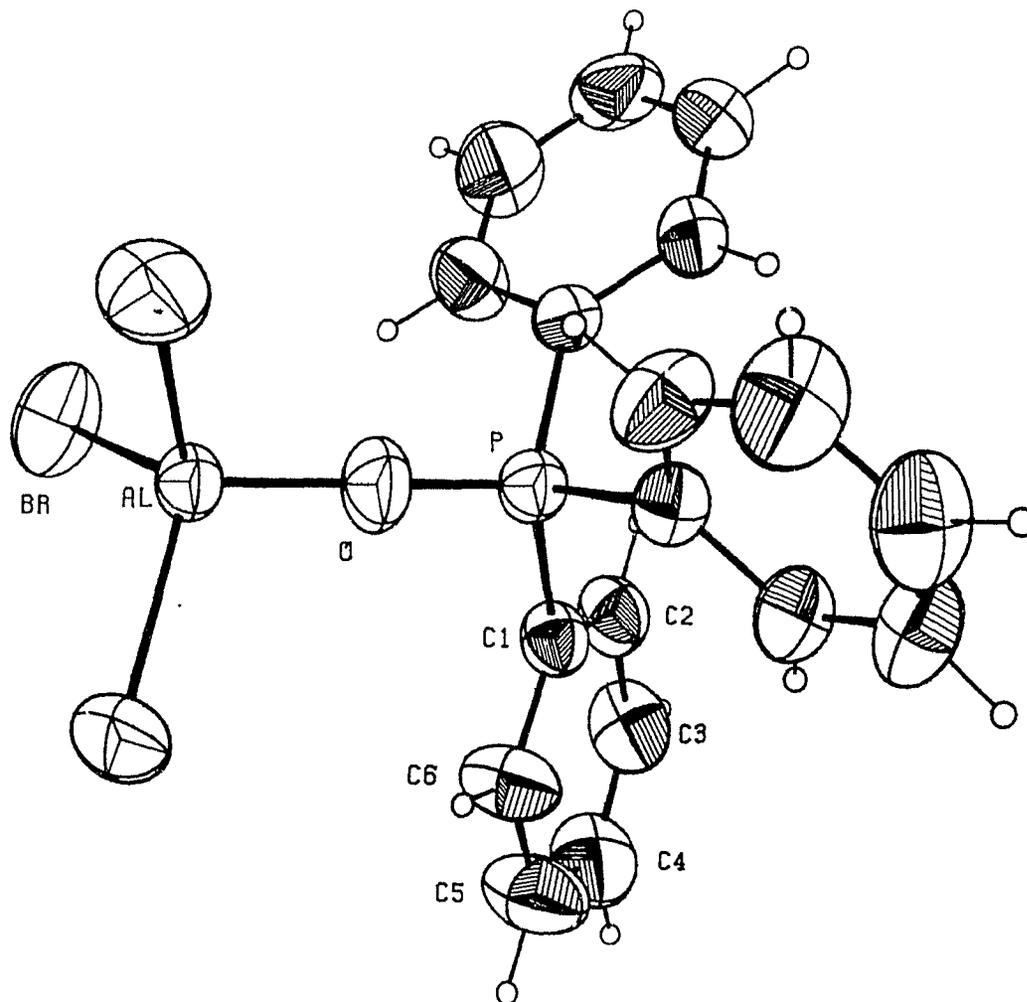


Figure 2.1.3.: Crystallographic view of $\text{Ph}_3\text{PO}\cdot\text{AlBr}_3$.

Table 2.1.3.: Selected bond lengths (Å) and angles (°) for $\text{Ph}_3\text{PO}\cdot\text{AlBr}_3$.

P-O	1.513 (7)	Al-Br	2.287 (2)
P-C(1)	1.791 (7)	O-Al	1.736 (7)
P-O-Al	180	O-P-C(1)	110.1 (2)
O-Al-Br	108.95 (8)	Br-Al-Br'	109.99 (8)
C(1)-P-C(1)'	108.8 (2)		

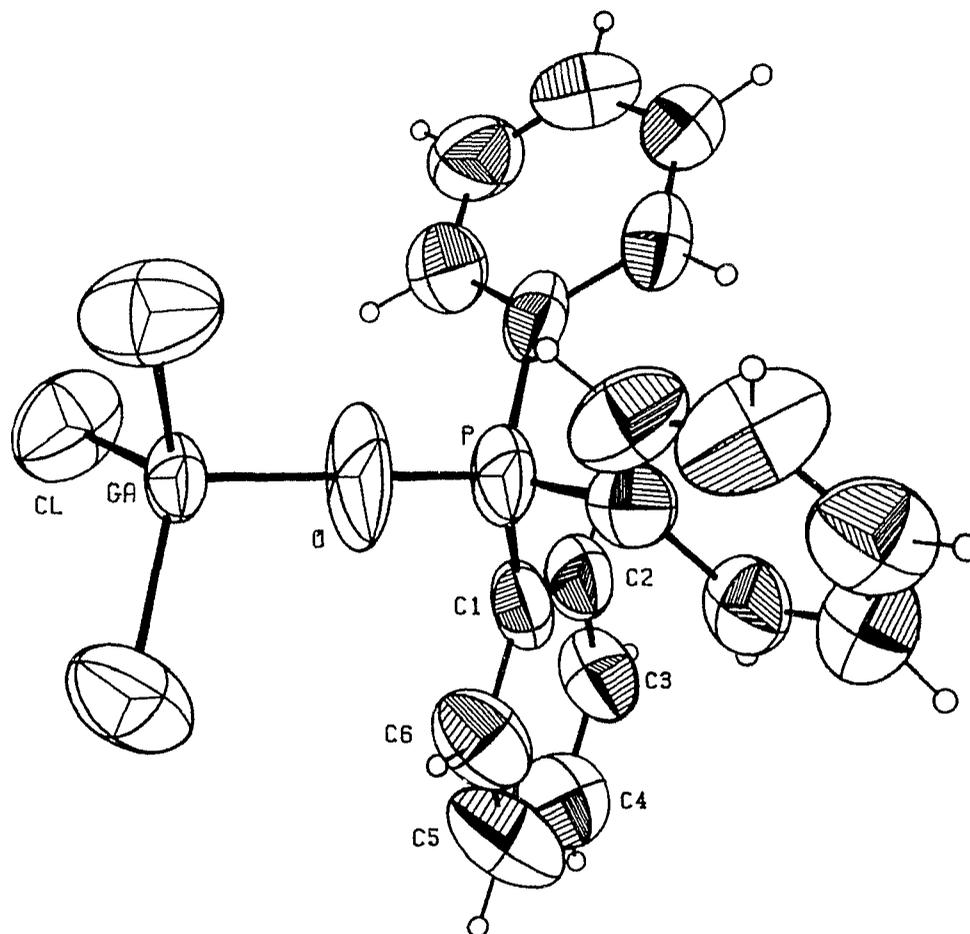


Figure 2.1.4.: Crystallographic view of $\text{Ph}_3\text{PO} \cdot \text{GaCl}_3$.

Table 2.1.4.: Selected bond lengths (Å) and angles (°) for $\text{Ph}_3\text{PO} \cdot \text{GaCl}_3$.

P-O	1.487 (11)	Ga-Cl	2.112 (6)
P-C(1)	1.761 (11)	O-Ga	1.818 (10)
P-O-Ga	180	O-P-C(1)	110.34 (29)
O-Ga-Cl	106.44 (19)	Cl-Ga-Cl'	112.32 (17)
C(1)-P-C(1)'	108.58 (30)		

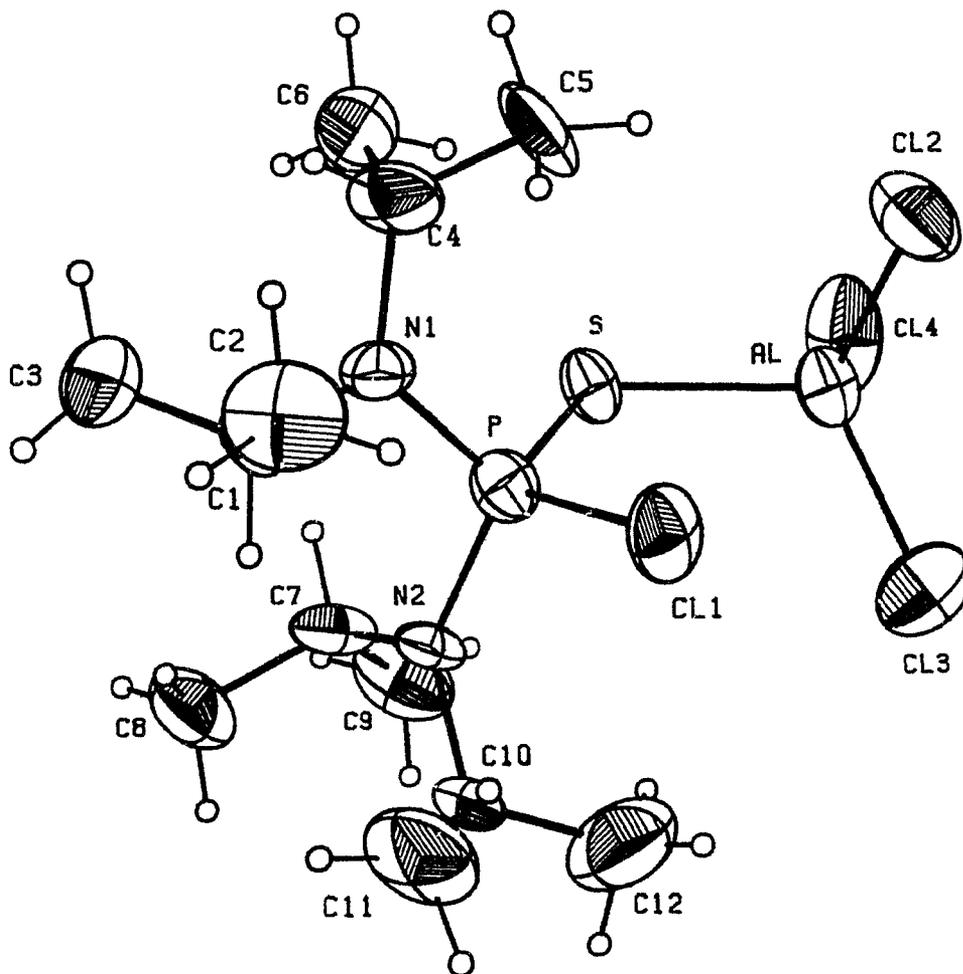


Figure 2.1.5.: Crystallographic view of $(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$.

Table 2.1.5.: Selected bond lengths (Å) and angles (°) for $(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$.

P-S	2.017 (6)	P-Cl(1)	1.987 (6)	P-N(1)	1.64 (1)
S-Al	2.291 (7)	Al-Cl(2)	2.110 (7)	P-N(2)	1.64 (1)
P-S-Al	112.2 (2)	S-P-N(1)	108.5 (5)		
S-P-Cl(1)	109.8 (3)	S-P-N(2)	112.7 (5)		
Cl(1)-P-N(1)	110.3 (5)	N(1)-P-N(2)	109.3 (6)		
Cl(1)-P-N(2)	106.3 (5)	S-Al-Cl(2)	109.5 (3)		
S-Al-Cl(3)	115.6 (3)	Cl(2)-Al-Cl(3)	111.2 (3)		
S-Al-Cl(4)	98.2 (3)	Cl(2)-Al-Cl(4)	111.3 (3)		
Cl(3)-Al-Cl(4)	110.4 (3)	P-N(1)-C(1)	118 (1)		
P-N(1)-C(4)	124 (1)	C(1)-N(1)-C(4)	115 (1)		
P-N(2)-C(7)	113.3 (9)	P-N(2)-C(10)	129 (1)		
C(7)-N(2)-C(10)	116 (1)				

1.604 Å in P_4O_{10} ,³ As-O, 1.79 Å in As_4O_6 ⁴⁸] and are generally consistent with those found in other Ph_3PnO complexes, Table 2.1.6.. This indicates significant retention of π character in the P-O bond of the adducts. The lengthening of the Pn-O bonds is consistent with the low Pn-O stretching frequency observed in the infrared spectra of many phosphoryl adducts, compared with that of the free bases.³⁵

The B-O bond lengths for $Ph_3PnO.BF_3$ [P, 1.516 (6) Å; As, 1.486 (5) Å] are typical σ : single bonds [range 1.43-1.55 Å].⁵¹ In contrast, the linear complexes have relatively short E-O bonds [$Ph_3PO.AlBr_3$, Al-O 1.736 (7) Å; $Ph_3PO.GaCl_3$, Ga-O 1.818 (10)] compared to the general single bond ranges [Al-O, 1.73-1.80 Å;⁵² Ga-O, 1.87-2.12 Å⁵³]. $Ph_3PO.AlCl_3$ also has a short Al-O bond (1.733 (4) Å).³⁶

(b) The Thiophosphoryl Complex, $(iPr_2N)_2P(Cl)S.AlCl_3$: The preparation and chemistry of this complex are discussed in detail in Chapter 2. The structure is presented here as an illustration of an $AlCl_3$ complex of a thiophosphoryl system.

Similar to P-Ch bond lengths found for other oxophosphoryl and thiophosphoryl complexes (Tables 2.1.6. and 2.1.7.), the P-Ch bond length in $(iPr_2N)_2P(Cl)S.AlCl_3$ (P-S 2.017 (6) Å) is significantly longer than in its free base $(iPr_2N)_2P(Cl)S$ [1.980 (2) Å, Chapter 2] although considerably shorter than a P-S single bond [$(PhS)_3P$, 2.112 (1) Å].⁵⁵ However, while linear P-Ch-E (Ch = O; E = Al, Ga) backbones and the short Ch-E bond lengths are observed for $Ph_3PO.AlCl_3$,³⁶ $Ph_3PO.AlBr_3$ and $Ph_3PO.GaCl_3$, $(iPr_2N)_2P(Cl)S.AlCl_3$ adopts a sharp angle at sulphur [P-S-Al, 112.2 (2)°], and the Al-S bond length [2.291 (7) Å] is close to that expected for a covalent bond (sum of covalent radii = 2.32 Å)⁵⁶ and comparable to that observed for aluminium sulphides [e.g. Al-S: α - $ZnAl_2S_4$, 2.36(3);⁵⁷ $Ce_6Al_{10/3}S_{14}$, Al-S(tetrahedral) 2.09, 2.29, Al-S(octahedral) 2.42, 2.65; α - Al_2S_3 , 2.26 Å].⁵⁸ $Ph_3PS.AlCl_3$ also has a severally bent P-S-Al angle [109.62 (8)°] and an identical Al-S bond

Table 2.1.6.: Comparison of Pn-O bond lengths (Å) and Pn-O-E angles (°) in some Lewis acid-base complexes with terminal oxophosphoryl and oxoarsenyl ligands.

Compound	P-O	P-O-M	Ref
Ph ₃ PO	1.483 (2)		46a
Ph ₃ PO.BF ₃	1.522 (3)	134.5 (2)	44
Ph ₃ PO.AlCl ₃	1.519 (4)	180	36
Ph ₃ PO.AlBr ₃	1.513 (7)	180	36
Ph ₃ PO.GaCl ₃	1.487 (11)	180	36
Ph ₃ PO.AlO ₃ (SiPh) ₇ O ₉	1.508 (4)	160.4 (3)	49a
[Ph ₃ PO.SeOCl ₂] ₂	1.497 (9)	143.4 (5)	49b
[Ph ₃ PO] ₂ .MnCl ₂	1.488 (6)	156.0 (4)	49c
[Ph ₃ PO] ₄ .Cu ₄ OCl ₆	1.51 (2)	180	12
[(Ph ₃ PO) ₂ NpO ₂] ²⁺	1.502 (9)	159.1 (4)	49d
[(Ph ₃ PO) ₂ UO ₂] ²⁺	1.505 (9)	160.0 (4)	49d
[(Ph ₃ PO) ₂ NpO ₂ Cl ₂]	1.50 (1)	167 (1)	49d
	1.55 (2)	153 (1)	
[{(Ph ₃ PO)ReCl ₂ (O)} ₂ O]	1.524 (4)	171.7 (3)	49e
<i>cis</i> -[{(Ph ₃ PO)Sm(η-C ₅ Me ₅) ₂ (C ₂ H ₄ O ₂)} ₂]	1.501 (10)	167.6 (6)	49f
	1.496 (11)	168.8 (5)	
<i>trans</i> -[{(Ph ₃ PO)Sm(η-C ₅ Me ₅) ₂ (C ₂ H ₄ O ₂)} ₂]	1.514 (7)	163.0 (5)	49f
	1.495 (8)	158.7 (5)	
[(Ph ₃ PO) ₂ (Cu ₂ (C ₃ H ₄ ClO ₂) ₄)]	1.507 (6)	146.7 (4)	49g
[(Ph ₃ PO)Cu(ClC ₃ H ₄ O ₂) ₂] ₂	1.477 (3)	149.0 (2)	49h
[(Ph ₃ PO) ₂ Os(OEP)] ^a	1.483 (8)	154.2 (5)	49i
[(Ph ₃ PO)La{N(SiMe ₃) ₂ } ₃]	1.52 (2)	174.6 (9)	49j
[(Ph ₃ PO) ₂ La ₂ (O ₂){N(SiMe ₃) ₂ } ₄]	1.51 (2)	172.6 (14)	49j
[(Ph ₃ PO) ₂ Co(NO ₃) ₂]	1.48 (1)	158.5 (8)	49k
[(Ph ₃ PO) ₂ CuCl ₂]	1.492 (4)	150.9 (3)	49l
[(Ph ₃ PO) ₆ Hg ₂ (ClO ₄) ₂]	1.50 (2)	131 (1)	49m
	1.52 (2)	160 (1)	
	1.50 (2)	152 (1)	
[(Ph ₃ PO) ₂ Ce(NO ₃) ₄]	1.531 (8)	169.2 (5)	49n
	1.526 (8)	173.2 (4)	
[(Ph ₃ PC) ₂ Th(NO ₃) ₄]	1.43 (2)	170.2 (11)	49o
	1.47 (2)	170.2 (10)	
[(Ph ₃ PO)UO ₂ (CH ₃ COO) ₂] ₂	1.49 (4)	143 (1)	49p
[(Ph ₃ PO)UO ₂ {(C ₂ H ₅) ₂ NCS ₂ } ₂]	1.49 (3)	162 (2)	49q
[(Ph ₃ PO)UO ₂ (CH ₃ CS ₂) ₂]	1.47 (2)	159 (1)	49r
[(Ph ₃ PO) ₂ UCl ₄]	1.524 (7)	165.1 (5)	49s
[(Ph ₃ PO)Sn(C ₆ H ₅) ₃ (NO ₃)]	1.47 (2)	153 (1)	49t
[(Me ₃ PO) ₂ Co(NO ₃) ₂]	1.53 (3)	139.6 (10)	49u
	1.55 (3)	133.2 (10)	
Me ₃ PO.SbCl ₅	1.56 (4)	144.9 (23)	49v

Table 2.1.6.: Comparison of Pn-O bond lengths (Å) and Pn-O-E angles (°) in some Lewis acid-base complexes with terminal oxophosphoryl and oxoarsenyl ligands (Continued).

Cl_3PO	1.45 (3)		3
$\text{Cl}_3\text{PO} \cdot \text{SbCl}_5$	1.47 (2)	145.0 (16)	49v
$\text{Cl}_3\text{PO} \cdot \text{NbCl}_5$	1.45 (2)	148.8 (12)	49v
$\text{Cl}_3\text{PO} \cdot \text{MoCl}_5$	1.459 (7)	143.7 (4)	49w
$\text{Cl}_3\text{PO} \cdot \text{ReCl}_5$	1.45 (1)	143.2 (8)	49x
$[\text{Cl}_3\text{PO} \cdot \text{MoNCl}_3]_4 \cdot \text{CCl}_4$	1.45 (2)	162.0 (8)	49w
	1.46 (2)	151.6 (9)	
	1.45 (1)	152 (1)	
	1.46 (1)	151.9 (7)	
$[\text{Cl}_3\text{PO} \cdot \text{WnCl}_3]_4$	1.393 (5)	152.4 (1)	49y
	1.530 (3)	146.9 (1)	
	1.534 (3)	146.6 (1)	
	1.517 (4)	157.9 (3)	
$(\text{H}_2\text{N})_3\text{PO}$	1.51 (1)		3
$(\text{Me}_2\text{N})_3\text{PO} \cdot \text{SnMe}_3\text{Cl}$	1.55 (3)	158 (1)	49z
$[\{(\text{Me}_2\text{N})_3\text{PO}\}_2\text{SnMe}_3]^+$	1.57 (2)	171 (2)	49z
$\text{Ph}_3\text{AsO} \cdot \text{H}_2\text{O}$	1.644 (7)		47
$\text{Ph}_3\text{AsO} \cdot \text{BF}_3$	1.690 (3)	125.7 (2)	44
$[(\text{Ph}_3\text{AsO})_2\text{CoCl}_2] \cdot \text{C}_2\text{H}_6\text{O}$	1.643 (21)	130.1 (13)	50a
	1.635 (20)	130.1 (13)	
$[(\text{Ph}_3\text{AsO})_2\text{Sn}(\text{ClC}_6\text{H}_4)_2\text{Ph}_2]^+$	1.667 (5)	149.2 (3)	50b
	1.673 (5)	142.7 (3)	
$[(\text{Ph}_3\text{AsO})\text{Sn}(\text{NO}_3)_2\text{Ph}_2]$	1.677 (4)	137.9 (6)	50c
$[(\text{Ph}_3\text{AsO})_3\text{Bi}_2\text{I}_6]$	1.67 (2)	142 (1)	50d
	1.69 (2)	147.3 (9)	
	1.69 (2)	153 (1)	
	1.66 (2)	143 (1)	
	1.69 (2)	146 (1)	
	1.69 (3)	151 (1)	
$[(\text{Me}_3\text{AsO})_9\text{Ca}_2][\text{ClO}_4]_4$	1.657 (7)	148.8 (5)	50e
$(\text{Et}_3\text{AsO})_2 \cdot \text{UCl}_4$	1.71	154	50f
$[(\text{Ph}_2\text{MeAsO})_4\text{Ni}(\text{NO}_3)]^+$	1.661 (6)	128.2 (4)	50g
$[(\text{CH}_2\text{Ph}_2\text{AsO})_2(\text{SnPh}_3\text{Cl})_2]$	1.665 (4)	134.5 (2)	50h
$[(\text{CH}_2\text{Ph}_2\text{AsO})_2(\text{SnPh}_3\text{NO}_3)_2]$	1.666 (6)	140.2 (3)	50i

^aOctaethylporphyrinate

Table 2.1.7.: Comparison of Pn-Ch bond lengths (Å) and Pn-Ch-E angles (°) in some Lewis acid-base complexes with terminal thio and seleno phosphoryl and thioarsenyl ligands.

Compound	P-Ch	P-Ch-M	Ref
$(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}$	1.980 (2)		Chap 2
$(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}.\text{AlCl}_3$	2.017 (6)	112.2 (2)	45
$(\text{Me}_3\text{SiN})(\text{Me}_2\text{Si})(\text{Me}_3\text{SiN})\text{P}(\text{Me})\text{S}.\text{GaCl}_3$	2.028 (1)	110.60 (6)	Chap 3
Ph_3PS	1.950 (3)		54a
$\text{Ph}_3\text{PS}.\text{AlCl}_3$	2.028 (2)	109.62 (8)	37
$\text{Ph}_3\text{PS}.\text{SI}_2$	2.007 (3)	107.0 (1)	54b
$\text{Ph}_3\text{PS}.\text{MoCl}_3$	2.041 (1)	111.31 (4)	54c
$\text{Ph}_3\text{PS}.\text{NbSCl}_3$	2.028 (5)	116.6 (2)	54d
	2.026 (6)	111.5 (2)	
Me_3PS	1.959 (2)		3
$\text{Me}_3\text{PS}.\text{Cr}(\text{CO})_5$	1.990 (3)	112.5 (1)	54e
$[(\text{Me}_3\text{PS})_3\text{Cu}]\text{ClO}_4$	1.967 (7)	110.3 (3)	54f
	2.009 (7)	104.3 (3)	
	2.007 (6)	107.2 (3)	
$[(\text{Me}_4\text{P}_2\text{S}_2)\text{CuCl}]_2$	1.995 (9)	109.5 (3)	54g
	1.991 (9)	113.1 (3)	
Ph_3PSe	2.106 (1)		54h
$\text{Ph}_3\text{PSe}.\text{AlCl}_3$	2.182 (2)	106.95 (7)	37
	2.181 (2)	107.15 (7)	
$\text{Ph}_3\text{PSe}.\text{HgCl}_2$	2.169 (6)	98.1 (1)	60
$\text{Ph}_3\text{PSe}.\text{AuCl}$	2.187 (5)	100.1 (1)	61
$[(\text{Me}_3\text{AsS})_4.\text{Co}][\text{ClO}_4]_2$	2.14 (1)	106.5 (4)	54i
	2.14 (1)	106.6 (4)	
	2.14 (1)	109.0 (4)	
	2.12 (1)	108.9 (4)	
	2.132 (8)	111.2 (3)	
	2.121 (8)	109.2 (4)	
	2.133 (8)	112.0 (4)	
	2.133 (8)	110.2 (3)	

length [2.297 (2) Å].³⁷

The amine units (C₂NP) are individually planar [s.o.a. = 357° (N1) and 358.3 (N2)] and the P-N bond lengths [1.64 (1), Å] are short (P-N single bond, 1.77 Å),³ indicative of substantial P-N π-interaction. Similar shortenings and planar nitrogen centres are also observed in the free base (Chapter 2) and other amino substituted phosphorus centres⁵⁹ (see also Chapters 2 and 3). The P-Cl bond (1.987 (6) Å; cf. PCl₅, 2.124 (3), 2.020 (3) Å)³ is also short, again as observed in the free base. This chlorine atom Cl(1) has a contact (3.581 (7) Å) with the aluminium centre. ⁱPr₂N units are sterically demanding, and it is likely that this contact is a function of the spatial requirements of the structure rather than a bonding interaction (see (Et₂N)₂P(Cl)NPh.AlCl₃ vs (ⁱPr₂N)₂P(Cl)NPh.AlCl₃, Chapter 2). The AlCl₃ moiety is distorted (S-Al-Cl(2), 109.5 (3)°; S-Al-Cl(3), 115.6 (3)°; S-Al-Cl(4), 98.2 (3)°) in such a way as to tilt the chlorine centres away from the phosphorus, permitting the aluminium to make contact [Al-P 3.579 (6) Å]. P-Al contacts are also found in Ph₃PS.AlCl₃ [3.538 (2) Å] and Ph₃PSe.AlCl₃ [3.727 (3), 3.706 (3) Å].³⁷ Furthermore, contacts are observed in the severely bent selenophosphoryl complexes Ph₃PSe.HgCl₂ (Hg-P, 3.53 Å)⁶⁰ and Ph₃PSe.AuCl [Au-P, 3.497 (7) Å].⁶¹

2.0.3. The Phosphorus-Chalcogen-Acid Linkage.

Comparison of the oxophosphoryl complexes in Table 2.1.6. reveals flexibility in the angles adopted at oxygen. In general, with three exceptions, the range of angles observed lie between 140 and 180°. In contrast, the angles observed at sulphur or selenium in the heavier chalcogenophosphoryl complexes, Table 2.1.7., are restricted to sharp angles of less than 116°. From these observations it is apparent that there are differences in the coordinative bonding modes of the chalcogenophosphoryls on descending group 16.

Linear geometry at an oxygen centre is not unique to the

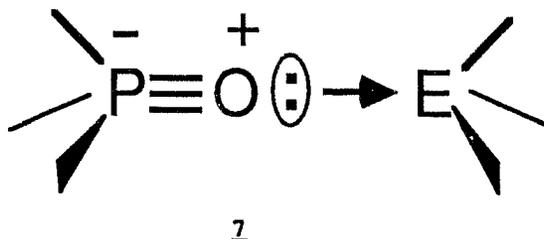
derivatives of $\text{Ph}_3\text{PO}\cdot\text{EX}_3$ ($\text{E} = \text{Al}, \text{Ga}; \text{X} = \text{halogen}$). Collinear bonding at oxygen has been reported¹² in the Ph_3PO ligands of the copper cluster $\text{Cu}_4\text{OCl}_6(\text{Ph}_3\text{PO})_4$. Furthermore, in the diphosphonium salt $[(\text{Me}_2\text{N})_3\text{P}-\text{O}-\text{P}(\text{NMe}_2)_3][\text{CF}_3\text{SO}_3]_2$ a linear P-O-P framework is observed,⁶² and linear geometries at oxygen are reported for the pyrophosphate anions^{63,64} and the siloxanes.^{63,65}

There are also reports of compounds containing both short Al-O bonds and unusually large angles at oxygen. An almost linear Al-O-Al [$178.0 (3)^\circ$] moiety is observed in $\text{Al}_2\text{O}(\text{C}_{10}\text{H}_8\text{NO})_4$.⁶⁶ Although the steric constraints of the chelating ligands may be enforcing linearity of the Al-O-Al framework, the unusual conformation and very short Al-O bonds [$1.676 (4)$ and $1.678 (4) \text{ \AA}$] are explained by the involvement of unoccupied d orbitals of the aluminium atoms in the bonding.⁶⁶ Analogous $p\pi-d\pi$ has been proposed for the siloxanes.^{63,65} However, Barron and co-workers theorise that the unoccupied $3d$ orbitals of aluminium are too high in energy to contribute to Al-O π bonding.⁶⁷ For the phenolate complexes $[\text{AlMe}_2(\text{OC}_6\text{H}_2\text{Me}-4-\text{tBu}_2-2,6)(\text{PMe}_3)]$ [Al-O-C $164.5 (4)^\circ$ and Al-O $1.736 (5) \text{ \AA}$] and $[\text{AlMeCl}_2(\text{OC}_6\text{H}_2\text{Me}-4-\text{tBu}_2-2,6)]^-$ [Al-O-C $164.0 (3)^\circ$ and Al-O $1.713 (4) \text{ \AA}$], Barron^{67,68} proposes a π interaction between the lone pairs of oxygen and a Al-X σ^* antibonding molecular orbital to explain the short Al-O bonds and wide C-O-Al angles. Steric effects are evident in these compounds, and may even be responsible for the distortion from linearity.

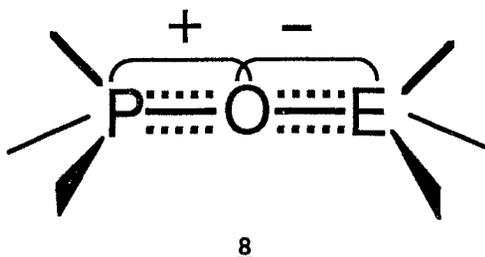
The bent geometry at oxygen in $\text{Ph}_3\text{PO}\cdot\text{BF}_3$ indicates that the observed linearity of the Al and Ga complexes is not sterically induced. Therefore, the structure of the adducts must be electronically controlled and dependent on the acceptor properties of the acid. Nevertheless, the P-O bond lengths of the Lewis acid adducts of Ph_3PO are essentially independent of the type of acid or molecular geometry of the adduct.

It is proposed that the linear $\text{Ph}_3\text{PO}\cdot\text{EX}_3$ ($\text{E} = \text{Al}, \text{Ga}; \text{X} = \text{halide}$)

are best viewed as σ complexes (using organometallic terminology), with the E centre bound to the axial lone pair of triply bonded model of the oxophosphoryl unit, illustrated in the Lewis structure 7.

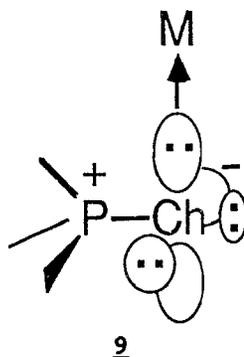


A similar bonding arrangement has been suggested for $\text{Cu}_4\text{OCl}_6(\text{Ph}_3\text{PO})_4$.¹² The potential for σ complexation for the oxides is believed to be a consequence of effective π bonding⁴ between the phosphorus and oxygen centres rendering the σ -type non-bonding pair of electrons highest in energy and therefore more available for donation. The short Al-O and Ga-O bonds observed in $\text{Ph}_3\text{PO} \cdot \text{EX}_3$ (E = Al, Ga) adducts indicate the presence of auxiliary bonding as observed in the phenolate complexes (see above). Therefore for oxophosphoryl adducts, in addition to σ acceptance by the acid centre, there is believed to be a π donation from the oxygen to the acid into either empty σ^* or d orbitals. Such an arrangement is depicted in 8. A similar π delocalised framework has been proposed for $[(\text{Me}_2\text{N})_3\text{P}-\text{O}-\text{P}(\text{NMe}_2)_3]^+$.⁶²



For the thio and selenophosphoryls complexes, many of the angles observed (Table 2.1.7.) at the chalcogen are consistent with the valence

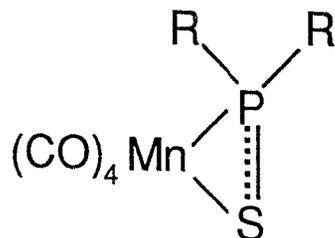
shell electron pair repulsion model for a two coordinate chalcogen centre. However, the P-Ch bond lengths are all significantly shorter than representative single bonds, implying some retention of π bonding in the complexes. Moreover, many of the observed angles are smaller than 109° and contacts are observed between the acid and phosphorus centres. Phosphorus-chalcogen π bonding has been shown^{4a} to be less pronounced on descending the p-block from oxygen, and it is likely that the π -type orbitals become more available for donation. Therefore, for the heavier chalcogen phosphoryls, it is proposed that they act as 'side on' donors or ' π donors' (using organometallic terminology) employing P-Ch π -bonding electrons for donation, rather than the σ lone pairs of electrons. This model is illustrated in the Lewis structure 9.



A linear P-N-P⁺ framework is found in the [(Ph₃P)₂N][V(CO)₆] salt.⁶⁹ However, other salts of the [(Ph₃P)₂N]⁺ cation, originating from the same (Ph₃P)₂NCl precursor, have a bent P-N-P framework.⁶⁹ This indicates a small energy differences between the bent and linear forms.⁶⁹ The majority of the oxophosphoryl complexes of Table 2.1.6. have wide angles at the oxygen centre consistent with ' σ ' donation to the acid centre. The slight deviations from linearity indicate that the σ -type non-bonding pair of electrons are only slightly lower in energy from the π -type electrons of the base, permitting partial π coordination.

π -type donation from a P-S bond has been observed by Roper,

Lindner and others.⁷⁰ For example,^{70b} in the manganese complex 10,



10

the $(C_6H_{11})_2PS$ fragment acts as a η^2 ligand while the vacant coordination site at the phosphorus allows for the formation of a full σ bond to the metal centre. The P-S bond length [2.006 (2) Å] is analogous to those found in the thiophosphoryl complexes of Table 2.1.7..

Nardelli⁷¹ reviewed the M-O-As angles of complexes with terminal Ph_3AsO ligands in 1977 and found them to range from 134 to 159°. This review, together with the more recently prepared adducts given in Table 2.1.6., demonstrates that $Ph_3AsO \cdot BF_3$ has one of the narrowest angles [125.7 (2)°] found in a terminal oxoarsenyl complex. From the observed As-O-M angles, the oxoarsenyl unit appears to act as a coincident π and σ donor. The complexes of thioarsenyls are not well characterised, Table 2.1.7., but from the limited structural data available they behave as π donors, similar to the thiophosphoryls.

In summary, the results show the coordinative bonding modes of the chalcogeno phosphoryls and arsenyls to be dependent on the pnictogen and the chalcogen. For the oxophosphoryls units, efficient $d\pi-p\pi$ bonding allows a significant degree of axial or σ complexation. However, substitution of the phosphorus or oxygen for a heavier pnictogen or chalcogen leads to primarily "side on" or π complexation.

Chapter 2

The Chemistry of the Bis(dialkylamino)phosphoryl Chlorides, $(R_2N)_2P(Cl)Ch$ ($R = Me, Et$ or iPr ; $Ch = NPh, O, S$ and Se), with $AlCl_3$, $AgSO_3CF_3$ and Other Halide Ion Abstracting Reagents.

An imino or chalcogeno phosphoryl centre with a chlorine substituent [$Y_2P(Cl)Ch$, $Ch = NR$, chalcogen] can react with Lewis acids to give coordination complexes (as in Chapter 1) or alternatively could give cationic species via halide ion abstraction. Wolf³⁰ and Appel²⁹ have both recognised the phosphoryl mono-chlorides as possible precursors to the rare²⁸ tricoordinate phosphonium (phosphoryl cation) centre. To establish the balance between complex formation and halide ion abstraction, the reactions and products of bis(dialkylamino)phosphoryl chlorides, $(R_2N)_2P(Cl)Ch$ ($R = Me, Et$ or iPr ; $Ch = NPh, O, S$ and Se) with $AlCl_3$ have been comprehensively examined. The results, together with those involving alternative halide ion abstracting reagents e.g. $AgSO_3CF_3$, allow for a better understanding of the ionic and covalent environments available to the phosphoryl unit.

2.2.1. N.m.r. and Structural Characterisation of the Diaminophosphoryl Chlorides, $(R_2N)_2P(Cl)Ch$ ($R = Me, Et, iPr$; $Ch = NPh, S, Se$) and $[(Me_3Si)_2N]_2P(Cl)S$.

The derivatives of $(R_2N)_2P(Cl)Ch$ ($R = Me, Et, iPr$; $Ch = NPh, S, Se$) were prepared by reaction of the corresponding phosphine with N_3Ph, S or Se . $[(Me_3Si)_2N]_2P(Cl)S$ was prepared by addition of Cl_3PS to $LiN(SiMe_3)_2$ and, like the Me and Et derivatives of $(R_2N)_2P(Cl)Ch$, is a distillable liquid. The iPr derivatives of $(R_2N)_2P(Cl)Ch$ and $[(Me_3Si)_2N]_2P(Cl)S$ have not been previously reported although $(iPr_2N)_2P(Cl)S$ has been identified⁷² as a possible reaction by-product (no characterisation details were given). The reactions of $[(Me_3Si)_2N]_2P(Cl)S$ are discussed in Chapter 3. ^{13}C and ^{31}P n.m.r. data

for the compounds are given in Table 2.2.1..

In contrast to the sterically less restricted Me and Et derivatives of $(R_2N)_2P(Cl)Ch$, the iPr derivatives and $[(Me_3Si)_2N]_2P(Cl)S$ show two methyl resonances in the ^{13}C n.m.r. spectra, indicating restricted rotation about the P-N bonds. Similar inequivalence is observed for $(iPr_2N)_2P(Cl)$. A high temperature (80 °C) study of $(iPr_2N)_2P(Cl)S$ in deuterated toluene revealed no significant change from the room temperature ^{13}C n.m.r. spectrum. While the ^{31}P chemical shifts of the iPr derivatives of $(R_2N)_2P(Cl)Ch$ are typical, the chemical shift of $[(Me_3Si)_2N]_2P(Cl)S$ is severely deshielded (204 ppm). To the author's knowledge, this represents the most deshielded tetracoordinate organophosphorus species known (general range +100 to -100 ppm).⁷³ Caution must be exercised in drawing structural conclusions on the basis of ^{31}P chemical shifts⁷⁴ and ready explanation of this novel chemical shift is not available.

The X-ray crystal structures of the iPr derivatives of $(R_2N)_2P(Cl)Ch$ have been determined by Dr. J. F. Richardson (Ch = NPh) and Dr. T. S. Cameron (Ch = S, Se).⁷⁵ Views of the molecules are shown in Figures 2.2.1.-2.2.3. and selected bond lengths and angles are given Tables 2.2.2.-2.2.4. respectively. The bond length and angles are generally as expected for the structural units involved.³ Disorder exists between the chlorine and chalcogen atoms for the thio and seleno phosphoryls.

2.2.2 Reactions Between Bis(dialkylamino)chalcogenophosphoryl Chlorides, $(R_2N)_2P(Cl)Ch$ (R = Me, Et or iPr ; Ch = NPh, O, S and Se) and $AlCl_3$.

Addition of a series of imino, oxo and thio bis(dialkylamino)phosphoryl chlorides, $(R_2N)_2P(Cl)Ch$ (R = Me, Et, iPr ; Ch = NPh, O, S) in CH_2Cl_2 to $AlCl_3$, under anhydrous conditions at room temperature, results in the formation of Lewis acid-base complexes in

Table 2.2.1.: Phosphorus-31 and ^{13}C n.m.r. data for derivatives of $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{S}$ and the products with AlCl_3 .

Chemical shifts in ppm.

Compound	^{31}P	^{13}C
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$	204	3.8, 2.7
$(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}$	12	
$(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}$	-8	147.4(i), 128.5(m), 122.4(o) 118.0(p), 47.5, 22.5, 22.2
$(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}.\text{AlCl}_3$	49	141.2(i), 129.7(m), 129.3(o) 127.1(p), 40.5, 12.1
$(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}.\text{AlCl}_3$	51	140.4(i), 130.9(m), 129.6(o) 127.4(p), 51.1, 24.4, 23.6
$(\text{Me}_2\text{N})_2\text{P}(\text{Cl})\text{O}$	32	36.5
$(\text{Me}_2\text{N})_2\text{P}(\text{Cl})\text{O}.\text{AlCl}_3$	32	37.0
$(\text{Me}_2\text{N})_2\text{P}(\text{Cl})\text{S}$	92	37.2
$(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{S}$	85	40.5, 13.2
$(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}$	70	48.1, 22.2, 21.9
$(\text{Me}_2\text{N})_2\text{P}(\text{Cl})\text{S}.\text{AlCl}_3$	79	38.3
$(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{S}.\text{AlCl}_3$	73	42.0, 13.0
$(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}.\text{AlCl}_3$	63	50.1, 22.6, 22.4
$(\text{Me}_2\text{N})_2\text{P}(\text{Cl})\text{SCH}_2\text{Cl}^+$	73	44.9, 38.6
$(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{SCH}_2\text{Cl}^+$	69	45.4, 43.0, 13.3
$(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{SCH}_2\text{Cl}^+$	61	51.5, 45.2, 22.9, 21.5
$(\text{Me}_2\text{N})_2\text{P}(\text{Cl})\text{Se}$	85 (901) ^a	37.7
$(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{Se}$	75 (893) ^a	40.8, 13.1
$(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{Se}$	53 (881) ^a	48.5, 22.6, 21.8
$(\text{Me}_2\text{N})_2\text{P}(\text{Cl})\text{Se}/\text{AlCl}_3$	267, 50-80 ^b	
$(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{Se}/\text{AlCl}_3$	264, 78-80, -8 (341) ^a	
$(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{Se}/\text{AlCl}_3$	313	

Aromatic carbon centres: (i) ipso, (o) ortho, (m) meta, (p) para

^a J_{PSe}/Hz

^b More than twenty peaks.

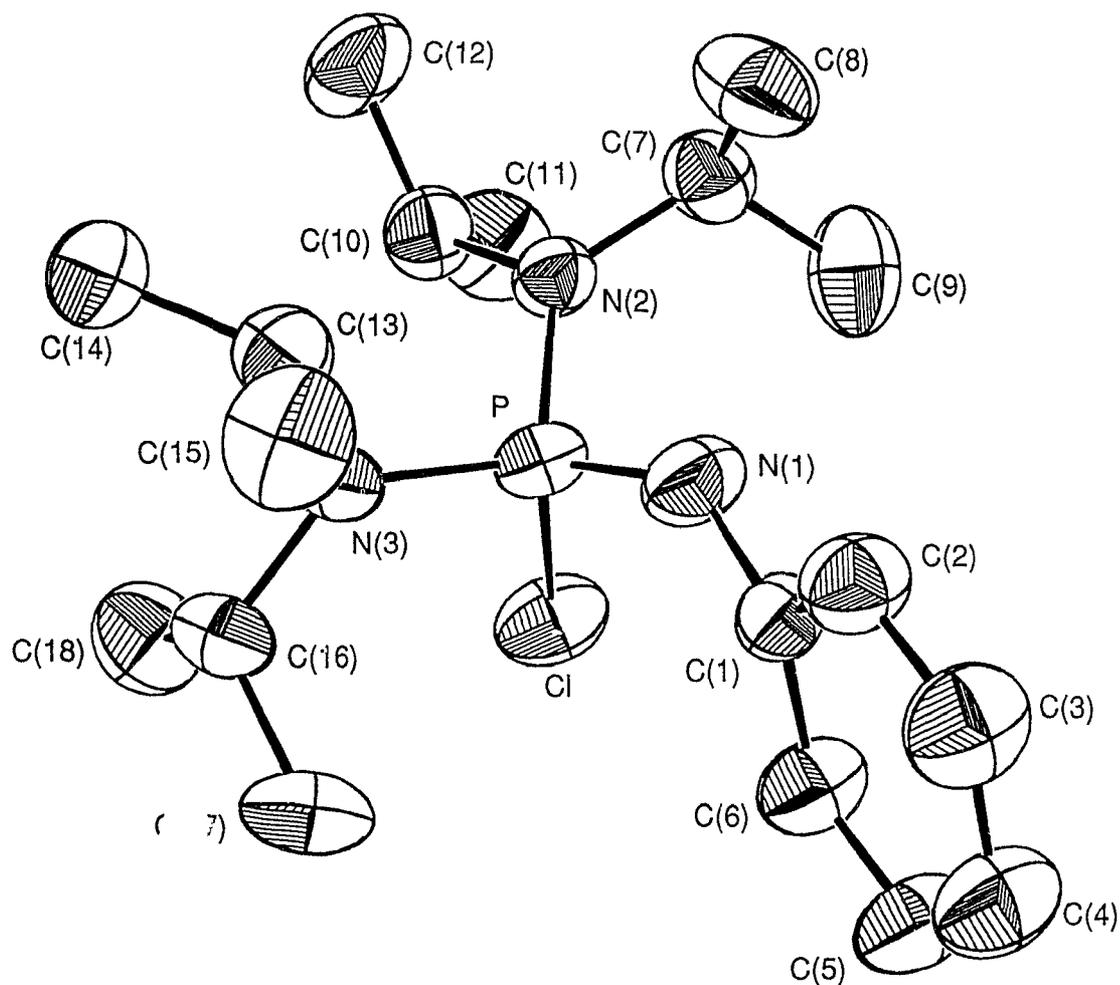


Figure 2.2.1.: Crystallographic view of $(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}$.

Table 2.2.2.: Selected bond lengths (Å) and angles (°) for $(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}$.

P-Cl	2.0809 (9)	P-N(1)	1.527 (2)
P-N(2)	1.643 (2)	P-N(3)	1.648 (2)
N(1)-C(1)	1.381 (3)		
Cl-P-N(1)	113.42 (8)	Cl-P-N(2)	104.84 (7)
Cl-P-N(3)	102.33 (7)	N(1)-P-N(2)	108.4 (2)
N(1)-P-N(3)	119.9 (2)	N(2)-P-N(3)	106.77 (9)
P-N(1)-C(1)	138.7 (2)	P-N(2)-C(7)	123.3 (2)
P-N(2)-C(10)	118.9 (2)	C(7)-N(2)-C(10)	115.7 (2)
P-N(3)-C(13)	112.1 (1)	P-N(3)-C(16)	129.1 (2)
C(13)-N(3)-C(16)	114.6 (2)		

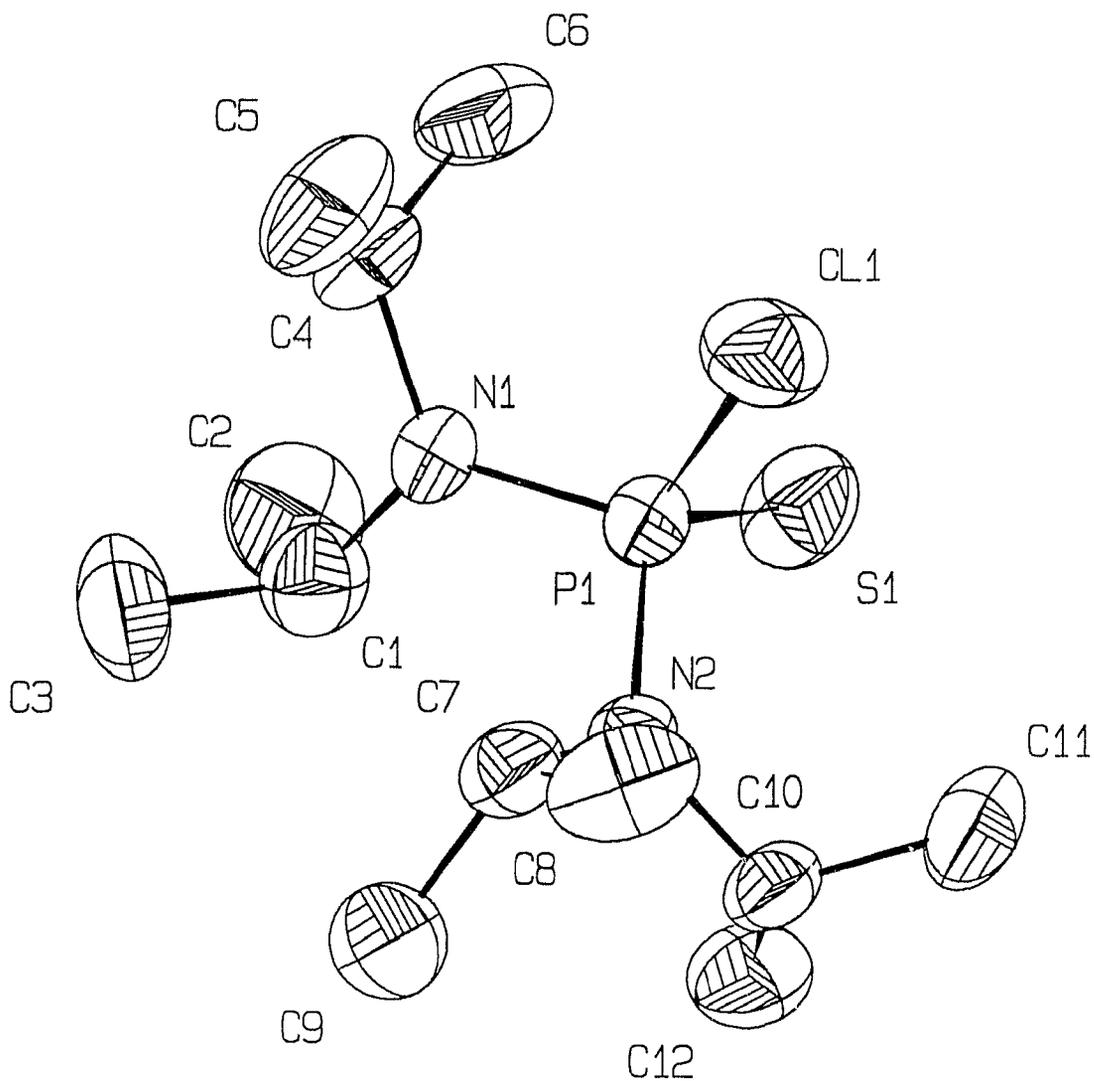


Figure 2.2.2.: Crystallographic view of $(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}$.

Table 2.2.3.: Selected bond lengths (Å) and angles ($^\circ$) for $(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}$.

P-Cl ^a	2.005 (2)	P-S ^a	1.980 (2)
P-N(1)	1.633 (4)	P-N(2)	1.637 (4)
Cl-P-Ch	108.93 (10)	S-P-N(1)	112.4 (2)
S-P-N(2)	111.1 (2)	Cl-P-N(1)	108.2 (2)
Cl-P-N(2)	110.3 (2)	N(1)-P-N(2)	105.8 (2)
P-N(1)-C(1)	124.9 (4)	P-N(1)-C(4)	116.9 (4)
C(1)-N(1)-C(4)	114.6 (4)	P-N(2)-C(7)	117.3 (3)
P-N(2)-C(10)	125.8 (3)	C(7)-N(2)-C(10)	113.8 (4)

^aDisorder exists between the Cl and S atoms and assignment is tentative.

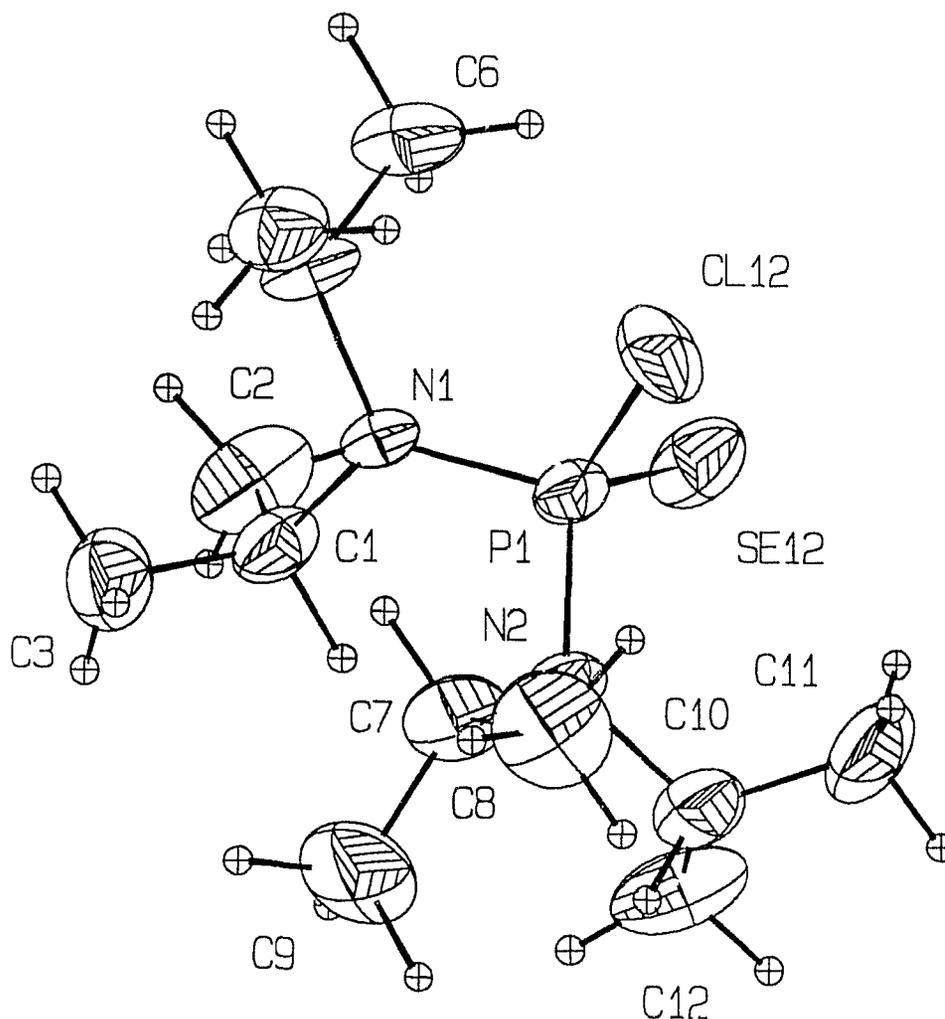


Figure 2.2.3.: Crystallographic view of $(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{Se}$.

Table 2.2.4.: Selected bond lengths (Å) and angles (°) for

$(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{Se}$.^a

Se(11)-P(1)	2.144 (3)	Cl(11)-P(1)	2.144 (3)
Se(12)-P(1)	2.087 (12)	Cl(12)-P(1)	1.93 (3)
P(1)-N(1)	1.631 (5)	P(1)-N(2)	1.657 (5)
Se(11)-P(1)-Cl(11)	107.9 (3)	Se(11)-P(1)-Se(11)	102.0 (3)
Se(11)-P(1)-N(1)	115.4 (2)	Se(11)-P(1)-N(2)	114.1 (2)
Cl(11)-P(1)-Cl(12)	118.1 (6)	Cl(11)-P(1)-N(1)	109.1 (4)
Cl(11)-P(1)-N(2)	103.8 (4)	Cl(12)-P(1)-Se(12)	111.9 (6)
Cl(12)-P(1)-N(1)	108.4 (5)	Cl(12)-P(1)-N(2)	111.0 (5)
Se(12)-P(1)-N(1)	107.1 (4)	Se(12)-P(1)-N(2)	112.3 (4)
N(1)-P(1)-N(2)	105.9 (3)	P(1)-N(1)-C(1)	118.5 (4)
P(1)-N(1)-C(4)	125.3 (4)	C(1)-N(1)-C(4)	113.6 (5)
P(1)-N(2)-C(7)	114.9 (4)	P(1)-N(2)-C(10)	124.8 (5)
C(7)-N(2)-C(10)	116.6 (6)		

^a Disorder exists between the Cl and Se atoms.

solution. The reaction mixtures have been examined by multinuclear n.m.r. and appear quantitative by ^{31}P n.m.r.. The ^{31}P and ^{13}C n.m.r. details for the complexes are given in Table 2.2.1..

The $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{N}(\text{Ph})/\text{AlCl}_3$, ($\text{R} = \text{Et}$ and ^iPr) reaction mixtures give a single broad ($\text{R} = \text{Et}$, 132 Hz; $\text{R} = ^i\text{Pr}$, 122 Hz) signal at 100 ppm in the ^{27}Al n.m.r., characteristic for an iminophosphoryl bound AlCl_3 unit (Chapter 3).^{30a,76} The ^{31}P chemical shifts ($\text{R} = \text{Et}$, 49; $\text{R} = ^i\text{Pr}$, 51 ppm) of the adducts are deshielded in comparison with the corresponding free base ($\text{R} = \text{Et}$, 12; $\text{R} = ^i\text{Pr}$, -8 ppm).

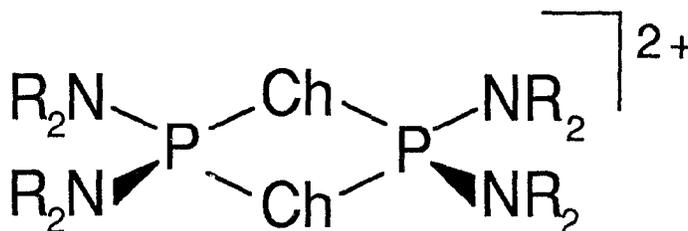
The ^{27}Al n.m.r. spectrum of $(\text{Me}_2\text{N})_2\text{P}(\text{Cl})\text{O}.\text{AlCl}_3$, consists of a single signal with a chemical shift (90 ppm) close to that of other oxo-phosphoryl- AlCl_3 adducts (Chapter 1). Asymmetry of the $(\text{Me}_2\text{N})_2\text{P}(\text{Cl})$ moiety or a non-linear P-O-Al framework may be responsible for the broad signal ($\Delta\nu_{1/2} = 73$ Hz) relative to the ^{27}Al signals of $(\text{Me}_2\text{N})_3\text{PO}.\text{AlCl}_3$ ($\Delta\nu_{1/2} = 18$ Hz) (Chapter 1). The ^{31}P chemical shift of the adduct is essentially identical to that of $(\text{Me}_2\text{N})_2\text{P}(\text{Cl})\text{O}$ (32 ppm).

The ^{27}Al n.m.r. spectral patterns observed for the $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{S}/\text{AlCl}_3$ reaction mixtures ($\text{R} = \text{Me}$, Et , ^iPr) contain a sharp signal at 102 ppm (AlCl_4^-),^{13,40} with a more substantial (> 80%) broad peak slightly down-field (106 ppm), consistent with the spectral patterns of other thiophosphoryl adducts of AlCl_3 (Chapter 1). ^{31}P n.m.r. spectra for these reaction solutions show single peaks with a chemical shift shielded from the corresponding free base thiophosphoryl chlorides, typical for amino substituted thiophosphoryl complexes (Chapter 1).

In contrast to the imines, oxides and sulphides, reactions between bis(dialkylamino)selenophosphoryl chlorides ($\text{R} = \text{Me}$, Et , ^iPr ; $\text{Ch} = \text{Se}$) and AlCl_3 produce exclusively ionic species in solution, as indicated by ^{27}Al n.m.r. (102 ppm, AlCl_4^-).^{13,40} The ^{31}P spectra show $(\text{Me}_2\text{N})_2\text{P}^+$ (268 ppm) and $(\text{Et}_2\text{N})_2\text{P}^+$ (264 ppm) as one of a number of species in solution for the Me/Se and Et/Se system, respectively. Complex

equilibria are evident in the Et/Se system (Figure 2.2.4.), involving the dimeric dication (vide infra) $[(\text{NEt}_2)_2\text{PSe}]_2^{2+}$ (-8 ppm, $J_{\text{P-Se}} = 341$ Hz, relative intensity of satellites = 14%), and other unidentified species. A triplet ($J_{\text{P-Se}} = 340$ Hz), consistent for $[(\text{NEt}_2)_2\text{PSe}]_2^{2+}$, has been observed in ^{77}Se n.m.r. spectrum. However, attempts to observe ^{77}Se signals for other solution species were unsuccessful. $(^i\text{Pr}_2\text{N})_2\text{P}^+$ (313 ppm)⁷⁷ is the only phosphorus containing product in the reaction of $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{Se}$ with AlCl_3 , and precipitation of elemental selenium renders the process irreversible.

The iminophosphoryl complexes have been prepared and isolated as analytically pure solids, empirical formulae $\text{R}_4\text{N}_2\text{PChAlCl}_4$ (Ch = NPh), by an alternative reaction pathway. The adduct structure of the ^iPr derivative in the solid has been confirmed by X-ray crystallography.^{75,78} Attempts to isolate $(\text{Me}_2\text{N})_2\text{P}(\text{Cl})\text{O}.\text{AlCl}_3$ yielded a viscous oil. Removal of solvent from the thio and seleno reaction solutions generally provides good yields (>75%) of crystalline solids with the empirical formulae $\text{R}_4\text{N}_2\text{PChAlCl}_4$ (Ch = S, Se). The low solubility of the precipitate obtained from the Me/Se system has prevented yield optimisation. The X-ray crystal structure of the $^i\text{Pr}/\text{S}$ confirms retention of the Lewis acid base complex in the solid (see Chapter 1). However, and in contrast to the solution chemistry, X-ray crystallographic analysis of the Et/S and Et/Se derivatives of the $\text{R}_4\text{N}_2\text{PChAlCl}_4$ show them to be salts of heterocyclic dications, 11.^{45,79}



11

The salts may be considered as dimers of the tricoordinate phosphonium

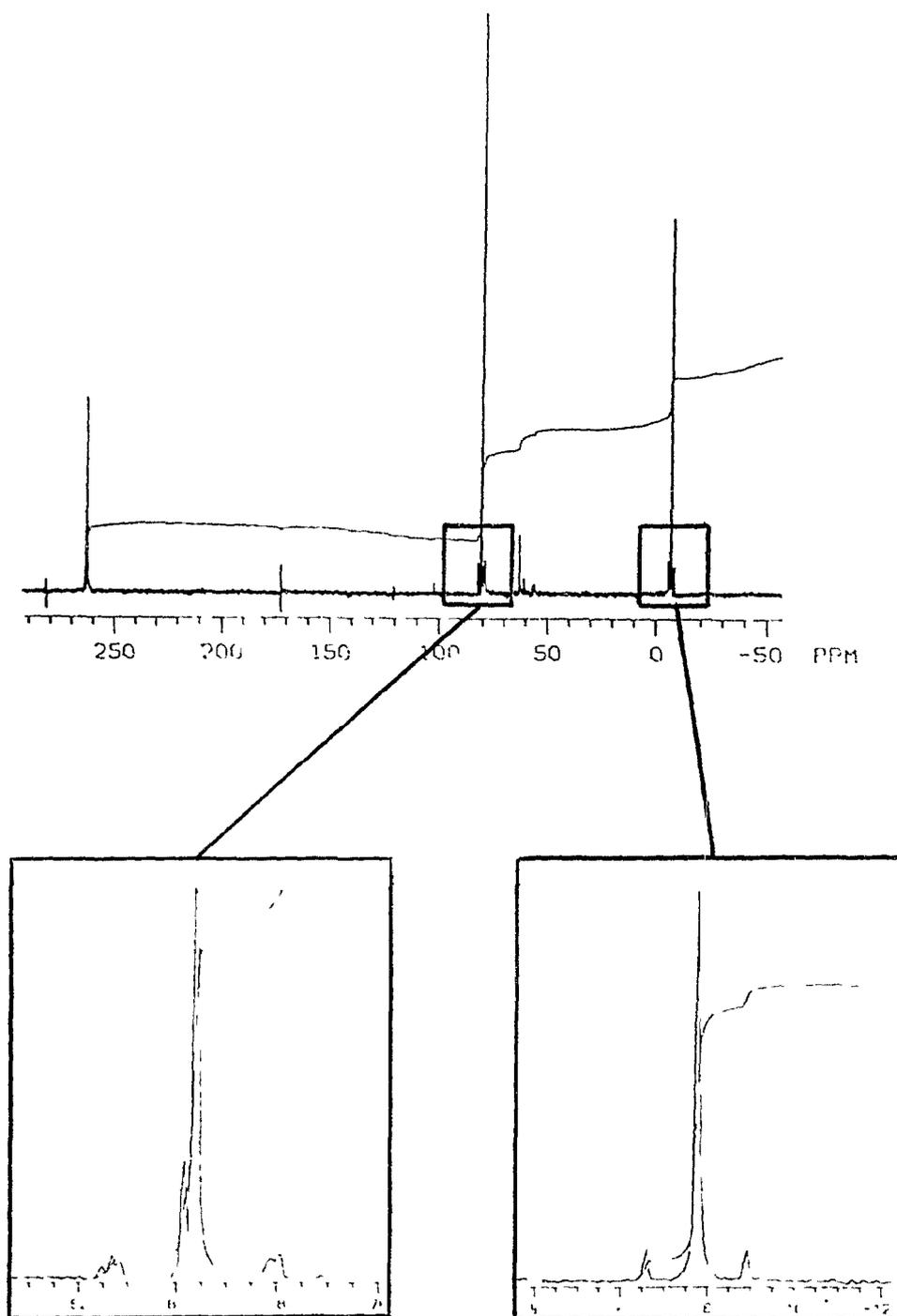


Figure 2.2.4.: ^{31}P -Phosphorus n.m.r. spectrum of the $(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{Se}/\text{AlCl}_3$ system in CH_2Cl_2 .

(phosphoryl cation) centre.

2.2.3. Alternative Preparation of $(R_2N)_2P(Cl)NPh \cdot AlCl_3$ (R = Et, iPr) Complexes. The Reactions of Phosphenium Cations with Phenyl Azide.

Reaction of $(R_2N)_2P(Cl)$ with $AlCl_3$ in CH_2Cl_2 yields the phosphenium cation salt $(R_2N)_2P^+ AlCl_4^-$.⁷⁷ Addition of PhN_3 to the reaction solution (R = Et or iPr) leads to nitrogen elimination and formation of the $(R_2N)_2P(Cl)NPh \cdot AlCl_3$ complex in essentially quantitative yield by ^{31}P n.m.r.. The air sensitive complexes were isolated from these reaction mixtures by addition of hexane and slow removal of solvent.

The iPr phosphenium cation is observed to react appreciably faster with PhN_3 than with its precursor phosphine $(iPr_2N)_2P(Cl)$.^{30a} Consistently, a kinetic study by Kukhar⁸⁰ found the cations to react approximately 250 faster. He suggests the reaction of the cations proceeds by an unusual nucleophilic attack by the azide on the phosphorus centre as opposed to the normal electrophilic attack. However, the reliability of the kinetic studies is unclear, as the ^{31}P chemical shifts of the products are consistent with hydrolysis of the iminophosphoryl $\cdot AlCl_3$ complex (see below).

2.2.4. Infra-red Spectroscopic Characterisation of Bis(dialkylamino)phosphoryl Chlorides, $(R_2N)_2P(Cl)Ch$ (R = Me, Et and iPr ; Ch = NPh, S and Se), and $R_4N_2PChAlCl_4$ Solids.

Comparison of the i.r. spectra for $(iPr_2N)_2P(NPh)Cl$ and the three derivatives of $(R_2N)_2P(S)Cl$ (R = Me,⁸¹ Et, iPr) and of $(R_2N)_2P(Se)Cl$ (R = Me,⁸² Et, iPr) provides support for the assignments of P-S and P-Se stretching frequencies, which can be monitored following reaction with $AlCl_3$. Two separate bands in the ranges $550-730\text{ cm}^{-1}$ and $658-802\text{ cm}^{-1}$ have been identified as being in some way related to the P=S

absorption.⁸³ Consequently, two bands (R = Me, 605, 735; R = Et, 610, 735; R = ⁱPr, 595, 705 cm⁻¹) are assigned to P-S stretching frequencies as these are the only bands which occur at lower wavenumber for the respective selenium derivatives (R = Me, 550, 700; R = Et, 555, 685; R = ⁱPr, 565, 640 cm⁻¹). These bands are not present in the spectra of (ⁱPr₂N)₂P(NPh)Cl and the Me/S, Et/S, Me/Se and Et/Se derivatives of R₄N₂PChAlCl₄ in the solid state. Moreover, one of the bands shifts to lower wavenumber in the spectra of (ⁱPr₂N)₂P(Cl)S.AlCl₃ (595, 640 cm⁻¹) and (ⁱPr₂N)₂P(Cl)S.GaCl₃ (595, 645 cm⁻¹). The later results are indicative of the higher wavenumber bands in the free base having the principle P=S character and imply a slight weakening of the P-S bond upon complex formation, consistent with previous studies.³⁵ The i.r. spectrum of (ⁱPr₂N)₂P(Cl)S.AlCl₃ is identical to that of (ⁱPr₂N)₂P(Cl)S.GaCl₃ above 550 cm⁻¹, and to that of Ph₃PS.AlCl₃ below 650 cm⁻¹. These observations confirm the coordination complex structures. The ionic nature of the Me/S, Et/S, Me/Se and Et/Se derivatives of R₄N₂PChAlCl₄ in the solid state, is demonstrated by the presence of the strong broad band centred at 485 cm⁻¹ in the i.r. spectra, characteristic of AlCl₄⁻.⁸⁴ A strong to medium band, observed in the region 400 cm⁻¹, is characteristic of the iminophosphoryl.AlCl₃ linkage (Chapter 3).⁷⁶

2.2.5. Mass Spectra of the R₄N₂PChAlCl₄ Solids.

All mass spectra were obtained under essentially the same conditions with an ionisation energy of 70 eV. Generally, both the adducts and dicationic heterocycles have a parent peak corresponding to the respective imino, thio or seleno free base, and the ensuing fragmentation patterns are similar to those species. Loss of the AlCl₃ is observed for other imino and thio phosphoryl adducts (see Chapter 3) and halide ion reabstraction by main group cations from AlCl₄⁻ has also been reported.⁸⁵ One exception to the above generalisation is the Me/S

dicationic heterocycle which has a parent peak of $m/z = 284$ ($C_4H_{12}Cl_2N_2P_2S_2$) consistent with at least some maintenance of a dimeric structure. The fragmentation patterns of the diamminophosphoryl chlorides generally include loss of chlorine and/or dialkylamino centres to give tricoordinate phosphonium centres, indicative of some stability for this species. The selenides have an additional alternative fragmentation pathway of selenium elimination, demonstrating the weakness of the P-Se bond.

2.2.6. Crystal Structures of $\{[(NEt_2)_2PS]\}_2[AlCl_4]_2$ and $\{[(NEt_2)_2PSe]\}_2[AlCl_4]_2$.

The X-ray crystal structures of $\{[(NEt_2)_2PS]\}_2[AlCl_4]_2$ and $\{[(NEt_2)_2PSe]\}_2[AlCl_4]_2$ were determined by Dr. R. D. Rogers^{45,79} at N.I.U.. Views of the compounds, with cation-anion contacts drawn, are presented in Figures 2.2.5. and 2.2.6. and selected bond lengths and angles are given in Tables 2.2.5 and 2.2.6..

Both crystal structures consist of discrete cationic and anionic units, although a number of long interionic contacts are evident (see below). The cation is a dimeric structure consisting of two NET_2PCh^+ (Ch = S, Se) fragments bound together as a P_2Ch_2 four membered ring. The heterocycle is planar by symmetry for the thio derivative and the maximum deviation from planarity for the seleno derivative is 0.003 Å. The ring planes are perpendicular to the planes formed by the four nitrogen centres. Distorted tetrahedral geometries are observed at phosphorus, enforced by the four-membered heterocyclic framework. The amine units (C_2NP) are individually planar with short P-N bond lengths [Ch = S, 1.601 (5), 1.607 (5) Å; Ch = Se, 1.614 (9), 1.60 (1), 1.58 (1), 1.625 (9) Å; c.f. P-N single bond 1.77 Å]³, indicating the presence of substantial P-N $p\pi-d\pi$ interaction. The P-S [2.109 (2), 2.083 (2) Å] and P-Se [2.257 (3), 2.249 (3), 2.238 (3), 2.262 (3) Å] bond lengths are generally typical of single bonds [P-S: (PhS)₃P, 2.112 (1) Å;⁵⁵ P₄S₁₀,

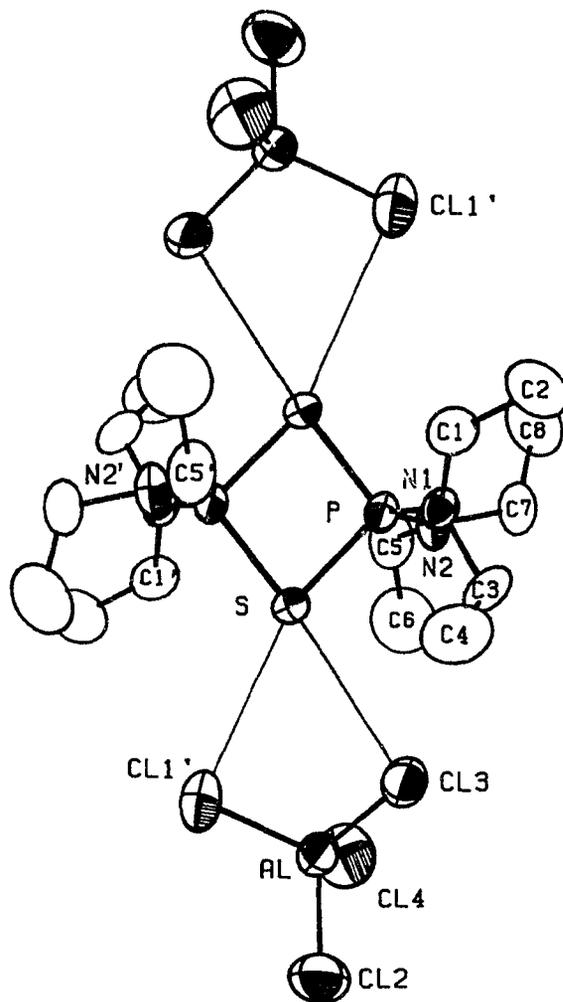


Figure 2.2.5.: Crystallographic view of $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$.

Table 2.2.5.: Selected bond lengths (Å) and angles (°) for

$[\{(Et_2N)_2PS\}_2][AlCl_4]_2$.

S-P	2.109 (2)	S-P'	2.083 (2)	P-N(1)	1.601 (5)
P-N(2)	1.607 (5)	Al-Cl(1)	2.134 (3)	Al-Cl(2)	2.109 (4)
Al-Cl(3)	2.126 (3)	Al-Cl(4)	2.113 (3)		

P-S-P'	84.0 (1)	S-P-S'	96.0 (1)
S-P-N(1)	113.1 (2)	S-P-N(2)	108.8 (2)
N(1)-P-N(2)	112.0 (3)	P-N(1)-C(1)	125.5 (5)
P-N(1)-C(3)	117.5 (4)	C(1)-N(1)-C(3)	117.0 (5)
P-N(2)-C(5)	119.6 (5)	P-N(2)-C(7)	123.9 (5)
C(5)-N(2)-C(7)	115.6 (6)	Cl(1)-Al-Cl(2)	110.3 (2)
Cl(1)-Al-Cl(3)	109.5 (1)	Cl(2)-Al-Cl(3)	108.1 (1)
Cl(1)-Al-Cl(4)	109.2 (1)	Cl(2)-Al-Cl(4)	109.6 (2)
Cl(3)-Al-Cl(4)	110.1 (2)		

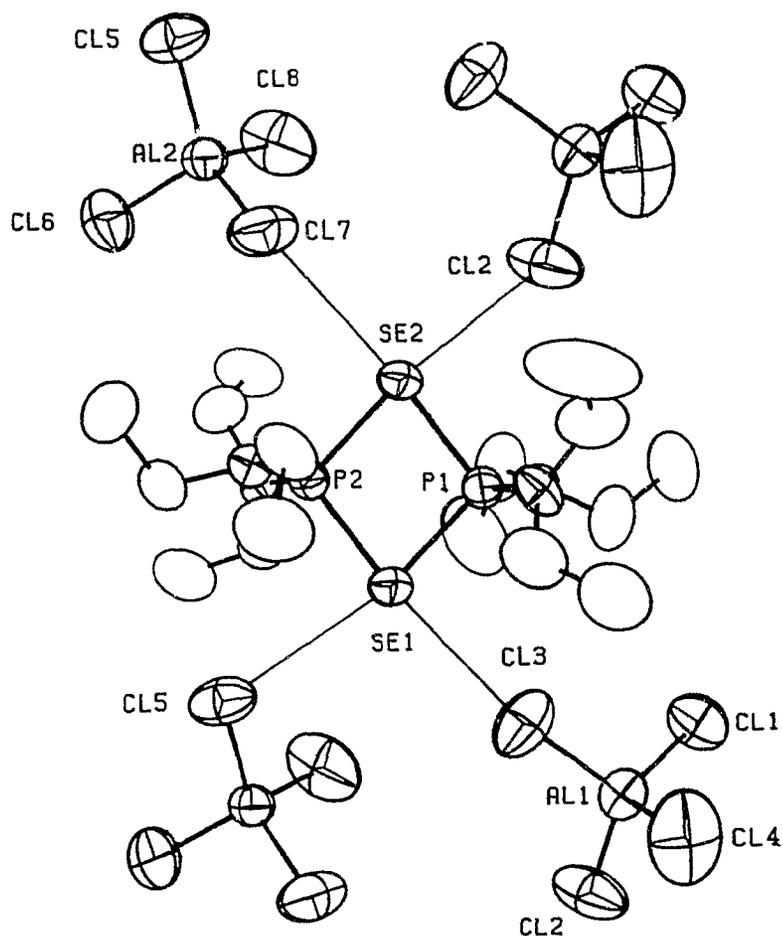


Figure 2.2.6.: Crystallographic view of $[(\text{Et}_2\text{N})_2\text{PSe}]_2[\text{AlCl}_4]_2$.

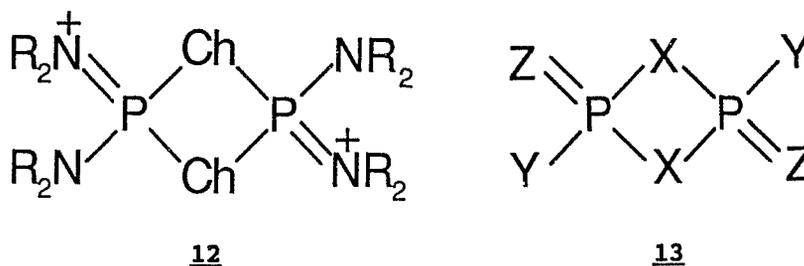
Table 2.2.6.: Selected bond lengths (Å) and angles (°) for

$[(\text{Et}_2\text{N})_2\text{PSe}]_2[\text{AlCl}_4]_2$.

Se(1)-P(1)	2.257 (3)	Se(1)-P(2)	2.238 (3)
Se(2)-P(1)	2.249 (3)	Se(2)-P(2)	2.262 (3)
P(1)-N(1)	1.614 (9)	P(1)-N(2)	1.58 (1)
P(2)-N(3)	1.60 (1)	P(2)-N(4)	1.625 (9)
Al(1)-Cl(1)	2.132 (5)	Al(1)-Cl(2)	2.103 (6)
Al(1)-Cl(3)	2.099 (6)	Al(1)-Cl(4)	2.113 (6)
P(1)-Se(1)-P(2)	82.9 (1)	P(1)-Se(2)-P(2)	82.6 (1)
Se(1)-P(1)-Se(2)	97.2 (1)	Se(1)-P(1)-N(1)	118.0 (4)
Se(2)-P(1)-N(1)	110.1 (4)	Se(1)-P(1)-N(2)	109.4 (4)
Se(2)-P(1)-N(2)	113.2 (4)	N(1)-P(1)-N(2)	108.7 (5)
Se(1)-P(2)-Se(2)	97.3 (1)	Se(1)-P(2)-N(3)	110.2 (4)
Se(2)-P(2)-N(3)	112.9 (4)	Se(1)-P(2)-N(4)	116.1 (4)
Se(2)-P(2)-N(4)	108.7 (4)	N(3)-P(2)-N(4)	111.0 (5)
P(1)-N(1)-C(1)	118.6 (9)	P(1)-N(1)-C(3)	125.4 (9)
C(1)-N(1)-C(3)	114 (1)	P(1)-N(2)-C(5)	125.8 (9)
P(1)-N(2)-C(7)	119.2 (9)	C(5)-N(2)-C(7)	114 (1)
Cl(1)-Al(1)-Cl(2)	109.6 (2)	Cl(1)-Al(1)-Cl(3)	107.7 (3)
Cl(2)-Al(1)-Cl(3)	110.2 (3)	Cl(1)-Al(1)-Cl(4)	108.8 (3)
Cl(2)-Al(1)-Cl(4)	109.6 (3)	Cl(3)-Al(1)-Cl(4)	110.8 (3)

2.10; P-Se: P_4Se_3 , 2.24 Å].³

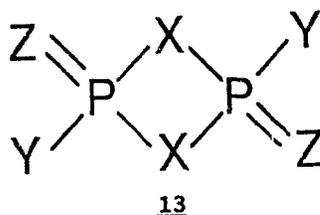
Consequently, the overall molecular bonding of the heterocycles is best viewed as resonance structures involving a delocalisation of the positive charge onto the amine centres, 12.



On this basis, the dications have an isoivalent relationship to numerous derivatives of the dichalcogenodiphosphetanes, 13 (X = S or Se).^{21,22} A structural comparison is made in Table 2.2.7..

In general, the angle at phosphorus is substantially wider, while the angle at the chalcogen is significantly narrower in the dications than in the neutral phosphetanes. This slight distortion of the cationic P_2Ch_2 rings, may be a function of the formal phosphonium character of the phosphorus centres. In addition, the influence of interactions between the cations and the anions is significant. Two long contacts exist between each chalcogen centre of the cation and the chlorine centres of the anions. While the S-Cl distances [S-Cl(1), 3.591 (3), S-Cl(3), 3.368 (3) Å] are within the sum of the van der Waal's radii (3.70 Å),⁵⁶ the Se-Cl interactions are substantially shorter [Se(1)-Cl(3), 3.211 (4) Å, Se(1)-Cl(5), 3.438 (5) Å, Se(2)-Cl(2), 3.499 (6) Å, Se(2)-Cl(7), 3.462 (4) Å; v.d.w, 3.80 Å].⁵⁶ As illustrated in Figures 2.2.5. and 2.2.6., one $AlCl_4^-$ unit is associated with each sulphur centre forming two contacts in a chelate fashion, while the chlorine centres of two different anions are associated with each selenium centre. Moreover, the observed distortions from tetrahedral geometry of the anions, evident in both

Table 2.2.7.: Structural parameters and ^{31}P n.m.r. chemical shifts for dichalcogenodiphosphetanes, 13.



X	Y	Z	P-X	XPX	XPX	^{31}P	Ref
S	NEt ₂	NEt ₂	2.109 (2) 2.083 (2)	96.0 (1)	84.0 (1)	21	45, 79
S	Me	S	2.141 (6)	94.54 (22)	85.46 (23)		86a
S	Ph	S	2.108 (2) 2.133 (2)	93.1 (1)	86.9 (1)	15	74
S	Mesityl	S	2.093 (1) 2.125 (1) 2.125 (1)	93.8 (1)	86.2 (1)	11	86b
S	NMe ₂	S	2.122 (1)	93.14 (3)	86.86 (3)	24	86c
S	N(SiMe ₃) ₂	N ^t Bu	2.160 (1)	90.35 (4)	89.20 (4)		86d
S	S ⁻ (Zn ²⁺)	S	2.117 (3) 2.124 (3) 2.125 (3) 2.110 (3)	94.0 (1) 94.2 (1)	86.0 (1) 85.8 (1)		86e
S	S ⁻ (Ag ⁺)	S	2.120 (2)	93.71 (8)	86.29 (8)		86f
Se	NEt ₂	NEt ₂	2.257 (3) 2.238 (3) 2.249 (3) 2.262 (3)	97.2 (1) 97.3 (1)	82.9 (1) 82.6 (1)	-8	45, 79
Se	^t Bu	Se	2.269 (2)	96.5 (1)	83.5 (1)		22a
Se	Ph	R ^{\$}	2.277 (2) 2.259 (2)	95.3 (1)	83.5 (1)		22b

^{\$} R = $\overline{\text{C-P(Se)(Ph)-SeP(Ph)-P(Se)Ph}}$.

bond lengths and bond angles are consistently more pronounced in the selenium system. Contacts of this nature are common for non-metal cations^{85,87} and are interpreted as electronic donations from the anion to the cation.⁸⁸ While the structural features of the cation imply localisation of the molecular charge in the P-N region, steric restrictions prevent the approach of the anion to these areas. Consistently, the contacts are specific to a single chalcogen centre, unlike many less sterically shielded non-metal cationic systems, which display bridging contacts over two bound centres.⁸⁵ Moreover, the interactions occur in the P_2Ch_2 plane. For $Ch = S$, the maximum deviation of any atom from the mean plane defined by P, S, Cl(1), Cl(3), P', S', Cl(1)' and Cl(3)' is 0.23 Å. Alternatively, the P, S, P', S' and S, Cl(1), Cl(3) planes intersect at only 15.6°. Similarly, for $Ch = Se$, the maximum deviation from planarity is 0.52 Å and the average dihedral angle is 8.5°. Therefore, the conformations of the cation-anion interactions appear to be defined by steric factors.

2.2.7. X-Ray Crystal Structure of $(iPr_2N)_2P(Cl)NPh.AlCl_3$.

The crystal structure of $(iPr_2N)_2P(Cl)N(Ph).AlCl_3$ was determined by Dr. John F. Richardson.^{75,78} A view of the molecule is presented in Figure 2.2.7. and selected bond lengths and angles are given in Table 2.2.8. The structure of the ethyl derivative $(Et_2N)_2P(Cl)NPh.AlCl_3$ has been reported.⁸⁹ In general, the bond lengths and angles in the two structures are similar. However, for the iPr derivative the phenyl group is in the *anti* conformation to the chlorine atom, while in the ethyl derivative it is *gauche*. The *gauche* arrangement is also observed in the iso-propyl free base, $(iPr_2N)_2P(Cl)NPh$ (see above). The conformations are likely under the control of steric factors.

2.2.8. Reaction between $(R_2N)_2P(Cl)S.AlCl_3$ and CH_2Cl_2 .

Solutions of $(R_2N)_2P(Cl)S.AlCl_3$ in CH_2Cl_2 heated to 80 °C undergo

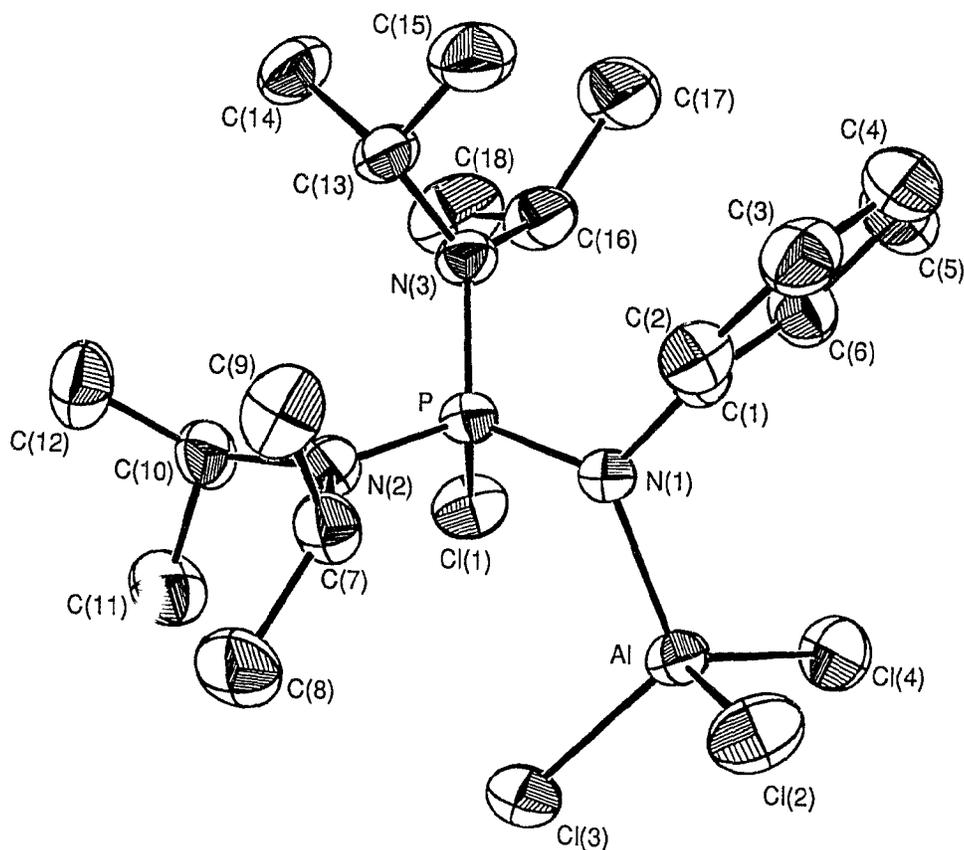


Figure 2.2.7.: Crystallographic view of $(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}.\text{AlCl}_3$.

Table 2.2.8.: Selected bond lengths (Å) and angles (°) for

$(i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}.\text{AlCl}_3$.

P-Cl(1)	2.033 (2)	P-N(1)	1.618 (3)	P-N(2)	1.624 (2)
P-N(3)	1.622 (3)	N(1)-C(1)	1.455 (3)	Al-N(1)	1.884 (3)
Al-Cl(2)	2.126 (1)	Al-Cl(3)	2.127 (1)	Al-Cl(4)	2.124 (1)
Cl(1)-P-N(1)	104.0 (1)	Cl(1)-P-N(2)	106.69 (9)		
Cl(1)-P-N(3)	105.0 (2)	N(1)-P-N(2)	112.3 (1)		
N(1)-P-N(3)	115.7 (1)	N(2)-P-N(3)	112.1 (1)		
P-N(1)-C(1)	119.6 (2)	P-N(2)-C(7)	121.6 (2)		
P-N(2)-C(10)	115.8 (2)	C(7)-N(2)-C(10)	122.6 (2)		
P-N(3)-C(13)	120.0 (3)	P-N(3)-C(16)	118.4 (2)		
C(13)-N(3)-C(16)	121.6 (3)	P-N(1)-Al	127.5 (1)		
Cl(2)-Al-N(1)	108.21 (9)	Cl(3)-Al-N(1)	111.78 (9)		
Cl(4)-Al-N(1)	108.26 (9)	Cl(2)-Al-Cl(3)	106.90 (6)		
Cl(2)-Al-Cl(4)	110.49 (6)	Cl(3)-Al-Cl(4)	111.18 (6)		

quantitative reactions to give ionic systems, which have been characterised by ^{13}C , ^{31}P (Table 2.2.1.) and ^{27}Al n.m.r. (AlCl_4^-). The process also occurs slowly at room temperature (fastest for $\text{R} = \text{}^i\text{Pr}$), and is irreversible. On a preparative scale, a mass-balance experiment ($\text{R} = \text{}^i\text{Pr}$) shows a molecular weight increase corresponding to an equimolar reaction between the adduct and CH_2Cl_2 . The identity of the cations as derivatives of $(\text{R}_2\text{N})_2\text{P}(\text{Cl})(\text{SCH}_2\text{Cl})^+$ is demonstrated by a triplet signal (not present in the spectra of the corresponding adducts) in the ^1H coupled ^{13}C n.m.r. spectra between 44 and 46 ppm, which is typical of a methylene group attached to sulphur.⁹⁰ On this basis, the process is rationalised as an acid induced electrophilic attack of the sulphur centre by the solvent, resulting in a chloride ion abstraction from the solvent to form AlCl_4^- .

A similar reaction is observed for $\text{Ph}_3\text{PS} \cdot \text{AlCl}_3$, but not for $(\text{Me}_2\text{N})_3\text{PS} \cdot \text{AlCl}_3$. Maier³² noted the formation of mercaptans, by way of their odour, while investigating the mechanism of the arylation of Cl_3PS in the presence of AlCl_3 in CH_2Cl_2 . He suggests they are formed via arylation of the sulphur centre. The investigation measured the conductivities of various arylthiophosphoryl chlorides solutions in the presence of AlCl_3 and the results are interpreted as being consistent with the formation of tricoordinate phosphonium centres. However, the interaction of the CH_2Cl_2 with the sulphides is not noted, and may have some bearing on Maier's observations.

The Et/Se system is also unstable in CH_2Cl_2 . However, at least three products are observed on heating the solutions and these have not been identified.

2.2.9. Chalcogenophosphonium Cations $[(\text{R}_2\text{N})_2\text{PCh}]_2^{2+}$ ($\text{Ch} = \text{S}, \text{Se}$) in Solution.

Derivatives of the thio and seleno dicationic heterocycles dissolve in CH_2Cl_2 provide n.m.r. spectra which are identical to those

of the reaction mixtures of the phosphoryl halides with AlCl_3 . The Et/Se derivative of the dication has been observed as a component of a complex equilibrium in solution. While the Me/Se derivative is believed to have similar behaviour, the low solubility of this system has precluded solution studies. In contrast, the sulphur derivatives favour the covalent adduct structures in solution. However, the Et/S derivative of the dication has been observed during the solvation process by means of ^{31}P n.m.r. (Et/S, 21 ppm), and is assigned by comparison with other phosphetane systems (Table 2.2.7.) and on the basis of the ^{27}Al n.m.r. spectrum (AlCl_4^-). Interestingly, the presence of excess AlCl_3 enhances the formation of the dicationic species in solution, and the Me/S (27 ppm) and $^i\text{Pr}/\text{S}$ (18 ppm) derivatives of heterocyclic dications have been identified by ^{31}P n.m.r.. Unfortunately, these solutions are unstable, as the reaction with the solvent is also enhanced resulting in the formation of $[(\text{R}_2\text{N})_2\text{P}(\text{Cl})(\text{SCH}_2\text{Cl})][\text{AlCl}_4]$ (see above). The role of AlCl_3 in adjustment of the equilibrium is not clear. The potential for forming the Al_2Cl_7^- anion may promote cation formation. The observation of the dication for the $^i\text{Pr}/\text{S}$ system in solution indicates a kinetic stabilisation of the complex $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$, possibly by virtue of steric influences. Addition of excess AlCl_3 to the iminophosphoryl. AlCl_3 complexes rapidly darkened the CH_2Cl_2 solutions to yield several unknown species.

2.2.10. The Iminophosphonium Cation and Hydrolysis of the $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}\cdot\text{AlCl}_3$ Complexes.

The quantitative formation of the $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}\cdot\text{AlCl}_3$ complexes from both the phosphonium cations and free base imines is in contrast to the results of Wolf and Sanchez.^{30a} They speculate the formation of the tricoordinate iminophosphonium cation $(\text{R}_2\text{N})_2\text{P}=\text{NPh}^+$ (R = Et, ^{31}P n.m.r. 37.1 ppm) together with the complex. In addition, they state that the

cation is formed quantitatively as a thermolysis product of the $(R_2N)_2P(Cl)NPh \cdot AlCl_3$ complex at 50 °C. However, my work shows the complexes to be thermally stable at 60 °C.

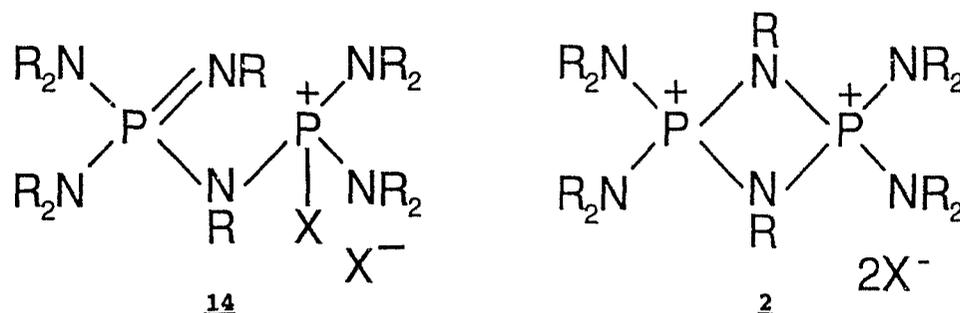
The iminophosphoryl $\cdot AlCl_3$ complexes are extremely air sensitive. Minimal air exposure results in hydrolysis to give $(R_2N)_2P(OH)NPh$, which has been spectroscopically characterised (^{31}P n.m.r.: R = Et, 39 ppm; R = Pr, 35 ppm). The ^{13}C n.m.r. spectrum of the ethyl derivative is identical to that reported for the tricoordinate iminophosphonium cation, as is the 1H n.m.r. spectrum excepted for a concentration dependent signal in the acidic range of the spectrum, not reported by Wolf. The hydrolysis reaction mixtures also give a sharp signal at 102 ppm in the ^{27}Al n.m.r. characteristic of $AlCl_4^-$. However, $AlCl_4^-$ can be detected at low concentrations,⁴⁰ and it is likely that much of the aluminium is contained in the hydrolysis precipitate. As part of this study, $(Et_2N)_2P(OH)NPh$ was also observed as an intermediate in the full hydrolysis of $(Et_2N)_2P(Cl)NPh$ to $(Et_2N)_2P(O)NPh^{91}$ by ^{31}P n.m.r., in the absence of $AlCl_3$.

It is clear from these results that Wolf and Sanchez unknowingly permitted hydrolysis of their reaction mixtures,^{30a} and that it is not possible to form the tricoordinate iminophosphonium cation from the iminophosphoryl $\cdot AlCl_3$ adducts. Therefore, considerable doubt must exist as to the validity of their investigations of related systems.^{30b}

2.2.11. The Monomeric Structure of $(^iPr_2N)_2P(Cl)NPh$ and the Dimerisation Process of the Thiophosphoryl Chlorides.

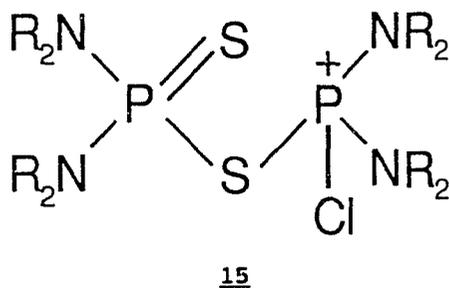
In contrast to the covalent monomeric structures observed for the thiophosphoryl chlorides and $(^iPr_2N)_2P(Cl)NPh$, Chernega¹⁷ has shown that the simple iminophosphoryl derivatives of $(R_2N)_2P(X)NR$ (R = Me, Et; X = Cl, Br) auto-ionise to either a monocationic cyclic dimer, **14** or a dicationic 1,3,2,4-diazadiphosphetidin-2,4-ium heterocycle, **2**. The heterocycles are thermally stable and in contrast to the $\{[(R_2N)_2PS]_2\}^{2+}$

derivatives, they do not dissociate in solution.



The structure observed for a particular $(R_2N)_2P(X)NR$ derivative is dependent on the polarisability of the P-halogen bond, the nucleophilicity of the imidic nitrogen atom (as dictated by its substituent), and the steric influence of the substituents.¹⁷ Consequently, the monomeric covalent structure of $(iPr_2N)_2P(Cl)NPh$ is understood in terms of the large steric influences of the iso-propyl substituents and the low nucleophilicity of the phenyl substituted imidic nitrogen. No ready explanation for the monomeric nature of the sterically unrestricted oxo, thio and seleno $(R_2N)_2P(Cl)Ch$ analogs is available.

The formation of the dicationic P_2N_2 heterocycles proceeds via the monocationic acyclic dimer 14.¹⁷ Therefore, the dimerisation of the thiophosphoryls may involve a similar intermediate, e.g 15.



The likely role of $AlCl_3$ in the production of dimeric products for the

thiophosphoryl chlorides is to increase the electrophilicity of the phosphorus centre. This would occur by adduct formation and/or chloride ion abstraction.

2.2.12. Alternative Halide Ion Abstracting Reagents with the Thiophosphoryl Chlorides, $(R_2N)_2P(Cl)S$.

^{31}P n.m.r. studies on $(Et_2N)_2P(Cl)S$ reveals no reaction with $NaPF_6$, $NaBF_4$ or $Me_3SiSO_3CF_3$. However, the reaction with $AgBF_4$ yields principally (70%) $(Et_2N)_2P(F)S$, identified by a doublet at 82 ppm with a typical⁹² P-F one bond coupling of 1031 Hz, and several other unidentified species.

$(iPr_2N)_2P(Cl)S$ reacts completely with two equivalents of $AgSO_3CF_3$, to give one unidentified product (^{31}P n.m.r., 66 ppm). On a preparative scale, attempts to isolate this species gave only a clear oil, insoluble in hexane and toluene. Only one equivalent of $AgCl$ precipitate was isolated from the reaction, indication that one molar equivalent of Ag remains in solution.

2.2.13. The Diaminophenyliminophosphoryl Chloride-Silver Triflate System.

$(R_2N)_2P(Cl)NPh$ ($R = Et, iPr$) reacts with $AgSO_3CF_3$ in CH_2Cl_2 to give $AgCl$ and $(R_2N)_2P(O)N(Ph)(SO_2CF_3)$ in essentially quantitative yield, as shown by ^{31}P n.m.r. The oxophosphoryl is also obtained from the reaction of $(iPr_2N)_2P^+ SO_3CF_3^-$ with PhN_3 . The isopropyl derivative $(iPr_2N)_2P(O)N(Ph)(SO_2CF_3)$ has been isolated as an air stable analytically pure solid.

The ^{31}P n.m.r. chemical shifts ($R = Et, 14$ ppm; $R = iPr, 13$ ppm) are in the range typical for tris(amino)oxophosphoryls⁷³ (c.f. $(Et_2N)_2P(O)NH(Ph)$, 15 ppm). Furthermore, the infrared spectrum ($R = iPr$) exhibits a strong peak at 1255 cm^{-1} characteristic of the $P=O$ stretching mode⁸³ and the mass spectrum [471 parent ion, 2^+ ($iPr_2N)_2PO^+$

base peak] is consistent with the structure.

The structure of the isopropyl oxophosphoryl has also been confirmed by X-ray crystallographic analysis, performed by Dr. J. F. Richardson.^{75,78} A view of the molecule is shown in Figure 2.2.8.. Selected bond lengths and angles are presented in Table 2.2.9., and are generally standard for the structural units involved.³ However, while the P-N(ⁱPr) bond lengths (P-N(2), 1.649 (3) Å and P-N(3), 1.639 (3) Å) are similar to those found in (ⁱPr₂N)₂P(Cl)NPh and (ⁱPr₂N)₂P(Cl)NPh.AlCl₃ the other P-N(S) bond length (P-N(1), 1.785 (3) Å) is considerably longer, close to a standard P-N single bond (1.77 Å).³ As mentioned previously, *dπ-pπ* bonding between phosphorus and nitrogen is commonly observed to significantly shorten most I-N bonds. The "long" P-N(1) bond is believed to be a function of competition for the lone pair of nitrogen by the sulphur centre. Consistently, the S-N bond (1.628 (3) Å) is relatively short (c.f. O₃SNH₃, S-N 1.76 Å).⁵¹

2.2.14. The Tricoordinate Phosphonium Electronic Environment.

The potential of the phosphoryl halides as precursors to the rare²⁸ tricoordinate phosphonium environment has been recognised by several research groups.^{29,30,33} This chapter has primarily examined the imino, thio and seleno bis(dialkylamino)phosphoryl chlorides reaction with AlCl₃, and has found a delicate energetic balance between covalent adduct and ionic forms for these phosphoryl units.

In solution the preferred species for the thio/AlCl₃ system (in 1:1 ratio) is a Lewis acid-base complex, while for the seleno/AlCl₃ system a complexed equilibrium process is evident, involving only cationic species. Addition of excess AlCl₃ to the thio species, however, leads to formation of the dicationic heterocycles observed in the solid state.

In the solid, it is clear that for the imino (from the results of Chernega),¹⁷ thio and seleno phosphoryl chlorides, the thermodynamically

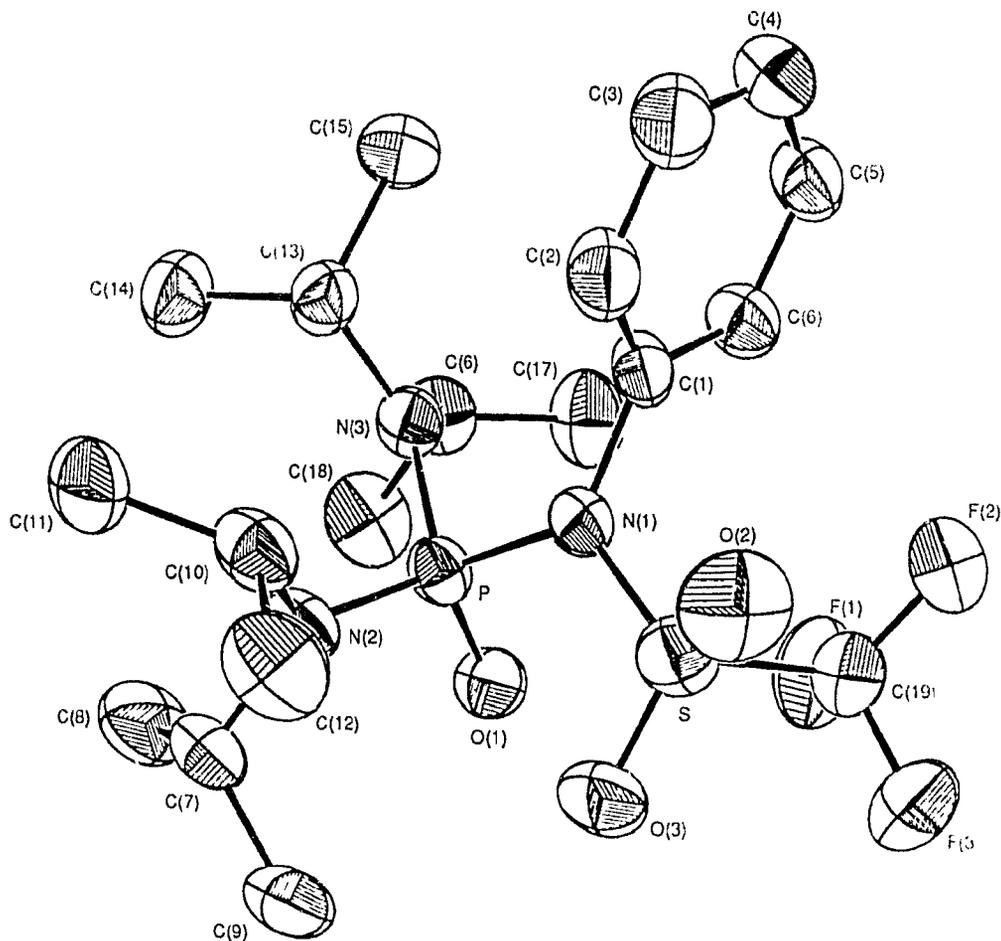


Figure 2.2.8.: Crystallographic view of $(i\text{-Pr}_2\text{N})_2\text{P}(\text{O})\text{N}(\text{Ph})(\text{SO}_2\text{CF}_3)$.

Table 2.2.9.: Selected bond lengths (Å) and angles (°) for

$(i\text{-Pr}_2\text{N})_2\text{P}(\text{O})\text{N}(\text{Ph})(\text{SO}_2\text{CF}_3)$.

P-N(1)	1.785 (3)	P-O(1)	1.464 (3)	P-N(2)	1.649 (3)
P-N(3)	1.639 (3)	N(1)-C(1)	1.458 (5)	N(1)-S	1.628 (3)
S-O(2)	1.422 (3)	S-O(3)	1.418 (3)	S-C(19)	1.851 (4)
O(1)-P-N(1)	109.7 (2)	O(1)-P-N(2)	113.9 (2)		
O(1)-P-N(3)	112.2 (2)	N(1)-P-N(2)	102.1 (1)		
N(1)-P-N(3)	104.5 (2)	N(2)-P-N(3)	113.5 (2)		
P-N(1)-C(1)	126.0 (2)	P-N(2)-C(7)	119.9 (2)		
P-N(2)-C(10)	124.7 (2)	C(7)-N(2)-C(10)	115.5 (3)		
P-N(3)-C(13)	122.8 (2)	P-N(3)-C(16)	121.5 (3)		
C(13)-N(3)-C(16)	114.8 (3)	P-N(1)-S	120.3 (2)		
O(2)-S-N(1)	110.6 (2)	O(3)-S-N(1)	109.5 (2)		
C(19)-S-N(1)	106.2 (2)	O(2)-S-O(3)	121.6 (2)		
O(2)-S-C(19)	103.4 (2)	O(3)-S-C(19)	104.1 (2)		

stable ionic form is that of the dicationic heterocycle, the dimer of the tricoordinate system. For the imino and thio systems with AlCl_3 , a kinetic Lewis acid base product may be isolated through the use of sterically bulky substituents.

No evidence exists for the involvement of the tricoordinate phosphonium cations in these systems. It is possible that the use of an alternative halide ion abstracting reagent might yield the phosphonium unit. For example, Paine³³ suggests PF_5 halide ion abstracts from a diaminothiophosphoryl fluoride. However, my preliminary attempts with alternative reagents were unsuccessful.

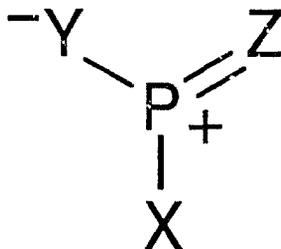
The oxophosphoryl product $(\text{R}_2\text{N})_2\text{P}(\text{O})\text{N}(\text{Ph})(\text{SO}_2\text{CF}_3)$ represents a covalent alternative to the tricoordinate iminophosphonium centre in the salt $[(\text{R}_2\text{N})_2\text{P}=\text{NPh}][\text{CF}_3\text{SO}_3^-]$. It also provides an interesting comparison to the recently synthesised tricoordinate phosphonium centre in bis(diisopropylamino)methylenephosphonium triflate $[(^i\text{Pr}_2\text{N})_2\text{P}=\text{C}(\text{SiMe}_3)_2][\text{SO}_3\text{CF}_3^-]$.²⁸ Thermodynamic preference for the covalent oxophosphoryl unit (the $\text{P}=\text{O}$ bond has a very high bond energy, $500\text{--}600 \text{ kJmol}^{-1}$)⁵⁶ is manifest in the imino derivative. Therefore, it is likely that isolation of the stable methylenephosphonium centre, is made possible by steric protection (kinetic stabilisation) of the $\text{P}=\text{C}$ bond, which is enhanced by the unusually large twist angle of 60° .²⁸ The steric protection offered by the phenyl substituent on the imine nitrogen centre is not nearly as uniform as, or as extensive as the two SiMe_3 units of the carbon analog, and evidently permits interaction between the cation and the anion for oxygen transfer. Thermodynamic control of the products for the imino system is demonstrated by the fact that $(^i\text{Pr}_2\text{N})_2\text{P}(\text{O})\text{N}(\text{Ph})(\text{SO}_2\text{CF}_3)$ was obtained from $(^i\text{Pr}_2\text{N})_2\text{P}^+ \text{CF}_3\text{SO}_3^-$, by means of a Staudinger type reaction, where the triflate anion is present prior to formation of the phosphonium cation, and from the iminophosphoryl centre, where triflate anion is released during reaction with AgSO_3CF_3 .

Chapter 3

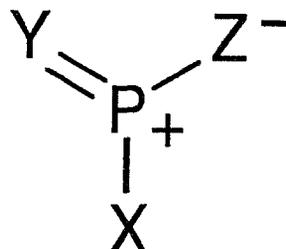
The Reactions and Cyclisation of the Novel Phosphoryls

$[(\text{Me}_3\text{Si})^t\text{BuN}](^t\text{BuN})\text{PS}$ and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$ with Lewis Acids.

Chapter 2, in part, explored the potential of the imino and chalcogeno bis(dialkylamino)phosphoryl chlorides as precursors to the tricoordinate phosphonium (phosphoryl cation) centre. Although novel reactivity and interesting products have been obtained on chloride ion abstraction, there is no evidence for the involvement of the tricoordinate phosphonium cation. The development of alternative routes to the phosphonium centre is therefore of interest.



16



17

Two ylide structures, 16 and 17, can be drawn as contributors to the overall structure of the neutral tricoordinate phosphoryl systems.⁹³ In this form there is an obvious relationship between the neutral and cationic tricoordinate phosphoryl systems. Addition of a Lewis acid to a tricoordinate phosphoryl with suitable substituents (e.g. NR, S) could potentially promote the ionic resonance structure containing the tricoordinate phosphonium centre. However, studies on the coordination chemistry of the tricoordinate phosphoryl have generally yielded heterocyclic products.^{25,94,95} Nevertheless, the potential for the formation of the cationic species remains.

Reported here are the reactions and products from the complexation of the tricoordinate phosphoryl $[(\text{Me}_3\text{Si})^t\text{BuN}](^t\text{BuN})\text{PS}$, I,³⁴ to ECl_3 ($\text{E} =$

Al, Ga) and H^+ ($SO_3CF_3^-$). Novel PNSiS heterocyclic products of type III (Figure 2.3.1) were obtained. Interestingly, further derivatives of III were gained by reaction of bis(bis(trimethylsilyl)amino)thiophosphoryl chloride, $[(Me_3Si)_2N]_2P(Cl)S$, II, with ECl_3 . The results indicate a transient tricoordinate phosphonium centre to be involved in the reactions of both I and II. Furthermore, it is demonstrated that the PNSiS heterocycles III can undergo an unusual rearrangement to thermodynamically more stable PNSiN heterocycles of type IV (Figure 2.3.1.)

J. Marc Whalen, an honours student in this laboratory, was responsible for the preliminary investigation of I with $AlCl_3$.

2.3.1. Isolation and Characterisation of PNSiS Heterocycles from the Reactions of $[(Me_3Si)^tBuN]^tBuNPS$, I, and $[(Me_3Si)_2N]_2P(Cl)S$, II with ECl_3 ($E = Al, Ga$) and $H^+SO_3CF_3^-$.

Reaction of the tricoordinate phosphoryl $[(Me_3Si)^tBuN]^tBuNPS$, I, with the Lewis acids ECl_3 ($E = Al, Ga$) and H^+ ($SO_3CF_3^-$) gives the PNSiS heterocycles III(a,b,c), with the acid centre bound to an exocyclic nitrogen atom. ^{31}P n.m.r. of the reaction mixtures reveals the heterocycles to be formed in high (>90%, H^+) or quantitative (ECl_3) yield and $(^tBuN)-(Me_2Si)-S-P(Me)[N(^tBu)(.AlCl_3)]$, III(a), and $\{(^tBuN)-(Me_2Si)-S-P(Me)[N(^tBu)(H)]\}SO_3CF_3$, III(c) have been isolated as air sensitive solids.

Further derivatives of PNSiS heterocycles, III(d) and III(e), have been isolated from the addition of $[(Me_3Si)_2N]_2P(Cl)S$, II, to ECl_3 ($E = Al, Ga$). In this case, the ^{31}P n.m.r. spectra of the reaction mixtures show two signals at 56 (III(d,e), 80%) and 74 ppm (20%). The minor component has also been isolated, as discussed below, and shown to be the ECl_3 complex of the PNSiN heterocycle IV.

The derivatives of III represent the first examples of the PNSiS heterocyclic framework. The structures of III(a),⁷⁶ III(c)⁷⁵ and

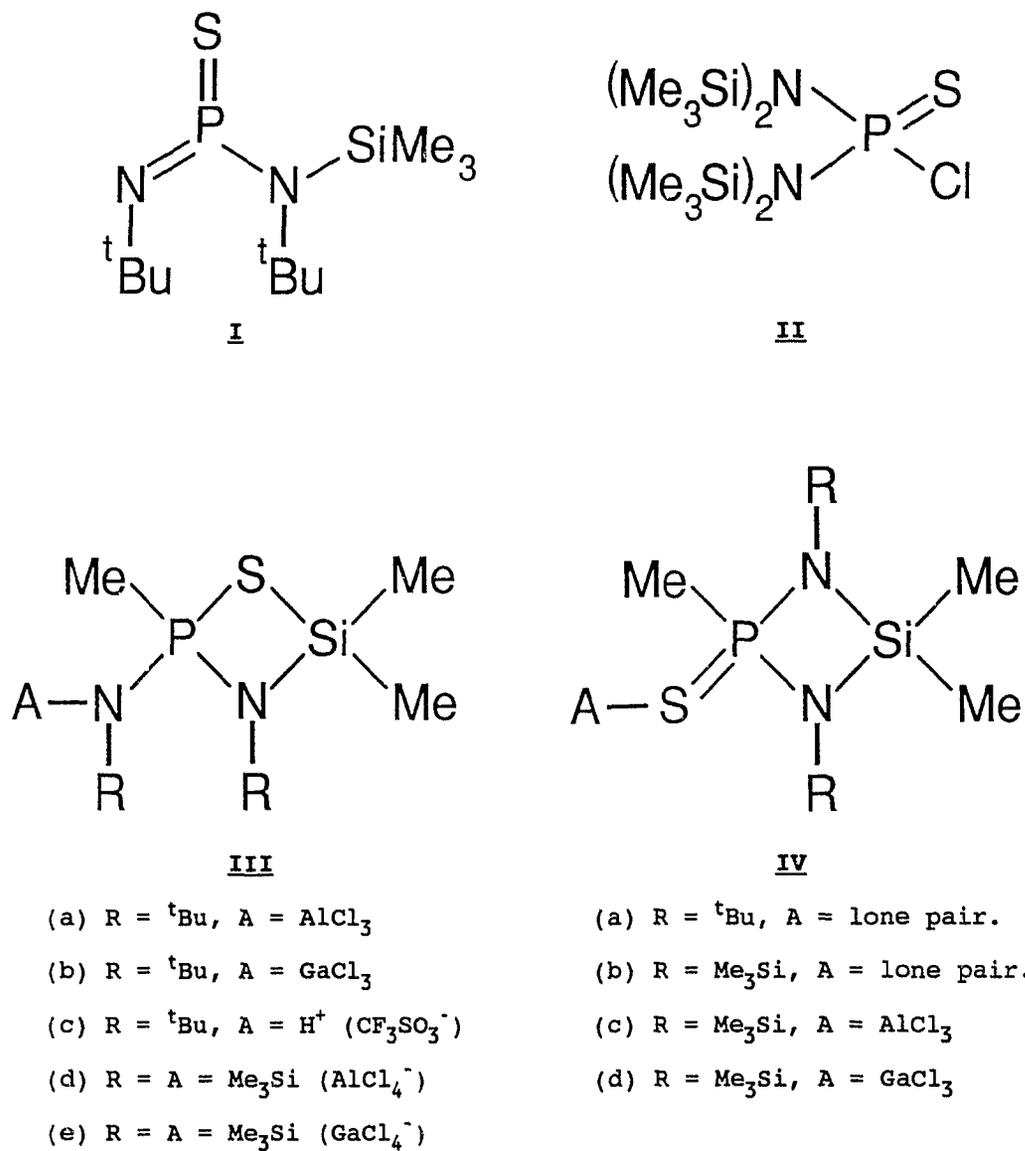


Figure 2.3.1.: The reactants and products of Chapter 3.

III(e)⁷⁶ have been confirmed by X-ray crystallography and views of the heterocycles are given in Figure 2.3.2.. Selected bond lengths and angles are presented in Table 2.3.1.. The structures were determined by Dr. J. F. Richardson.^{75,76} III(c) has two molecules in the asymmetric unit.

The bond lengths within the rings and around the phosphorus are generally indistinguishable in the three heterocycles. In this context, III(a) can be viewed as a zwitterion possessing a phosphonium centre and an aluminate centre. The P-N(1) [(a), 1.654 (4) Å; (c), 1.642 (5) and 1.631 (5) Å; (e), 1.642 (6) Å], P-N(2) [(a), 1.615 (4) Å; (c), 1.608 (6) and 1.606 (6) Å; (e), 1.615 (7) Å] and P-S [(a), 2.075 (2) Å; (c), 2.045 (3) and 2.056 (3) Å; (e), 2.060 (3) Å] bond lengths are short (c.f. single bonds P-N, 1.77,³ P-S, 2.112 (1) Å),⁵⁵ indicating substantial $d\pi-p\pi$ bonding over the SPN_2 moiety. The Si(1)-N(1) bond lengths [(a), 1.762 (4) Å; (c), 1.771 (5) and 1.756 (5) Å; (e), 1.762 (7) Å] are longer than commonly observed (1.72-1.74 Å)⁵¹ for compounds in which a high degree of $d\pi-p\pi$ exists between the silicon and nitrogen atoms. A similar observation has been made for the 1,3-diaza-2-sila-4-phosphenium cations⁹⁶ and implies that the cationic phosphorus centre dominates the π -type lone pair of N(1). The S-Si(1) [(a), 2.169 (2) Å; (c), 2.163 (3) and 2.162 (3) Å; (e) 2.179 (3) Å] bond lengths are typical of single bonds (c.f. 2.143 (3) Å in $[MePhSiS]_3$).⁹⁷

The endocyclic bond angles are indistinguishable for the ^tbutyl derivatives III(a) and III(c), and exhibit minor differences to those of III(e), presumably imposed by the differing steric requirements of the ^tbutyl and trimethylsilyl groups. The rings are distorted from planarity, with very narrow angles found at sulphur, [(a), 77.17 (7)°; (c), 77.71 (9)° and 77.7 (1)°; (e), 75.8 (1)°], which is compensated for by wide angles at the planar N(1) [(a), 101.6 (3)°; (c), 101.4 (3)° and 102.7 (3)°; (e), 99.9 (3)°].

N.m.r. details for the derivatives of III are given in Table

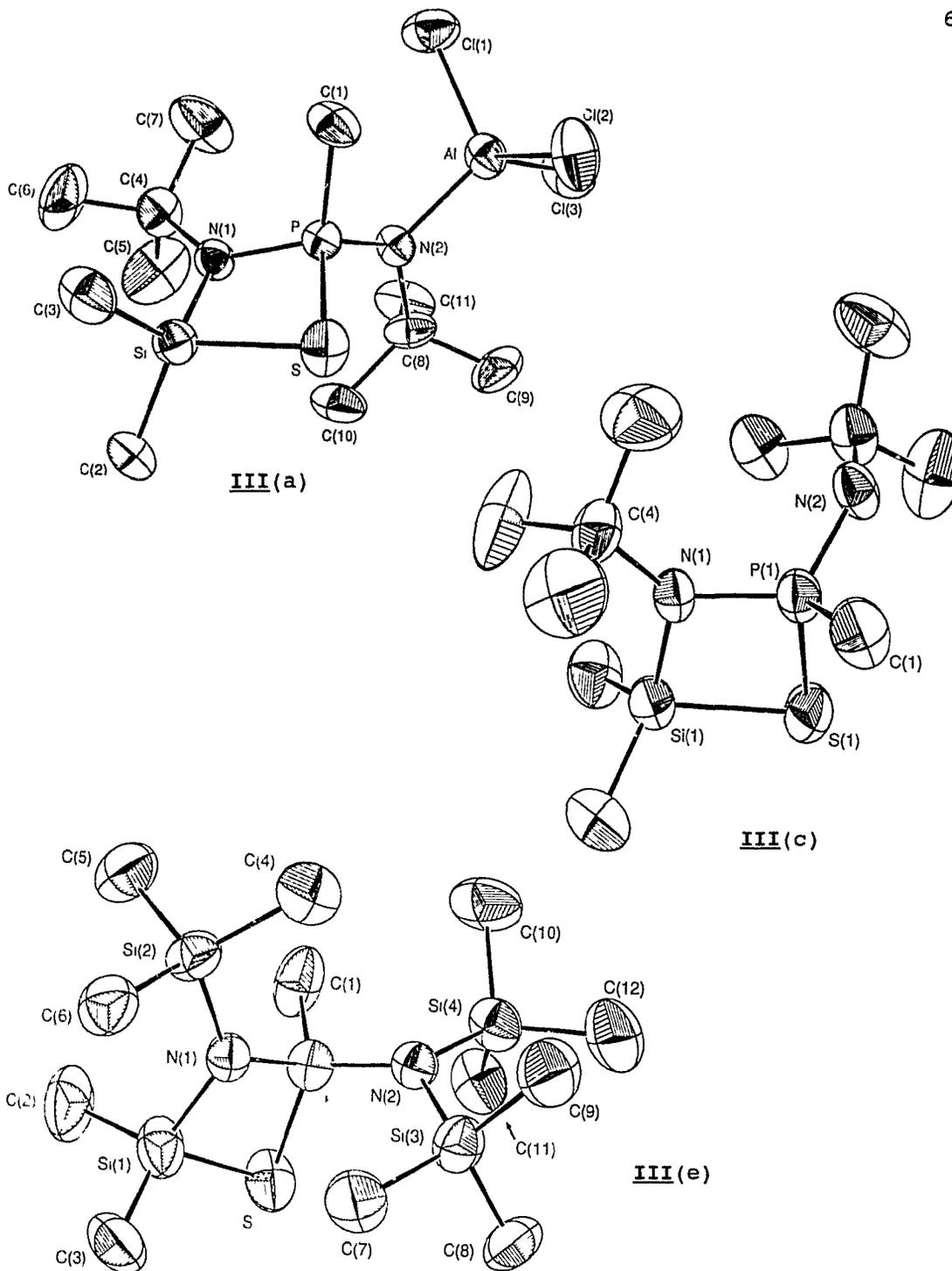


Figure 2.3.2.: Crystallographic views of
 $\{^t\text{BuN}-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\cdot\text{AlCl}_3)]\}$, **III(a)**,
 $\{(^t\text{BuN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\text{H})]\}\{\text{SO}_3\text{CF}_3\}$, **III(c)** and
 $\{(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(\text{Me}_3\text{Si})_2]\}\{\text{GaCl}_4\}$, **III(e)**.

Table 2.3.1.: Selected bond lengths (Å) and angle (°) for

$(^t\text{BuN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\cdot\text{AlCl}_3)]$, **III** (a),
 $\{(^t\text{BuN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\text{H})]\}\{\text{SO}_3\text{CF}_3\}$, **III**(c) and
 $\{(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(\text{Me}_3\text{Si})_2]\}\{\text{GaCl}_4\}$, **III**(e).

	III (a)	III (c)*	III (e)
P(1)-S(1)	2.075 (2)	2.045 (3) 2.056 (3)	2.060 (3)
S(1)-Si(1)	2.169 (2)	2.163 (3) 2.162 (3)	2.179 (3)
N(1)-Si(1)	1.762 (4)	1.771 (5) 1.756 (5)	1.762 (7)
P(1)-N(1)	1.654 (4)	1.642 (5) 1.631 (5)	1.642 (6)
P(1)-N(2)	1.615 (4)	1.608 (6) 1.606 (6)	1.615 (7)
P(1)-S(1)-Si(1)	77.17 (7)	77.71 (9) 77.7 (1)	75.8 (1)
S(1)-P(1)-N(1)	93.4 (2)	94.0 (3) 93.2 (2)	95.1 (2)
S(1)-Si(1)-N(1)	87.2 (1)	86.5 (2) 86.2 (2)	87.8 (2)
P(1)-N(1)-Si(1)	101.6 (3)	101.4 (3) 102.7 (3)	99.9 (3)
P(1)-N(1)-C(4)[Si(2)]	128.8 (3)	128.0 (4) 128.5 (4)	129.3 (3)
Si(1)-N(1)-C(4)[Si(2)]	128.7 (3)	128.8 (5) 128.0 (5)	127.9 (3)

* Two molecules in the asymmetric unit. Values for both are reported.

2.3.2.. Generally the n.m.r. data are similar for the heterocycles, including the ^{31}P chemical shifts. However, the ^{13}C chemical shift of the P-Me of III(c) (24.3 ppm) is considerably more shielded than in the other derivatives [(a), 31.6 ppm; (d)(e), 31.2 ppm,) possibly by virtue of the reduced steric crowding at N(2). Rigidity of the heterocycles is demonstrated by the inequivalence of the endocyclic silicon methyl groups in the ^1H and ^{13}C n.m.r..⁹⁸ The amine proton of III(c) is observed as a doublet at 6.02 ppm ($^2J_{\text{HP}} = 18$ Hz) in the ^1H n.m.r. and in the i.r. spectrum as a broad peak at 3170 cm^{-1} . The i.r. signal is slightly outside the normal ranges for N-H frequencies⁹⁰ but no equivalent signal is observed for the AlCl_3 adduct III(a).

2 3.2. PNSiN Heterocycles IV. Thermolysis and Isomerisation of the PNSiS Heterocycles, III.

As described above, addition of $[(\text{Me}_3\text{Si})_2\text{N}] \text{P}(\text{Cl})\text{S}$, II, to ECl_3 gives two signals in the ^{31}P n.m.r. spectra of the reaction mixtures at 73 (20%) and 56 (III(d,e), 80%) ppm. However, reaction mixtures from the slow addition of GaCl_3 to II show a new peak at 60 ppm (90%) with the peaks at 73 and 56 ppm as only minor components. Attempts to isolate this new species were unsuccessful. However, heating ($80\text{ }^\circ\text{C}$, 30 h) of these reaction mixtures was found to give the 74 ppm species almost quantitatively by ^{31}P n.m.r., permitting its isolation and identification as the phosphetidine PNSiN heterocycle $(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-(\text{Me}_3\text{SiN})-\text{P}(\text{Me})[\text{S}.\text{GaCl}_3]$, IV(d), where the exocyclic sulphur centre is coordinated to GaCl_3 .

N.m.r. data for IV(d) are given in Table 2.3.2.. The ^{31}P chemical shift, 74 ppm, is near that reported for the free base phosphetidine $(^t\text{BuN})-(\text{Me}_2\text{Si})-(^t\text{BuN})-\text{P}(\text{Me})[\text{S}]$ (73.2 ppm), IV(a).^{95b}

The X-ray crystal structure of IV(d) has been determined by Dr. J. F. Richardson.⁷⁵ A view of the complex is shown in Figure 2.3.3. and selected bond lengths and angles are given in Table 2.3.3. The P-S bond

Table 2.3.2: 1-Hydrogen, ^{13}C , and ^{31}P n.m.r. data the PNSiS and PNSiN heterocycles III and IV.

Chemical shifts in ppm, coupling constants () in hertz.

Compound	^{31}P	^{13}C [^1H]			
		N^tBu^a	SiMe_2	PMe	
<u>III</u> (a) ^b	49	60.7, 58.5 32.5, 31.8 [1.80, 1.45]	5.5, 5.3 [0.78, 0.77]	31.6 (82.8) [2.87 (14.2)]	
<u>III</u> (c) ^c	45	59.1, 56.2 31.7, 30.6 [1.43, 1.39]	5.5, 5.4 [0.84, 0.82]	24.3 (81.8) [2.30 (14.7)]	
<u>III</u> (d,e) ^d	56	NSiMe_3	$\text{N}(\text{SiMe}_3)_2$	SiMe_2	PMe
		1.7 [0.39]	5.3 [0.56]	5.7, 6.0 [0.94, 0.91]	31.2 (80.3) [2.57 (13.2)]
<u>IV</u> (d) ^e	74	1.1 [0.3]		4.0, 4.2 [0.56, 0.68]	29.1 (71.7) [2.40 (13.8)]

^a Not possible to conclusively assign ^{13}C and ^1H signals to the two types of ^tBu .

^b ^{27}Al : 102 (AlCl_4^-), 40 100 ($\Delta\nu_{1/2} = 170$ Hz) ppm.

^c $\text{H-N}^t\text{Bu}$: ^1H , 6.02 (18.1); CF_3SO_3^- : ^{13}C , 120.3 ($^1J_{\text{CF}} = 320$ Hz).

^d III(d) [^{27}Al , 102 ppm (AlCl_4^-) 40] and III(e) [^{71}Ga , 249 ppm (GaCl_4^-) 40] have identical n.m.r details.

^e ^{71}Ga : 249 (GaCl_4^-), 40 257 ($\Delta\nu_{1/2} = 2500$ Hz) ppm.

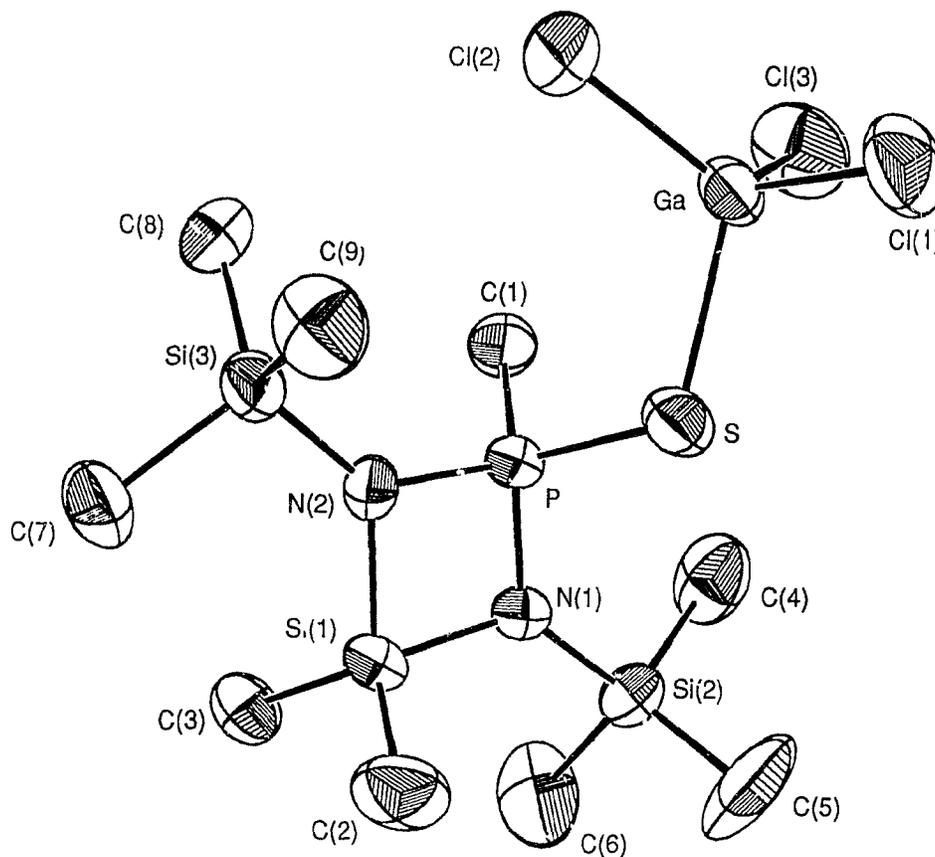


Figure 2.3.3.: Crystallographic view of
 $(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-(\text{Me}_3\text{SiN})-\text{P}(\text{Me})[\text{S.GaCl}_3]$, **IV(d)**.

Table 2.3.3.: Selected bond lengths (Å) and angles (°) for
 $(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-(\text{Me}_3\text{SiN})-\text{P}(\text{Me})\text{S.GaCl}_3$, **IV(d)**.

P-S	2.008 (1)	S-Ga	2.280 (1)	P-N(1)	1.632 (3)
P-N(2)	1.637 (3)	N(1)-Si(1)	1.769 (3)	N(2)-Si(1)	1.771 (4)
Ga-S-P	110.60 (6)	N(1)-P-N(2)	92.7 (2)		
P-N(1)-Si(1)	91.7 (2)	N(1)-Si(1)-N(2)	83.9 (2)		
P-N(2)-Si(1)	91.6 (2)	P-N(1)-Si(2)	133.4 (3)		
P-N(2)-Si(3)	135.4 (2)	Si(1)-N(1)-Si(2)	134.4 (3)		
Si(1)-N(2)-Si(3)	133.0 (3)				

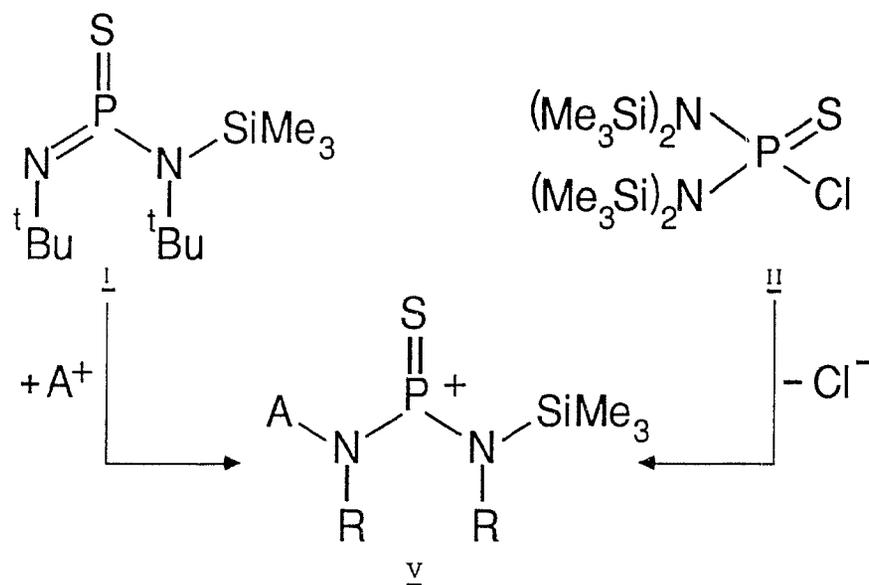
length [2.028 (1) Å] and P-S-Ga angle [110.60 (6)°] are typical of thiophosphoryl complexes (see Chapter 1). The heterocycle is planar, with trigonal planar nitrogen atoms [s.o.a.: 359.5° (N1), 360° (N2)] and the P-N [P-N(1), 1.632 (3) Å; P-N(2), 1.637 (3) Å] and the Si-N [Si(1)-N(1), 1.769 (3) Å; Si(1)-N(2) 1.771 (4) Å] bond lengths are similar to those found in the PNSiS rings, III.

Prolonged heating (1 week, 80 °C) of solutions of the PNSiS ECl_4^- salts, III(d,e), yields the PNSiN complexes IV(c,d) (90%) and another species (^{31}P n.m.r., 72.4 ppm, 10%), believed to be the reaction product of IV(c,d) with CH_2Cl_2 (see Chapter 2). In contrast, the imino. AlCl_3 adduct, III(a), and the triflate salt III(c), are found to be thermally stable in solution. However, addition of Ph_3PO to solutions containing III(a) or III(d) in both cases gives the respective free base PNSiN heterocycle IV and $\text{Ph}_3\text{PO}.\text{AlCl}_3$. The thermal and base induced isomerisation of the PNSiS heterocycles III to the PNSiN heterocycles IV is indicative of the latter being the thermodynamically preferred product. However, attachment of a Lewis acid (e.g. ECl_3 , H^+ , Me_3Si) to the imine centre of III (A = lone pair of electrons) clearly prohibits the rearrangement.

2.3.3. Modes of Cyclisation for I and II: A Common Intermediate Tricoordinate Phosphonium Cation?

Isolation of the same PNSiS heterocycle III from the reactions of I and II with Lewis acids is indicative of a common intermediate. Consistently low temperature ^{31}P n.m.r. studies of the reactions of I and II with GaCl_3 both give a significant signal at 61 ppm during the course of the reaction. [In the case of I this is the only observable intermediate to III. However, two other intermediates are observed during the reaction of II, one of which (177 ppm) is apparently formed after the appearance of the 61 ppm species.] If indeed a common intermediate is present, it is tempting to assign it as a tricoordinate

phosphonium centre, e.g. V, formed either by halide ion abstraction from II or by coordination of a Lewis acid to the imine nitrogen of I.



In contrast to the ECl_3 and triflic acid reactions of I, Scherer reports the reaction of I with $\text{Re}(\text{CO})_5\text{Br}$ to yield IV(a) with the exocyclic sulphur datively bound to rhenium.^{95a} The alternative cyclisation pathways for $[(\text{Me}_3\text{Si})^t\text{BuN})(^t\text{BuN})\text{PS}$, I, are considered to be a function of the initial site of complexation of the Lewis acid. With the "hard" acids, ECl_3 and H^+ , attack at principally the "hard" nucleophilic imine centre is envisaged, as observed in the products, prohibiting its involvement in ring formation. For the "soft" rhenium acid, however, attack at the "soft" sulphur centre might be expected, leading to a cyclisation through the imine nitrogen centre.

The observation of the PNSiN heterocycle IV(c,d) in the reactions of II with ECl_3 is not well understood. The fact that it is observed consistently in a 1:4 ratio with III(d,e), irrespective of the rate of addition of II to ECl_3 or the temperature of the reaction, is perhaps indicative of III(d,e) and IV(c,d) being formed from a common precursor that decays intramolecularly by two alternative pathways.

SECTION 3: CONCLUSIONS AND FUTURE WORK

Conclusions and Future Work.

The interaction of a number of phosphoryl compounds with the Group 13 trihalides and other Lewis acids have been comprehensively examined. The results allow several conclusions:

- (1) The coordinative bonding mode of the tetracoordinate chalcogenophosphoryls is shown to change with the chalcogen. The oxophosphoryls tend to act as σ donors, allowing collinear bonding at the oxygen, while the thio and seleno phosphoryls act as "side-on" or π donors, leading to narrow angles at the chalcogen.
- (2) The imino, oxo, thio and seleno bis(dialkylamino)phosphoryl chlorides, $(R_2N)_2P(Cl)Ch$ ($Ch = NR, O, S, Se$) react with $AlCl_3$ to give covalent or ionic products. The nature of the products is dependent on Ch , whether the products are observed in solution or the solid, and the steric requirements of the substituents.
- (3) The thermodynamically preferred arrangement of the ionic products from $(R_2N)_2P(Cl)Ch$ is a novel dimeric dicationic heterocycle.
- (4) No evidence exists for the involvement of a tricoordinate phosphonium centre in the $(R_2N)_2P(Cl)Ch/AlCl_3$ ($R = \text{alkyl}$) system.
- (5) The recently²⁸ characterised first example of a tricoordinate phosphonium centre appears to be kinetically (sterically) stabilised.
- (6) The novel tetracoordinate and tricoordinate silylaminothiophosphoryls $[(Me_3Si)_2N]_2P(Cl)S$ and $[(Me_3Si)^tBuN]^tBuN]PS$ both give novel PNSiS heterocyclic products on reaction with ECl_3 ($E = Al$ or Ga). A tricoordinate phosphonium (phosphoryl cation) system is postulated as an intermediate to the rings.

This work has demonstrated a diverse and interesting reactivity for the tetracoordinate and tricoordinate phosphoryl systems. Several avenues of future work are apparent.

Firstly, the reactions of the methylenephosphoryl chlorides with halide ion abstractors should be thoroughly examined. Bertrand²⁸ has

demonstrated the stability of the P=C linkage in the tricoordinate methylenephosponium centre and potentially a number of other derivatives might be prepared by the halide ion abstraction route.

Secondly, the effects of introducing a sterically bulky substituent at the imine centre of the iminophosphoryl chlorides $(R_2N)_2P(Cl)NR$ on the reactions with $AgSO_3CF_3$ should be investigated. A kinetically stabilised tricoordinate iminophosponium cation could result.

Thirdly, a more comprehensive study into the oxophosphoryl chloride- $AlCl_3$ system should be done to investigate the products in the solid state. Can derivatives $(R_2N)_2P(Cl)O$ form ionic products?

Finally, a theoretical assessment of the monomeric/dimeric balance of the tetracoordinate chalcogenophosphoryls is necessary. No adequate explanation currently exists for their general monomeric nature.

SECTION 4: EXPERIMENTAL

Experimental

4.0.1. General Procedures

The chemical reactions handled within this thesis were generally extremely sensitive. Stringent handling techniques to exclude air and moisture were employed.

Solids were handled in a Vacuum Atmosphere HE-243-2 nitrogen-filled glove-box. Liquids were handled in a glove-bag under either nitrogen or argon. Glass equipment was flame dried before use. Reactions were generally performed in an evacuated (10^{-3} Torr) double-compartment vessel, equipped with Ace Glass Inc. taps and threaded fittings.^{85,99} However, when large volumes (> 50 ml) of solvent were required, Schlenk apparatus was employed.

Chlorinated and alkane solvents were dried over P_2O_5 and CaH_2 . THF, benzene and toluene were distilled over sodium and benzophenone. Anhydrous ether (Aldrich) was taken immediately from opened cans. Deuterated solvents were vacuum distilled over P_2O_5 . Generally all solvents were stored in evacuated glass bulbs and transferred by distillation on the vacuum line.

The following reagents were obtained commercially (Aldrich, Pfaltz and Bauer) and used without purification: Ph_3P , Ph_3PO , Ph_3As , Ph_3AsO , $NOBF_4$, $AlBr_3$, $(Me_2N)_3P$, $(Me_2N)_3PO$, BF_3 , S_8 , Se_8 , Me_2NH , Et_2NH , iPr_2NH , PCl_3 , $(Me_3Si)_2NH$, Cl_3PS , n -butyllithium (1.6 M hexane solution), $AgSO_3CF_3$, PhN_3 (20% hexane solution) and $(Me_2N)_2P(Cl)O$. $AlCl_3$ and $GaCl_3$ were sublimed and HSO_3CF_3 was distilled before use (all Aldrich). $(iPr_2N)PCl$,¹⁰⁰ $(R_2N)_2P(Cl)Ch$ ($R = Me$ or Et ; $Ch = S$ ¹⁰¹ or Se ¹⁰²), $(Me_3Si)(tBu)NH$ ¹⁰³ and $[(tBu)(Me_3Si)N](tBu)P(S)$ ³⁴ were prepared by literature procedures. $(Me_2N)_3PS$ was prepared by reaction of $(Me_2N)_3P$ with S in Et_2O at $0^\circ C$. $(Et_2N)_2P(Cl)NPh$ was prepared by reaction of $(Et_2N)_2PCl$ with PhN_3 in hexane and characterised by n.m.r..⁹²

Melting points were recorded on a Fischer-Johns apparatus and are

uncorrected. Elemental analyses were obtained by Beller Laboratories, Gottingen, Germany. Infrared spectra were recorded on Nujol mulls or neat liquids on CsI plates using a Perkin-Elmer 283B spectrophotometer. N.m.r. spectra were recorded on a Nicolet NT-360 spectrometer in CH_2Cl_2 , CD_2Cl_2 or CDCl_3 in 5 or 10 mm pyrex flame sealed tubes. Chemical shifts are reported in ppm relative to external standards (85% H_3PO_4 for ^{31}P ; $\text{Et}_2\text{O} \cdot \text{BF}_3$ for ^{11}B ; $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ for ^{27}Al ; $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ for ^{71}Ga ; ^{77}Se signals externally referenced initially to selenous acid and then re-referenced to SeMe_2) and relative to the internal solvent signal for ^1H and ^{13}C . Mass spectra were obtained by using a CEC Model 21-104 mass spectrometer. Air sensitive crystals for X-ray crystallography were mounted in flame sealed glass capillaries. All X-ray crystal structure determinations were performed Drs. Cameron and Linden (Dalhousie University), Dr. Rogers (Northern Illinois University) or Dr. Richardson (University of Louisville), as noted in the script.

4.0.2. Preparation and Characterisation of the Compounds of Section 2, Chapter 1.

Preparation of the Chalcogeno Phosphoryl and Arsonyl Complexes
 $\text{Y}_3\text{PnCh} \cdot \text{EX}_3$ ($\text{Y} = \text{Ph}$ or Me_2N ; $\text{Pn} = \text{P}$ or As ; $\text{E} = \text{B}$, Al or Ga ; $\text{X} = \text{F}$, Cl or Br): $\text{Ph}_3\text{PO} \cdot \text{AlBr}_3$, $\text{Ph}_3\text{PO} \cdot \text{GaCl}_3$, and $(\text{Me}_2\text{N})_3\text{PCh} \cdot \text{AlCl}_3$ ($\text{Ch} = \text{O}$, S) were prepared by addition of the chalcogenophosphoryl to one equivalent of the group 13 trihalide. $\text{Ph}_3\text{PnO} \cdot \text{BF}_3$ ($\text{Pn} = \text{P}$, As) was prepared by addition of Ph_3Pn to two equivalents of NOBF_4 . The complexes were isolated by slow removal of the CH_2Cl_2 solvent under vacuum.

I.r. data and m.p. of $(\text{Me}_2\text{N})_3\text{PS} \cdot \text{AlCl}_3$ (not previously reported): 1295m, 1160m, 1060w, 970s, 745s, 675m, 540m, 490vs, 435vs, 385w, 345w cm^{-1} ;
 m.p. 75-7 °C.

4.0.3. Preparation and Characterisation of the Compounds of Section 2, Chapter 2.

Preparation of Bis(di-isopropylamino)phenyliminophosphoryl

Chloride: A solution of PhN_3 (1.73 g, 14.6 mmol) in CH_2Cl_2 (10 ml) was added to a solution of $(^i\text{Pr}_2\text{N})_2\text{PCl}$ (3.52 g, 13.2 mmol) in CH_2Cl_2 (11 ml) and the reaction mixture was heated to 95 °C for 48 h. The volatiles were removed from the purple solution and the resulting solid purified by double vacuum sublimation at 115 °C under vacuum and recrystallised from warm hexane to give a large single colourless crystal of $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}$. Yield: 0.48 g, 1.3 mmol, 10%; m.p. 86 °C; mass spectrum [m/z (rel. int.)]: 357 (26), 322 (22), 314 (68), 166 (74), 100 (100).

Anal. Calcd: C, 60.40; H, 9.29; N, 11.74%.

Found: C, 59.59; H, 9.24; N, 12.21%.

I.r.: 1600s, 1505s, 1200s, 1175s, 1160sh, 1125s, 1095m, 1070w, 1015m, 990s, 970sh, 885m, 850w, 750s, 690s, 665m, 615m, 560sh, 540s, 505sh, 450w, 410w, 385w cm^{-1} .

A second crop of crystals (2.20 g, total yield of 2.68 g, 7.46 mmol, 57%) was obtained from the hexane solution. The compound is air sensitive and hydrolyses slowly over several months in the solid state.

Preparation of Bis(di-isopropylamino)chalcogenophosphoryl Chloride

$(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{Ch}$ (Ch = S and Se): A stirred mixture of $(^i\text{Pr}_2\text{N})_2\text{PCl}$ (Ch = S, 3.12 g, 11.7 mmol; Ch = Se, 4.26 g, 16.0 mmol), elemental chalcogen (S, 0.38 g, 11.9 mmol; Se, 1.63 g, 16.0 mmol) and AlCl_3 (Ch = S, 0.08 g, 0.56 mmol; Ch = Se, 0.13 g, 0.94 mmol) in CH_2Cl_2 (Ch = S, 25.7 g; Ch = Se, 25 g) was heated (Ch = S, 60 °C for 24 h; Ch = Se, 95-100 °C for 70 h).

Ch = S: The solvent was removed to yield an orange/yellow solid which was vacuum sublimed twice at 80 °C and recrystallised from hot hexane to

give large white elongated crystals of $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}$. Yield: 1.69 g, 5.67 mmol, 50%; m.p. 105 °C; mass spectrum [m/z (rel. int)]: 298 (11), 166 (28), 100 (100);

Anal. Calcd: C, 48.23; H, 9.44; N, 9.37; P, 10.36; S, 10.73%.

Found: C, 48.07; H, 9.27; N, 9.40; P, 10.32; S, 10.86%.

I.r.: 1195s, 1170s, 1155s, 1120s, 990vs, 970vs, 880w, 850w, 840w, 705vs, 650w, 595m, 550m, 535m, 495m, 430m, 385w cm^{-1} .

Ch = Se: The solvent was removed and the resulting solid was extracted with hexane (14 g) to leave a green precipitate and an orange solution. The orange slurry produced upon removal of the hexane was vacuum sublimed three times at 95 °C and recrystallised from hot hexane to give large white elongated crystals of $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{Se}$. Yield: 0.794 g, 2.3 mmol, 15%; m.p. 111-112 °C; mass spectrum [m/z (rel. int)]: 346 (8), 266 (18), 231 (18), 166 (100);

Anal. Calcd: C, 41.69; H, 8.16; N, 8.10%.

Found: C, 42.05; H, 8.44; N, 8.01%.

I.r.: 1195s, 1170s, 1150s, 1115s, 990vs, 970vs, 875w, 850w, 840w, 640s, 565s, 550m, 535m, 495m, 465w, 415w, 385w cm^{-1} .

N.m.r. Studies of Reactions Between $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{Ch}$ ($\text{R} = \text{Me}, \text{Et}$ or $i\text{Pr}$; $\text{Ch} = \text{NPh}, \text{O}, \text{S}$ or Se) and AlCl_3 : Equimolar reaction mixtures of the phosphoryl chlorides and AlCl_3 in CH_2Cl_2 were examined by ^{13}C , ^{31}P and ^{27}Al n.m.r.. Characteristic spectra for Lewis acid-base complexes of the form $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{Ch}.\text{AlCl}_3$ were observed for all of the imino, oxo and thio sulphur derivatives as quantitative solution products. For the Me/Se and Et/Se derivatives, a number of signals were observed in the ^{31}P spectrum and a single sharp line at 102 ppm in the ^{27}Al spectrum corresponding to AlCl_4^- . The ^{31}P and ^{27}Al spectra of the $i\text{Pr}/\text{Se}$ system show $(^i\text{Pr}_2\text{N})_2\text{P}^+ \text{AlCl}_4^-$ to be the only species in solution. A red precipitate was isolated from the reaction mixture which gave no bands in the IR spectrum, indicative of it being elemental selenium.

Preparation of 2,2,4,4-Tetrakis(dialkylamino)-2 λ^5 ,4 λ^5 -cyclodi-(phosphoniathiane) Bis(tetrachloroaluminate) (Alkyl = Me or Et): A solution of $(R_2N)_2P(Cl)S$ (R = Me, 0.493 g, 2.64 mmol; R = Et, 5.03 g, 20.7 mmol) in CH_2Cl_2 (R = Me, 20 ml; R = Et, 69 g) was added to $AlCl_3$ (R = Me, 0.353 g, 2.64 mmol; R = Et, 2.77 g, 20.7 mmol) and the mixture was stirred at room temperature. A vigorous reaction occurred with solvation of $AlCl_3$. After several hours the solvent was slowly removed from the clear pale yellow solution to yield white crystals. The supernatant liquid was decanted and the crystals were washed in cooled solvent by local cooling back distillation of CH_2Cl_2 .

R = Me. The crystals were characterised as $[(Me_2N)_2PS]_2[AlCl_4]_2$.

Yield: 0.65 g, 1.02 mmol, 77%; m.p. 128 °C; mass spectrum [m/z (rel. int)]: 284 (13), 186 (18), 151 (19), 44 (100), 144 (26);

Anal. Calcd: C, 15.01; H, 3.78; N, 8.75; P, 9.68; S, 10.01%

Found: C, 15.11; H, 3.67; N, 8.67; P, 9.51; S, 9.90%.

I.r.: 1300m, 1160m, 1055m, 1010s, 985s, 760w, 705m, 665w, 635m, 615w, 485vs,br, 370w, 305w cm^{-1} .

R = Et. The crystals were characterised as $[(Et_2N)_2PS]_2[AlCl_4]_2$.

Yield: 6.688 g, 8.89 mmol, 86%; m.p. 100 °C; mass spectrum [m/z (rel. int)]: 242 (21), 207 (25), 72 (100);

Anal. Calcd: C, 25.55; H, 5.36; N, 7.45%.

Found: C, 25.61; H, 5.36; N, 7.30%.

I.r.: 1300m, 1205s, 1150s, 1100m, 1065m, 1025s, 960m, 930m, 840w, 790s, 745m, 705w, 675m, 630m, 490vs,br, 350m cm^{-1} .

Preparation of Bis(di-isopropylamino)thiophosphoryl Chloride-Aluminium Trichloride Adduct: A solution of $(iPr_2N)_2P(Cl)S$ (1.075 g, 3.6 mmol) in CH_2Cl_2 (13.7 g) was added to $AlCl_3$ (0.485 g, 3.63 mmol) and shaken until solvation of $AlCl_3$ was complete. Slow removal of solvent from the clear reaction mixture gave small white crystals. The supernatant liquid was decanted and the crystals washed twice with small

aliquots of cool CH_2Cl_2 , and were characterised as $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$.

Yield: 1.28 g, 2.96 mmol, 82%; m.p. 152 °C; mass spectrum [m/z (rel.

int)]: 298 (6), 163 (28), 120 (24), 100 (100);

Anal. Calcd: C, 33.35; H, 6.53; N, 6.48; P, 7.17; S, 7.42%.

Found: C, 33.20; H, 6.54; N, 6.44; P, 7.33; S, 7.48%.

I.r.: 1195s, 1165s, 1140s, 1110s, 1005vs, 995vs, 965vs, 875w, 845m, 640s, 595vs, 550s, 515vs, 500vs, 440s, 415s cm^{-1} .

The $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{GaCl}_3$ adduct has been prepared in a similar manner to the aluminium derivative. Yield: 53%; m.p. 184 °C; I.r.: 1195s, 1165s, 1140 s, 1110s, 1005vs, 995vs, 965vs, 875w, 845m, 640s, 595vs, 550s, 510w, 470w, 485w, 390s, 375s, 350s cm^{-1} .

Preparation of 2,2,4,4-Tetrakis(dialkylamino)-2 λ^5 ,4 λ^5 -cyclo-di-(phosphoniaselenone) Bis(tetrachloroaluminate) (Alkyl = Me or Et): A solution of $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{Se}$ (R = Me, 1.01 g, 4.33 mmol; R = Et, 2.24 g, 7.74 mmol) in CH_2Cl_2 (R = Me, 15.4 g; R = Et, 26.3 g) was added to AlCl_3 (R = Me, 0.58 g, 4.36 mmol; R = Et, 1.03 g, 7.74 mmol) and the mixture was stirred at room temperature. Yellow solutions were formed rapidly and the AlCl_3 was consumed.

R = Me. Precipitation of a pale yellow solid occurred within seconds. The orange solution was decanted and the solid was washed by back distillation of solvent, and characterised as $[\{(\text{Me}_2\text{N})_2\text{PSe}\}_2][\text{AlCl}_4]_2$. Yield: 0.796 g, 1.08 mmol, 50%; m.p. 128 °C; mass spectrum [m/z (rel.int)]: 234 (41), 199 (13), 154 (20), 119 (26), 110 (100); IR: 1290m, 1150m, 1050m, 995s, 970s, 685m, 545w, 480vs cm^{-1} .

R = Et. The solution went through a number of colour changes (yellow, orange, red, orange and yellow). After 4 h, the solvent was slowly removed to give bright yellow crystals of $[\{(\text{Et}_2\text{N})_2\text{PSe}\}_2][\text{AlCl}_4]_2$. Yield: 3.118 g, 3.68 mmol, 95%; m.p. 119 °C; mass spectrum [m/z (rel.int)]: 290 (16), 255 (11), 210 (3), 138 (100);

Anal. Calcd: C, 22.72; H, 4.77; N, 6.62; P, 7.32; Se, 18.67%.

Found: C, 22.67; H, 4.96; N, 6.62; P, 7.31; Se, 18.63%.

I.r.: 1290w, 1205s, 1145m, 1100m, 1050m, 1015s, 980w, 955m, 925w, 795s, 660w, 540w, 485vs cm^{-1} .

Isolation of Bis(dialkylamino)phenyliminophosphoryl

Chloride-Aluminium Trichloride Adduct (Alkyl = Et or ⁱPr): A solution of $(\text{R}_2\text{N})_2\text{P}^+\text{AlCl}_4^-$ was prepared *in situ*⁷⁷ by the reaction of $(\text{R}_2\text{N})_2\text{P}(\text{Cl})$ (R = Et, 1.31 g, 6.22 mmol; R = ⁱPr, 2.419 g, 9.08 mmol) with AlCl_3 (R = Et, 0.83 g, 6.22 mmol; R = ⁱPr, 1.212 g, 9.08 mmol) in CH_2Cl_2 (R = Et, 38 g; R = ⁱPr, 46 g). Upon solvation of AlCl_3 the solution was cooled to -78°C and a solution of phenyl azide (R = Et, 0.74g, 6.22 mmol; R = ⁱPr, 1.08 g, 9.08 mmol) in CH_2Cl_2 (R = Et, 13 g; R = ⁱPr, 23 g) was added in small aliquots. Evolution of N_2 began as the solution warmed to room temperature and the reaction was complete after several hours stirring at room temperature. The coloured solutions (R = Et, yellow; R = ⁱPr, orange) were degassed, two thirds of the CH_2Cl_2 was removed, and hexane (5 mL) was added. Slow removal of solvent yielded a crystalline solid, which was recrystallised by slow cooling of the warm (55°C) solvent mixture, to give large transparent crystals.

R = Et. The crystals were characterised as $(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}.\text{AlCl}_3$.

Yield: 1.11 g, 2.55 mmol, 41%; m.p. $163-165^\circ\text{C}$; mass spectrum [m/z (rel. int): 301 (27), 266 (12), 229 (19), 194 (13), 138 (100);

Anal. Calcd: C, 38.64; H, 5.79; N, 9.66; P, 7.12%.

Found: C, 38.71; H, 5.92; N, 9.57; P, 7.00%.

I.r.: 1595m, 1490sh, 1340sh, 1285w, 1200s, 1150s, 1115w, 1095w, 1075w, 1040s, 1020s, 975w, 950w, 920w, 910w, 850s, 810m, 795 m, 765m, 710w, 695m, 680m, 625m, 565s, 525sh, 500s, 490s, 460sh, 435w, 400s cm^{-1} .

R = ⁱPr. The crystals were characterised as $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}.\text{AlCl}_3$.

Yield: 0.953 g, 1.94 mmol, 21%; m.p. 179°C ; mass spectrum [m/z (rel. int): 357 (10), 314 (40), 271 (12), 257 (14), 166 (62), 157 (11), 137

(19), 112 (45), 100 (100);

Anal. Calcd: C, 44.01; H, 6.77; N, 8.55%.

Found: C, 44.01; H, 6.83; N, 8.56%.

I.r.: 1595m, 1410sh, 1305w, 1210s, 1165sh, 1150s, 1125sh, 1075w, 1035sh, 1015s, 980sh, 885w, 870w, 840s, 830sh, 755w, 695s, 655m, 640s, 570s, 555m, 530sh, 885s, 440w, 425w, 395m cm^{-1} .

The isolated yields are not optimised. N.m.r. studies of identical reaction mixtures reveal a principal (>95%) signal in the ^{31}P spectrum corresponding to the adduct, indicating an essentially quantitative reaction.

N.m.r. Studies on the Reaction of $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$ (R = Me, Et or ^iPr) with CH_2Cl_2 : N.m.r. samples of $[\{(\text{Me}_2\text{N})_2\text{PS}\}_2][\text{AlCl}_4]_2$ (0.06 g), $[\{(\text{Et}_2\text{N})_2\text{PS}\}_2][\text{AlCl}_4]_2$ (0.03g) and $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$ (0.11g) in CH_2Cl_2 (3.55 g, 2.47 g, and 3 g, respectively) were warmed to 80 °C for 24 h. ^{31}P n.m.r. spectra showed quantitative formation of new species with chemical shifts of 73, 69 and 61 ppm, respectively. The ^{27}Al n.m.r. spectra of all three solutions consist of only a single sharp peak at 102 ppm (corresponding to AlCl_4^-). In a preparative experiment $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$ (0.66 g, 1.5 mmol) was dissolved in CH_2Cl_2 (17.8 g) and the solution was heated to 80 °C for 18 h. After removal of the solvent the sample weight had increased by 0.13 g corresponding to an uptake of CH_2Cl_2 (1.5 mmol).

A 0.058 M CH_2Cl_2 solution of $\text{Ph}_3\text{PS}\cdot\text{AlCl}_3$ was heated for 1 week at 80 °C. The ^{31}P and ^{27}Al n.m.r. spectra showed peaks at 46 and 102 ppm (AlCl_4^-) respectively. The ^{13}C n.m.r. spectrum is consistent with the formation of $\text{Ph}_3\text{PS}\cdot\text{CH}_2\text{Cl}^+$ [136.7 (p), 134 (o), 130.9 (m), 117 (i), 44.5 ppm].

Variable-temperature ^{31}P N.m.r Studies on the Dissolution of

$[\{(\text{Et}_2\text{N})_2\text{PS}\}_2][\text{AlCl}_4]_2$: A sample of $[\{(\text{Et}_2\text{N})_2\text{PS}\}_2][\text{AlCl}_4]_2$ (0.052 g) was

placed in a 10 mm n.m.r. tube and CH_2Cl_2 (3 ml) was introduced at -196 °C. The sample was warmed to -78 °C immediately prior to placement in the n.m.r. probe, which had been previously cooled to -70 °C. Each spectrum was obtained after a 5 min temperature equilibration period. The spectra were observed during data acquisition and therefore spectra for a particular temperature represent an average over the data acquisition period. After 20 min at -70 °C, 30 min at -40 °C and 10 min at -20 °C, no signals were observed. After 15 min at 0 °C, two single peaks were observed at 75 (20%) and 21 ppm (80%). After 5 min at 20 °C, the signal at 75 ppm was not observed and the peak at 21 ppm (70%) dominated the spectrum, with a new signal at 22 ppm (30%) observed as a shoulder. The 22 ppm signal increased over the next 5 min and became the dominant peak. After 30 min two small peaks of approximately equal intensity were also observed at 75 and 73 ppm. After another 2 h at room temperature (22 °C) the spectrum consisted of a small peak at 75 ppm and two equal intensity peaks at 73 and 22 ppm. Complete dissolution of the crystals occurred on standing at room temperature for 3 d, and the spectrum contained only the signal at 73 ppm which corresponds to $(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$.

N.m.r. Studies of the Reactions Between $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{S}\cdot\text{AlCl}_3$ and Excess AlCl_3 : Three solutions: $[\{(\text{Me}_2\text{N})_2\text{PS}\}_2][\text{AlCl}_4]_2$ (0.06 g, 0.08 mmol) and AlCl_3 (0.06 g, 0.4 mmol) in 3.85 g of CH_2Cl_2 , $[\{(\text{Et}_2\text{N})_2\text{PS}\}_2][\text{AlCl}_4]_2$ (0.04 g, 0.05 mmol) and AlCl_3 (0.03 g, 0.2 mmol) in 3.85 g of CH_2Cl_2 , and $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{S}$ (0.03 g, 0.1 mmol) and AlCl_3 (0.03 g, 0.2 mmol) in 1.70 g of CH_2Cl_2 , were prepared and studied by ^{31}P n.m.r. spectroscopy. After 5 d the spectra show signals at: R = Me, 78 (30%), 73 (20%), 27 (50%); R = Et, 73 (10%), 69 (20%), 21 (70%); R = ^iPr , 60 (60%), 18 (40%).

Exposure of $(\text{R}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}\cdot\text{AlCl}_3$ Complexes to Air: Ground

crystals of $(R_2N)_2P(Cl)NPh \cdot AlCl_3$ ($R = Et, iPr$) were exposed to the air for 10 min and then placed in $CDCl_3$ (used as delivered). White precipitates formed and the solutions were examined by ^{31}P and ^{27}Al n.m.r. spectroscopy. The only species present in solution was tentatively characterised as $(R_2N)_2P(NPh)OH$, ^{31}P : $R = Et$, 39 ppm, $R = iPr$, 35 ppm; ^{13}C : $R = Et$, 136.4 (i), 129.6 (m), 125.1 (p) 120.6 (o), 41.3, 13.1 ppm; $R = iPr$, 136.5 (i), 129.2 (m), 125.2 (p), 122.4 (o) ($J_{PC} = 6.8$ Hz), 50.5, 23.1 ppm; 1H : $R = Et$, 9.57 (1H, Doublet $J_{HP} = 12$ Hz) (chemical shift concentration dependent. Range 9.5-11.4), 7.3-7.1 (5H, aromatic), 3.4-3.2 (8H, doublet of quartets), 1.26 (12H, Triplet $J_{HH} = 7.2$ Hz); $R = iPr$, 11.45 (1H, Doublet $J_{HP} = 14$ Hz) (chemical shift concentration dependent), 7.5-7 (5H, aromatic), 4.1-4 (4H, multiplet), 1.59 (12H, Doublet $J_{HH} = 6.9$ Hz), 1.47 (12H, Doublet $J_{HH} = 6.8$ Hz). These compounds could not be isolated. $AlCl_4^-$ was identified as being in solution by ^{27}Al n.m.r. (102 ppm).

Addition of $(R_2N)_2P(Cl)S$ ($R = Et$ or iPr) to Alternative Halide Ion

Abstractors: A solution of $(Et_2N)_2P(Cl)S$ (0.88 g, 3.6 mmol) in CH_2Cl_2 (13.6 g) was divided in four and added to n.m.r. tubes containing 1 mmol of $NaPF_6$, $NaBF_4$, $Me_3SiSO_3CF_3$, and $AgBF_4$. The ^{31}P n.m.r. spectra of the solutions revealed no reaction with the first three reagents. However, the ^{31}P n.m.r. of the $AgBF_4$ reaction mixture gave four peaks at 82 ($J_{PF} = 1031$ Hz), 78, 68, 62 and 28 ppm.

To a n.m.r. tube containing $(iPr_2N)_2P(Cl)S$ (0.110 g, 0.37 mmol) and $AgSO_3CF_3$ (0.095 g, 0.37 mmol) was added CH_2Cl_2 (3.6 g). The ^{31}P n.m.r. spectrum of the reaction mixture showed, in addition to a signal (70 ppm) for the starting thiophosphoryl, another peak of equal integral at 67 ppm. In a similar reaction, $(iPr_2N)_2P(Cl)S$ (0.126 g, 0.42 mmol), two equivalents of $AgSO_3CF_3$ (0.216 g, 0.84 mmol) and CH_2Cl_2 (3.2 g), only a single signal at 66 ppm was observed. On a preparative scale $(iPr_2N)_2P(Cl)S$ (0.374 g, 1.25 mmol) in CH_2Cl_2 (19 g) was added to

AgSO_3CF_3 (0.644 g, 2.51 mmol) and the reaction mixture was stirred overnight. The solution was decanted from the AgCl precipitate (approx. 1.25 mmol) and the solvent slowly distilled away to yield a clear oil, found to be insoluble in hexane and toluene.

Reaction of $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}$ with AgSO_3CF_3 and Isolation of Bis(di-isopropylamino)phenyltrifluoromethylsulphonaminoxophosphoryl: A solution of $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}$ (0.743 g, 2.08 mmol) in CH_2Cl_2 (20 ml) was added to AgSO_3CF_3 (0.534 g, 2.08 mmol). Reaction occurred immediately and the solution was stirred overnight. The CH_2Cl_2 was removed, hexane (20 ml) was added, and the resulting pale yellow solution was decanted from the precipitate. Slow removal of the solvent yielded an off-white air stable solid, which was recrystallised six times from hexane, and characterised as $(^i\text{Pr}_2\text{N})_2\text{P}(\text{O})\text{N}(\text{Ph})(\text{SO}_2\text{CF}_3)$. Yield: 0.343 g, 0.73 mmol, 35%; m.p.. 117-8 °C; mass spectrum [m/z (rel. int.)]: 471 (1), 247 (100); ^{31}P , 13 ppm; ^{13}C , 136.4 (i), 131.9 (m), 129.9 (p), 129.6 (o), 120.3 ($^1J_{\text{CF}} = 325$ Hz), 48.7, 23.6, 23.0 ppm; Anal. Calcd.: C, 48.40; H, 7.05; N, 8.91%. Found: C, 48.45; H, 7.17; N, 8.98%. I.r.: 1600w, 1255s, 1225w, 1200s, 1170w, 1130m, 1070w, 1020s, 970s, 940s, 915m, 880s, 870sh, 705s, 680s, 620m, 605s, 580m, 565sh, 550s, 525s, 445m, 405w, 385w cm^{-1} . N.m.r. studies on the reaction mixture show the reaction to be quantitative. Similarly, reactions of $(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{NPh}$ with excess AgSO_3CF_3 gave only a single product (^{31}P , 14 ppm).

Reaction of $(^i\text{Pr}_2\text{N})_2\text{P}^+ \text{CF}_3\text{SO}_3^-$ with Phenyl Azide: To a stirred solution of $(^i\text{Pr}_2\text{N})_2\text{P}^+ \text{CF}_3\text{SO}_3^-$ (prepared *in situ*, 2.09 mmol $\text{AgSO}_3\text{CF}_3^-$, 2.08 mmol $(^i\text{Pr}_2\text{N})_2\text{P}(\text{Cl})$) in CH_2Cl_2 (20 ml) was added PhN_3 (2.08 mmol) in CH_2Cl_2 (10 ml). A ^{31}P n.m.r. spectrum of the reaction mixture revealed $(^i\text{Pr}_2\text{N})_2\text{P}(\text{O})\text{N}(\text{Ph})(\text{SO}_2\text{CF}_3)$ to be the principal (>80%) component.

$(^i\text{Pr}_2\text{N})_2\text{P}^+$ and $(^i\text{Pr}_2\text{N})_2\text{PCl}$ were the only other phosphorus containing species present.

Additional Characterisation Details for Known Compounds:

I.r. data for $(\text{Et}_2\text{N})_2\text{P}(\text{S})\text{Cl}$: 1300s, 1255w, 1205s, 1165s, 1105s, 1065s, 1025s, 945s, 790s, 735s, 695s, 610s, 500s, 440w, 390w, 340m, 245m cm^{-1} .

I.r. data for $(\text{Et}_2\text{N})_2\text{P}(\text{Se})\text{Cl}$: 1300s, 1260w, 1205s, 1165s, 1025s, 950s, 790s, 685s, 555s, 505m, 470w, 430w, 330m cm^{-1} .

Carbon-13 n.m.r. data for $(^i\text{Pr}_2\text{N})_2\text{PCl}$: 47.4 ($^2J_{\text{PC}} = 13 \text{ Hz}$), 24, 22.9 ($^3J_{\text{PC}} = 10.4 \text{ Hz}$) ppm.

4.0.4. Preparation and Characterisation of the Compounds of Section 2, Chapter 3.

Isolation of 1,1-dimethyl-3-methyl-3-^tbutylamino-4-^tbutyl-cyclo[4]-1-sila-2-thia-4-aza-3-phosph(V)ane-Aluminium Trichloride Adduct, III(a) from the Reaction of $[(\text{Me}_3\text{Si})^t\text{BuN}](^t\text{BuN})\text{P}(\text{S})$, I, with AlCl_3 : A solution of $[(\text{Me}_3\text{Si})^t\text{BuN}](^t\text{BuN})\text{P}(\text{S})$ (1.08 g, 3.88 mmol) in CH_2Cl_2 (24 g) was added to AlCl_3 (0.515, 3.85 mmol). The AlCl_3 dissolved within minutes to give a clear solution. Slow solvent removal under vacuum resulted in the precipitation of a white crystalline solid. The supernatant liquid was decanted and the solid was washed in cooled solvent by local back distillation. The crystals were characterised as $(^t\text{BuN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\text{AlCl}_3)]$, III(a). Yield 0.529 g, 1.28 mmol, 33%; m.p. 174-176 °C; mass spectrum [m/z (rel. int.)]: 278 (23), 263 (73), 206 (100);

Anal. Calcd: C, 32.08; H, 6.61; N, 6.80; S, 7.79; Cl, 25.83; P, 7.52;
Al, 6.55%

Found: C, 32.21; H, 6.77; N, 6.81; S, 7.80; Cl, 25.76; P, 7.46;
Al, 6.65%

I.r.: 1260m, 1225w, 1190m, 1170w, 1070s, 1045m, 995s, 935m, 905m, 880m,

845m, 820w, 805m, 775m, 685m, 585m, 570w, 525w, 480s, 430m, 410s cm^{-1} .

Yields of up to 44% have been obtained.

Isolation of 1,1-dimethyl-3-methyl-3-^tbutylamino-4-^tbutyl-cyclo[4]-1-sila-2-thia-4-aza-3-phosphonium Triflate, III(c) from Reaction of $[(\text{Me}_3\text{Si})^t\text{BuN}](^t\text{BuN})\text{PS}$, I, with HSO_3CF_3 : A suspension of triflic acid (0.94 g, 6.26 mmol) in CH_2Cl_2 (6 g) was added over a 5 min period to a solution of $[(\text{Me}_3\text{Si})^t\text{BuN}](^t\text{BuN})\text{PS}$ (1.69 g, 6.07 mmol) in CH_2Cl_2 (14 g). After shaking for 10 min, hexane (5 mL) was introduced and the solvent was slowly removed from the mixed solvent system under vacuum. A white solid precipitated which was recrystallised from the warm (55 °C) residual solvent to give block-shaped white crystals of $\{(\text{Me}_2\text{Si})^t\text{BuN}-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\text{H})]\}\{\text{SO}_3\text{CF}_3\}$, III(c). Yield 0.408 g, 0.95 mmol, 16%; m.p. 130 °C; mass spectrum [m/z (rel. int.)]: 279 (11), 278 (27), 264 (18), 263 (67), 206 (54), 97 (100);

Anal. Calcd.: C, 33.63; H, 6.59; N, 6.54; P, 7.23; S, 14.96%

Found: C, 33.91; H, 6.57; N, 6.59; P, 7.00; S, 14.99%.

I.r.: 3170s,br, 1250br, 1155, 1095, 1055, 1025, 940, 925, 910, 880w, 850m, 800s, 770w, 760w, 685m, 630s, 590w, 570w, 515s, 485w, 445m, 415m cm^{-1} .

A further 1.26 g (total yield 1.67 g, 63%) was obtained from the residual reaction mixture.

³¹P N.m.r. Studies on Reactions of $[(\text{Me}_3\text{Si})^t\text{BuN}](^t\text{BuN})\text{P}(\text{S})$, I:

Equimolar reaction mixtures prepared in a similar manner to those described above were examined by ³¹P n.m.r. spectroscopy, which showed the complexes $(^t\text{BuN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\text{A})]$ (A = AlCl_3 , GaCl_3 , H^+), III(a,b,c), as the principal component (> 90%) in each case.

A reaction of $[(\text{Me}_3\text{Si})^t\text{BuN}](^t\text{BuN})\text{PS}$ (0.33 g, 1.2 mmol) with GaCl_3 (0.21 g, 0.12 mmol) was examined at low temperature by warming the sample from -196 °C to -20 °C and monitoring the reaction between -20 and +20 °C.

At $-20\text{ }^{\circ}\text{C}$ a signal for I at 140 ppm was observed together with a trace signal at 61 ppm. At $0\text{ }^{\circ}\text{C}$ the signal at 61 ppm and a new third signal at 49 ppm dominated the spectrum. After mixing (shaking) the spectrum contained a single peak at 49 ppm assigned to $(^t\text{BuN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\text{GaCl}_3)]$, III(b).

Preparation of Bis[bis(trimethylsilyl)amino]thiophosphoryl Chloride, II: $^{104}\text{ }^n\text{BuLi}$ (1.6 M, 78 cm^3 , 125 mmol) was added dropwise to a stirred solution of $(\text{Me}_3\text{Si})_2\text{NH}$ (20 g, 124 mmol) in Et_2O (100 cm^3), and the mixture was set to reflux for 30 min. After cooling to $-10\text{ }^{\circ}\text{C}$, a solution of Cl_3PS (10.5 g, 61.9 mmol) in Et_2O (50 cm^3) was added rapidly dropwise. The solution was stirred overnight, filtered through celite and the volatiles were removed under vacuum. Vacuum distillation (short path apparatus, bath temperature up to $160\text{ }^{\circ}\text{C}$) of the resulting orange oil gave a clear liquid characterised as $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$. Yield: 10.31 g, 24.6 mmol, 40%; b.p. $90-96\text{ }^{\circ}\text{C}/10^{-3}$ torr; Anal. Calcd: C, 34.40; H, 8.59, N, 6.68; S, 7.65%. Found: C, 35.26; H, 8.81; N, 6.74; S, 7.35%. (N.B. Analysis difficulties are often associated with silicon containing liquids). I.r. (neat liquid): 1255s, 925s, 900s,br, 760s, 685s, 645m, 620m, 490m, 435s, 375w, 365m, 320w, 270m cm^{-1} .

Isolation of 1,1-dimethyl-3-methyl-3-bis(trimethylsilyl)amino-4-trimethylsilyl-cyclo[4]-1-sila-2-thia-4-aza-3-phosphonium Tetrachloro-aluminate (-gallate), III(d) and III(e) from Reaction of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$, II, with ECl_3 (E = Al, Ga): A solution of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{S})\text{Cl}$ (E = Al, 1.43 g, 3.41 mmol; E = Ga, 1.57 g, 3.75 mmol) in CH_2Cl_2 (E = Al, 38 g; E = Ga, 11 g) was added rapidly to solid ECl_3 (E = Al, 0.456g, 3.41 mmol; E = Ga, 0.66 g, 3.75 mmol). Immediate reaction gave an intense purple solution which became pale yellow/orange on stirring overnight. Some of the solvent was removed

under vacuum and hexane (3 mL) was introduced. Clear block shaped crystals were obtained on cooling to $-10\text{ }^{\circ}\text{C}$.

E = Al. The crystals were characterised as

$\{(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(\text{Me}_3\text{Si})_2]\}\{\text{AlCl}_4\}$, III(d). Yield 0.374 g, 0.68 mmol, 20%; m.p. $129\text{ }^{\circ}\text{C}$; mass spectrum [m/z (rel. int.)]: 310 (27), 295 (100).

Anal. Calcd. C, 25.71; H, 6.65; N, 5.42; P, 5.89; S, 6.05%.

Found: C, 26.10; H, 6.52; N, 5.07; P, 5.61; S, 5.81%.

I.r.: 1275m, 1260s, 1025s, 995s, 920m, 895m, 840s, 795s, 690w, 675w, 640w, 630w, 560m, 480s, 400m, 360w cm^{-1} .

E = Ga. The crystals were characterised as

$\{(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(\text{Me}_3\text{Si})_2]\}\{\text{GaCl}_4\}$, III(e). Yield 0.88 g, 1.48 mmol, 39%; m.p. $130\text{ }^{\circ}\text{C}$; mass spectrum [m/z (rel. int.)]: 310 (6), 295 (25), 93 (100).

I.r.: 1275m, 1260s, 1025s, 995s, 920m, 900m, 840s, 795s, 690w, 675w, 645w, 635w, 560m, 460m, 410m, 375s, 360w cm^{-1} .

Isolation of 1,1-dimethyl-3-methyl-2,4-(trimethylsilyl)-cyclo[4]-1-sila-7,4-diaza-3-thiophosphoryl-Gallium Trichloride Adduct, IV(d), from the Reaction of GaCl_3 with $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$, II: A solution of GaCl_3 (0.446 g, 2.53 μmol) in CH_2Cl_2 (21 g) was added dropwise over 3-5 h to a stirred solution of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$ (1.06 g, 2.53 mmol) in CH_2Cl_2 (4 g). The reaction mixture was then heated to $80\text{ }^{\circ}\text{C}$ for 30 h to give an orange solution. A portion (21 g) of the solvent was removed and hexane (2 g) was added. Large clear crystals were obtained on cooling to $-10\text{ }^{\circ}\text{C}$, characterised as

$(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-(\text{Me}_3\text{SiN})-\text{P}(\text{Me})[\text{S.GaCl}_3]$, IV(d). Yield 0.265 g, 0.54 mmol, 21%; m.p. $147-148\text{ }^{\circ}\text{C}$; mass spectrum [m/z (rel. int.)]: 310 (25), 295 (100).

Anal. Calcd: C, 22.21; H, 5.59; N, 5.76%.

Found: C, 21.19; H, 5.27; N, 5.77%.

I.r.: 1300m, 1260s, 1125m, 1035s, 915w, 890w, 840s, 805w, 760w, 690w, 635m, 565s, 460s, 425m, 380s, 360s, 325m cm^{-1} .

^{31}P N.m.r. Studies on the Reactions of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$, II:

Addition of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$ to equimolar or excess ECl_3 (E = Al and Ga): Solutions of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$ were added at different rates to equimolar quantities of ECl_3 and the reaction mixtures consistently showed signals at 56 ppm [assigned to III(d,e)] and 74 ppm [assigned to IV(c,d)] with an intensity ratio of 4:1, respectively. The corresponding compounds have been isolated as described above. Similar spectra were obtained with up to three times excess ECl_3 , however, the initial intense purple colour of the reaction mixtures is more persistent (E = Al, 1 m, E = Ga, 24 h). The loss of colour has no effect on the spectra.

Addition of excess $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$ to AlCl_3 : A solution of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$ (1.53 g, 3.66 mmol) in CH_2Cl_2 (18 g) was added rapidly to AlCl_3 (0.24 g, 1.8 mmol). The initially pale yellow reaction mixture became colourless after four hours. Fifteen minutes after the total solvation of AlCl_3 the ^{31}P n.m.r. spectrum showed peaks at 73 (60%) and 56 (40%) ppm. After two weeks the spectrum contained an additional peak at 74 and at least 8 other trace peaks. After heating (20 h, 80 °C) the peak at 56 ppm was not observed and the peak at 74 ppm [assigned to IV(c)] dominated a complex spectrum (50%).

Addition of HSO_3CF_3 to $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$: A suspension of triflic acid (0.58 g, 3.9 mmol) in CH_2Cl_2 (13 g) was added rapidly to a solution of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$ (1.53 g, 3.66 mmol) in CH_2Cl_2 (2 g), and the ^{31}P n.m.r. spectrum contained more than 20 peaks between 0 and 100 ppm.

Addition of GaCl_3 to equimolar $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$: A solution of GaCl_3 (0.375 g, 2.1 mmol) in CH_2Cl_2 (34 g) was added over 5.5 h to a solution of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$ (0.90 g, 2.1 mmol; CH_2Cl_2 , 8 g). The ^{31}P n.m.r. spectrum showed signals at 74 (2%), 60 (90%) and 56 (8%) ppm.

Low Temperature Studies of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$ with GaCl_3 :

$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}(\text{Cl})\text{S}$ (0.25 g, 0.60 mmol) in CH_2Cl_2 (4.1 g) was added to an n.m.r. tube containing GaCl_3 (0.11 g, 0.65 mmol) at -196°C . The sample was warmed to -20°C and the reaction was monitored between -20 and $+20^\circ\text{C}$. The signal at 205 ppm (II), observed at -20°C , was quantitatively replaced by a signal at 73 ppm between -10 and 0°C . The sample was shaken and two new signals, 177 (30%) and 61 (70%) ppm replaced the signal at 73 ppm. At $+10^\circ\text{C}$ the integral of the two peaks became 60% and 40%, respectively, and two new signals appeared at 74 and 56 ppm. After 45 minutes the spectrum contained only two signals at 74 ppm [20%, assigned to IV(d)] and 56 ppm [80%, assigned to III(e)].

^{31}P N.m.r. Study of the Solution Thermolysis of

$\{(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}[\text{N}(\text{Me}_3\text{Si})_2](\text{Me})\}\{\text{ECl}_4^-\}$, III(d,e) (E = Al, Ga):
Solutions of the salts (AlCl_4^- 0.17 g; GaCl_4^- 0.17 g) in CH_2Cl_2 (3.12 g and 2.05 g, respectively) were warmed to 80°C for 1 week. The ^{31}P n.m.r. spectrum contained a signal at 74 ppm [$> 90\%$, assigned $(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-(\text{Me}_3\text{SiN})-\text{P}(\text{Me})[\text{S.ECl}_3]$, IV(c,d)], and a small signal at 72 ppm [tentatively assigned to $\{(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-(\text{Me}_3\text{SiN})-\text{P}(\text{Me})[\text{SCH}_2\text{Cl}]\}\{\text{AlCl}_4\}$].

^{31}P N.m.r. Study of the Reaction of

$(^t\text{BuN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\text{AlCl}_3)]$, III(a), with Ph_3PO : CH_2Cl_2 (3.1 g) was condensed into an n.m.r. tube containing Ph_3PO (0.08 g, 0.27 mmol) and $(^t\text{BuN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(^t\text{Bu})(\text{AlCl}_3)]$ (0.11 g, 0.26 mmol). The ^{31}P n.m.r. spectrum of the reaction mixture gave two integral equivalent signals at 74 [assigned to $(^t\text{BuN})-(\text{Me}_2\text{Si})-(^t\text{BuN})-\text{P}(\text{Me})[\text{S}]$, IV(a)] and 44 ($\text{Ph}_3\text{PO}.\text{AlCl}_3$) ppm.

^{31}P N.m.r. Study of the Reaction of

$\{(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}(\text{Me})[\text{N}(\text{Me}_3\text{Si})_2]\}\{\text{AlCl}_4\}$, III(d), with Ph_3PO : III(d)

was prepared *in situ* by reaction of II (0.74 mmol) with AlCl_3 (0.73 mmol) in CH_2Cl_2 (27 g), and the solution was added to Ph_3PO (0.74 mmol) in CH_2Cl_2 (8 g). A ^{31}P n.m.r. spectrum of the reaction mixture revealed three signals at 4 ppm (50%, $\text{Ph}_3\text{PO}\cdot\text{AlCl}_3$), 60 ppm (5 %) and 74 ppm [45%, assigned to $(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-(\text{Me}_3\text{SiN})-\text{P}(\text{Me})[\text{S}]$, IV(b)].

SECTION 5: APPENDIX OF CRYSTALLOGRAPHIC DATA

Appendix of Crystallographic Data

Full details of the crystal structure determinations listed in the Appendix are available from Dr. Neil Burford, Dalhousie University.

Table 5.0.1.: Structural parameters for derivatives of $(iPr_2N)_2P(Cl)Ch$ (Ch = NPh,[#] S,[§] and Se[§]).

Formula	$C_{18}H_{33}ClN_3P$	$C_{12}H_{28}ClN_2PS$	$C_{12}H_{28}ClN_2PSe$
M	341.78	298.85	345.75
Crystal Class	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	8.400 (2)	9.740 (1)	9.723 (2)
b/Å	16.496 (3)	14.206 (1)	14.203 (2)
c/Å	15.061 (3)	12.693 (1)	12.826 (2)
$\beta/^\circ$	90.70 (2)	100.33	99.73 (2)
Z	4	4	4
R	0.039	0.0537	0.0633
R_w	0.038	0.0591	0.0703

[#]Structure determined by Dr. J. F. Richardson.

[§]Structure determined by Dr. T. S. Cameron.

Table 5.0.2.: Structural parameters[#] for (ⁱPr₂N)₂P(Cl)NPh.AlCl₃ and (ⁱPr₂N)₂P(O)N(Ph)(SO₂CF₃).

Formula	C ₁₈ H ₃₃ AlCl ₄ N ₃ P	C ₁₉ H ₃₃ F ₃ N ₃ O ₃ PS
M	491.25	471.53
Crystal Class	Monoclinic	Monoclinic
Space Group	P2 ₁	P2 ₁ /n
a/Å	8.719 (2)	10.594 (3)
b/Å	15.553 (2)	13.222 (3)
c/Å	9.509 (2)	17.084 (3)
β/°	102.73 (2)	97.71 (2)
Z	2	4
R	0.029	0.048
R _w	0.030	0.046

[#]Structures determined by Dr. J. F. Richardson.

Table 5.0.3.: Structural parameters[#] for $\{(\text{}^t\text{BuN})-(\text{Me}_2\text{Si})-\text{S}-\text{P}[\text{N}(\text{}^t\text{Bu})(\text{H})]\}$
 $\{\text{CF}_3\text{SO}_3\}$, III(c), and $(\text{Me}_3\text{SiN})-(\text{Me}_2\text{Si})-(\text{Me}_3\text{SiN})-\text{P}(\text{Me})[\text{S.GaCl}_3]$, IV(d).

Formula	$\sim_{24}\text{H}_{56}\text{F}_6\text{N}_4\text{O}_6\text{P}_2\text{S}_4\text{Si}_4$	$\text{C}_9\text{H}_{27}\text{Cl}_3\text{GaN}_2\text{PSSi}_3$
M	857.10	486.70
Crystal Class	Triclinic	Monoclinic
Space Group	P1	P2 ₁ /n
a/Å	13.206 (3)	10.980 (1)
b/Å	13.211 (3)	17.744 (2)
c/Å	12.662 (3)	12.170 (2)
α/°	99.04 (2)	-
β/°	91.18 (2)	101.24 (2)
γ/°	80.54 (2)	-
Z	4	4
R	0.065	0.037
R _w	0.067	0.038

[#]Structures determined by Dr. J. F. Richardson.

SECTION 5: REFERENCES

References

1. See, for example, 'Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1972, Vol. 1-5.
2. See, for example, 'J. March, Advanced Organic Chemistry,' Wiley-Interscience, New York, 1985, Chap. 16, p. 780.
3. D. E. C. Corbridge, 'The Structural Chemistry of Phosphorus,' Elsevier, New York, 1974.
4. (a) M. W. Schmidt and M. S. Gordon, *J. Am. Chem. Soc.*, 1985, **107**, 1922; (b) *Can. J. Chem.*, 1985, **63**, 1609; (c) M. W. Schmidt, S. Yabushita, and M. S. Gordon, *J. Phys. Chem.*, 1984, **88**, 382.
5. P. Molina, M. Alajarin, C. L. Leonardo, R. M. Claramunt, M. de la Concepcion Foces-Foces, F. H. Cano, J. Catalan, J. L. G. de Paz, and J. Elguero, *J. Am. Chem. Soc.*, 1989, **111**, 355; M. M. Francl, R. C. Pellow, and L. C. Allen, *ibid.* 1988, **110**, 3723; W. Kutzelnigg, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 272.
6. D. Gonbeau, G. Pfister-Guillouzo, M. R. Mazieres and M. Sanchez, *Can. J. Chem.*, 1985, **63**, 3242.
7. E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 1961, 2459.
8. G. Trinquier and J-P. Malrieu, *J. Am. Chem. Soc.*, 1979, **101**, 7169.
9. (a) G. A. Bowmaker, R. Herr, and H. Schmidbaur, *Chem. Ber.*, 1983, **116**, 3567; (b) H. Schmidbaur, *Angew. Chem. Int. Ed. Engl.*, 1983, **22**, 907.
10. G. W. Adamsen and J. C. J. Bart, *J. Chem. Soc. A*, 1970, 1452.
11. M. J. E. Hewlins, *J. Chem. Soc. B*, 1971, 94.
12. J. A. Bertrand, *Inorg. Chem.*, 1967, **6**, 495.
13. J. J. Delpuech, in 'NMR of Newly Accessible Nuclei,' ed. P. Laszlo, Academic Press, New York, 1983, vol. 2, p. 153.
14. See, for reviews on the dimerisation, (a) A. Schmidpeter, in 'The Chemistry of Inorganic Homo- and Heterocycles,' eds. I. Haiduc and D. B. Sowerby, Academic Press, New York, 1987, vol 2, p. 617; (b)

- H. G. Heal, 'The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus,' Academic Press, New York, 1980; (c) M. Bermann, *Adv. Inorg. Chem. Radiochem.*, 1972, 14, 1.
15. See, for a review, C. W. Allen, in 'The Chemistry of Inorganic Homo- and Heterocycles,' eds. I. Haiduc and D. B. Sowerby, Academic Press, New York, 1987, vol 2, p. 501.
16. N. Burford and M. J. Schriver, unpublished results.
17. A. P. Marchenko, V. V. Miroschnichenko, V. A. Kovenya, A. M. Pinchuk, A. N. Chernega, M. Yu. Antipin, and Yu. T. Struchkov, *Zh. Obshch. Khim.*, 1988, 58, 1758; *J. Gen. Chem. (USSR)*, 1989, 59, 1569; A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov, I. E. Boldeskul, A. P. Marchenko, and A. M. Pinchuk, *Zh. Strukt. Khim.*, 1987, 28, 135; *J. Struct. Chem.*, 1987, 28, 274.
18. I. Haiduc, 'The Chemistry of Inorganic Ring Systems,' Wiley-Interscience, London, 1970, Part 2, Chap. 5, p. 787.
19. R. Appel, F. Knoll, and H-D. Wihler, *Angew. Chem. Int. Ed. Engl.*, 1977, 16, 402; V. J. Weiss and B. Nuber, *Z. Anorg. Allg. Chem.*, 1981, 473, 101.
20. B. Neumuller, H. Riffel, and E. Fluck, *Z. Anorg. Allg. Chem.*, 1990, 588, 147; J. Svara, E. Fluck, and H. Riffel, *Z. Naturforsch., Teil B*, 1985, 40, 1258.
21. See, for example, D. B. Sowerby, in 'The Chemistry of Inorganic Homo- and Heterocycles,' eds. I. Haiduc and D. B. Sowerby, Academic Press, New York, 1987, vol. 2, p. 681.
22. (a) J. T. Shore, W. T. Pennington, M. C. Noble, and A. W. Cordes, *Phosphorus Sulfur*, 1988, 39, 153; (b) J. C. Fitzmaurice, D. J. Williams, P. T. Wood, and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1988, 741.
23. M. Regitz and G. Mass, *Top. Curr. Chem.*, 1981, 97, 71. See, for a recent example, M. P. Coogan and M. J. P. Harger, *J. Chem. Soc., Chem. Commun.*, 1990, 1745.

24. A. H. Cowley and N. C. Norman, *Prog. Inorg. Chem.*, 1986, 34, 1.
25. See, for a review, H. Germa and J. Navech, *Phosphorus Sulfur*, 1986, 26, 327.
26. (a) S. Pohl, E. Niecke, and B. Krebs, *Angew. Chem. Int. Ed. Engl.*, 1975, 14, 261; (b) R. Appel, F. Knoch, and H. Kunze, *ibid.*, 1983, 22, 1004; (c) *ibid.*, 1984, 23, 157.
27. M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, 1983, 862.
28. A. Igau, A. Baceiredo, H. Grutzmacher, H. Pritzkow, and G. Bertrand, *J. Am. Chem. Soc.*, 1989, 111, 6853.
29. R. Appel and R. Schmitz, *Chem. Ber.*, 1983, 116, 3521.
30. (a) M. R. Marre, M. Sanchez, and R. Wolf, *Phosphorus Sulfur*, 1982, 13, 327; M. Sanchez, M. R. Marre, J. F. Brazier, J. Bellan, and R. Wolf, *ibid.*, 1983, 14, 331. (b) See, for related work, M. R. Marre, M. Sanchez, and R. Wolf, *J. Chem. Soc., Chem. Commun.*, 1984, 566; M. R. Mazieres, M. Sanchez, J. Bellan, and R. Wolf, *Phosphorus Sulfur*, 1986, 26, 97.
31. See, for example, D. S. Payne, in 'Non-Aqueous Solvent Systems,' ed. T. C. Waddington, Academic Press, New York, 1965, Chap. 8, p. 301.
32. L. Maier, *Z. Anorg. Allg. Chem.*, 1966, 343, 29.
33. R. W. Light and R. T. Paine, *Phosphorus Sulfur*, 1980, 8, 255.
34. O. J. Scherer and N. Kuhn, *Angew. Chem. Int. Ed. Engl.*, 1974, 13, 811.
35. See, for example, E. Lindner, R. Lehner, and H. Scheer, *Chem. Ber.*, 1967, 100, 1331; W. v. d. Veer and F. Jellinek, *Rec. Trav. Chim. Pays-Bas*, 1966, 85; M. J. Frazer, W. Gerrard, and R. Twaits, *J. Inorg. Nucl. Chem.*, 1963, 25, 637; F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 1960, 2199; S. D. Radosavljevic and D. D. Poleti, *Glas. Hemi. Drus. Beograd.*, 1979, 44, 639; S. Milicev and D. Hadzi, *Inorg. Chim. Acta.*, 1977, 21, 201; M. E.

- Peach and T. C. Waddington, *J. Chem. Soc.*, 1962, 3450; M. Zackrisson and K. I. Alden, *Acta Chem. Scand.*, 1960, 14, 994.
36. N. Burford, B. W. Royan, R. E. v. H. Spence, T. S. Cameron, A. Linden, and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1990, 1521.
37. N. Burford, B. W. Royan, R. E. v. H. Spence, and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1990, 2111.
38. T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Org. Chem.*, 1975, 40, 3437.
39. T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, 1975, 97, 940.
40. J. W. Akitt, in 'Multinuclear NMR,' Ed. J. Mason, Plenum Press, New York, 1987, p. 259.
41. H. Noth and B. Wrackmeyer, 'NMR: Basic Principles and Progress,' vol. 14, eds. P. Diehl, E. Fluck and R. Kosfeld, Springer-Verlag, New York, 1978.
42. D. E. H. Jones, *J. Chem. Soc., Dalton Trans.*, 1972, 567; R. G. Kidd and D. R. Truax, *J. Am. Chem. Soc.*, 1968, 90, 6867.
43. J. S. Hartman and G. J. Schrobilgen, *Inorg. Chem.*, 1974, 13, 874.
44. N. Burford, R. E. v. H. Spence, A. Linden and T. S. Cameron, *Acta Crystallogr., Sect. C*, 1990, 46, 92.
45. N. Burford, R. E. v. H. Spence and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1990, 3611.
46. (a) G. Ruban and V. Zabel, *Cryst. Struct. Comm.*, 1976, 5, 671; (b) G. Bandoli, G. Bortolozzo, D. A. Clemente, U. Croatto and C. Panattoni, *J. Chem. Soc. A*, 1970, 2778.
47. G. Ferguson and E. W. Macaulay, *J. Chem. Soc. A*, 1969, 1.
48. D. B. Sowerby, in 'The Chemistry of Inorganic Homo- and Heterocycles,' eds. I. Haiduc and D. B. Sowerby, Academic Press, New York, 1987, vol. 2, p. 713.
49. (a) F. J. Feher, T. A. Budzichowski, and K. J. Weller, *J. Am.*

Chem. Soc., 1989, 111, 7288; (b) Y. Hermodsson, *Arkiv. Kemi.*, 1969, 30, 15; (c) K. Tomita, *Acta Crystallogr., Sect. C*, 1985, 41, 1832; (d) N. W. Alcock, M. M. Roberts and D. Brown, *J. Chem. Soc., Dalton Trans.*, 1982, 25; (e) J. K. Felixberger, J. G. Kuchler, E. Herdtweck, R. A. Paciello and W. A. Hermann, *Angew. Chem. Int. Ed. Engl.*, 1988, 27, 946; (f) W. J. Evans, W. Grate and R. J. Doedens, *J. Am. Chem. Soc.*, 1985, 107, 1671; (g) B. Koren, P. Sivy, F. Valach, M. Melnik and J. Jecny, *Acta Crystallogr., Sect. C*, 1988, 44, 646; (h) P. Sharrock, M. Melnik, F. Belanger-Gariepy and A. L. Beauchamp, *Can. J. Chem.*, 1985, 63, 2564; (i) C-M. Che, T-F. Lai, W-C. Chung, W. P. Schaefer and H. B. Gray, *Inorg. Chem.*, 1987, 26, 3907; (j) D. C. Bradley, J. S. Ghotra, F. A. Hart, M. B. Hursthouse and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1977, 1166; (k) A. M. G. Dias Rodrigues, R. H. P. Francisco and J. R. Lechat, *Cryst. Struct. Comm.*, 1982, 11, 847; (l) J. A. Bertrand and A. R. Kalyanaraman, *Inorg. Chem. Acta*, 1971, 5, 341; (m) D. L. Kepert, D. Taylor, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1973, 1658; (n) M. U. Haque, C. N. Caughlan, F. A. Hart, and R. VanNice, *Inorg. Chem.*, 1971, 10, 115; (o) K. M. A. Malik and J. W. Jeffery, *Acta Crystallogr., Sect. B*, 1973, 29, 2687; (p) C. Panattoni, R. Graziani, G. Bandoli, B. Zarli, and G. Bombieri, *Inorg. Chem.*, 1969, 8, 320; (q) R. Graziani, B. Zarli, A. Cassol, G. Bombieri, E. Forsellini, and E. Tondello, *Inorg. Chem.*, 1970, 9, 116; (r) G. Bombieri, U. Croatto, E. Forsellini, B. Zarli, and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1972, 560; (s) G. Bombieri, D. Brown, and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1975, 1873; (t) M. Nardelli, C. Pelizzi, and G. Pelizzi, *J. Organomet. Chem.*, 1976, 112, 263; (u) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, 1963, 85, 2402; (v) C. I. Branden and I. Lindqvist, *Acta Chem. Scand.*, 1963, 17, 353; (w) T. Ernst, A. El-Kholi, U. Muller and K. Dehnicke, *Z. Anorg. Allg. Chem.*,

- 1988, 566, 7; (x) P. Klingelhofer, U. Muller, H. G. Hauck and K. Dehnicke, *Z. Naturforsch., Teil B*, 1984, 39, 135; (y) W. Musterle, J. Strahle, W. Liebelt and K. Dehnicke, *Z. Naturforsch., Teil B*, 1979, 34, 942; (z) L. A. Aslanov, V. M. Attiya, V. M. Ionov, A. B. Permin, and V. S. Petrosyan, *Zh. Strukt. Khim.*, 1977, 18, 1113.
50. (a) P. Prick, P. T. Beurskens, and P. J. M. W. L. Birker, *Cryst. Struct. Comm.*, 1977, 6, 437; (b) N. W. Kong, C. Wei, V. G. K. Das, and R. J. Butcher, *J. Organomet. Chem.*, 1989, 361, 53; (c) M. Nardelli, C. Pelizzi, G. Pelizzi, and P. Tarasconi, *Inorg. Chem. Acta*, 1978, 30, 179; (d) F. Lazerini, L. Golic, and G. Pelizzi, *J. Cryst. Mol. Struct.*, 1976, 6, 113; (e) Y. S. Ng, G. A. Rodley and W. T. Robinson, *Acta Crystallogr., Sect. B*, 1977, 33, 931; (f) J. G. H. Du Preez, B. J. Gellatly, and M. Laing, *J. Inorg. Nucl. Chem.*, 1976, 38, 1872; (g) L. R. Falvello, M. Gerloch, and P. R. Raithby, *Acta Crystallogr., Sect. C*, 1987, 43, 2029; (h) C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1983, 847; (i) S. Dondi, M. Nardelli, C. Pelizzi, G. Pelizzi, and G. Predieri, *J. Organomet. Chem.*, 1986, 308, 195.
51. A. F. Wells, 'Structural Inorganic Chemistry,' Oxford University Press, Oxford, 1984.
52. J. L. Atwood and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1983, 302.
53. M. J. Zaworotko, R. D. Rogers and J. L. Atwood, *Organometallics*, 1982, 1, 1179, and refs. therein.
54. (a) P. W. Coddington and K. A. Kerr, *Acta Crystallogr., Sect. B*, 1978, 34, 3785; (b) W. W. Schweikert and E. A. Meyers, *J. Chem. Phys.*, 1968, 72, 1561; J. W. Bransford and E. A. Meyers, *Cryst. Struct. Comm.*, 1978, 2, 697; (c) C. D. Garner, N. C. Howladar, F. E. Mabbs, P. M. Boorman and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1978, 1350; P. M. Boorman, C. D. Garner, F. E. Mabbs and T. J. King, *J. Chem. Soc., Chem. Commun.*, 1974, 663; (d) M. G. B.

- Drew and R. J. Hobson, *Inorg. Chim. Acta.*, 1983, **72**, 233; (e) E. N. Baker and B. R. Reay, *J. Chem. Soc., Dalton Trans.*, 1973, 2205; (f) P. G. Eller and P. W. R. Corfield, *J. Chem. Soc., Chem. Commun.*, 1971, 105; (g) F. A. Cotton, B. A. Frenz, D. L. Hunter and Z. C. Mester, *Inorg. Chim. Acta.*, 1974, **11**, 119; (h) P. W. Coddington and K. A. Kerr, *Acta Crystallogr., Sect. B*, 1979, **35**, 1261; (i) P. C. Tellinghuisen, W. T. Robinson, and C. J. Wilkins, *J. Chem. Soc., Dalton Trans.*, 1985, 1289.
55. N. Burford, B. W. Royan, and P. S. White, *Acta Crystallogr., Sect. C*, 1990, **46**, 274.
56. J. E. Huheey, 'Inorganic Chemistry,' Harper and Row, New York, 1983.
57. G. A. Steigmann, *Acta Crystallogr.*, 1967, **23**, 142.
58. J. Flahaut and P. Laruelle, in 'The Chemistry of Extended Defects in Non-metallic Solids,' eds. L. Eyring and M. O'Keefe, North Holland, Amsterdam, 1970.
59. See, for example, S. A. Weissman, S. G. Baxter, A. M. Arif, and A. H. Cowley, *J. Am. Chem. Soc.*, 1986, **108**, 529; D. Schomburg, G. Bettermann, L. Ernst, and R. Schmutzler, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 975.
60. L. S. Dent Glasser, L. Ingram, M. G. King, and G. P. McQuillan, *J. Chem. Soc. A*, 1969, 2502.
61. M. S. Hussain, *J. Cryst. Spectrosc. Res.*, 1986, **16**, 91.
62. A. Aaberg, T. Gramstad, and S. Husebye, *Acta Chem. Scand. A*, 1980, **34**, 717.
63. R. Steudel, 'Chemistry of the Non-Metals,' English eds. F. C. Nachod and J. J. Zuckerman, Walter de Gruyter, New York, 1977.
64. C. Calvo, *Can. J. Chem.*, 1965, **43**, 1139; 1147.
65. C. Glidewell and D. C. Liles, *J. Chem. Soc., Chem. Commun.*, 1977, 632.
66. Y. Kushi and Q. Fernando, *J. Am. Chem. Soc.*, 1970, **92**, 91.

67. M. D. Healy, D. A. Wierda, and A. R. Barron, *Organometallics*, 1988, 7, 2543.
68. A. R. Barron, K. D. Dobbs, and M. M. Francl, *J. Am. Chem. Soc.*, 1991, 113, 39.
69. R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, 1974, 96, 7601.
70. See, for example, (a) D. S. Bohle, C. E. F. Rickard, W. R. Roper, and P. Schwerdtfeger, *Organometallics*, 1990, 9, 2068; (b) E. Lindner, V. Kass, W. Hiller, and R. Fawzi, *Angew. Chem. Int. Ed. Engl.*, 1989, 28, 448; E. Lindner, C. P. Krieg, W. Hiller, and R. Fawzi, *ibid*, 1984, 23, 523; E. Lindner, K. E. Frick, R. Fawzi, W. Hiller, and M. Stangle, *Chem. Ber.*, 1988, 121, 1075; H. P. M. M. Ambrosius, J. H. Noordik, and G. J. A. Ariaans, *J. Chem. Soc., Chem. Commun.*, 1980, 832.
71. M. Nardelli, C. Pelizzi, and G. Pelizzi, *J. Organometal. Chem.*, 1977, 125, 161.
72. J. M. Sotiropoulos, A. Baceiredo, and G. Bertrand, *J. Am. Chem. Soc.*, 1987, 109, 4711.
73. K. R. Dixon, in 'Multinuclear NMR,' Ed. J. Mason, Plenum Press, New York, 1987, p. 369.
74. C. Lensch, W. Clegg, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 723.
75. Full details of the structure(s) are available from Dr. N. Burford, Dalhousie University. Some crystallographic details are given in Section 5: Appendix.
76. N. Burford, R. E. v. H. Spence, J. M. Whalen, R. D. Rogers, and J. F. Richardson, *Organometallics*, 1990, 9, 2854.
77. A. H. Cowley and R. A. Kemp, *Chem. Rev.*, 1985, 85, 367.
78. N. Burford, R. E. v. H. Spence, and J. F. Richardson, *J. Chem. Soc., Dalton Trans.*, In press.
79. N. Burford, R. E. v. H. Spence, and R. D. Rogers, *J. Am. Chem. Soc.*, 1989, 111, 5006.

80. L. F. Kasukhin, M. P. Ponomarchuk, T. V. Kim, and V. P. Kukhar, *Dokl. Akad. Nauk SSSR*, 1986, **290**, 1375.
81. . Kottgen, H. Stoll, A. Lentz, P. Pantzer, and J. Goubeau, *Z. Anorg. Allg. Chem.*, 1971, **385**, 56.
82. I. A. Nuretdinov, N. P. Grechkin, N. A. Buina, and L. K. Nuretdinov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1969, **7**, 1535; *Akad. Nauk. SSSR, Bulletin Division of Chemical Science*, 1969, 1423.
83. L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Chapman and Hall, London, 1975.
84. K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' 4th edn., Interscience, Toronto, 1986.
85. B. W. Royan, PhD Thesis, Dalhousie University, 1990 and references therein.
86. (a) J. J. Daly, *J. Chem. Soc.*, 1964, 4065; (b) C. Lensch and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 2855; (c) E. Fluck, G. Gonzalez, K. Peters, and H.-G. von Schnering, *Z. Anorg. Allg. Chem.*, 1981, **473**, 51; (d) S. Pohl, *Chem. Ber.*, 1976, **109**, 3122; (e) M. Bouchetiere, P. Toffoli, P. Khodadad, and N. Rodier, *Acta Crystallogr., Sect. B*, 1978, **34**, 384; (f) M. Bouchetiere, P. Toffoli, P. Khodadad, and N. Rodier, *Acta Crystallogr., Sect. B*, 1978, **34**, 3561.
87. See, for example, G. Cardinal, R. J. Gillespie, J. F. Sawyer, and J. E. Vekris, *J. Chem. Soc., Dalton Trans.*, 1982, 765; R. J. Gillespie, J. P. Kent, and J. F. Sawyer, *Inorg. Chem.*, 1990, **29**, 1251.
88. R. F. W. Bader, R. J. Gillespie, and P. J. MacDougall, in 'Molecular Structure and Energetics,' Vol 11, 'From Atoms to Polymers,' eds. J. F. Liebman and A. Greenberg, VCH, New York, 1989, p. 1.
89. M. R. Mazieres, T. C. Kim, R. Wolf, and M. Sanchez, *Zeitschrift*

- fur Kristallographie*, 1988, 184, 147.
90. D. H. Williams and I. Fleming, 'Spectroscopic Methods in Organic Chemistry,' 3rd Ed., McGraw-Hill, UK, 1980.
 91. V. Gutmann, Ch. Kamenater and K. Utvary, *Mh. Chem.*, 1965, 96, 836.
 92. See, for example, V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, in 'Topics in Phosphorus Chemistry,' vol. 5. eds. M. Grayson, and E. Griffith, Wiley-Interscience, New York, 1967.
 93. S. Pohl and B. Krebs, *Chem. Ber.*, 1977, 110, 3183.
 94. E. Niecke, R. Kroher, and S. Pohl, *Angew. Chem. Int. Ed. Engl.*, 1977, 16, 864; O. J. Scherer, N. T. Kulbach, and W. Glassel, *Z. Naturforsch., Teil B*, 1978, 33, 652.
 95. (a) O. J. Scherer, J. Kerth, and R. Anselmann, *Phosphorus Sulfur*, 1983, 18, 271; (b) O. J. Scherer and J. Kerth, *J. Organomet. Chem.*, 1983, 243, C33.
 96. M. Veith, B. Bertsch, and V. Huch, *Z. Anorg. Allg. Chem.*, 1988, 559, 73.
 97. L. Pazdernik, F. Brisse, and R. Rivest, *Acta Crystallogr., Sect. B*, 1977, 33, 1780.
 98. O. J. Scherer, M. Puttmann, C. Kruger, and G. Wolmershauser, *Chem. Ber.*, 1982, 115, 2076.
 99. A modification of the H-tube reaction vessel (A. L. Wayda and J. L. Dye, *J. Chem. Educ.*, 1985, 62, 356) made by J. Mueller.
 100. A. H. Cowley, R. A. Kemp, J. G. Lasch, N. C. Norman, C. A. Stewart, B. R. Whittlesey, and T. C. Wright, *Inorg. Chem.*, 1986, 25, 740; R. B. King and P. M. Sundaram, *J. Org. Chem.*, 1984, 49, 1784; M. J. S. Gynane, A. Hudson, M. F. Lappert, P. P. Power, and H. Goldwhite, *J. Chem. Soc., Dalton Trans.*, 1980, 2428.
 101. A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, 1958, 80, 1107; C. Steube and H. P. Lankelma, *J. Am. Chem. Soc.*, 1956, 78, 976.
 102. I. A. Nuretdinov, N. P. Grechkin, N. A. Buina, and L. K. Nuretdinov, *Akad. Nauk. SSSR, Bulletin Division of Chemical*

Science, 1969, 1423.

103. O. J. Scherer and R. Anselmann, *Inorg. Synth.*, 1989, 13, 8.
104. A modification of the procedure described by L. Kling (III), C. B. Colburn, and W. E. Hill, *J. Inorg. Nucl. Chem., Supplement*, 1976, 5.