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I. Synthesis and Characterisation of New Main Group Heteronaphthalenic Cations

II. An Investigation of the Triphenylphosphine Chalcogenide-Trichloroaluminium(III) Adduct Systems

by

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Submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

at

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Halifax, Nova Scotia

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Canada

To my parents, and to Britta

"The intensity of the conviction that a hypothesis is true has no bearing on whether it is true or not"

Sir Peter Medawar

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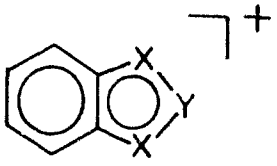
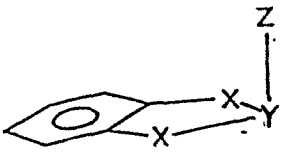
ABSTRACT

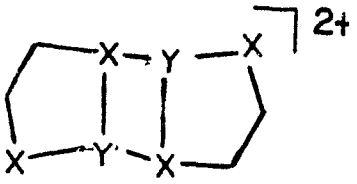
In part I of the thesis, the preparation and characterisation of a series of heteronaphthalenic cations, **1**, are described. **1** contain previously unreported $p\pi$-bonding between sulphur and the heavier elements of Group 15 (P, As, Sb). The cations are stabilised by a combination of positive charge, a weakly nucleophilic counter ion and a Hueckel, 10π-electron count. The thermodynamic stability of **1** is demonstrated by the near planar structures of the halothiazapnictoles, **2g(Cl),g(Br),h**. Attempts to prepare non-aromatic derivatives of **1** have resulted in the isolation of novel heterocyclic dications, **21,24**.



1 X = NR, S, Se
Y = P, As, Sb



2g(Cl),g(Br),h X = NH, S
Y = P, As; Z = Cl, Br



21 X = S, Y = As
24 X = NMe, Y = As

Part II of the thesis contains a comprehensive spectroscopic and structural study of the Lewis acid-base adducts, $Ph_3PCh.AlCl_3$ (Ch = O, S, Se). $Ph_3PO.AlCl_3$ exhibits a unique linear backbone both in solution and in the solid state. However, $Ph_3PS/Se.AlCl_3$ are severely bent at the chalcogen centre. The contrasting modes of acid coordination are rationalised in terms of the different contributions of π- and σ-components to the bonding schemes of the free bases.

LIST OF ABBREVIATIONS USED IN TEXT

fw	formula weight	^{o}C	degrees Celcius
mpt	melting point	^{o}	degree
bpt	boiling point	min	minute
dpt	decomposition point	m	medium
pm	picometre	w	weak
IR	infrared	s	strong
NMR	nuclear magnetic resonance	v	very
MCD	magnetic circular dichroism	sh	shoulder
UV	ultraviolet	br	broad
h	hour	Ph, Me	phenyl, methyl
a.u.	atomic unit	MO	Molecular Orbital
J	joule	λ	wavelength
cm	centimetre	mm	millimetre
nm	nanometre	o.d.	outer diameter
mol	mole	M	molar
mmol	millimole	ε	extinction coefficient
ppm	part per million	Hz	hertz

AO	Atomic Orbital
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied molecular Orbital
FMO	Frontier Molecular Orbital
CSA	Chemical Shielding Anisotropy
PPP	Pariser, Parr, Pople

ACKNOWLEDGEMENTS

First off, I would like to thank Neil Burford, who has been a quite outstanding supervisor. It is hard to believe that three years ago the "Burford Group" consisted of him, me and an empty lab on the 5th floor. Special thanks also to Rupert Spence and Bill Power for their help and friendship during my time at Dalhousie.

I would also like to acknowledge here the assistance of the many co-workers who have contributed to the research reported in this thesis: Anne Dipchand for her excellent work on **1f,g**$AlCl_4$; Marc Whalen for his preliminary investigations into **17**$AlCl_4$; Patrick Cho for producing "buckets" of **1c**$AlCl_4$; Chris Levy for his efforts on the very difficult **2i/1i**$AlCl_4$ system; Jurgen Mueller for his glass-blowing expertise; Ron Curtis and Dr. Rod Wasylishen for the solid state ^{31}P NMR spectra of **1b,c,g**$AlCl_4$; Dr. Josef Michl for allowing me to come to the University of Texas at Austin and obtain MCD specta of **1**$AlCl_4$, and Dr. Jacek Waluk for helping me to use the spectro-polarimeter (also thanks to Brad Arnold and Allan McKinley for looking after me in Austin); Dr. Don Hooper, Bruce Macdonald, Maureen Yeats and Rupert for running many of the solution NMR spectra (all solution spectra were obtained at the Atlantic Regional Magnetic Resonance Centre, Dalhousie University); Dr. Kathy Darvesh for her assistance with the molecular orbital calculations; Drs. T. Stanley Cameron and Tony Linden (Dalhousie University), Robin Rogers (Northern Illinois University), Peter White (University of New Brunswick), John Richardson (University of Louisville) and Rosemary Hynes and Eric Gabe (National Research Council,

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PART I: SYNTHESIS AND CHARACTERISATION OF NEW MAIN GROUP HETERO-NAPHTHALENIC CATIONS

I.1 INTRODUCTION

Part I of the thesis describes the preparation and characterisation of new heteronaphthalenic cations which contain thermodynamically stable $p\pi$-$p\pi$ bonding between the heavier elements of Groups 15 and 16. The purpose of this introduction is to demonstrate that this work represents a significant contribution to the development of Main Group chemistry.

The chemistry of carbon, or organic chemistry, is by far the most extensive and diverse branch of the chemical sciences.[1] However, many of the properties exhibited by carbon are present in the chemistry of other elements. For example, a number of the heavier Main Group elements are capable of catenation, in particular sulphur, selenium and phosphorus, while first row non-metals form strong π bonds.[2,3] One important consideration is that carbon compounds display a kinetic stability to chemical oxidation which allows them to survive in the Earth's oxidising atmosphere.[4] However, the unique thermodynamic balance between σ- and π-bonding in organic chemistry is believed by many chemists to be the key to carbon's protean abilities, as carbon is the only element which can form energetically competitive σ- and π-bonds, both to itself and to other elements such as nitrogen and oxygen.[5]

In contrast to carbon (and the other first row non-metals), the chemistry of the heavier Main Group elements is dominated by σ-bonding and has been severely restricted by the dearth of stable $p\pi$-bonds.[2,3] Indeed, the scarcity of heavy element $p\pi$-bonding led to the postulation of the "Double Bond Rule",[6] which asserted that elements with a valence

principal quantum number of three or greater would not form stable $p\pi$-$p\pi$ bonds. Compounds containing such bonds were often referred to as "non-existent".[7] However, the last 15 years have witnessed the preparation and characterisation of stable $p\pi$ bonds between many of the heavier Main Group elements and this research represents some of the most exciting chemistry of the last decade.

The dichotomy in bonding characteristics within the Main Group has many common manifestations. Consider, for example, the elements of the first two rows of Groups 15 and 16. Elemental oxygen and nitrogen occur as multiply bonded dimers and, as a result, are gases at normal temperatures and pressures. However, the most thermodynamically stable forms of sulphur and phosphorus under ambient conditions are fully σ-bonded polyatomic molecules which occur as solids.[2,3]

As with any generalisation, there are some well known exceptions to the "Double Bond Rule". Sulphur and selenium can form $p\pi$-bonds with carbon, for example CS_2 and CSe_2, but such bonds are often not as stable as their first row analogues.[8]

Several theories have been advanced to rationalise the "Double Bond Rule" and for detailed accounts the reader is referred to important papers by Kutzelnigg[5(a)] and Schmidt *et al.*[9] However, some salient points are worthy of discussion here.

In 1948, Pitzer[10] proposed that since heavier elements have longer bonds, their $p\pi$-$p\pi$ overlap integrals should be less than those of first row elements. Chemists often assume that bond strengths are proportional to overlap integrals and this qualitative approach is still frequently used to account for the lack of $p\pi$-bonds between the heavier

p-block elements. In fact, this postulate is incorrect. Calculations carried out by Mulliken[11] in 1950, and confirmed recently at higher levels of computation by Gordon's group,[9] show that overlap integrals do not decrease significantly when heavy atoms are used in place of their first-row counterparts. Indeed, the more recent work has demonstrated that the $p\pi$-$p\pi$ overlap integral is larger for the phosphorus-phosphorus (-P=P-) double bond than for the analogous nitrogen system.[9]

Another common fallacy is that the σ-bond strengths are greater for heavier elements. Actually, this is not always the case, as C-C and N-N σ-bonds (368 and 268 $kJmol^{-1}$, respectively) are stronger than their Si-Si and P-P counterparts (309 and 255 $kJmol^{-1}$, respectively).[9] A parallel trend is also observed for many heteroatomic bonds; for example, phosphorus-halogen bonds (P-X: X = F, 490 $kJmol^{-1}$; X = Cl, 326 $kJmol^{-1}$; X = Br, 264 $kJmol^{-1}$; X = I, 184 $kJmol^{-1}$).[12] Nevertheless, the heavier non-metals are reluctant to form $p\pi$-$p\pi$ bonded systems as they are themselves significantly weaker than the σ-bonded alternatives.

The most satisfactory explanation for the σ-bond preference of the *p*-block elements is provided by Kutzelnigg,[5(a)] who contends that the heavier non-metals behave "normally". The σ-bonds of the anomalous first row elements are greatly weakened by lone pair, or core, electron repulsions. The repulsions are very much reduced for the heavier non-metals because of the more diffuse nature of the atomic core. Therefore, the predominance of the π-bond in the first row is a result of σ-bond weakness as opposed to π-bond strength, as the effectiveness of π-bonding does not appear to be significantly affected by increased lone pair repulsions. Carbon forms significantly stronger σ-bonds than

the other first row non-metals as it has much weaker core electron repulsions and this electronic property is revealed experimentally in the energetic balance between σ- and π-bonding found in organic chemistry.

The initial $p\pi$ multiple bonds involving heavier Main Group elements were formed to first row elements, in particular carbon, and are listed in Table I.1.i. The isolation of a stable (*i.e.* isolable and "indefinitely" stable at room temperature under a suitably inert atmosphere) carbon-Group 15 element $p\pi$ bond was achieved by Dimroth as far back as 1964 when his group prepared the first phosphacyanine.[26] Since then many other compounds containing such bonds have been prepared, such as the pnictabenzenes[27] and the phosphenes.[28] Even sterically protected phosphorus-carbon[29] and arsenic-carbon triple bonds[30] have been synthesised. Many of these compounds have shown great versatility as synthetic reagents.[28(c),29] Carbon-Group 14 multiple bonding proved considerably more elusive as it was not until 1981 that a stable silene was isolated.[13] For more details, the reader is referred to any of the many excellent reviews available on this topic.[15(a),31]

With the exception of boron-chalcogen[21] and nitrogen-sulphur systems,[23] the preparation of stable $p\pi$-bonds between the heavier *p*-block elements and the first row elements other than carbon has proved difficult and reports of the synthesis of compounds containing such bonds are relatively recent. However, rapid progress in this field is anticipated especially for boron-Group 15 and nitrogen-Group 14 bonds as the initial breakthroughs have now been achieved.[14,15,17,25]

The isolation of stable compounds containing a double bond between

Table I.1.i. Stable $p\pi$-Bonds Between the First Row Non-Metals and the Heavier Main Group Elements

		HEAVY MAIN GROUP ELEMENTS		
		Group 14	Group 15	Group 16
FIRST	B		P=B[17]	S=B, Se=B[21]
ROW	C	Si=C[13] Ge=C[15(a)]	P=C, As=C, Sb=C[6b]	S=C, Se=C, Te=C[22]
NON	N	Si=N,[14] Ge=N[15] (Sn=N)[16]	P=N,[18] As=N[19] (Sb=N)[16]	S=N,[23] Se=N[24]
METALS	O		P=O[20]	

two heavy *p*-block elements has relied primarily on either the use of bulky substituents, which impart kinetic stability, or positive charge, where the stabilisation is thermodynamic in origin. This review shall consider first the better known of the two approaches: steric stabilisation.

Steric stabilisation of a double bond between two heavier Main Group elements was first achieved in 1976 by Lappert and co-workers,[32] who determined the solid state structure of the hindered stannylene, $\{Sn[CH(SiMe_3)_2]_2\}$ (and that of the analogous germylene), to be dimeric, with two tricoordinate tin centres and a tin-tin multiple bond. However, this bond is not truly olefinic in character as neither tin centre is planar and there is an almost negligible shortening of the tin-tin bond when compared to a regular σ-bond.[33] Therefore, it was not until 1981 that genuine, stable heavy element double bonds were prepared when West and co-workers reported the first silicon-silicon double bond[5(b),34] and Yoshifugi's group published the isolation and crystal structure of a diphosphene.[35]

Many more such bonds have now been prepared, usually through relatively simple metathetical techniques, and these are listed in Table I.1.ii.[36] Sterically demanding ligands, such as mesityl (1,3,5-trimethylbenzene), supermesityl (1,3,5-tri-*t*-butylbenzene) or trimethylsilyl, afford kinetic stabilisation by preventing the close contact of monomeric units which would otherwise lead to the formation of thermodynamically stable fully σ-bonded products.[42]

Table I.1.ii clearly demonstrates an important limitation to this method of stabilisation as the double bonds isolated by this approach

TABLE I.1.ii. Sterically Stabilised $p\pi$ Bonds between the Heavier Main Group Elements

Si=Si[5(b)]	Si=P[39]	P=P[35,38]	As=P[38]
Ge=Ge[37]	Ge=P[40]	As=As[38]	Sb=P[38]
	Sn=Sn[32]	Sn=P[41]	

are restricted to the heavier elements of Groups 14 and 15. Unfortunately, the electron rich nature of the elements on the right hand of the *p*-block excludes the possibility of a steric shield. Instead, many research groups, in particular those of Gillespie, Passmore and Corbett, have made use of molecular positive charge to stabilise $p\pi$-bonding between the heavier Group 16 and 17 elements.[43] Salts containing cations such as Ch_4^{2+} (Ch = S, Se, Te),[44] X_2^+ (X = Br, I)[45] and sulphur/selenium iodides[46] have been prepared and shown, mainly through structural studies, to contain multiple bond character. Many of the above compounds were isolated and characterised before those displaying sterically stabilised Group 14 and 15 multiple bonds. However, their significance, both in terms of primogenicity and in the potential generality of the method, has been somewhat overlooked until recently.[43(c)]

It has been shown that, although charge provides an inherent kinetic barrier to oligomerisation, these delocalised π-bonded species are thermodynamically stable with respect to potential σ-bonded decomposition products.[43(c)] Indeed, it is important to recognise that charge alone is not necessarily sufficient to prevent interaction between two such cations. For instance, the dimerisation of I_2^+ to I_4^{2+} through a π^*-π^* interaction is well documented.[43(c),47] The stabilising influence of the positive charge is thought to derive from less diffuse $p\pi$-orbitals which are able to form a more effective π-overlap.[43(c)] In complete contrast to the sterically protected systems, the use of positive charge has been limited to the preparation of chalcogen and/or halogen multiple bonds. Additionally, it should be noted that the

polyatomic Main Group cations can only be isolated in the presence of complex, weakly basic anions such as tetrachloroaluminate(III) and hexafluoroarsenate(V).[43(c)]

Aromaticity has also been invoked to account for the stability of some of the chalcogen ring systems. For example, the Ch_4^{2+} cations, which at least formally possess 6π-electrons, are planar and exhibit short Ch-Ch bonds.[44] Such conjectures have been supported by semi-empirical INDO-type calculations, which clearly demonstrate a delocalised, Hueckel π-manifold for these systems.[48] Therefore, Hueckel resonance energy may play a role in the stabilisation of such cations.

The greater number of compounds containing heavy element *p*π-bonding has been stabilised by using either one or other of the preceeding methodologies. However, other systems demonstrating Main Group multiple bonding have been identified. Of these, the pnictogen Zintl phase anions, such as Pn_4^{2-} (Pn = As, Sb, Bi)[49] which are isovalent with the Ch_4^{2+} cations,[44] were the first to be characterised and remain the most important. Indeed, Bi_4^{2-} represents the only characterised bismuth *p*π bond. These anions, together with the related P_6^{4-} and As_6^{4-} systems,[49] are planar, have bond orders greater than one and are believed to contain significant *p*π-*p*π bonding. Charge cannot account for the preparation of these rather unusual compounds, at least in the sense proposed for the chalcogen/halogen cations. However, in light of their relationship to the Ch_4^{2+} cations, it can be theorised that their Hueckel electron counts (6π-electrons in Pn_4^{2-}, 10π-electrons in Pn_6^{4-}) contribute significantly to their stability. In this context, it should be noted that Ch_6^{4+} cations do not occur as planar, π-bonded

units. Such systems would be anti-aromatic, possessing 8π-electrons and, in fact, Te_6^{4+} has a trigonal prismatic structure.[50]

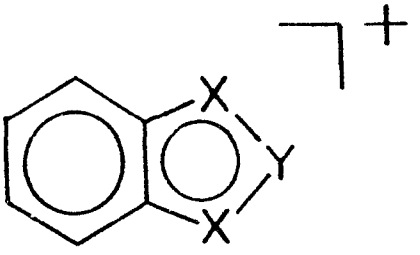
As yet, Zintl phases represent a somewhat uncertain area of chemistry, existing in a No-man's land intermediate to metallic and ionic bonding. Consequently, the factors determining the stability and composition of these systems are still not well understood. Indeed, there are almost as many definitions as to what constitutes a Zintl phase as there are reviews on the subject. However, work is in progress to further utilise the potential of anionic environments to stabilise heavy element multiple bonds through more systematic approaches. Phosphorus, in particular, appears adept at forming such bonds.[51]

Recent research has also demonstrated that it may be possible to stabilise olefinic heavy element double bonds without resorting to sterically demanding substituents. It has been established that heavy element *pπ*-bonding can be stabilised intramolecularly through the presence of a basic functional group such as an amine.[52] In addition, the use of substiuents with unusual electronic properties, in particular the trifluoromethyl (CF_3) group, can stabilise multiple bonds between nitrogen and the heavier pnictogens.[15(b),18(a),19(a)] An extension of this methodolgy to include two heavy Group 15 elements in the multiple bond is expected.

At the outset of the research reported in thesis, stable compounds containing *pπ*-*pπ* bonds between the heavier elements from the opposite sides of the *p*-block were unknown.[53] This was not due to a lack of effort on the part of synthetic chemists. For example, unsuccessful attempts had been made by workers to prepare sterically stabilised Group

14/15-Group 16 $p\pi$-$p\pi$ double bonds.[54,55] Therefore, although it had been possible to capture reactive intermediates containing Group 15-Group 16 multiple bonds either as transition metal complexes[56] or using organic trapping reagents,[57] a template incorporating stabilising features which would allow general, stable $p\pi$-bonding throughout the *p*-block had not been developed (Scheme I.1). As a consequence, such bonds remained the realm of matrix isolation and gas phase chemists.[31,58]

Part I of this thesis describes the identification of such a molecular template. Use of the bicyclic, heteronaphthalenic cation, **1**, (a framework known for several years with mainly or entirely first row elements as heteroatoms)[59-65] has allowed the preparation of thermodynamically stable $p\pi$-bonds between the heavier elements of Groups 15 and 16 through a combination of positive charge and a Hueckel, 10π-electron count. A detailed account of the synthesis, spectroscopic and structural characterisation of several heavy element derivatives of **1** is provided and the results of studies aimed at determining the importance of aromaticity to the stabilization of the framework are reported.



1 X = NR, S, Se

Y = P, As, Sb

SCHEME I.1

Methods of Stabilising Heavy Element $p\pi$-Bonds

Steric Stabilisation	Homo- and Heteroatomic Cations
Zintl Anions	
Al, Si, P	S
Ge, As	Se, Br
Sn, Sb	Te, I
Bi	

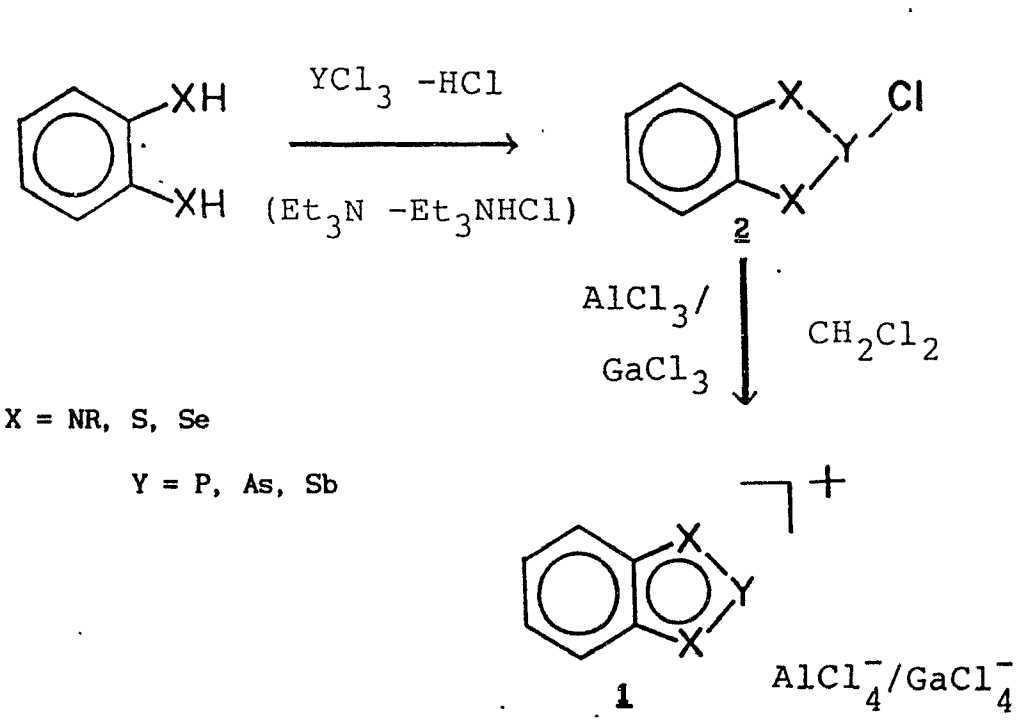
I.2. RESULTS AND DISCUSSION

I.2.1. General Synthetic Considerations

1.2.1(a). Preparation of the 2-Halo-1,3,2-benzodithia-, diaza- and thiaza-pnictoles, 2b-i.

2b-f are known compounds and are made using the literature procedures or minor modifications thereof.[66,67,68] The preparation of 2g(Cl) is only briefly mentioned, without details, by Pudovik and co-workers.[69] 2g(Br),h,i are new compounds and are obtained using the standard cyclisation procedures reported for the syntheses of their literature analogues [Scheme I.2.1(a)]. If the product contains an amine functionality, a base such as triethylamine is added to the

SCHEME I.2.1(a).

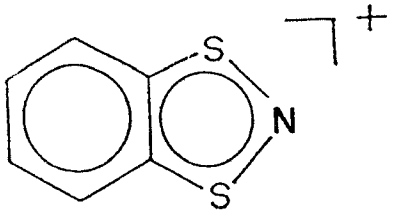


reaction mixture to remove the HCl released in the methathetical process. The much reduced basicity of dicoordinate sulphur centres allows the isolation of the dithia- derivatives without the addition of triethylamine. The instability of *o*-benzenediselenol requires the *in situ* generation of the dilithiated species immediately prior to reaction with PCl_3. The desired products are purified either by distillation under reduced pressure or by recrystallisation. The halobenzopnictoles are air- and moisture-sensitive and must be stored under an inert gas atmosphere or *in vacuo*. Physical characterisation data for the new compounds can be found in Table I.2.1(a). Full experimental details are given in Part III.

1.2.1(b). Synthesis of the New Heteronaphthalenic Cations, 1b-i, as Tetrachloroaluminate or Tetrachlorogallate Salts.

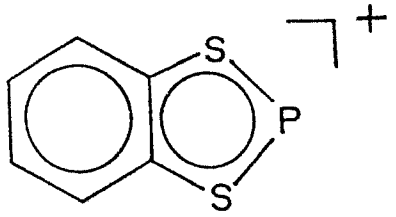
Cations **1b-i** are prepared, at room temperature and under rigorously anaerobic and anhydrous conditions, by the addition of **2b-i** in CH_2Cl_2 to a stirred suspension/solution of an equimolar quantity of alumimium (III) or gallium(III) chloride,[70] also in CH_2Cl_2 [Scheme I.2.1(a)]. This approach has been used successfully to prepare dicoordinate amino-substituted phosphenium cations, and has recently been extended to include related arsenium, stibenium and bismuthenium salts.[18(d),19(b)] Physical and analytical data are given in Table I.2.1(b). Detailed descriptions of the synthesis of each salt can be found in Part III.

It has been observed that $AlCl_3$ in CH_2Cl_2 can function as an oxidising agent if the valence electron binding energy of the substrate is less than approximately 7.9 eV.[71] However, the binding energy for benzo π-electrons is typically 9 eV[72] and, although this will be reduced



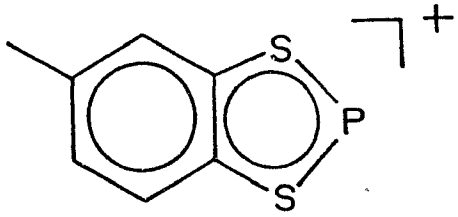
1a

1,3,2-Benzodithiazolium



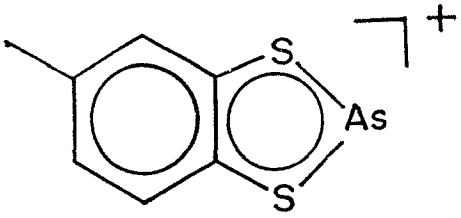
1b

1,3,2-Benzodithiaphospholium



1c

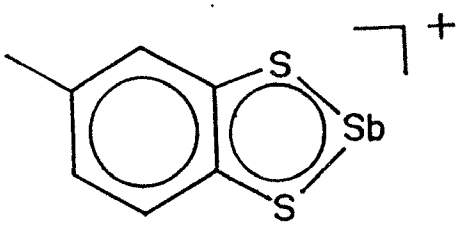
5-Methyl-1,3,2-benzodithiaphospholium



1d

5-Methyl-1,3,2-benzo-

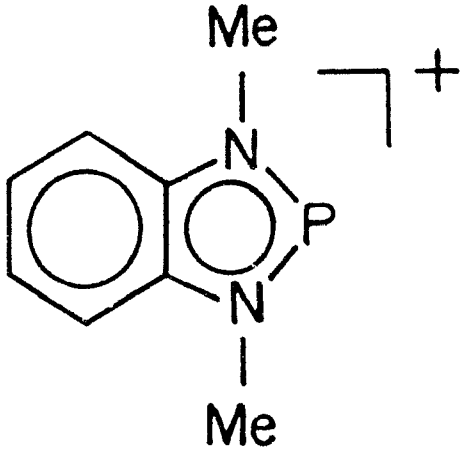
dithiarsolium



1e

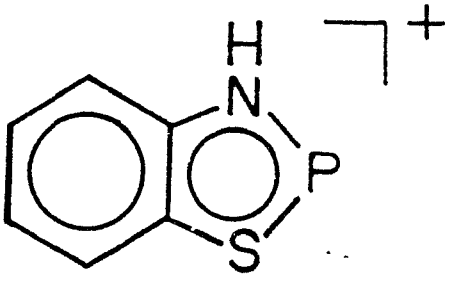
5-Methyl-1,3,2-benzo-

dithiastibolium



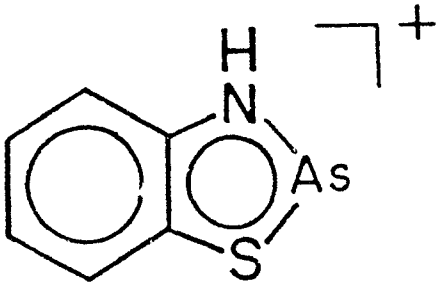
1f

N,N'-Dimethyl-1,3,2-benzo-diazaphospholium



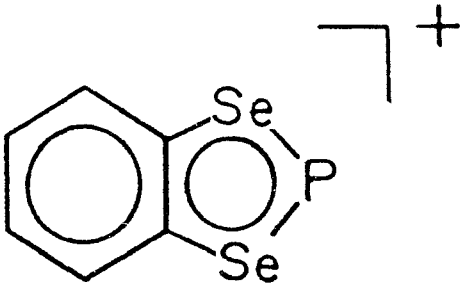
1g

1,3,2-Benzazathiaphospholium



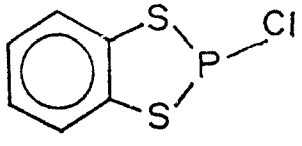
1h

1,3,2-Benzothiazarsolium

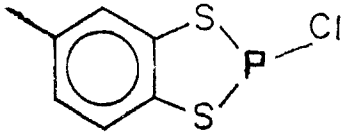


1i

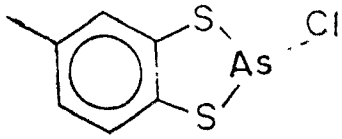
1,3,2-Benzodiselenaphospholium



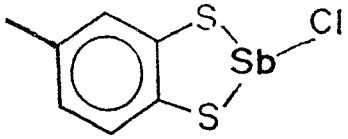
2b



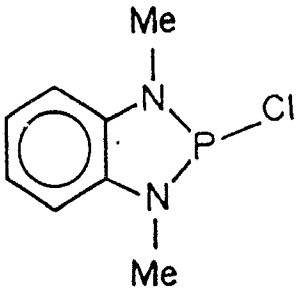
2c



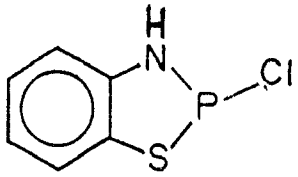
2d



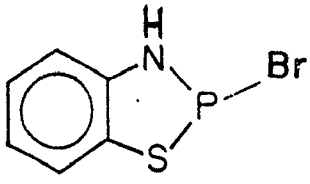
2e



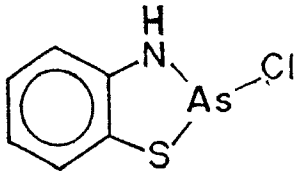
2f



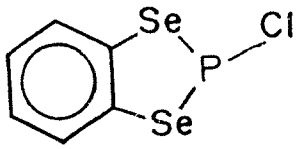
2g(Cl)



2g(Br)



2h



2i

TABLE I.2.1(a). Physical Characterisation Data for the New Halobenzopnictoles, 2g(Cl),g(Br),h

	Mpt. (^{o}C)	Elemental Analyses (%)	
		Calcd.	Found
2g(Cl)	83-84 (Et_2O)	C, 38.01; H, 2.66; N, 7.39.	C, 37.77; H, 3.14; N, 7.34.*
2g(Br)	139-142 (CH_2Cl_2/Et_2O, 1:1)	C, 30.79; H, 2.16; N, 5.99.	C, 30.85; H, 2.38; N, 5.93.
2h	135-137 (CH_2Cl_2)	C, 30.85; H, 2.16; N, 6.00.	C, 30.63; H, 2.19; N, 5.91.

* Analysis sample recrystallised from CH_2Cl_2

TABLE I.2.1(b). Physical Characterisation Data for Derivatives of the Heteronaphalenic Cations, 1

	Mpt. (°C)	Elemental Analyses (%)	
		Calcd.	Found
1bAlCl$_4$	*ca.* 80, dec	C, 21.18; H, 1.18; S, 18.82; P, 9.12; Al, 7.94; Cl, 41.76.	C, 21.02; H, 1.22; S, 18.71; P, 8.97; Al, 8.15; Cl, 41.43.
1cAlCl$_4$	*ca.* 107, dec	C, 23.73; H, 1.69; S, 18.08; P, 8.76.	C, 23.72; H, 1.83; S, 17.78; P, 8.83.
1cAlCl$_x$Br$_{4-x}$	*ca.* 75, dec (CH_2Cl_2/*n*-hexane)		
1dAlCl$_4$	121-123	C, 21.13; H, 1.52; S, 16.11; As, 18.83.	C, 20.97; H, 1.78; S, 15.82; As, 18.50.
1eAlCl$_4$	*ca.* 145, dec (ppts. from CH_2Cl_2)		
1eGaCl$_4$	*ca.* 130, dec (ppts. from CH_2Cl_2)		
1fAlCl$_4$	126-128		
1gAlCl$_4$	123-125	C, 22.33; H, 1.57; N, 4.34.	C, 22.12; H, 1.88; N, 4.33.
1hAlCl$_4$	125-128	C, 19.64; H, 1.38; N, 3.82; S, 8.74.	C, 19.78; H, 1.24; N, 3.80; S, 8.87.

All salts obtained in pure form by recrystallisation from CH_2Cl_2 unless otherwise stated.

significantly in **2** by interaction between the delocalised π-cloud of the aromatic ring and the heteroatom lone pairs, there is no evidence of radical formation in the reactions of **2** with $AlCl_3$ in CH_2Cl_2.

$AlCl_3$ and some derivatives of **2** demonstrate only poor solubility in CH_2Cl_2.[73] However, on combination of the two reactants, vigorous stirring results in homogeneous reaction mixtures. In general, the initial colourless or pale yellow solutions of the reactants become bright yellow/orange on addition to the Lewis acid. The majority of **1**$AlCl_4$ can be isolated in pure form by slow evaporation of solvent from the reaction mixture. However, **1a**$AlCl_4$ (partially) and **1d**$AlCl_4/GaCl_4$ (mostly) precipitate out of the reaction mixture shortly after complete addition of reactants. The **1a**$AlCl_4$ precipitate can be recrystallised quantitively as pure crystalline material. However, this is not possible for **1d**$AlCl_4/GaCl_4$ which appear to be rather insoluble and unstable in CH_2Cl_2 solution [see Section I.2.2.(c)]. As yet, **1i** has only been prepared *in situ*.

The range of solvents in which derivatives of **1** can be manipulated is restricted by the high reactivity and ionic structure of the salts. For instance, **1c**$AlCl_4$ is totally insoluble in *n*-heptane, **1c**$AlCl_4$ and **d**$AlCl_4$ are destroyed by carefully dried acetonitrile and attempts to recrystallise **1e**$AlCl_4$ from SO_2 give a white solid, presumably an oxidation product. The thermodynamic strength of the Al(Ga)-O bond rules out the use of organic oxygen containing solvents, such as ethers.[74]

All derivatives of **1** are extremely air- and moisture- sensitive, but are stable when handled in an atmosphere from which water and

oxygen have been rigorously excluded. Samples stored as solids in glass tubes under N_2 have shown no visible signs of decomposition over the last two years.

I.2.1(c). Concentration Dependence of Chloride Abstraction Process

Studies on the **2b,c**/$AlCl_3$/**1b,c**$AlCl_4$ systems demonstrate that the yield and ease of isolation of product are influenced by the concentration of the precursor chlorophosphole. High concentrations give a much darker, red reaction solution and, on workup, lead to low (< 50%) yields of the desired product, and substantial quantities of an unidentified, air-sensitive red oil. In contrast, highly dilute reaction solutions give a much paler orange/yellow colour and result in almost quantitative yields of the pure salt. Furthermore, when only a tenth of the required stoichiometric amount of $AlCl_3$ is used, a red oil is the sole product. However, on addition of the remaining nine-tenths to the reaction mixture, it is possible to obtain crystalline **1a**$AlCl_4$ in upto 47% isolated yield.

These results indicate that the cationic species rapidly reacts with the chlorophosphole and that the reaction is only partially reversible. The exact nature of the interaction between **1b,c** and **2b,c** is examined more thoroughly in Section I.2.5. Although these observations refer specifically to **1b,c**, they are believed to be generally applicable to the preparation of all derivatives of **1**. Consequently, all such halide abstraction reactions should be carried out under conditions of high dilution.

I.2.2. Spectroscopic Characterisation and Comparison of 1 and 2.

Table I.2.2. provides a summary of the spectroscopic techniques used to establish the identities of the salts of 1 and the corresponding halobenzopnictoles, 2, both in the solid state and solution.

I.2.2(a). Infra-Red Spectroscopy

Full listings of ν_{max} for the infra-red spectra are tabulated in Part III.

The ionic nature of the derivatives of 1 in the solid state is clearly demonstrated by spectral bands due to the complex anion. All tetrachloroaluminate salts show a very strong absorption at approximately 485 cm^{-1}, a result of ν_3 fundamental vibration of the tetrahedral anion.[75] The analogous band for the tetrachlorogallate anion is observed at 370 cm^{-1} in the spectrum of 1d$GaCl_4$, while peaks consistent with $MoCl_6^-$ and $AlCl_xBr_{4-x}^-$ are present in the spectra of the respective salts of 1b.[75] In addition, absorptions observed for 2, which are associated with the pnictogen-halogen stretching vibrations (2b, 415; 2c 405; 2d, 310;[67] 2e, 275;[67] 2g(Cl), 295; 2g(Br), 250; 2h, 230 cm^{-1}), are absent from the spectra of the salts. Strong peaks are found at 760 cm^{-1} for the C-H out-of-plane deformations of the four adjacent aromatic hydrogens in the spectra of 1b,f-i, while the bands due to the 1,3,4-substitution pattern of hydrogens are present between 810 and 815 cm^{-1} in the spectra of the tolyl derivatives.[76]

The infra-red spectra of 1c$AlCl_4$ and 1d$AlCl_4/GaCl_4$ are important to their identification in the solid state, as X-ray crystal structures determinations and satisfactory elemental analyses (1d$AlCl_4/GaCl_4$) have not been obtained. The spectral evidence is most clearly demonstrated

TABLE I.2.2. Spectroscopic Techniques Employed in the Characterisation of Derivatives of 1 and 2

	IR	Mass Spec.	Multinuclear NMR Spectroscopy			
			^{31}P	^{27}Al	^{1}H	^{13}C
1b$AlCl_4$	X	X	X	X	X	X
1c$AlCl_4$	X	X	X	X	X	X
1c$AlCl_xBr_{4-x}$	X	X	X		X	
1c$MoCl_6$	X					
1d$AlCl_4$	X	X		X	X	X
1e$AlCl_4$	X	X		X	X	X
1e$GaCl_4$	X	X			X	
1f$AlCl_4$	X		X	X		
1g$AlCl_4$	X	X	X	X	X	X
1h$AlCl_4$	X	X		X	X	X
1i$AlCl_4$			X	X		
2b	X	X	X		X	X
2c	X	X	X		X	X
2d	X	X			X	X
2e	X	X			X	X
2f[68]					X	X
2g(Cl)	X	X	X		X	X
2g(Br)	X	X	X		X	X
2h	X	X			X	X
2i	X		X		X	X

TABLE I.2.2. Spectroscopic Techniques Employed in the Characterisation of Derivatives of 1 and 2 (Continued)

	Electronic Absorption Spectroscopy		Solid State ^{31}P NMR
	UV/Visible	MCD	
1b$AlCl_4$	X	X	X
1c$AlCl_4$	X	X	X
1d$AlCl_4$	X	X	
1g$AlCl_4$	X	X	X
1h$AlCl_4$	X	X	
2c	X		
2g(Cl)	X		
2g(Br)	X		
2h	X		

by referring to Fig. I.2.2(a), which compares the infra-red spectrum of the fully characterised **1c**$AlCl_4$ with those of **1d**$AlCl_4$ and **1e**$AlCl_4$. The similarity of these spectra indicates that the structures of **1d** and **1e** are closely related to that of **1c**. Furthermore, the spectrum of **1e**$GaCl_4$ differs from that of **1e**$AlCl_4$ only in the absorption bands associated with the anions.

1b-e,g,h contain previously unknown $p\pi$-bonds between the heavier pnictogens and sulphur, and each should display new infra-red absorptions. However, the spectra do not exhibit strong bands in the region where such absorptions would be anticipated, *ca.* 800-500 cm^{-1}.[77] This is not unexpected considering the similar electronegativies of phosphorus, arsenic, antimony and sulphur.[78]

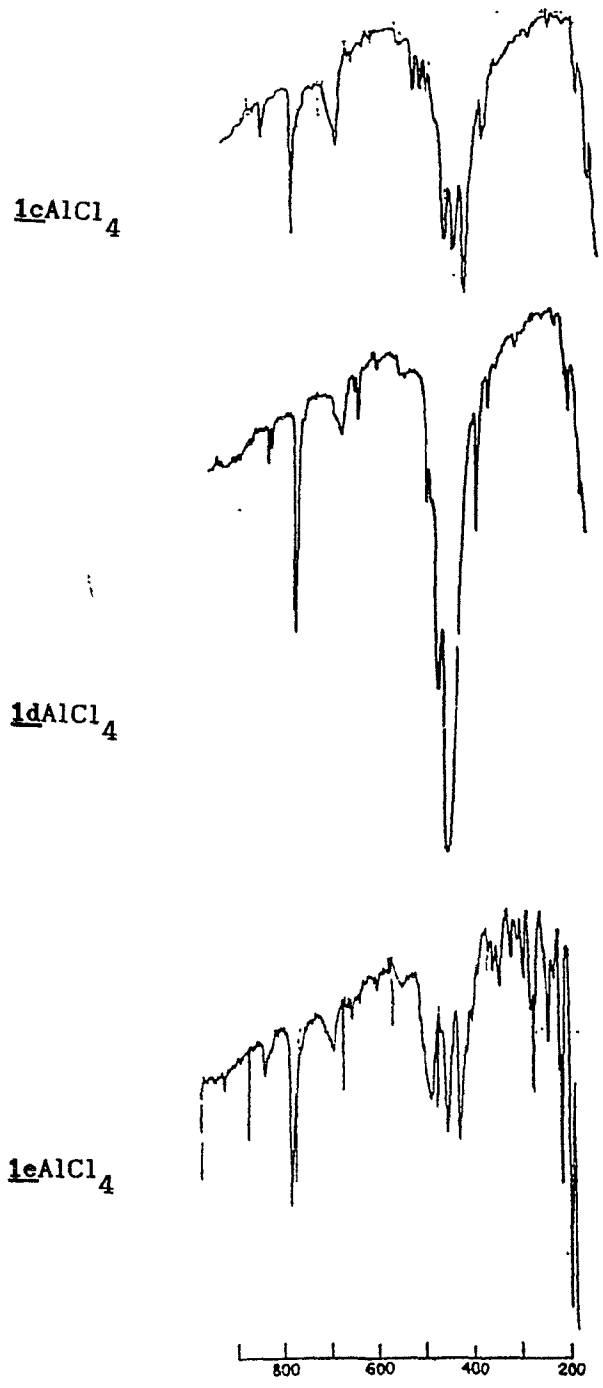
I.2.2(b). Mass Spectrometry

Full listings of the major fragmentation peaks are proved in Part III.

The mass spectra of the **1b-e,g,h** salts are essentially identical to those of the corresponding chlorobenzopnictoles. In common with other non-metal salts,[79] the data are consistent with halide ion reabstraction in the mass spectrometer source. Indeed, the $AlCl_xBr_{4-x}$ salt of **1c** gives a mass spectrum indicative of both chloride and bromide reabstraction. Therefore, the base peaks of the dithiabenzopnictolium, **1b-e**, salts result from loss of halogen radical from the precursor halide radical cations. No significant fragmentation of the base peaks is observed at an ionising voltage of 70 eV, implying a high gas-phase stability for the cations **1b-e**.[80]

The mass spectra of **1g,h** also demonstrate halide ion reabstraction

FIGURE I.2.2(a). Infra-red Spectra of 1c,d,eAlCl$_4$ (200 - 1000 cm^{-1})



in the source. However, the base peaks obtained for both salts correspond to loss of HCl from the pnictoles, although loss of Cl may remain a significant fragmentation pathway. Again, little further fragmentation is observed.

I.2.2(c). Multinuclear Solution NMR Spectroscopy

Table I.2.2(c)i provides multinuclear (^{1}H, ^{13}C, ^{31}P and ^{27}Al) NMR data for **1**, **2** and related systems.

The ^{1}H NMR spectra of the benzo derivatives, **1b,g,h** and **2b,g(Cl),g(Br),h,i**, have spectral patterns indicative of AA'BB'(X) spin systems for the species with C_{2v}/C_s symmetry and ABCD(X) systems for the asymmetric derivatives. The proton spectra of the tolyl derivatives, **1c-e** and **2c-e**, are first order and the proton-proton coupling constants are reported in Table I.2.2(c)i. The *ortho* coupling constants observed for the cations (*ca.* 8.5 Hz) are significantly larger than those of the analogous halobenzopnictoles (*ca.* 8.1 Hz) and this is consistent with a change from a 6π- to a 10π-aromatic system.[81] The spectra also clearly show the aromatic protons of **1** to be significantly deshielded from the precursor neutral halides, indicative of effective delocalisation of positive charge throughout framework **1**. Furthermore, the chemical shift ranges are similar to those of the 1,3-benzodithiolium, **1j**, 1,3-benzazathiolium, **1k**, and 1,3,2-benzodithiazolium, **1a**, systems [Table I.2.2(c)i], all of which are regarded as 10π-electron, aromatic systems.[59,60,64] Similar deshielding is also observed in the ^{13}C spectra [Table I.2.2(c)i].

TABLE I.2.2(c)i. ^{1}H, ^{13}C, ^{31}P and ^{27}Al NMR Data for 1, 2 and Related Compounds[+]

^{1}H (361.0 MHz)

1b$AlCl_4$	1c$AlCl_4$	1c$AlCl_xBr_{4-x}$	1d$AlCl_4$	1e$AlCl_4$	1e$GaCl_4$
8.25-7.32	8.54 (d)	8.43	8.33 (d)	See Text and	
(AA'BB'X)	8.46 (s)	8.35	8.26 (s)	Figure I.2.2(c)	
$^{3}J_{HH}$= 6	7.92 (d)	7.83	7.75 (d)		
$^{2}J_{HH}$= 2.5	2.72 (s)	2.66	2.66 (s)		
$^{4}J_{PH}$= 1	$^{3}J_{HH}$= 8.5		$^{3}J_{HH}$= 8.6		

1g$AlCl_4$	1h$AlCl_4$	1a[59]	1j(i)[60$]	1j(ii)[60$]	1k[64]
8.34-7.93	8.40-7.60	9.2-8.1 (Cl^-)	8.90-7.95	8.73	8.60-7.88
ABCDX	ABCD	8.0-7.0 (Br_3^-)	AA'BB'	8.67	ABCD
8.3 (NH)	8.4 (NH)	AA'BB'		8.00	
				2.73	
				$^{3}J_{HH}$= 8.5	

2b	2c	2d	2e	2g(Cl,Br)	2h	2i
7.70-7.29	7.55 (d)	7.48 (d)	7.45 (d)	7.60-7.10	7.53-6.99	7.70-7.25
AA'BB'X	7.49 (s)	7.43 (s)	7.39 (s)	ABCDX	ABCD	AA'BB'X
	7.12 (d)	7.05 (d)	6.93 (d)	6.7 (NH)	6.6 (NH)	
	2.39 (s)	2.37 (s)	2.35 (s)	$^{2}J_{PH}$= 30		
	$^{3}J_{HH}$= 8.1	$^{3}J_{HH}$= 8.1	$^{3}J_{HH}$= 8.0			

$ Methine signals omitted

TABLE I.2.2(c)i. ^{1}H, ^{13}C, ^{31}P and ^{27}Al NMR Data for 1, 2 and Related Compounds[+] (Continued)

$^{13}C\{^{1}H\}$ (90.8 MHz)

1b$AlCl_4$	1c$AlCl_4$	1d$AlCl_4$	1g$AlCl_4$
149, 131, 128	153, 150, 144, 133, 128, 127, 22	153, 150, 142, 131, 129, 128, 21	148 (d), $^{2}J_{CP}$= 3 136 (d), $^{2}J_{CP}$= 3 131, 129, 126, 119

1h$AlCl_4$	1j(i)[60$]	1j(ii)[60$]
130, 128, 127, 119. Quaternary carbons not observed.	145, 132, 128	146, 144, 143, 134, 127, 127, 22

2b	2c	2d	2e
138, 127, 126	139, 136, 128, 126, 126, 120, 21	139, 136, 136, 127, 127, 126, 21	140, 137, 136, 130, 130, 127, 21

2g(Cl)	2g(Br)	2h	2i
143 (d), $^{2}J_{CP}$= 16 126, 125, 124, 122, 114	127, 125, 122, 115. Quaternary carbons not observed	147, 126, 126, 124, 121, 115	136, 129, 127

$ Methine signals omitted

TABLE I.2.2(c)i. ^{1}H, ^{13}C, ^{31}P and ^{27}Al NMR Data for 1, 2 and Related Compounds[+] (Continued)

$^{31}P\{^{1}H\}$ (146.2 MHz)

1b	1c$AlCl_4$	1c$AlCl_xBr_{4-x}$	1f	1g$AlCl_4$	1g$AlCl_xBr_{4-x}$	1i*
408	414	406	212	306[85]	300	495
						$^{1}J_{PSe}$ = 565

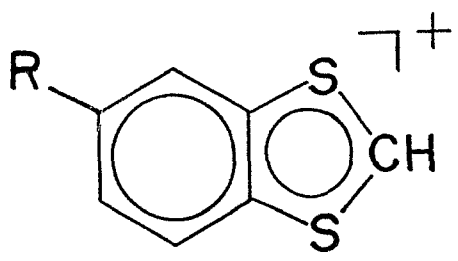
2b	2c	2g(Cl)	2g(Br)	2i
157	161	160	175	150
				$^{1}J_{PSe}$ = 330

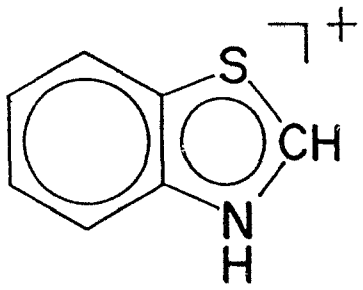
^{27}Al (94.1 MHz)

1b,c,d$AlCl_4$	1e$AlCl_4$
102 (150 < $\Delta\nu_{1/2}$ < 200 Hz)	102, 98, 92
	Integration Ratio *ca.* 1:1:1
1f,g,h$AlCl_4$	1i$AlCl_4$*
102 ($\Delta\nu_{1/2}$ < 40 Hz)	102, ($\Delta\nu_{1/2}$ = 740 Hz)

* Reaction mixture

+ All chemical shifts are reported in parts per million (ppm) and referenced either internally by using the residual protio-solvent resonance (^{1}H) or the solvent carbon resonance (^{13}C), both relative to tetramethylsilane, or externally by using 85% H_3PO_4 (^{31}P) or $Al(H_2O)_6^{3+}$ (^{27}Al). Spectra recorded in $CDCl_3$, CD_2Cl_2 or CH_2Cl_2. Coupling constants are given in Hertz (Hz).





1j **1k**

1j(i) R = H

1j(ii) R = CH_3

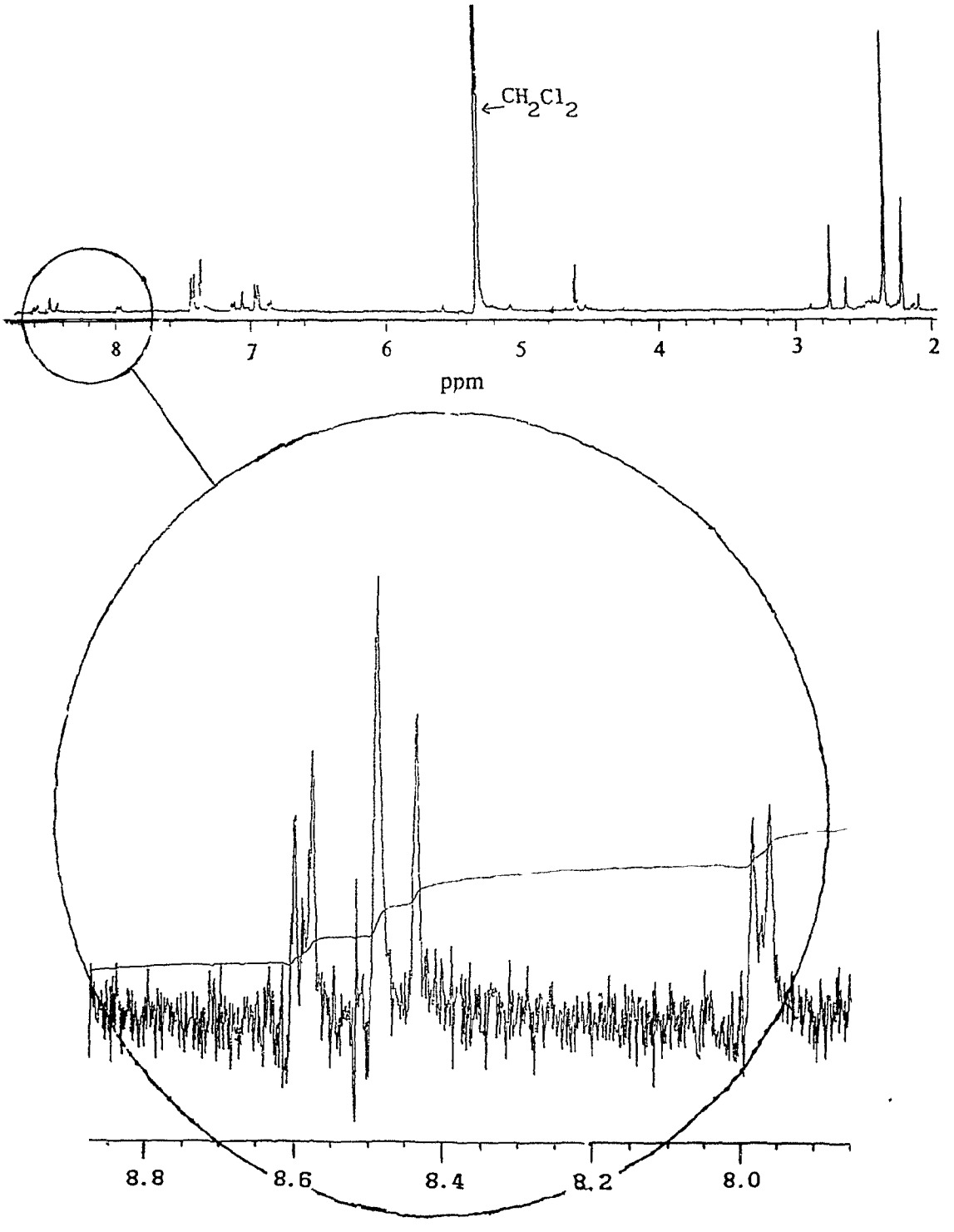
In the hybrid systems **1g,h** and **2g,h**, a dramatic deshielding of the amino proton chemical shifts is observed upon chloride abstraction [**2g(Cl)**, 6.75; **2g(Br)**, 6.71: **1g**, 8.3 ppm. **2h**, 6.63; **1h**, 8.4 ppm]. Therefore the nitrogen centres carry a significant amount of positive charge, although the chemical shift change is not as large as that observed on protonation of an aromatic secondary amine.[82] Such deshielding could be the result of induction or, alternatively, the hydrogen atoms may access the charge through hyperconjugation effects.[83] Poorly resolved two bond ^{1}H-^{31}P couplings of *ca.* 30 Hz are present in the spectra of the **2g(Cl),g(Br)**, suggesting that the amine protons are not readily exchangeable in chlorinated solvents. This perhaps indicates that the molecules display a high degree of association in

solution (presumably through hydrogen bonding) and is consistent with their low solubilities in CH_2Cl_2. The couplings are not apparent in the spectrum of **1g**$AlCl_4$.

Both the tetrachloro-aluminate and -gallate salts of **1e** are unstable in CH_2Cl_2. The ^1H spectrum obtained for the tetrachloro-aluminate salt is illustrated in Fig. I.2.2(c). It is identical to that of **1e**$GaCl_4$. The spectrum is complex but the predominant peaks clearly belong to the chlorobenzodithiastibole, **2e** [Table I.2.2(c)i]. However, deshielded from these signals are resonances [inset in Fig. I.2.2(c)] which exhibit chemical shifts and coupling constants close to those recorded for **1c** and **1d**. Presumably, the redissolution of the **1e** salts in CH_2Cl_2 initiates a series of reactions in which chloride ion reabstraction is the first step.

The aromatic character of framework **1** is emphasised by comparison of the ^1H and ^{13}C spectra of **1c,d** and **2c,d**. The methyl protons of **1c,d** are appreciably deshielded from those of **2c,d** [Table I.2.2(c)i] and toluene-3,4-dithiol (2.25 ppm). It could be argued that this is the result of σ-induction of the positive charge. However, in contrast to the deshielding observed for the benzo carbons of **1c,d** with respect to **2c,d**, due to π-delocalisation of charge, the chemical shifts of the methyl carbon nuclei are essentially the same. Close inspection of the ^1H and ^{13}C spectra of toluene and 2-methylnaphthalene reveals a comparable effect. Anisotropic effects dominate proton chemical shifts because of the small frequency range of the nucleus (typically *ca.* -5 - +15 ppm). This is an anomaly, as the heavier nuclei, like ^{13}C, have much larger chemical shift ranges (*e.g. ca.* -10 - +240 ppm for ^{13}C) and

FIGURE I.2.2(c). ^{1}H NMR Spectrum of <u>1e</u>$AlCl_4$



inductive effects become paramount. The magnetic anisotropy (ring current) of 10 delocalised π-electrons is greater than that of 6 delocalised π-electrons.[84] Therefore, the larger ring current of the 10π-electrons may account for the disparity in the relative differences in chemical shifts of the ^{1}H and ^{13}C nuclei of exocyclic methyl groups of 6π- and 10π-systems.

^{31}P NMR chemical shifts for phosphorus containing derivatives of **1** and **2** are given in Table I.2.2(c)i. The ^{31}P NMR signals of some typical dicoordinate phosphorus cations are listed in Table I.2.2(c)ii.[18(d)] **1b,c,i** exhibit very deshielded ^{31}P resonances, **1g** has a chemical shift which is typical for Main Group dicoordinate phosphorus, while the signal for **1f** is in fact more shielded than for PCl_3 (221 ppm).

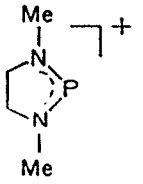
^{31}P chemical shifts are notoriously difficult to rationalise, but comparisons within a structurally and electronically related group of compounds have some validity.[86] The ^{31}P shifts of **2b,c,g(Cl),g(Br),i** occur within 15 ppm of each other and are standard for halophosphines.[86] Therefore, the large differences observed for the shifts of the corresponding cations is of immediate interest. This may be a consequence of the superior ability of nitrogen, in comparison to sulphur and selenium, to donate π-electron density to an electron deficient, dicoordinate phosphorus centre. Despite the large change in electronegativity from nitrogen to sulphur (selenium), which should strongly influence the degree of σ-withdrawal of electron density from the phosphorus centres, the observed chemical shifts imply that, for **1**, π-effects are predominant. The ^{31}P chemical shift of **1e** is considerably shielded from those of structurally related but saturated cations, such

as N,N'-dimethyl-1,3,2-diaminophospholidinium [Table I.2.2(c)ii], supporting the proposal that cationic dicoordinate phosphorus centres can be shielded (and stabilised) by effective delocalisation of the charge into multicentre π-bonded systems.[18(d)]

The differing contributions of **1b,c,f,g,i** to the paramagnetic component of the chemical shielding at phosphorus provide an alternative explanation for the variation in ^{31}P chemical shifts.[87] The paramagnetic term results from the interaction of specific excited states with the ground electronic state in the presence of a magnetic field. One such interaction allowed by selection rules to contribute to this term is the n-π^* transition. The replacement of a nitrogen by a sulphur (selenium) in framework **1** will change the energies of the respective n-π^* transitions and, consequently, may cause significant differences in the ^{31}P chemical shifts. This possibility is further examined when the results of molecular orbital calculations on **1** are presented in Section I.2.4.

The signal shapes of the ^{31}P resonances of **1b,c** exhibit a noticeable temperature dependence. The peaks are broad at room temperature but sharpen on cooling to $-80^{\circ}C$ without any significant variation of chemical shift. This behaviour is attributed to a rapid exchange process with a very small equilibrium constant, most likely involving halide ion reabstraction. **1f,g** and, somewhat surprisingly, **1i**, give sharp phosphorus resonances at room temperature. The spectra of **1b,c** contain secondary peaks of relatively low intensity which increase in intensity with time and are the result of cation decay in solution. The most important of these occurs at approximately 218 ppm

TABLE I.2.2(c)ii ^{31}P Chemical Shifts (ppm, with respect to 85% H_3PO_4) of Selected Dicoordinate Phosphorus Cations*

$(C_5H_5)_2P^+$	184
$(Me_2N)_2P^+$	264
	264
$(Me_2N)(iPr_2N)P^+$	290
$(iPr_2N)_2P^+$	313
$Cl(Me_2N)_2P^+$	325
$(Me_2N)[(Me_3Si)_2N]P^+$	354
$[Me_3Si)_2N]_2P^+$	451
tBu$(Me_2N)P^+$	510

* Taken from reference 18(d).

and is strongest in the spectrum of **1c**$AlCl_{4-x}Br_x$. The long term solution behaviour of the other phosphorus containing derivatives of **1** has not been investigated.

The identification of **1i** is based almost entirely on the ^{31}P solution spectrum. This consists of a resonance at 495 ppm (the most deshielded chemical shift of the phosphorus containing derivatives of **1**) and accompanying selenium satellites (^{77}Se: I = 1/2; natural abundance, 7.6%). The satellites account for *ca.* 15% of the overall signal, confirming the phosphorus connectivity to two magnetically equivalent selenium centres. The magnitude of the one bond ^{31}P-^{77}Se coupling constant (565 Hz) is more than 1.5x greater than that observed for **2i** (330 Hz), although less than those of phosphine selenides.[88] ^{31}P-^{77}Se coupling constants have been related to the hybridisation of the phosphorus centre, in that an increase in *s*-character leads to a corresponding increase in the observed coupling.[89] Therefore, a change in hybridisation from approximately sp^3 in **2i** to approximately sp^2 in **1i** may explain the difference in coupling constants.

^{27}Al NMR spectroscopy has proven a useful tool in the study of solutions containing $AlCl_4^-$, as the anion gives a sharp (>50 Hz) resonance at 102 ppm with respect to $Al(H_2O)_6^{3+}$. (The high symmetry of the tetrahedral anion leads to a narrow signal despite the quadrupolar nature of the nucleus. This trait of quadrupolar NMR is further discussed in Part II).[90] The ^{27}Al spectra of **1b,c,d,g,h**$AlCl_4$ contain resonances attributable to the anion [Table I.2.2(c)i]. However, the signals of the dithia- derivatives, **1b,c,d**, are broader ($150 < \Delta\nu_{1/2} < 200$ Hz) than those of **1f,g,h**$AlCl_4$ ($\Delta\nu_{1/2}$ <40 Hz). The spectra of **1b,c,d**

also contain a minor signal (*ca.* 90 ppm) which may be due to $AlCl_3$. This observation is consistent with the equilibrium process implied by the temperature dependent ^{31}P NMR signals of **1b,c** and strongly suggests a reduced solution stability for **1b,c,d**. In accord with the ^{1}H spectrum, the ^{27}Al spectrum of **1e**$AlCl_4$ is more complex containing three peaks of approximately equal intensity, one of which is due to $AlCl_4^-$. The resonance obtained for **1i** is very broad ($\Delta\nu_{1/2}$ = 740 Hz) but this may be due to the large excess of $AlCl_3$ present in the reaction mixture.

I.2.2(d) Electronic and MCD Absorption Spectroscopies

The work described in this section was carried out at the University of Texas at Austin in the laboratories of Professor Josef Michl, under the direct supervision of Dr. Jacek Waluk. The electronic absorption and magnetic circular dichroism (MCD) spectra of CH_2Cl_2 solutions of **1b-d,g,h**$AlCl_4$ have been recorded and are presented in Figures I.2.2.(d)i-v, together with the results of Pariser, Parr, Pople (PPP) π-electron calculations performed by Jacek Waluk.[91]

The electronic absorption spectra give single broad bands. The energies of these absorptions depend on the identity of the heteroatoms involved. Cation **1d** displays the lowest energy transition at approximately 24000 cm^{-1} (420 nm), **1b,c,h** have an absorption maximum around 26500 cm^{-1} (380 nm), while **1g** exhibits the highest energy absorption with a maximum at about 28800 cm^{-1} (350 nm). Therefore, heavier heteroatoms within framework **1** lower the energies of the absorption maxima. The observed spectra are in accordance with the colours of the salts (**1b**, yellow; **1c**; orange; **1d**, red; **1g**, pale yellow; **1h**, red/orange). In particular, the relatively faint colour of **1g** is

FIGURE 1.2.2(d)i. Electronic Absorption Spectra of 1bAlCl$_4$ in CH_2Cl_2 at 293 K. Bottom: absorption spectrum (oscillator strengths given). Centre: MCD spectrum (magnetically induced molar ellipticity in units of $degG^{-1}m^{-1}M^{-1}$, B terms in units of $10^{-3}\beta_e D^2/cm^{-1}$). Top: Results of PPP calculations (solid bars: transitions polarized vertically with respect to the plane of 1b, broken bars polarized horizontally).

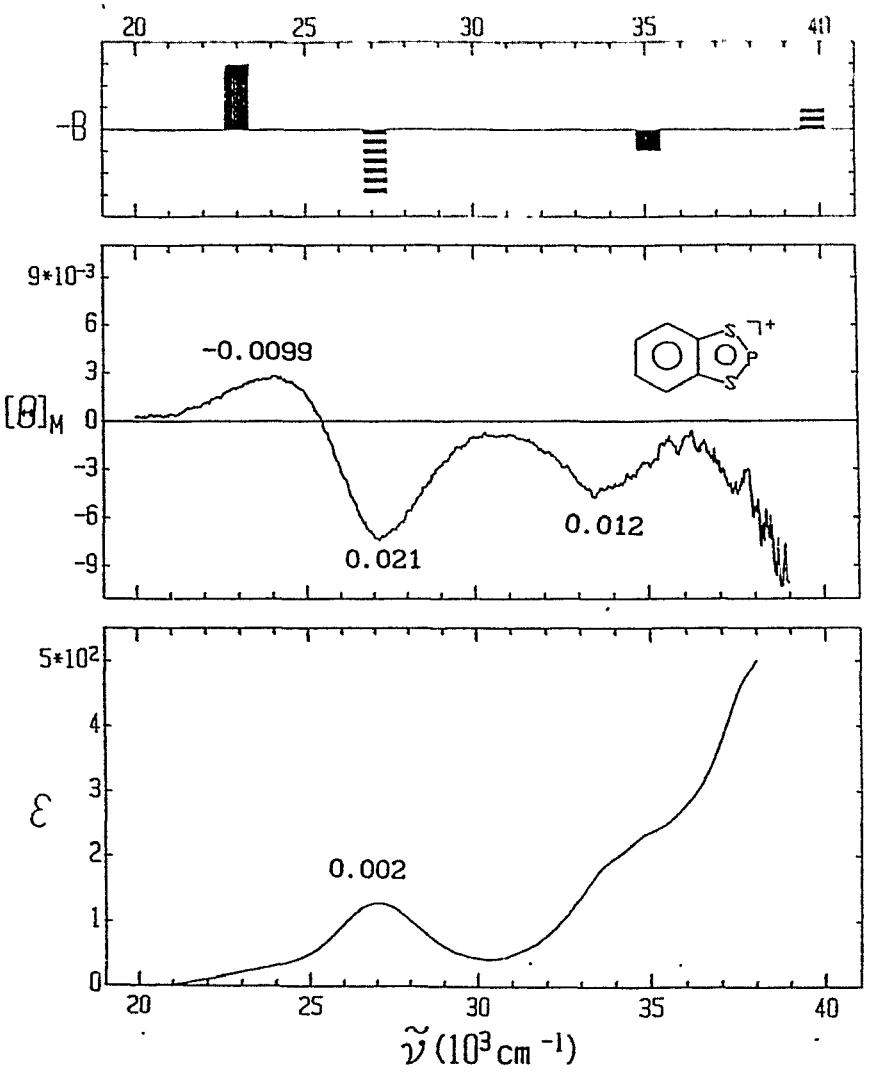


FIGURE I.2.2(d)ii. Electronic Absorption Spectra of 1cAlCl$_4$ in CH_2Cl_2 at 293 K.

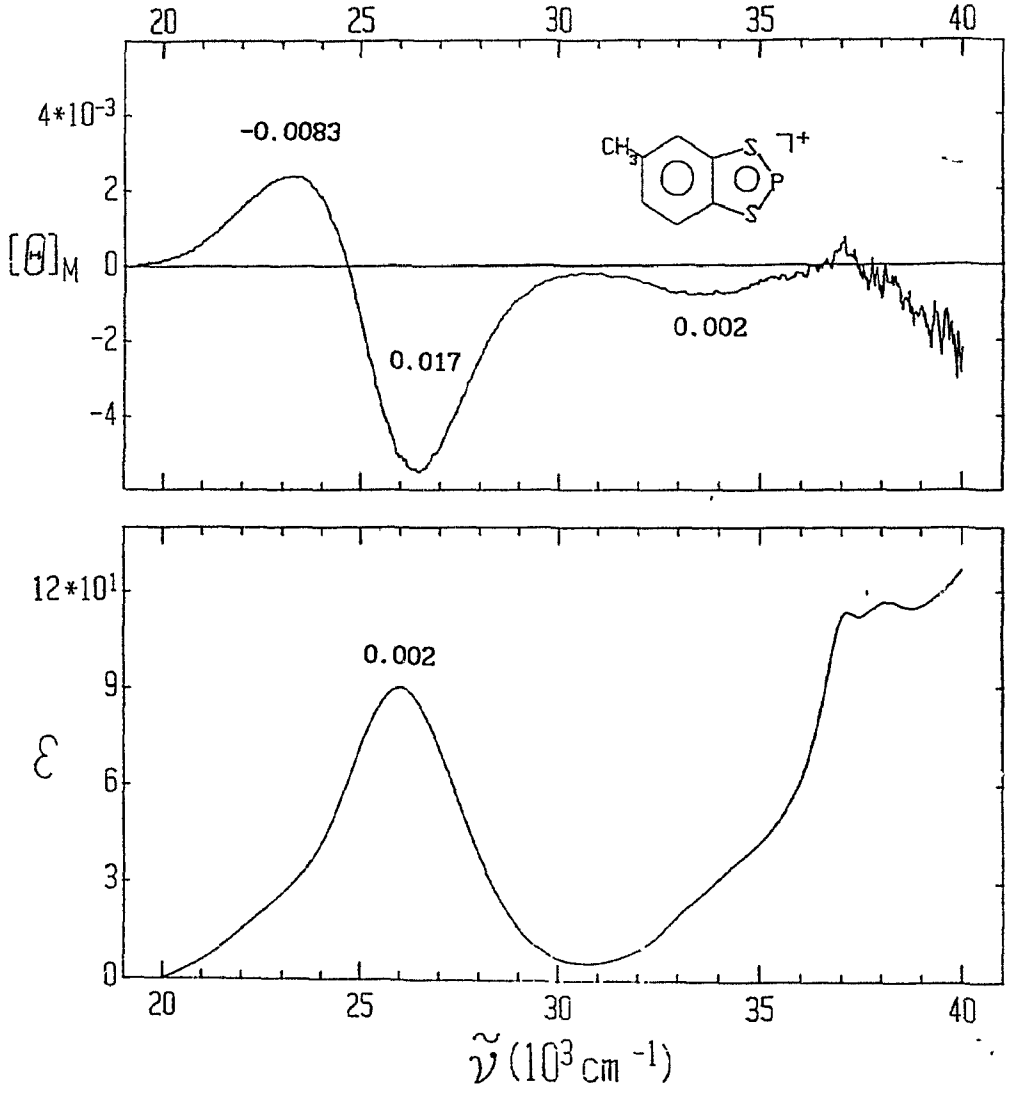


FIGURE I.2.2(d)iii. Electronic Absorption Spectra of 1dAlCl$_4$ in CH_2Cl_2 at 293 K.

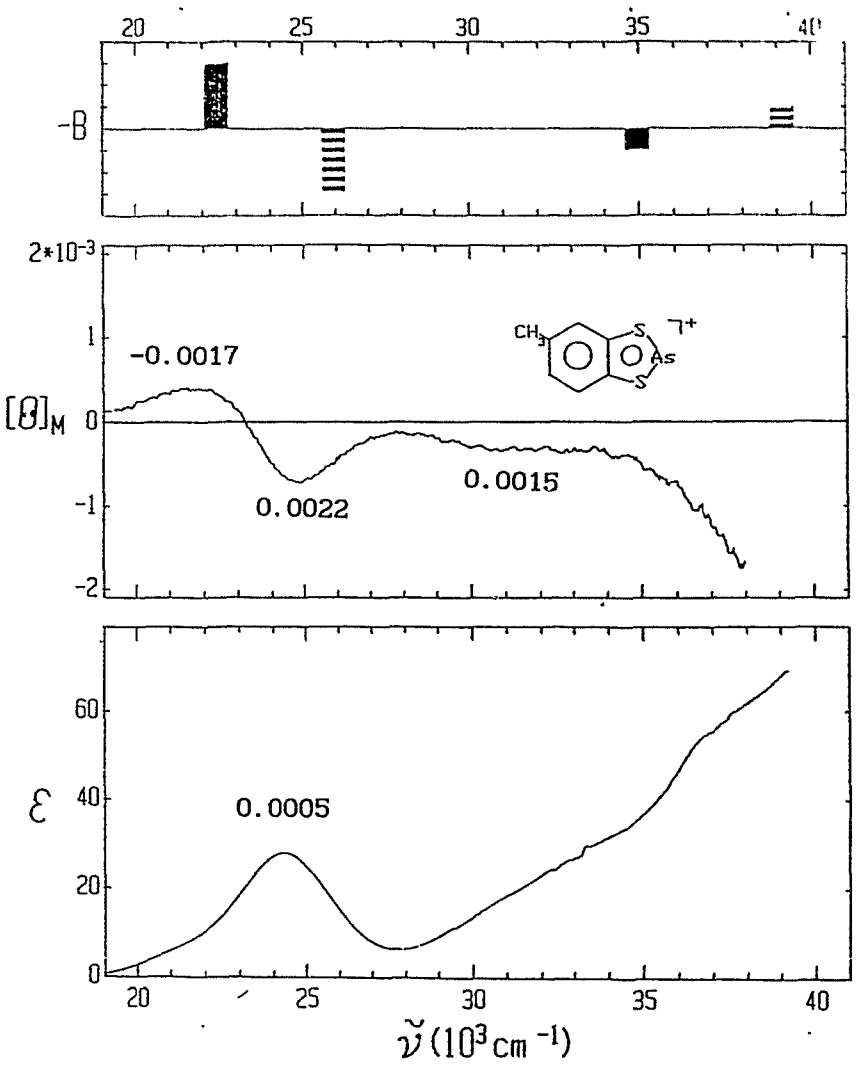


FIGURE I.2.2(d)iv. Electronic Absorption Spectra of 1gAlCl$_4$ in CH_2Cl_2 at 293 K.

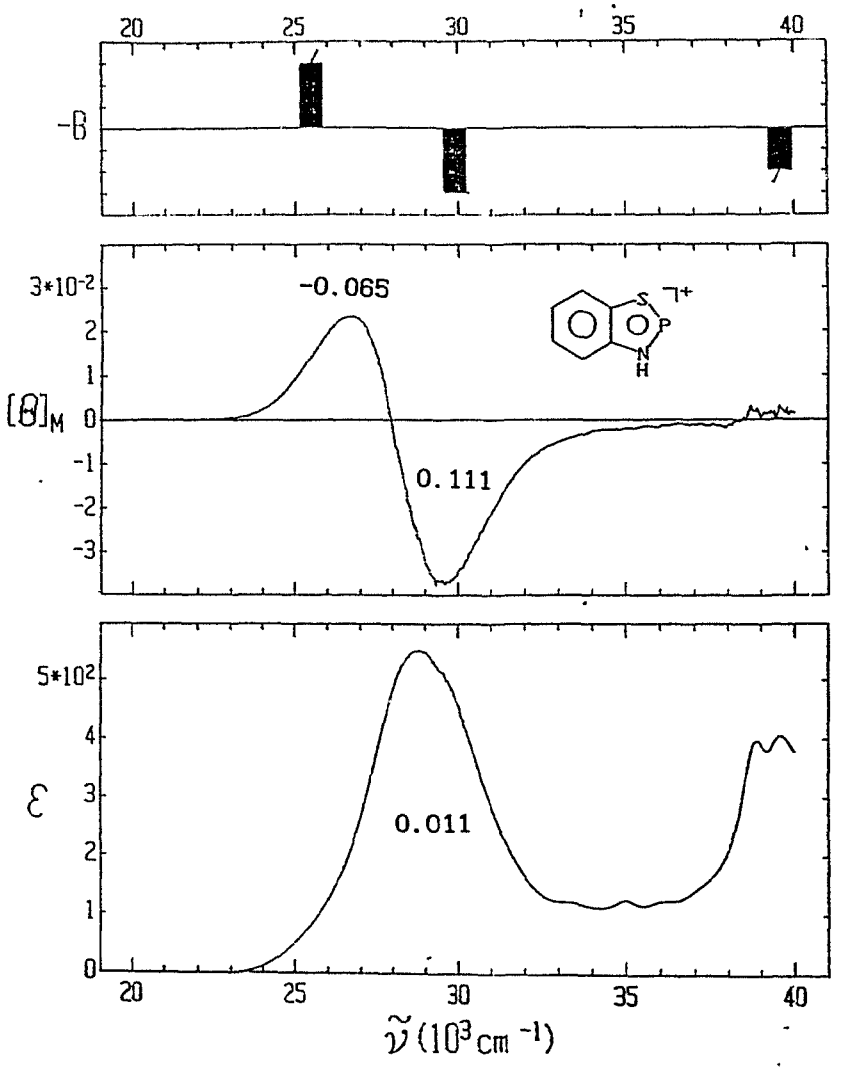
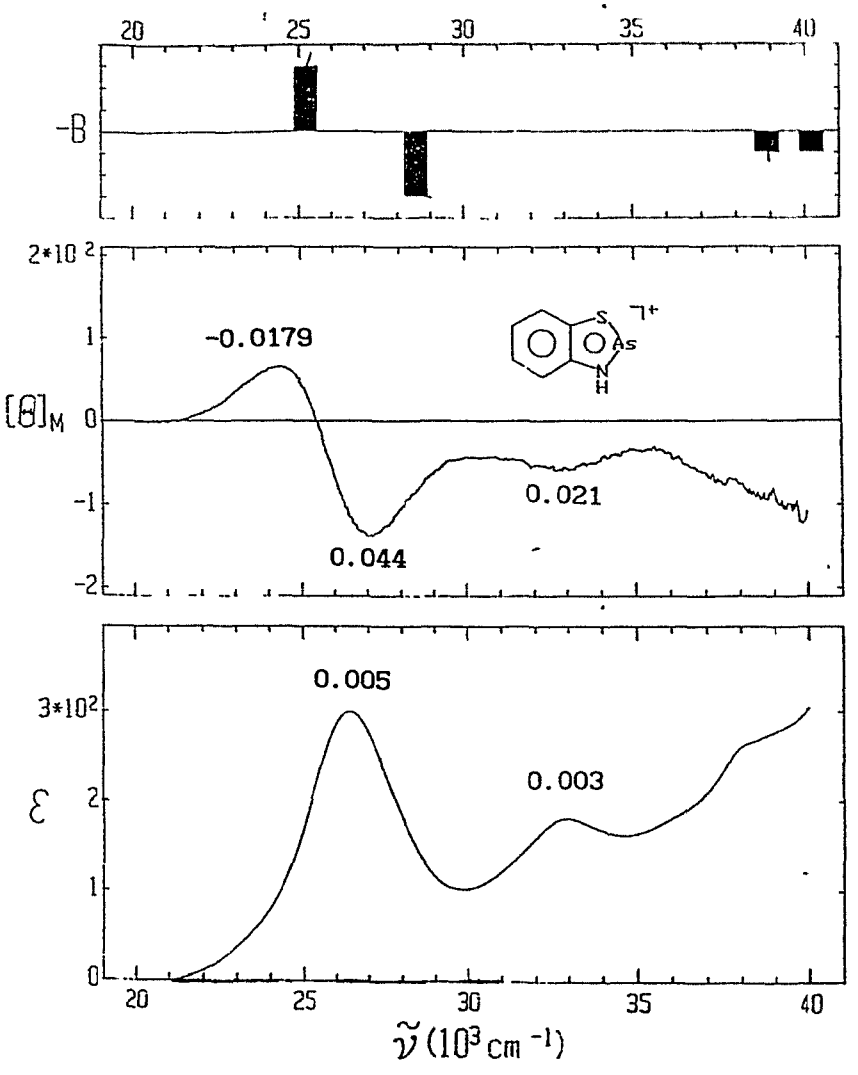


FIGURE I.2.2(d)v. Electronic Absorption Spectra of 1hAlCl$_4$ in CH_2Cl_2 at 293 K.



now readily understood as it represents the visible tail of an ultraviolet absorption. The absorption spectra of two salts (Cl^- and Br/Br_3^-) of **1a** have been reported and are essentially independent of the anion.[59(b)] The lowest energy absorption has a maximum at approximately 25380 cm^{-1} (394 nm), occurring at a lower energy than those of **1b,c**. Therefore, **1a** does not follow the trend observed for its heavier analogues, perhaps indicating subtle differences in electronic structure.

The absorption extinction coefficient (ε) is also a function of the heteroatom, decreasing with increasing atomic number. However, ε values for the heavy element derivatives are suprisingly low. The largest, that of **1g**, is only about 580. By comparison, ε for the lowest energy absorption in **1a** is greater than 3000. The PPP calculations carried out on these systems predict the relative ordering of the observed ε values (oscillator strengths) but greatly overestimate their magnitude.[92] The low values may be an artefact of experimental procedure, due to the difficulties in handling and accurately weighing very small quantities of such sensitive compounds. Alternatively, they may indicate that the transitions are not as strongly allowed as those of **1a**.

The MCD spectra of **1b-d,g,h** demonstrate the existence of two transitions at low energy, which are designated B terms in MCD terminology. The electronic absorption spectra display only one peak for **1g,h**, while shoulders can be distinguished on the main absorption bands of **1b,c,d**. The spectra of **1b-d,h** also display a third so-called B term absorption.[93]

If the characteristics of perturbing heteroatoms and/or

substituents are known (more specifically, their resonance integrals and electronegativities), the signs of the B terms of delocalised π-electron structures derived from a (4N+2)-electron perimeter can be readily predicted by an analysis of the energy splittings of the frontier π-molecular orbitals using a theory developed by Michl.[94,95,96] There are two contributions to the MCD B terms of an aromatic molecule with low symmetry. The first is called the μ^- contribution, and it is proportional to the difference of the magnetic moments of the perimeter orbitals involved in the transitions. It is always present, but relatively smal and has a sign largely independent of molecular structure. The second, μ^+, which is proportional to the sum of the magnetic moments of the perimeter orbitals, is usually an order of magnitude greater than μ^-. However, it is only non-zero when the energy splitting between the two highest occupied molecular π-orbitals (ΔHOMO) differs from that between the two lowest unoccupied π-orbitals (ΔLUMO). When the μ^+ contribution dominates, Michl's theory predicts a +,-,+ sequence of B terms for the three lowest energy π-π^* transitions for ΔHOMO > ΔLUMO. For ΔHOMO < ΔLUMO, the opposite sequence, -,+,- is anticipated. If ΔHOMO = ΔLUMO, the μ^+ contribution vanishes and μ^- now dictates the signs of the B terms. An inequality of ΔHOMO and ΔLUMO can be induced even by weak perturbations to the system (*e.g.* substitution of a hydrogen by a methyl) and so MCD chromophores where ΔHOMO is approximately equal to ΔLUMO are designated "soft". In contrast, if ΔHOMO and ΔLUMO are very different then it is unlikely that substitution will lead to change in the sign ΔHOMO - ΔLUMO and, consequently, the signs of the B terms. Therefore, such chromophores are designated as

"positive-hard", for ΔHOMO > ΔLUMO, and "negative hard", for ΔHOMO < ΔLUMO.

The MCD spectra obtained for the derivatives of **1** exhibit a common pattern. A positive MCD signal is observed for the first band (note that this corresponds to a negative B term) followed by a positive B term (negative signal) for the second transition. These are followed in **1b,c** by another positive B term. The signs of the first two signals clearly demonstrate that **1b,c,d,g,h** are negative-hard chromophores, *i.e.* ΔHOMO < ΔLUMO. This agrees well with the results of calculations carried out at Texas by Dr. Waluk[91] and at Dalhousie (Section I.2.4) as ΔHOMO is predicted to be in the order of 1eV, whereas ΔLUMO is approximately 5eV. The source of the dramatic imbalance is the very low energy of the π-LUMO. Indeed, ΔLUMO is so great that the first three excited states calculated by the PPP method involve electron promotion into the LUMO from the first, second and third π-orbitals, respectively.[91] The state which involves the third highest occupied MO is not described by Michl's model and usually lies very high in energy.[91,95] The third signal clearly visible in the spectra of **1b-d,h** could be the result of such a transition. However, it may also be due to an n-π^* excitation and the results of STO-3G calculations on **1b,f,g** (Section I.2.4) indicate that the third highest occupied molecular orbitals have large contributions from the $3s, p_{x,y}$ atomic orbitals of the phosphorus centres *i.e.* the phosphorus "lone pairs".

Whatever the origin of the third absorption, the first two transitions can be unequivocally assigned to the first two π-π^* excitations of a perturbed (4N+2) π-electron perimeter with B term signs

correctly predicted by Michl's theory. Therefore, in the electronic spectroscopic sense, cations **1** are aromatic.

Absorption maxima and extinction coefficients of the electronic absorption spectra of **2c,g(Cl),g(Br),h** in acetonitrile are listed in Table I.2.2(d). The spectra of **2g(Cl),g(Br)** are very similar showing three absorbance bands. The spectrum of **2h** exhibits only two transitions although a third may be present as a shoulder. The spectrum of **2c** is of a somewhat different form but also reveals two absorptions. However, the spectra of **2** are clearly different to those of **1**, indicating dissimilar electronic structures.

I.2.2(e) Phosphorus-31 Solid State NMR Spectroscopy

The information gleaned from solution NMR studies is isotropic, as the rapid (Brownian) motions of a solute in a solvent averages out any anisotropy (orientation dependence) of the chemical shift. However, such motion is greatly reduced in solids. Therefore, static solid state NMR spectra consist of broad envelopes of resonance frequencies, so-called powder patterns, which contain information on the three dimensional nature of the chemical shift tensor.[97] If a single nucleus is under investigation, then the width of the observed band is designated the chemical shielding anisotropy (CSA). The anisotropic information can be averaged to an isotropic value (δ_{iso}) if the sample is physically rotated about an axis inclined at the "magic angle", 54° 44' 11" with respect to the magnetic field, B_o. Under such circumstances, if the frequency of rotation is greater than the CSA, then the powder pattern collapses to give a "solution-like" spectrum containing a single, narrow resonance line for each nucleus at a

TABLE I.2.2(d) Absorption Maxima (λ_{max}) and Extinction Coefficients (ε) for Acetonitrile Solutions of 2c,g(Cl),g(Br),h

	λ_{max}, cm^{-1} (nm)	ε
2c	33×10^3 (300), 40×10^3 (250)	2000, 5150
2g(Cl)	33×10^3 (300), 40×10^3 (250)	- -
	48×10^3 (210)	-
2g(Br)	34×10^3 (295), 41×10^3 (245)	3050, 8000,
	48×10^3 (210)	27600
2h	33×10^3 (300), 45×10^3 (220)	5500, 33970

crystallographically non-equivalent site. If the spinning frequency is less than the CSA, the single resonance is accompanied by a series of spinning sidebands, the intensities and distribution of which reflect the magnitude of the CSA.

Recent research has demonstrated that the CSA of a nucleus is a sensitive probe of its local electronic environment. For example, Zilm, Grant and others have demonstrated that $p\pi$-bonded nuclei exhibit exceptionally large CSA's.[98] Also, it has been recognised for many years that a large anisotropy in magnetic susceptibility is a characteristic property of aromatic molecules.[99] Therefore, the phosphorus-containing derivatives of **1** represent worthwhile candidates for study by solid-state NMR.

^{31}P solid-state spectra of the tetrachloroaluminate salts of **1b,c,g** were obtained in collaboration with Ronald Curtis and Professor Roderick Wasylishen of Dalhousie University. Full experimental details will be published elsewhere.[100]

The magic angle spinning (MAS) spectra [Fig. I.2.2(e)i] demonstrate that the cations exhibit abnormally large CSA's for the phosphorus nuclei, as spinning sidebands are observed even at spinning rates of 2.8 kHz. δ_{iso} (ppm) for the three phosphorus centres [**1b**: 424.5 (obs'd), 424.3 (calc'd); **1c**: 416.6 (obs'd), 416.7 (calc'd); **1g**: 323.2 (obs'd), 323.3 (calc'd)] are very close to the solution ^{31}P chemical shifts [Table I.2.2.(c)i]. The static spectra [Fig. I.2.2(e)ii] reveal standard powder patterns for species with non-axially symmetric shielding tensors.[101] Computer simulation[100] of the spectra provides the three principal components of the chemical shift tensors, (δ_{11}, δ_{22},

FIGURE I.2.2(e)i. Magic Angle Spinning Solid State ^{31}P Spectra of $\underline{1b}AlCl_4$ Obtained at 2.8 kHz (Similar Spectra were Obtained for $\underline{1c,g}AlCl_4$)

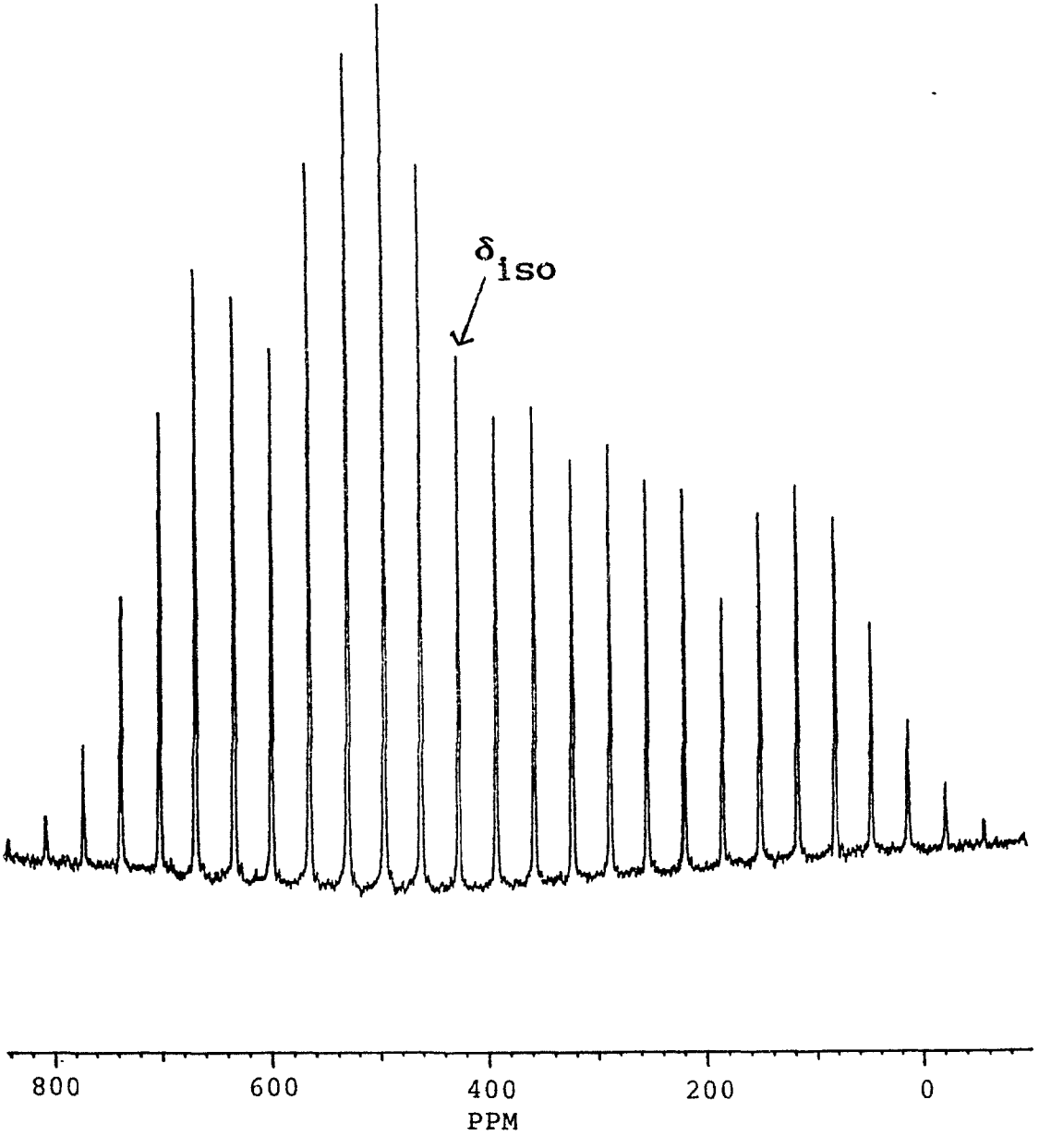
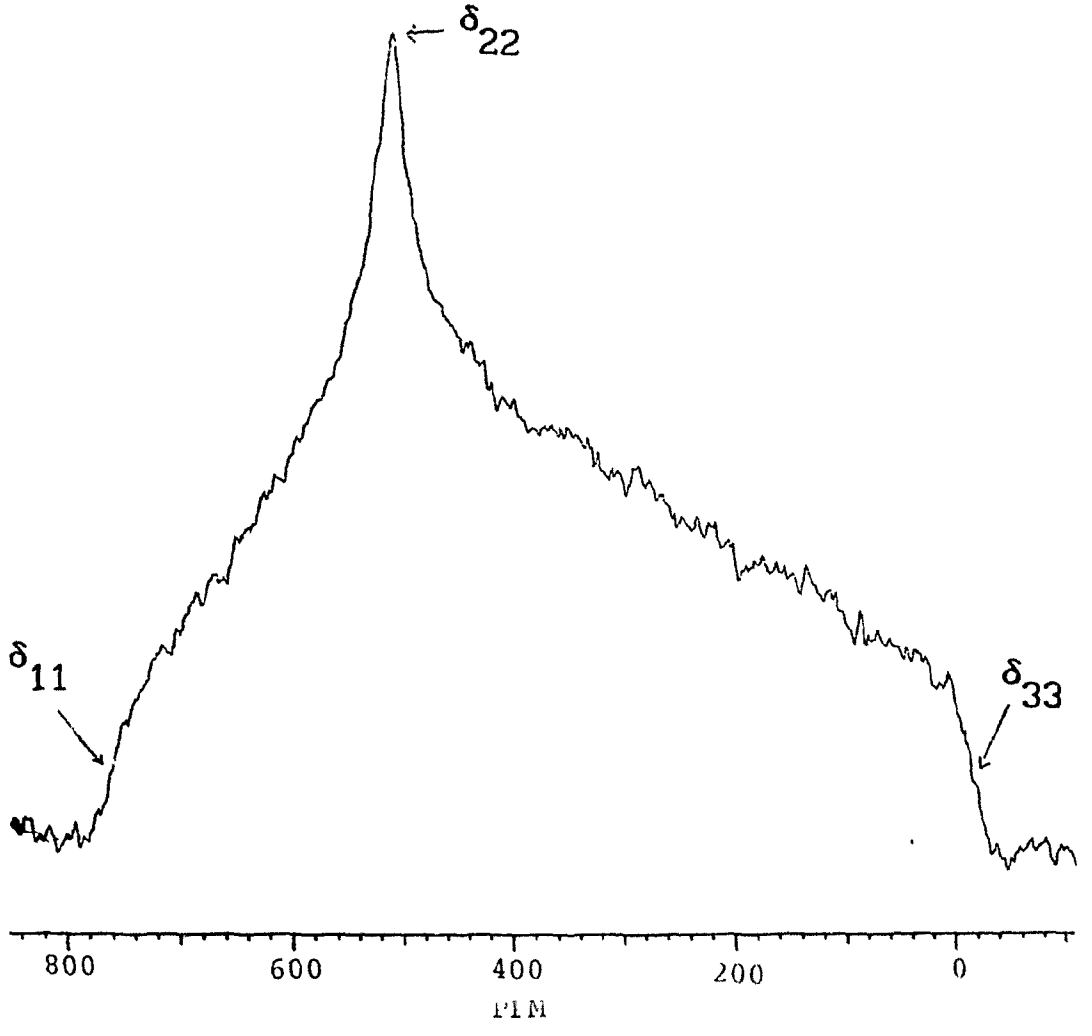


FIGURE I.2.2(e)ii. Static Solid State ^{31}P NMR Spectra of 1b$AlCl_4$

(Similar Spectra were Obtained for 1c,g$AlCl_4$)



1b:	δ_{11} = 766	δ_{22} = 520	δ_{33} = -13 ppm
1c:	δ_{11} = 755	δ_{22} = 520	δ_{33} = -25 ppm
1g:	δ_{11} = 684	δ_{22} = 252	δ_{33} = 34 ppm

δ_{33}), and gives values of 779, 780 and 718 ppm for the CSA's ($\Delta\delta = \delta_{11} - \delta_{33}$) of **1b,c,g**, respectively. These values are listed in Table I.2.2(e) together with values obtained for other phosphorus compounds. The CSA's of **1c,g** are clearly much greater than those reported for fully σ-bonded phosphine [phosphorus(III)] compounds or those containing $p\pi$-$d\pi$ multiple bonds,[102] and are closer in value to those obtained for species with full -P=P- $p\pi$-$p\pi$ bonds.[98(a)]

I.2.3 Structural Studies

The solid-state structures of **1b,c,f,g,h**$AlCl_4$ and **2g(Cl),g(Br),h** have been established by single crystal X-ray diffraction techniques. The structures of two neutral phosphines, *tris*(phenylthio)-phosphine, [$(PhS)_3P$], and 5-methyl-2-phenyl-1,3,2-benzodithiaphosphole, **3**, have also been determined for comparison. Crystallographic details are provided in Appendix 1.

I.2.3(a). Crystal Structure of *Tris*(phenylthio)phosphine, [$(PhS)_3P$].

The literature provides very little structural information on P(III)-S single bonds which are free from steric or electronic distortions. It is essential that such data be available so that meaningful comparisons to the P-S bond distances in **1b,c,g** can be made. Therefore, the crystal structure of the acyclic phosphine, $(PhS)_3P$ has been established. Crystals of $(PhS)_3P$ were grown by slow evaporation of CCl_4. The structure was determined by Dr. Peter S. White at the University of New Brunswick. Important bond lengths and angles are provided in Table I.2.3(a) and illustrations of the molecule and the unit cell are given in Fig. I.2.3(a).[103,104]

TABLE I.2.2(e). Chemical Shielding Anisotropies (CSA's) of Some Phosphorus Containing Compounds

Compound	CSA (ppm)
1b	779
1c	780
1g	718
$Mes^{*}P{=}PMes^{*}$	1239
$Mes^{*}PCl_2$	90
$Mes^{*}HP{-}PHMes^{*}$	85
Ph_3P	50
$Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}PPh_2)$	179
$Ph_3P{=}NPh$	135
$Ph_3P{=}O$	200

Mes^{*} = 2,4,6-tri-*t*-butylphenyl

Values taken from references 98(a), 102.

The structure is made up of discrete molecules and each phosphorus centre resides on a C_3 axis. The PS_3 unit adopts the standard pyramidal phosphine geometry,[2] while the phenyl groups assume a *cis* orientation with respect to the lone pair on phosphorus. This has sometimes been denoted as an *exo* configuration.[105(a)] The P-S bond length of 212.2 (1) confirms a typical P-S single σ-bond distance of about 210 pm *e.g.* P_4S_3, 209 (1);[106] **4**, 218.0 (2);[107] **5** (mean) 207.2 (2);[108] **6** [electron diffraction (e.d.)] 208 (2);[109] $(MeS)_3P$ (e.d.) 211.5 (4);[105(a)] $MeSPCl_2$ (e.d.) 208 (1);[105(b)] $MeSPBr_2$ (e.d.) 212 (2) pm.[105(b)] The C-S bond length [178.5 (2) pm] is shorter than those found for standard σ-bonds such as $(MeS)_3P$ [183.4 (7) pm][105] and Me_2S [e.d.: 180.2 (2) pm].[110] Presumably, this is indicative of a weak π-interaction between the sulphur centres and the aromatic rings.

Studies on $(MeS)_3P$ indicate the presence of at least two conformers in the liquid[111] and gas[105] phases and show that the *cis* (*exo*) conformation is less favoured. However, the steric constraints of the phenyl derivative enforce the observed C_3 solid state geometry.

$(PhS)_3P$ is isostructural with its arsenic analogue,[112] both compounds exhibiting sterically active lone pairs. However, the structure of $(PhS)_3N$ contains a planar nitrogen and short N-S bonds, evidently the result of a significant *pπ-dπ* interaction between the nitrogen and the sulphur centres.[113]

I.2.3(b). Crystal Structure of 5-Methyl-1,3,2-benzodithiaphosphole, 3.

Crystals of **3**,[114] were obtained by cooling a saturated *n*-hexane solution. The structure was determined at Dalhousie by Drs. Anthony Linden and T. Stanley Cameron. Selected bond lengths and angles are

FIGURE I.2.3(a). Diagrams of the Molecular Structure and Unit Cell of $(PhS)_3P$

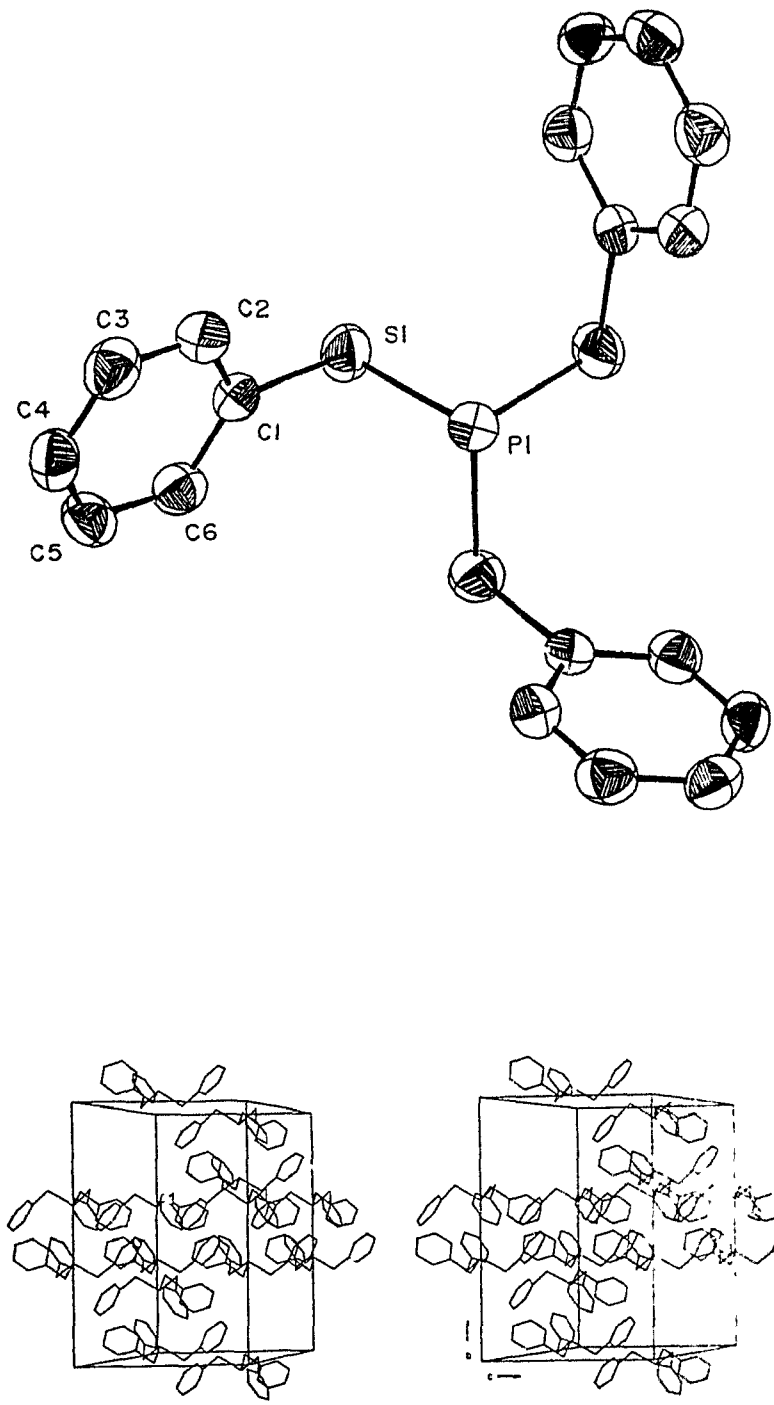
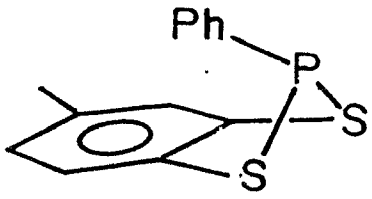


TABLE I.2.3(a). Selected Bond Lengths (pm) and Angles (^{o}) for *Tris*(thiophenyl)phosphine, $(PhS)_3P$

P-S(1)	211.2 (1)
S(1)-C(1)	178.5 (2)
S(1)-P-S(1)'	97.45 (5)
P-S(1)-C(1)	100.03 (7)
S(1)-C(1)-C(2)	120.1 (2)



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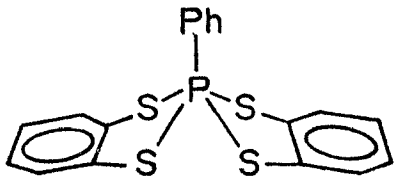

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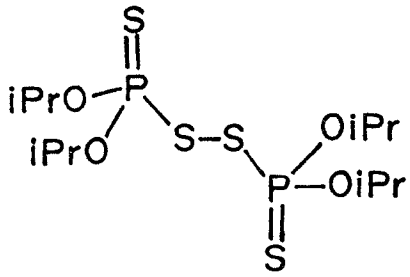

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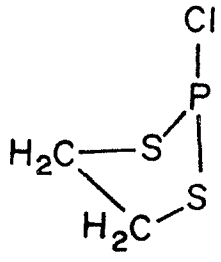
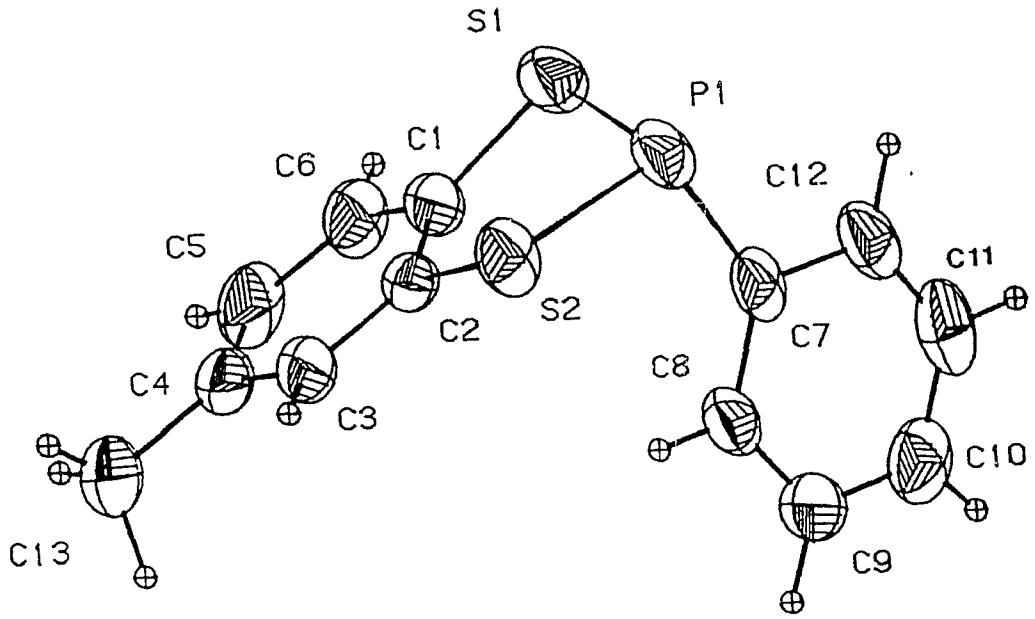


6

provided in Table I.2.3(b) and SNOOPI[115] views of the compound and the crystal packing are given in Fig. I.2.3(b). The structure consists of discrete molecular units with no significant intermolecular contacts. The bicyclic ring system is folded by an angle of 25.2° about the S-S vector so that the phosphorus atom is removed by 53 pm from the plane of the dithiobenzene unit. The geometry at the phosphorus centre is distorted tetrahedral indicative of a stereochemically active lone pair.

3 exhibits standard P-S bond lengths [mean 210.6 (2) pm]. The S-C bonds [mean 176.3 (6) pm] are shorter than typical single bonds[105,110] and similar to those of $(PhS)_3P$. Again, this may be attributed to some π-interaction between the sulphur centres and the aromatic ring. The endocyclic angles of the five-membered ring are similar to those determined for **4**.[107] The P-C-C angles are different and this inequality, thought to be steric in origin, has been observed for many phenyl substituted phosphorus centres.[116] The phenyl substituent itself is twisted so that one of the ortho hydrogens atoms lies almost directly above S(2) and the observed S(2)-P-C(7)-C(8) torsion angle is 1.0 (7)°. The distance between the sulphur centre and the hydrogen centre is 28 pm, which is within the sum of the van der Waals radii (18.5 and 12 pm, respectively). However, this conformation is thought to be the result of crystal packing, as indicated by the unusual asymmetry of the angles at the phosphorus centre and C(9). Furthermore, the ^{13}C NMR spectrum shows the *ortho* carbon atoms to be equivalent in solution. The P-C bond distance [182.7 (4) pm] is comparable to those reported for other phosphines, for example 182.2 (5) - 183.1 (5) pm in triphenylphosphine.[117]

FIGURE I.2.3(b). Diagrams of the Molecular Structure and Unit Cell of 5-Methyl-2-phenyl-1,3,2-benzodithiaphosphole, 3



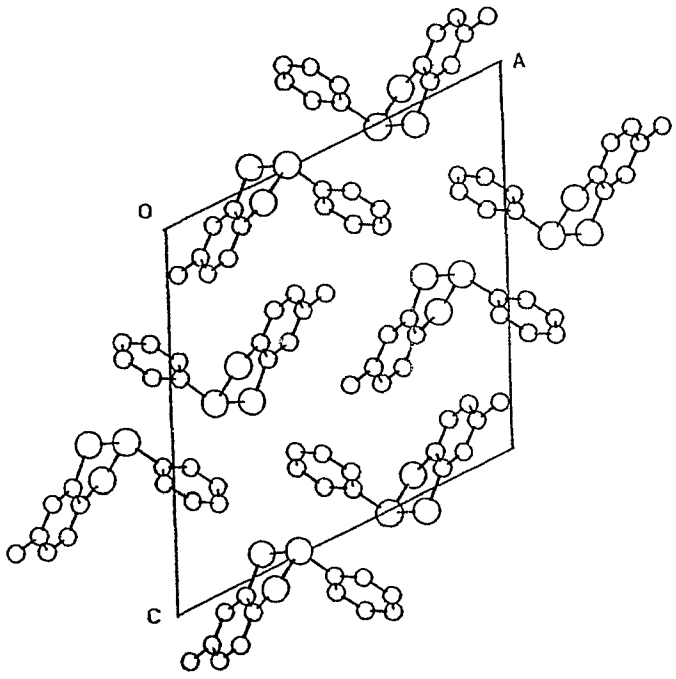


TABLE I.2.3(b). Selected Bond Lengths (pm) and Angles (°) for 5-Methyl-2-phenyl-1,3,2-benzodithiaphosphole, 3

P-S(1)	211.0 (2)	P-S(2)	210.2 (2)
C(1)-S(1)	176.1 (5)	C(2)-S(2)	176.5 (6)
C(1)-C(2)	140.1 (6)	P-C(7)	182.7 (4)
S(1)-P-S(2)	94.9 (1)	P-S(1)-C(1)	99.1 (2)
P-S(2)-C(2)	99.6 (2)	S(1)-C(1)-C(2)	118.8 (4)
S(2)-C(2)-C(1)	118.8 (4)	S(1)-P-C(7)	101.0 (2)
S(2)-P-C(7)	104.5 (2)	P-C(7)-C(8)	126.6 (3)
		P-C(7)-C(12)	115.5 (3)

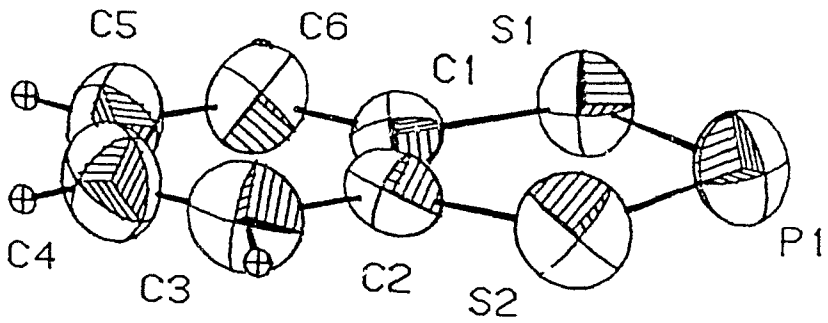
I.2.3(c). Crystal Structures of 1,3,2-Benzodithiaphospholium, 1b, Tetrachloroaluminate and 5-Methyl-1,3,2-benzodithiaphospholium, 1c, Tetrachloroaluminate.

Crystals of both salts were grown by slow evaporation of CH_2Cl_2 and the structures determined by Drs. Linden and Cameron. Selected bond lengths (pm) and angles (^{o}) are provided in Table I.2.3(c). Stereoview packing diagrams of **1b,c**$AlCl_4$ are given in Figs. I.2.3(c)i,ii.[115,104] The substitution of a proton by a methyl group on the benzo moiety has a significant effect on the crystal packing although the overall molecular features of the two cations are very similar.

Illustrations[115] of cations **1b,c** are provided in Figures I.2.3(c)i,ii. In contrast to **3** [Section I.2.3(b)], the cations are planar, as demonstrated by the sum of the endocyclic angles of the five and six membered rings (within experimental error, 540 and 720^{o}, respectively). The maximum deviation from the best plane occurs at P (2.7 pm) for **1b** and C(5) (2.0 pm) for **1c**.

The P-S bond lengths for **1b** and **1c** are (mean) 201.6 (2) and (mean) 202.0 (3) pm, respectively, and are approximately 4% shorter than a standard P-S single bond [Section I.2.3(a)]. Similar bond lengths are found in Lewis acid-base adducts of phosphorus(V) sulphides and in (η^2-thioxophosphorus)metal complexes. For example, the P-S bond lengths of $Ph_3PS.MoOCl_3$, $Ph_3PS.NbSCl_3$ and **7** are 204.1 (1) 202.7 (6) and 203.3 (2) pm, respectively.[118,119,56] Although the P-S bonds determined for **1b,c** are appreciably longer than the very short distances found in free phosphorus sulphides (*ca.* 190 pm),[120] they are the shortest yet reported for a phosphorus(III)-sulphur bond.

FIGURE I.2.3(c)i. Diagrams of the 1,3,2-Benzodithiaphospholium Cation, 1b, and the Unit Cell of 1bAlCl$_4$



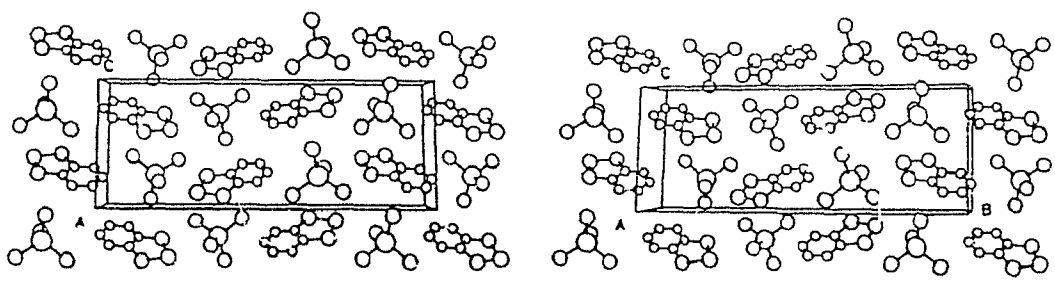
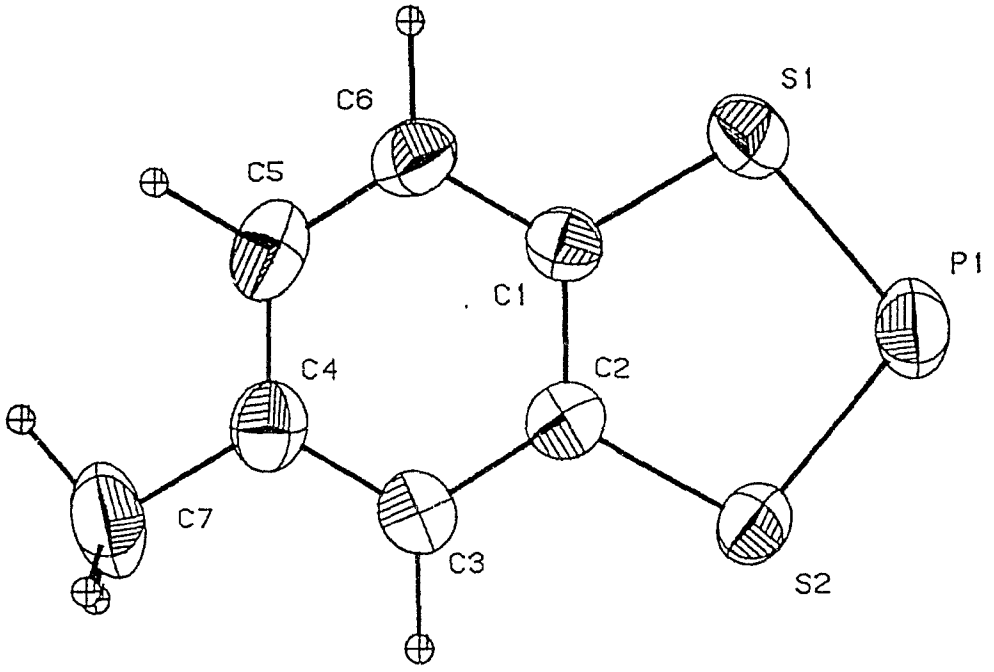
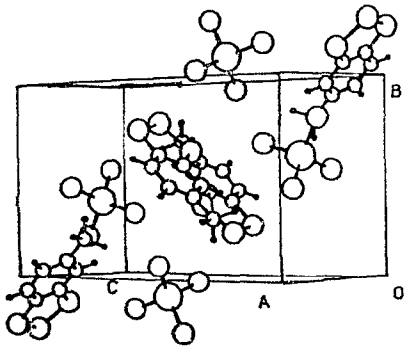


FIGURE I.2.3(c)ii. Diagrams of the 5-Methyl-1,3,2-benzodithiaphospholium Cation, 1c, and the Unit Cell of 1cAlCl$_4$





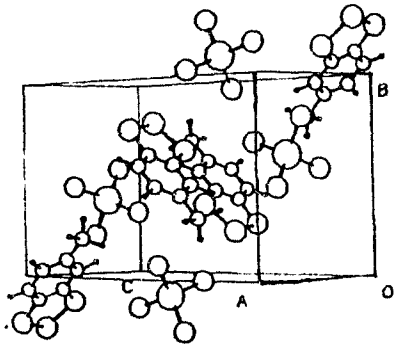


TABLE I.2.3(c) Selected Bond Lengths (pm) and Angles (°) for 1,3,2-Benzodithiaphospholium, 1b, Tetrachloroaluminate and 5-Methyl-1,3,2-benzodithiaphospholium, 1c, Tetrachloroaluminate

	$C_6H_4S_2PAlCl_4$	$C_7H_6S_2PAlCl_4$
P-S(1)	201.6 (3)	201.6 (3)
P-S(2)	201.5 (3)	202.3 (3)
S(1)-C(1)	172.8 (5)	173.2 (7)
S(2)-C(2)	171.1 (6)	173.7 (7)
C(1)-C(2)	138.3 (7)	138.7 (11)
S(1)-P-S(2)	97.6 (1)	98.3 (1)
P-S(1)-C(1)	102.6 (2)	102.2 (2)
P-S(2)-C(2)	102.5 (2)	102.0 (2)
S(1)-C(1)-C(2)	117.8 (4)	119.0 (5)
S(2)-C(2)-C(1)	119.5 (4)	118.6 (5)

The C-S bond lengths of **1b,c** [mean 172.0 (6) and 173.4 (7) pm, respectively] are also significantly less than a standard C-S single bond distance [180 pm][110] and the somewhat shorter distances found for $(PhS)_3P$ [178.5 (2) pm] and **3** [mean 176.3 (6) pm] [Section I.2.3(a)i]. Comparable C-S bond distances to those in **1b,c** are found in molecules which exhibit substantial π-electron delocalisation, such as thiourea [171 (1) pm], thiophene [174 (3) pm] and **1a** [170.8 (2) pm].[121,122,59]

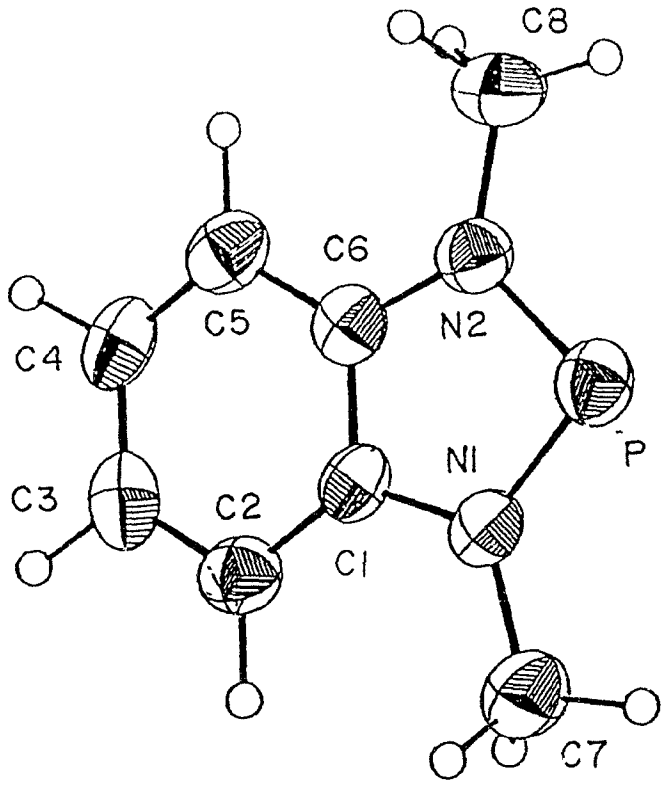
The bond angles within the heterocyclic units of **1b,c** differ greatly. The largest are found at the bridgehead carbons [mean 118.7 (5)°] and the smallest at the phosphorus atoms [mean 97.9 (1)]. In contrast, the five-membered ring of the isolobal, carbocyclic indenyl anion, **8**, has approximately equal [108 (2)°] endocyclic angles.[123]

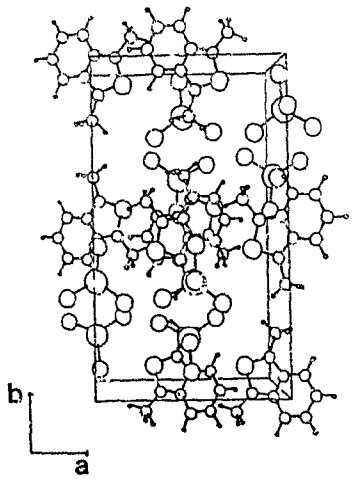
I.2.3(d) Crystal Structure of N,N'-Dimethyl-1,3,2-benzodiaza-phospholium (1f) Tetrachloroaluminate.

Crystals were grown by slow evaporation of CH_2Cl_2. The structure was determined by Dr. White. Diagrams of the crystal packing and the cation are provided in Fig. I.2.3(d).[104,103] Relevant bond lengths (pm) and bond angles (°) are provided in Table I.2.3(d), with the related values for some diaminophosphenium cations and metallo-phosphenium complexes.

1f is planar with a maximum deviation from the best plane of 8.8 pm at C(7). The P-N bond lengths [mean 164.3 (6) pm] are comparable to or slightly longer than those of the other phosphenium compounds listed in Table I.2.3(d), indicative of substantial *pπ-pπ* bonding between the heteroatomic centres. The endocyclic C-N bonds [mean 137.9 (9) pm] are noticeably shorter than the exocyclic counterparts [mean 147.9

FIGURE I.2.3(d). Diagrams of the N,N'-Dimethyl-1,3,2-benzodiazaphospholium Cation, 1f, and the Unit Cell of 1fAlCl$_4$





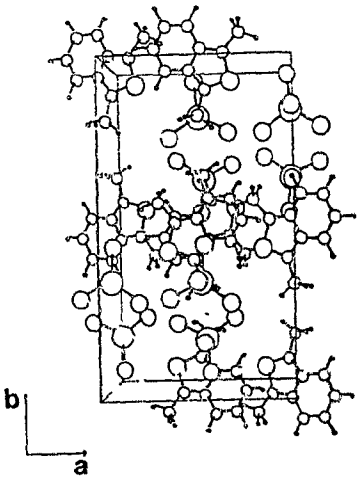


TABLE I.2.3(d). Selected Bond Lengths (pm) and Angles (°) for N,N'-Dimethyl-1,3,2-benzodiazaphospholium, 1f, Tetrachloroaluminate and Some Related Aminophosphenium Systems

$C_8H_{10}N_2PAlCl_4$

P-N(1)	163.8 (6)	P-N(2)	164.8 (6)
N(1)-C(1)	137.8 (9)	N(2)-C(6)	138.0 (9)
N(1)-C(7)	147.7 (10)	N(2)-C(8)	147.4 (10)
N(1)-P-N(2)	91.3 (3)	P-N(1)-C(1)	114.2 (5)
P-N(1)-C(7)	113.2 (5)	P-N(2)-C(6)	113.2 (5)
P-N(2)-C(8)	123.5 (5)	N(1)-C(1)-C(6)	110.1 (6)
N(2)-C(6)-C(1)	111.1 (6)	N(1)-C(1)-C(2)	128.9 (6)
C(1)-N(1)-C(7)	122.0 (6)	N(2)-C(6)-C(5)	127.7 (7)
		C(6)-N(2)-C(8)	123.3 (6)

$(iPr_2N)_2P^+$		$Me_2Si(tBuN)_2P^+$		$Cl_2Al[(Me_3Si)_3N]_2P$	
mean P-N	161.3 (4)	P-N	163.3 (3)	P-N	161.4 (6)
mean C-N	151.3 (6)	C-N	150.7 (5)	N-P-N	97.4 (4)
N-P-N	114.8 (2)	N-P-N	90.2 (1)		

$RNCH_2CH_2N(R)PMo(\eta\text{-}C_5H_5)(CO)_2$

R = Me		R = $PhCH_2$	
mean P-N	164.5 (5)	mean P-N	165.5 (7)
mean N-C *exo*:	144.9 (9)	mean N-C *exo*:	144.4 (11)
endo:	142.9 (9)	*endo*:	146.5 (13)
N-P-N	92.1 (3)	N-P-N	92.5 (4)

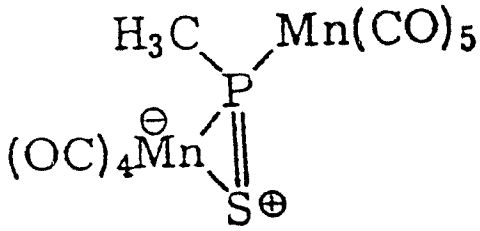
Values taken from references 19(b), 124-127.

(9) pm] and are identical to those found in the benzotriazolium, 9, cation.[128] In comparison, the C-N bond distances of the quinodal 2,1,3-benzoselenadiazole, 10, [mean 132.4 (9) pm][129] are much shorter, similar in length to a full >C=N- double bond.[130] The angle at phosphorus in 1f is noticeably narrower than those of 1b,c, while the angles at the nitrogen centres are wider than those at the sulphurs of 1b,c.

I.2.3(e). Crystal Structure of 1,3,2-Benzazathiaphospholium, 1g, Tetrachloroaluminate.

Crystals were grown by slow evaporation of CH_2Cl_2. The structure has been determined by Dr. White. The crystal structure of 1g$AlCl_4$ is isostructural with that of 1b$AlCl_4$. A unit cell diagram of 1g$AlCl_4$ and an illustration of cation 1g are provided in Figure I.2.3(e).[103,104] Salient bond lengths (pm) and angles (^{o}) are given in Table I.2.3(e)i. The ring system is planar with a maximum deviation from the best plane of 4.5 pm at C4.

1g represents a structural hybrid of 1b,c and 1f. The P-S and C-S bond lengths in 1g [203.4 (1) and 173.2 (4) pm respectively] are almost identical to those determined for 1b,c. Likewise, the P-N and N-C bond lengths [164.3 (3) and 138.7 (4) pm, respectively] are indistinguishable from those of 1f. The N-P-S angle [93.7 (1)^o] is intermediate to those found for the phosphorus centres of 1b,c and 1f. The presence of both sulphur and nitrogen centres in the the planar five-membered ring causes large differences in the other heterocyclic angles. The P-S-C angle [96.5 (1)^o] is less than those in 1b,c while the P-N-C angle [121.1 (2)^o] is greater than the analogous angles in 1f. The S-C-C and N-C-C



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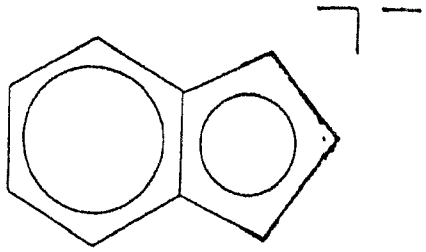

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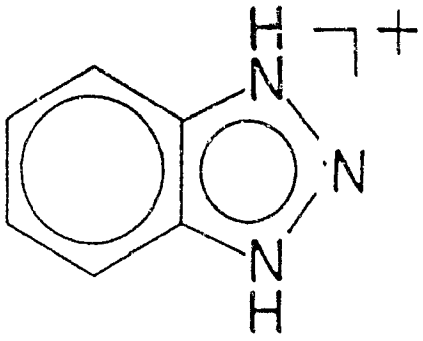

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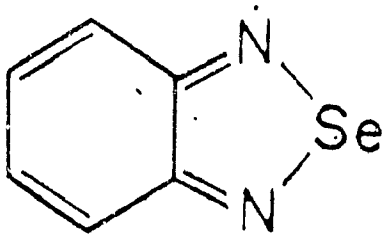

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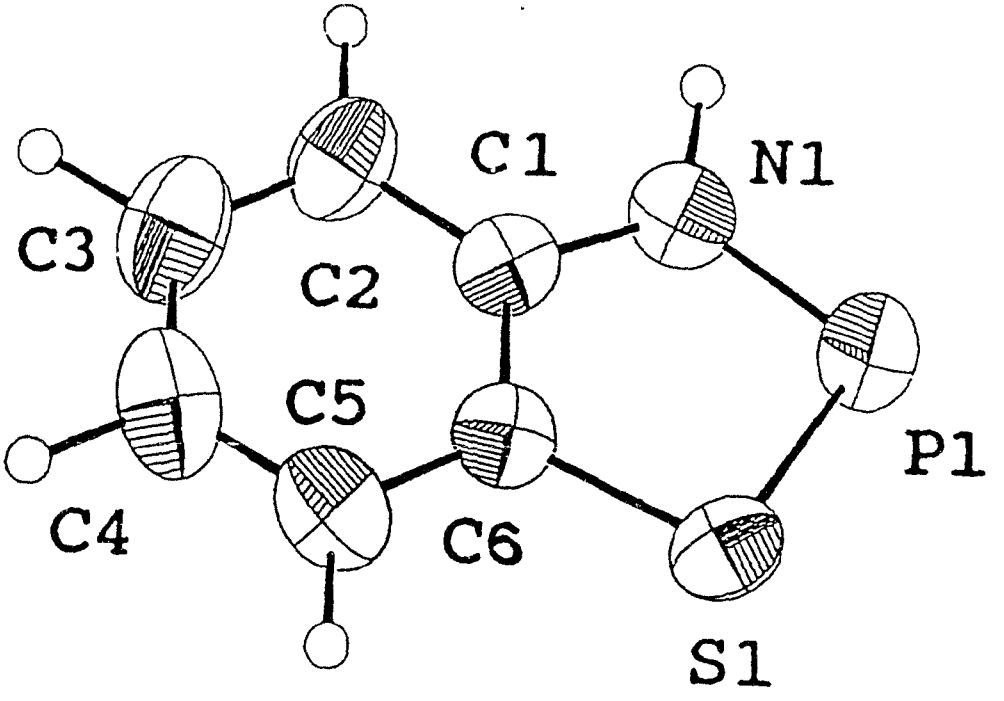
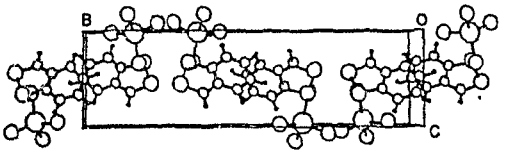
FIGURE I.2.3(e). Diagrams of the 1,3,2-Benzazathiaphospholium Cation, 1g, and the Unit Cell of 1gAlCl$_4$





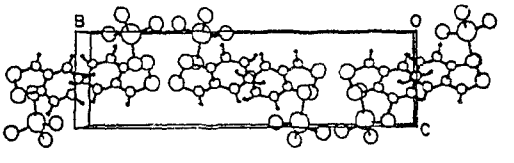


TABLE I.2.2(e). Selected Bond Lengths (pm) and Angles (°) for 1,3,2-Benzazathiaphospholium, 1g, Tetrachloroaluminate

$C_6H_5NSPAlCl_4$

P-S	203.37 (14)
P-N	164.3 (3)
N(1)-C(1)	138.7 (4)
S(1)-C(6)	173.2 (4)
C(1)-C(6)	139.4 (5)

S-P-N	93.74 (11)
C(1)-N-P	121.1 (2)
C(6)-S-P	96.54 (12)
S-C(6)-C(1)	114.1 (3)
N-C(1)-C(6)	114.5 (3)

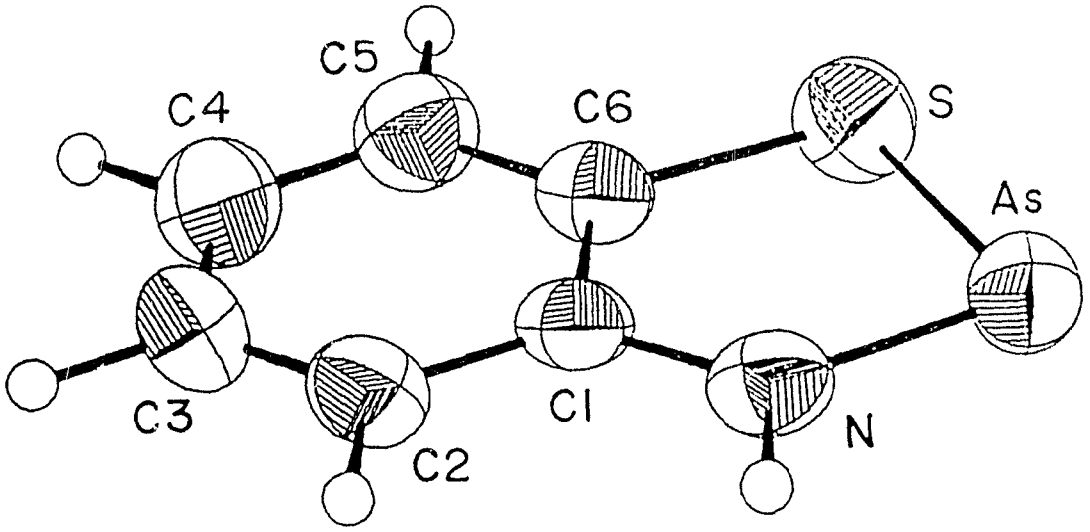
angles of **1g** are identical [114.1 (3) and 114.5 (3)°, respectively]. The former is narrower than those of **1b,c** while the latter is wider than those of **1f**. In light of the uniformity of bond lengths, the severe angular variations found in **1b,c,f,g** are intriguing. The results suggest that the changes in heterocyclic ring strain imposed by the substitution of different atomic centres are better accomodated by angle distortion than by adjustments in bond lengths.

I.2.3(f). The Crystal Structure of 1,3,2-Benzothiazarsolium, 1h, Tetrachloroaluminate.

Crystals were grown by slow evaporation of CH_2Cl_2. The structure was determined by Dr. White. **1h**$AlCl_4$ is isostructural with both **1b**$AlCl_4$ and **1g**$AlCl_4$. A stereoview of the unit cell of **1h**$AlCl_4$ and a diagram of **1h** are provided in Figure I.2.3(f).[103,104] Selected bond lengths and angles are given in Table I.2.3(f). The cation is planar with maximum deviation from best plane of 5 pm at C(4).

The As(III)-S bond distance [215.36 (15) pm] is the shortest yet reported,[131] intermediate to those of arsenic(V) sulphides (*e.g.* 208.2 pm in Ph_3AsS)[132] and typical As-S single bonds [*e.g.* 224.3 (1) pm in $(PhS)_3As$, 220.9(3) pm in **2d**].[112,67] The C-S bond [177.6 (5) pm] is identical to those determined for **1b,g** [see Section I.2.3(c),(e)]. The As(III)-N bond [177.6 (4) pm] is also unusually short [*c.f.* 183.2 (3) pm in the cyclic arsine, $Me_2Si(tBuN)_2AsCl$].[133] Comparable As(III)-N bond lengths have been reported for the unusual cage compound, $Ph_6As_6N_5H_3$, which displays coplanar NAs_3 fragments with bond distances as short as 172 (2) pm.[134] The As-N bond lengths of $(C_6H_2tBu_3)NHAs{=}N(C_6H_2tBu_3)$ are 171.4 (7) and 174.5 (7) pm.[135] As(V)-N $d\pi$-$p\pi$ bonds in compounds

FIGURE I.2.3(f). Diagrams of the 1,3,2-Benzothiazarsolium Cation, 1h, and the Unit Cell of 1hAlCl$_4$



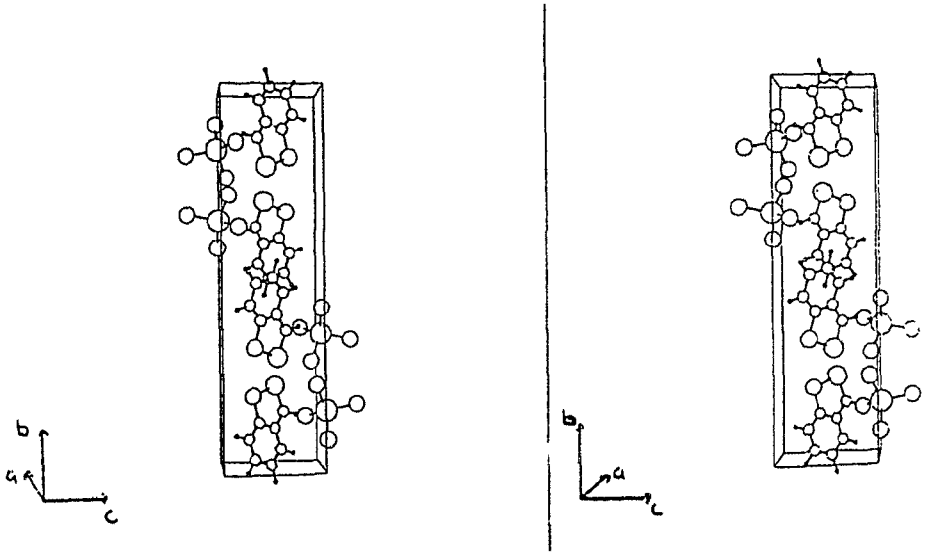


TABLE I.2.3(f). Selected Bond Lengths (pm) and Angles (°) for 1,3,2-Benzothiazarsolium, 1h, Tetrachloroaluminate

$C_6H_4AsNSAlCl_4$

As-N	177.6 (4)
As-S	215.36 (15)
N-C(1)	138.2 (7)
S-C(6)	173.6 (5)
C(1)-C(6)	138.3 (7)
N-As-S	89.27 (14)
As-N-C(1)	121.6 (3)
As-S-C(6)	97.0 (2)
N-C(1)-C(6)	115.8 (5)
S-C(6)-C(1)	116.4 (4)

such as the cyclotri- or cyclotetra-arsazenes are ca. 173 pm.[136] The C-N bond length [138.2 (7) pm] is indistinguishable from those found in **1f,g** [see Sections I.2.3(d),(e)].

The As-N-C angle [121.6 (3)°] is identical to the P-N-C angle of **1g** [see Section I.2.3(e)], however, the As-S-C angle [97.0 (1)°] is much sharper than the P-S-C angle of **1b** [102.6 (2)°]. Also, the S-As-N angle [89.3 (1)°] is markedly narrower than the apical angles determined for the other derivatives of **1** [**1b**, 97.6 (1); **1c**, 98.3 (1); **1f**, 91.3 (3); **1g**, 93.7 (1)°]. Presumably such adjustments are necessary to compensate for the longer pnictogen-heteroatom bond lengths of **1h**.

I.2.3(g). Cation-Anion Interactions in the Crystal Structures of 1AlCl$_4$

The crystallographically characterised derivatives of **1**AlCl$_4$ consist of discrete cationic and anionic units. However, contacts exist between the tetrachloroaluminate anions and heteronaphthalenic cations which are within or at the sum of the van der Waals radii of the elements concerned.[137] Three distinct contact arrays are observed, the characteristics of which are determined by the type and degree of ring substitution:

[A] the interactions displayed by isostructural series **1b,g,h**AlCl$_4$, in which the cation has only proton substituents.

An illustration of the contacts in **1g**AlCl$_4$, which is representative of the isostructural group, **1b,g,h**AlCl$_4$, is provided in Figure I.2.3(g)i. The important contact distances and angles for the **1g**AlCl$_4$ structure are listed in Table I.2.3(g)i. The contacts are localised on the heterocyclic unit of the ring system in a *quasi*-symmetrical fashion. They result in a macrostructure of layers which run approximately

FIGURE I.2.3(g)i. Illustration of Intermolecular Contacts in 1g$AlCl_4$, which is Representative of the Isostructural Group, 1b,g,h$AlCl_4$

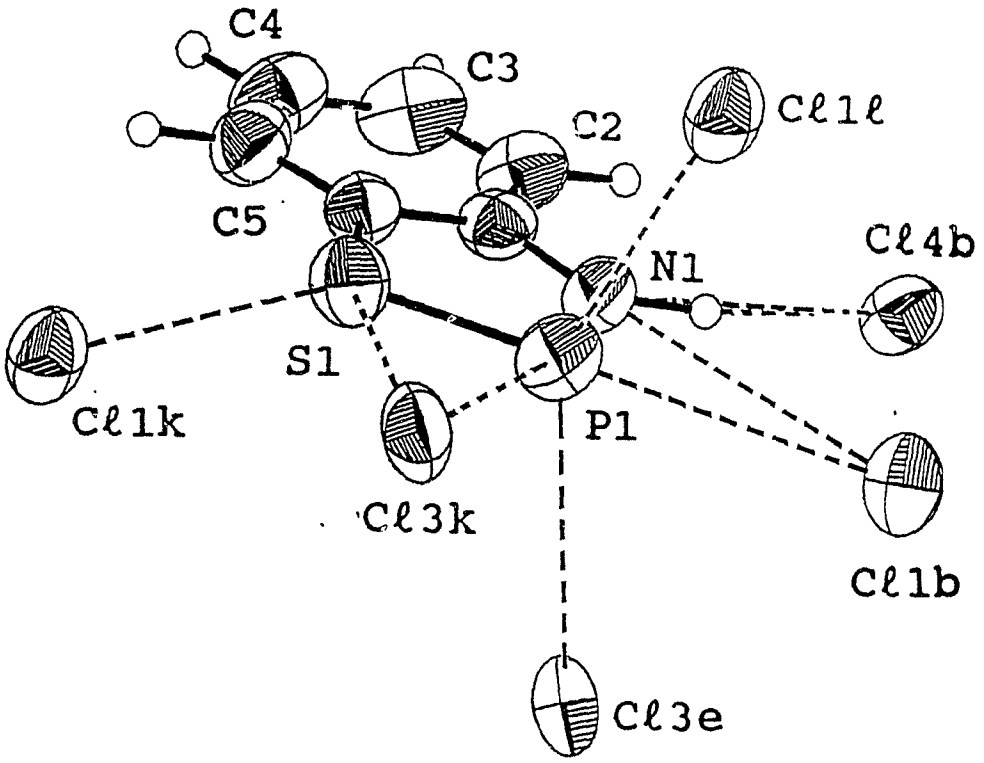


TABLE I.2.3(g)i. Important Intermolecular Contact Distances (pm) and Angles (°) in $\underline{1g}AlCl_4$

P-Cl(1)1	340.5 (2)	P-Cl(1)b	339.3 (1)
P-Cl(3)e	364.2 (2)	P-Cl(3)k	345.4 (1)
S-Cl(3)k	355.1 (1)	S-Cl(1)k	371.1 (1)
N-Cl(1)b	347.1 (3)	N-Cl(4)b	344.1 (3)
H-Cl(1)b	279.6 (1)	H-Cl(4)b	242.0 (1)

Cl(1)1-P-Cl(3)k	71.94 (3)	Cl(1)1-P-Cl(3)e	149.51 (4)
Cl(1)b-P-Cl(1)1	81.40 (3)	Cl(1)b-P-Cl(3)e	67.78 (3)
Cl(3)e-P-Cl(3)k	109.34 (4)	Cl(1)1-P-N	106.1 (1)
Cl(1)b-P-N	78.8 (1)	Cl(3)e-P-N	78.5 (1)
Cl(1)1-P-S	104.34 (5)	Cl(3)e-P-S	105.39 (5)
Cl(3)k-P-S	75.78 (4)	P-S-Cl(3)k	70.50 (4)
Cl(1)k-S-Cl(3)k	57.23 (2)	Cl(1)k-S-C(6)	136.3 (1)
P-N-Cl(1)b	73.5 (1)	Cl(1)b-N-Cl(4)b	59.22 (5)
Cl(4)b-N-C(1)	106.1 (2)	P-Cl(3)k-S	33.72 (3)
N-Cl(1)b-P	27.67 (5)		

perpendicular to the *b*-axis. Two of the contacts are localised at the phosphorus (arsenic) centre above and below the heterocyclic plane. Of the four in-plane cation/anion interactions, two bridge the P-S and P-N bonds, while the others are directed to the sulphur and nitrogen atoms. In **1g,h**$AlCl_4$, the N---Cl interaction also leads to a close contact between the chlorine and the amine proton. This can perhaps be viewed as a weak hydrogen bond, although the tetrachloroaluminate anion is a notoriously poor donor.[138]

Similar contact arrays have been observed in the salts of a number of homopolyatomic non-metal cations, in particular Ch_4^{2+} (Ch = S, Se, Te).[139] This is consistent with the isolobal[140] relationship between the heteroatomic unit of the cation and any three atom segment of a Ch_4^{2+} cation. Moreover, the heterocyclic ring of the cation is isovalent with Ch_4^{2+}.

[B] the interactions found in **1f**$AlCl_4$ in which methyl substituents are at positions 1 and 3 of the cation.

Two important intermolecular contacts, above and below the phosphorus centre, are present in **1f**$AlCl_4$, in comparable positions to those found in **1b,g,h**$AlCl_4$. The interactions are pictured in Figure I.2.3(g)ii and the relevant distances and angles are given in Table I.2.3(g)ii. The steric presence of the N-methyl substituents apparently prevents the bond bridging contacts observed in **1b,g,h**$AlCl_4$ and any lateral interaction between the nitrogen centres and anions. Veith and co-workers observe similar contacts for the tetrachloroaluminate salt of the cyclic $(CH_3)_2Si(t\text{BuN})_2P^+$ cation.[19(b)] However, no intermolecular interactions are reported for the acyclic $[(i\text{Pr}_2\text{N})_2\text{P}]AlCl_4$.[124]

FIGURE 2.2.3(g)ii. Illustration of Intermolecular Contacts in 1f$AlCl_4$

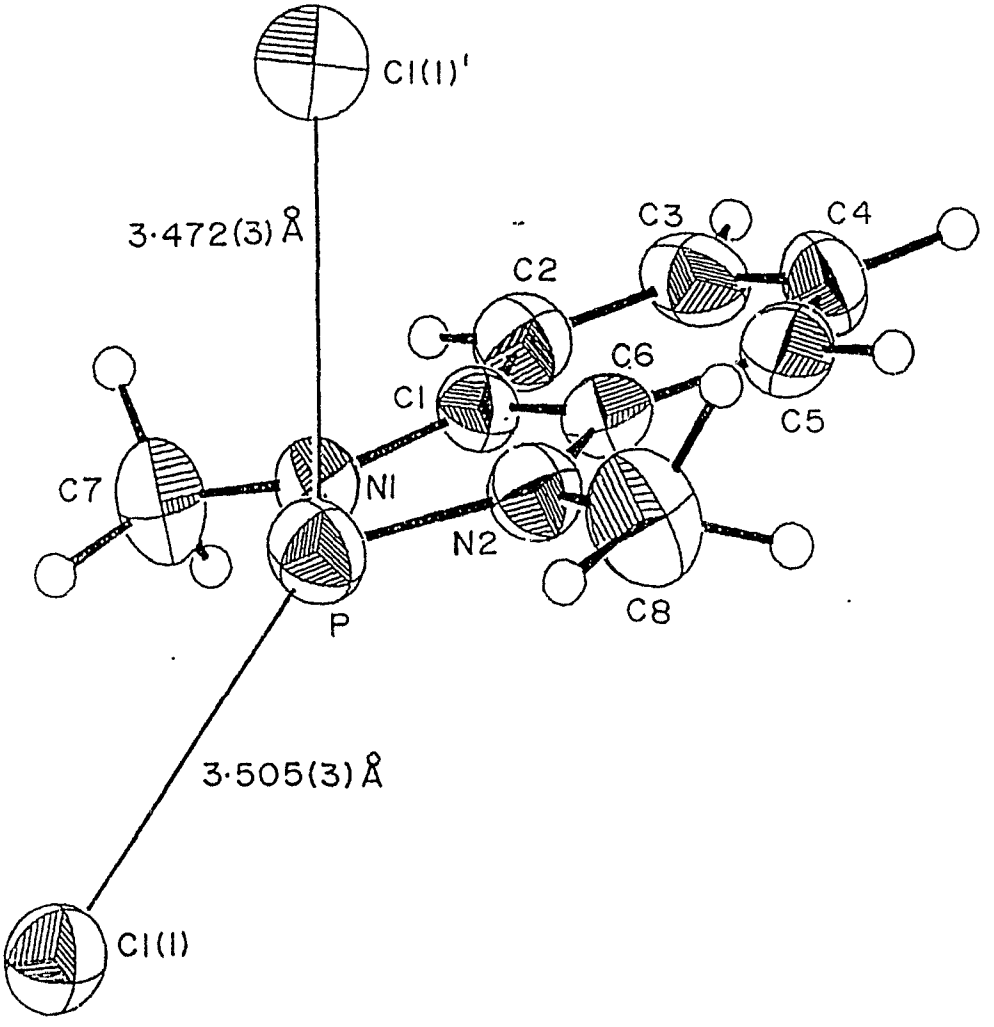


TABLE I.2.3(g)ii. Important Intermolecular Contact Distances (pm) and Angles (^{o}) in $\underline{1f}AlCl_4$

P-Cl(1)	350.5 (3)
P-Cl(1)'	347.2 (3)
Cl(1)-P-Cl(1)'	146.2 (2)
Cl(1)-P-N(1)	96.3 (3)
Cl(1)-P-N(2)	138.8 (3)
Cl(1)'-P-N(1)	84.6 (3)
Cl(1)'-P-N(2)	74.7 (3)

[C] the contacts observed for **1c**$AlCl_4$, where a proton is replaced by a methyl group at the 5 position of the bicyclic ring.

The methyl at the 5 position of **1c** dramatically changes the contact array of **1c**$AlCl_4$ in comparison to that of the unsubstituted **1b**$AlCl_4$. A diagram of the former is provided in Figure I.2.3(g)iii and important distances and angles are listed in Table I.2.3(g)iii. Many of the in-plane contacts of **1b**$AlCl_4$ have been replaced by out-of-plane contacts in the **1c**$AlCl_4$. In addition, the phosphorus-anion contact found below the heterocyclic plane in **1b**$AlCl_4$ [as illustrated for **1g**$AlCl_4$ in Figure I.2.3(g)i] is absent from **1c**$AlCl_4$.

The origin and chemical significance of these intermolecular interactions remains uncertain. The contacts present in the Ch_4^{2+} salts have been modelled by calculations, which indicate that they are weak nucleophilic (charge transfer) donations from the anion to the electrophilic centres of the cations.[141] Certainly, a localisation of positive charge is suggested by the congregation of the contacts around the heteroatoms of the ring systems. However, as demonstrated by the difference in the structures of the salts of **1b** and **1c**, the interactions are weak and do not significantly influence the electronic structure of the cations. This is emphasised by the geometries of the anions which are close to tetrahedral with typical Al-Cl bond lengths [Table I.2.3(g)iv].[139(a)] In contrast, many Main Group and Transition metal cation-aromatic π-complexes have severely distorted $AlCl_4^-$ anions and closer metal-anion contacts,[142] while the anion in $LiAlCl_4$ is dramatically distorted by the small, polarizing cation.[143]

FIGURE I.2.3(g)iii. Illustration of Intermolecular Contacts in 1cAlCl$_4$

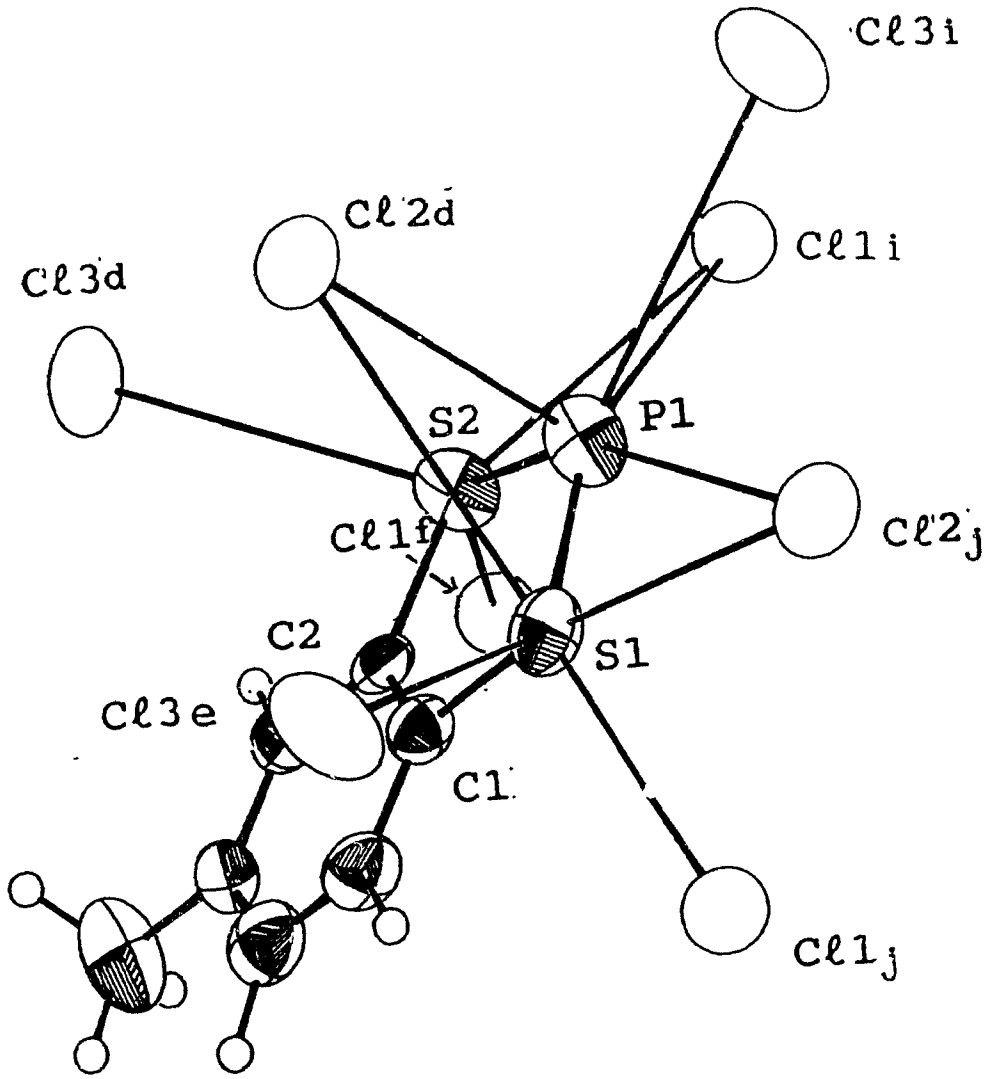


TABLE I.2.3(g)iii. Important Intermolecular Contact Distances (pm) and Angles (^{o}) in $\underline{1c}AlCl_4$

P-Cl(1)i	336.5 (3)	P-Cl(2)d	336.7 (3)
P-Cl(2)j	389.1 (2)	P-Cl(3)i	378.3 (3)
S(1)-Cl(1)j	345.1 (3)	S(1)-Cl(2)d	389.1 (3)
S(1)-Cl(2)j	338.9 (3)	S(1)-Cl(3)e	370.9 (3)
S(2)-Cl(1)f	356.4 (3)	S(2)-Cl(1)i	351.9 (3)
S(2)-Cl(3)d	393.2 (3)		

S(1)-Cl(2)d-P	31.19 (5)	S(1)-P-Cl(2)d	88.89 (9)
P-S(1)-Cl(2)d	59.92 (7)	S(2)-Cl(1)i-P	34.10 (5)
S(2)-P-Cl(1)i	77.12 (9)	P-S(2)-Cl(1)i	68.78 (9)
S(1)-Cl(2)j-P	31.19 (5)	S(1)-P-Cl(2)j	60.53 (8)
Cl(1)j-S(1)-Cl(3)e	67.54 (5)	Cl(1)j-S(1)-Cl(2)j	61.11 (5)
Cl(1)j-S(1)-Cl(2)d	138.45 (6)	Cl(1)i-P-Cl(2)j	119.57 (7)
Cl(1)i-P-Cl(3)i	57.84 (5)	Cl(1)i-P-Cl(2)d	114.18 (7)
Cl(1)f-S(2)-Cl(3)d	112.23 (6)	Cl(1)i-S(2)-Cl(3)d	64.41 (5)
Cl(1)f-S(2)-Cl(1)i	83.63 (5)	Cl(2)d-P-Cl(3)i	82.52 (6)
P-S(1)-Cl(2)j	88.29 (9)		

TABLE I.2.3(g)iv. Ranges and Average Values for the Bond Lengths (pm) and Angles (°) of the Tetrachloroaluminate Anions of 1b,c,f-h

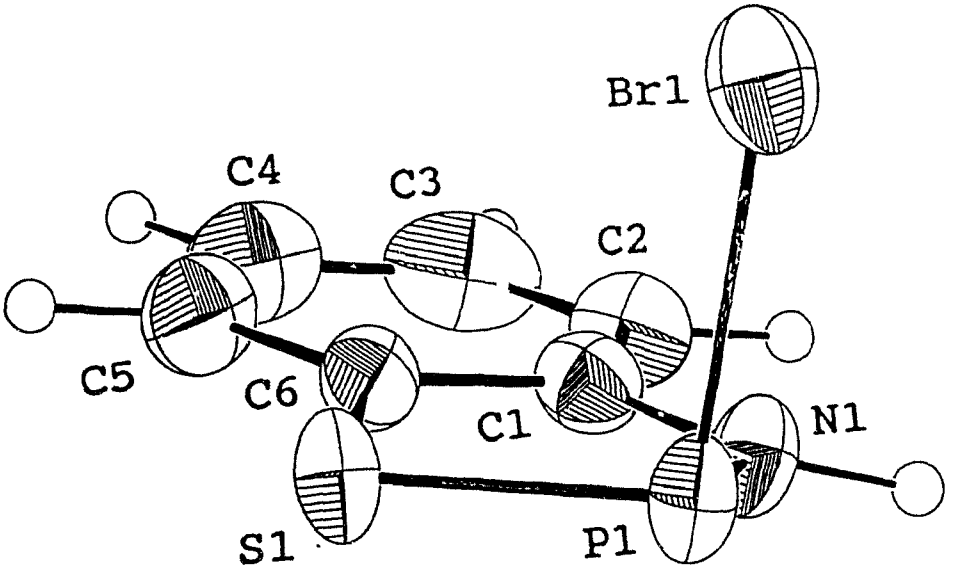
	Al-Cl	Cl-Al-Cl
	1b$AlCl_4$	
Range	211.0 (2) - 213.6 (2)	107.66 (8) - 110.82 (8)
Average	212.5 (2)	109.40 (8)
	1c$AlCl_4$	
Range	211.4 (3) - 214.6 (3)	107.6 (1) - 109.9 (1)
Average	213.0 (3)	109.5 (1)
	1f$AlCl_4$	
Range	212.2 (3) - 213.8 (3)	108.5 (2) - 111.3 (2)
Average	212.8 (3)	109.5 (2)
	1g$AlCl_4$	
Range	214.1 (1) - 210.9 (1)	105.97 (5) - 112.00 (6)
Average	212.9 (1)	109.45 (6)
	1h$AlCl_4$	
Range	210.9 (2) - 213.7 (2)	106.46 (8) - 111.29 (8)
Average	212.8 (2)	109.46 (8)

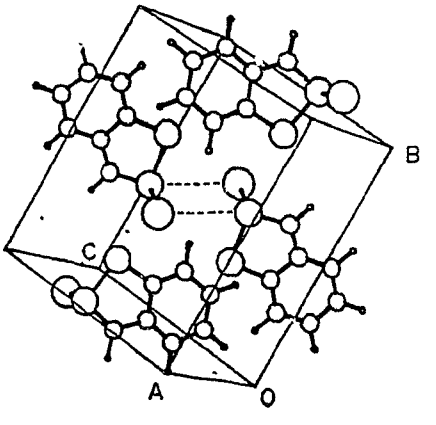
I.2.3(h). Crystal Structures of 2-Chloro-1,3,2-benzazathiaphosphole, 2g(Cl) and 2-Bromo-1,3,2-benzazathiaphosphole, 2g(Br)

The removal, *in vacuo*, of solvent from a dilute diethyl ether solution of **2g(Cl)** gave a beige residue which crystallised overnight while under vacuum. Crystals of **2g(Br)** were grown by slow evaporation of a CH_2Cl_2/Et_2O (*ca.* 1:1) solution. Both structures were solved by Dr. White and they are isostructural. Long intermolecular contacts between the phosphorus and halogen centres gives dimeric units of **2g(Cl),g(Br)**. The dimer is further associated with other dimeric units through interactions between the amine hydrogens and the halogen atoms [**2g(Cl)**: 249.47 (7); **2g(Br)**: 240.5 (2) pm]. A diagram of the unit cell of **2g(Br)** is provided in Figure I.2.3(h)i.[104] An illustration of the monomeric unit of **2g(Br)** is also provided in Figure I.2.3(h)i,[103] and a diagram of the dimer of **2g(Cl)** is given in Fig. I.2.3(h)ii.[103] Important bond lengths (pm) and angles (°) for both molecules are listed in Table I 2.3(h).

The monomeric units are related by an inversion centre. The bridging P_2X_2 (X = Cl, Br) four-membered ring is planar and consists of two unequal phosphorus-halogen interactions. The shorter distances [P-Cl, 224.42 (9) pm; P-Br, 248.7 (2) pm] are unusually long for covalent phosphorus-halogen bonds (*c.f.* 204.3 (3) pm in PCl_3, 222.0 (3) pm in PBr_3)[144,145] while the long P-X interactions [P-Cl, 3.5786 (9); P-Br, 3.568 (2) pm] are within the sum of the respective van der Waals radii.[137] The heterocycles are more or less coplanar and perpendicular to the four membered ring. The plane of the P_2X_2 ring does not bisect the bicyclic ring systems but is displaced so that halogens are

FIGURE I.2.3(h)i. Diagrams of the Molecular Unit and Unit Cell of 2-Bromo-1,3,2-benzazathiaphosphole, 2g(Br).





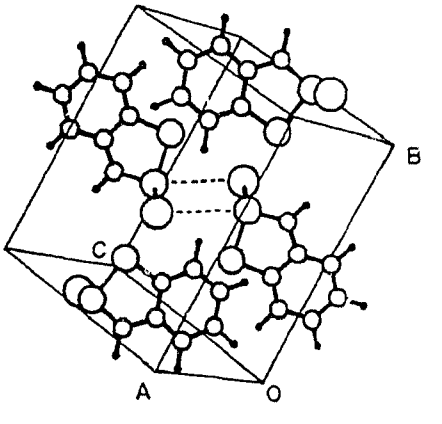
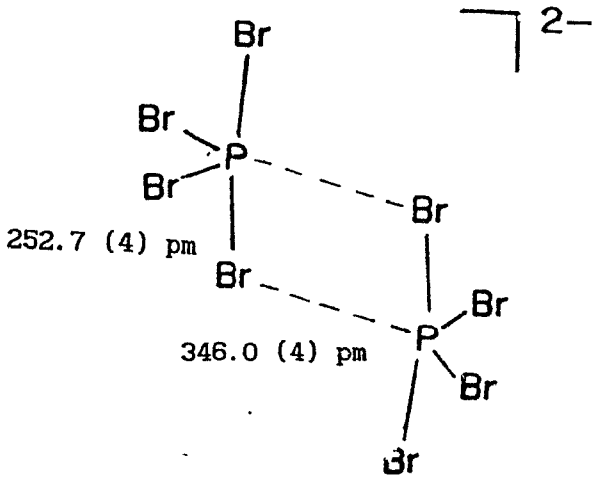


TABLE I.2.3(h). Selected Bond Lengths (pm) and Angles (°) for 2-Chloro-1,3,2-benzazathiaphosphole, 2g(Cl), and 2-Bromo-1,3,2-benzazathiaphosphole, 2g(Br)

	C_6H_5ClNPS	C_6H_5BrNPS
P-X (X = Cl, Br)	224.43 (9)	248.7 (2)
P-X'	357.86 (9)	356.8 (2)
P-N	165.5 (2)	165.9 (5)
P-S	208.66 (8)	208.1 (2)
P-P'	413.2 (1)	430.9 (3)
P-S'	344.93 (8)	343.7 (2)
S-X'	347.15 (9)	354.2 (2)
N-X'	343.0 (2)	351.6 (4)
N-C(1)	140.1 (3)	139.9 (8)
S-C(6)	176.5 (2)	175.3 (6)
C(1)-C(6)	138.2 (3)	139.8 (8)
X-P-X'	92.76 (3)	91.13 (5)
P-X-P'	87.24 (3)	88.87 (5)
X-P-N	102.72 (7)	103.1 (2)
X-P-S	99.65 (3)	99.91 (7)
N-P-S	92.80 (7)	92.8 (2)
P-N-C(1)	120.8 (2)	120.8 (4)
P-S-C(6)	104.08 (7)	104.8 (2)
N-C(1)-C(6)	115.1 (2)	115.4 (5)
S-C(6)-C(1)	114.4 (2)	113.6 (4)

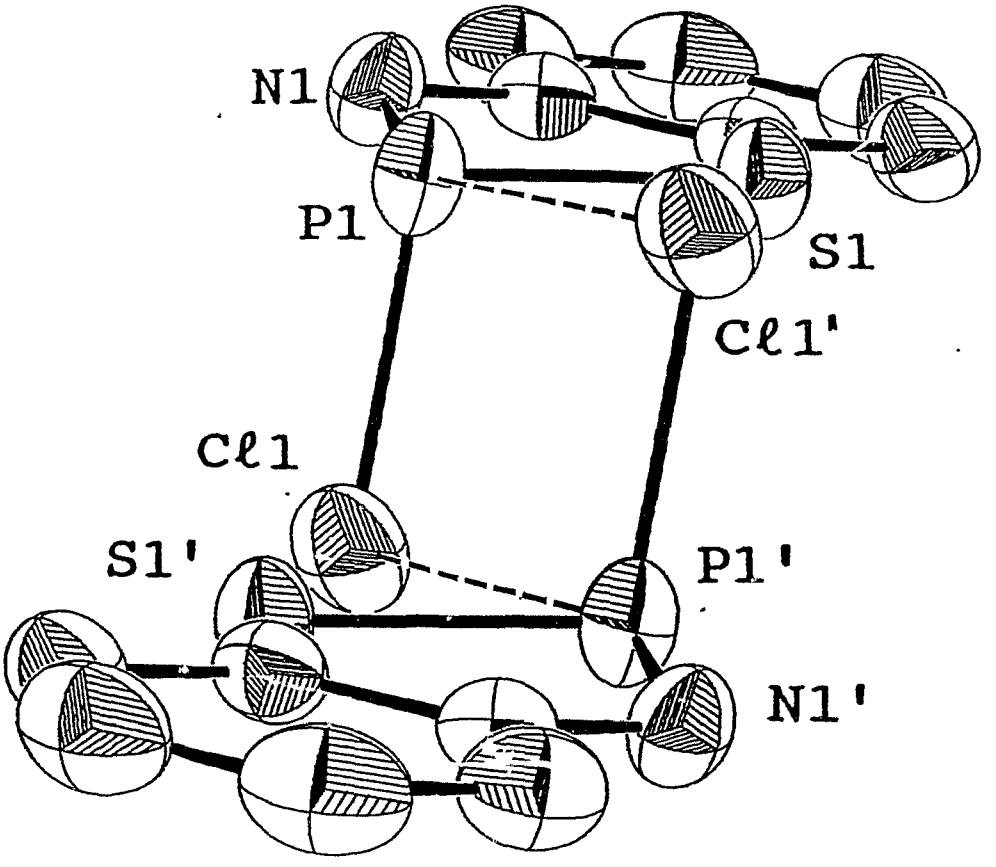
also in contact with the sulphur centres [S---Cl' 347.1(9) pm, S---Br' 354.2 (2) pm], as illustrated in Figure I.2.3(h)ii. The interaction of the chlorine with the heavy elements of the ajacent ring is reminiscent, both in distance and orientation, of the anion contacts to the phosphorus and sulphur centres of **1b.gAlCl$_4$**.

Similar dimeric interactions have been reported for halogenophosphate anions (**11**), such as PBr_4^- and $PX(CN)_4^-$ (X = Br, I), which can be regarded as trapped S_N2 intermediates.[146,147] While the latter anion has equivalent P-Br bond lengths [305.8 (1)], the former exhibits alternating P-Br distances [252.7 (4) pm, 346.0 (4) pm] similar to those in **2g(Br)**. However, other derivatives of PX_4^- do not dimerise in the solid state.[148,149] Solid state and solution ^{31}P NMR studies indicate that the dimeric structures of **11** are maintained in solution.[146] As yet, no solid state ^{31}P NMR spectra of **2g(Cl),g(Br)** have been obtained but the solution ^{31}P chemical shifts obtained are standard for halophosphines [Section I.2.2(c)].



11

FIGURE I.2.3(h)ii. A View of the Dimer of 2g(Cl)



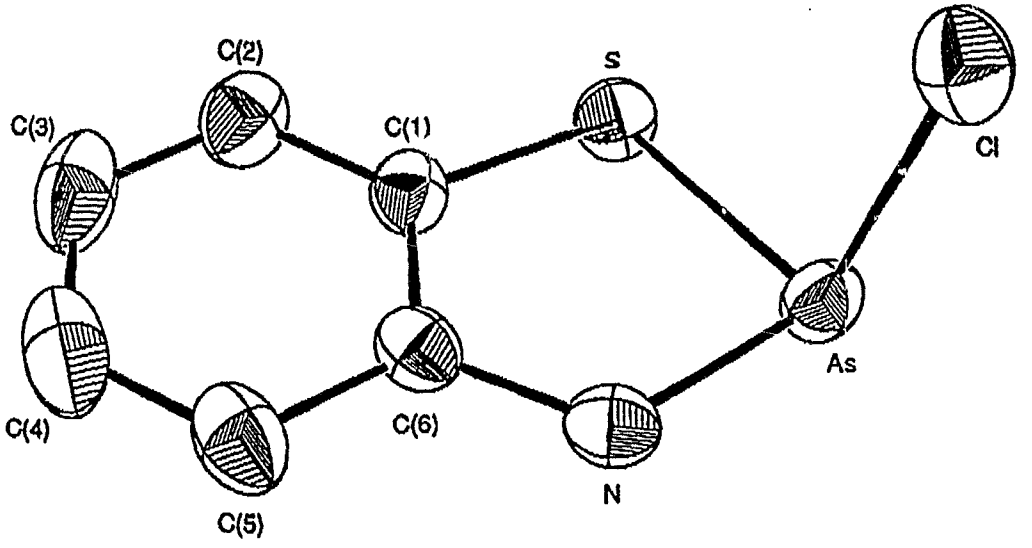
The structural characteristics of the bicyclic units of **2g(Cl), g(Br)** are remarkably similar to those of **1g**. The heterocycles are close to planar with maximum deviations from planarity at the nitrogen centres [19.8 (2) and 17.3 (6) pm, respectively]. The P-N and C-N bond lengths [**2g(Cl)**: P-N = 165.5 (2), N-C = 140.1 (3) pm. **2g(Br)**: P-N = 165.9 (5), N-C = 139.9 (8) pm. **1g**: P-N = 164.3 (3), N-C = 138.7 (4) pm] are essentially identical and only small differences exist in the bond angles of the heterocyclic moieties. The P-S bond distances of **2g(Cl), g(Br)** [208.86 (9) and 208.1 (2) pm respectively] are somewhat longer than in **1g** [203.37 (14) pm], but are still significantly shorter than those of the standard P-S single bonds of **3** and $(PhS)_3P$ [*ca.* 210 pm, see Sections I.2.3(a)-(b)]. The C-S bonds of **2g(Cl)** [176.5 (2) pm] and **2g(Br)** [175.9 (6) pm] are identical to those of **3** and therefore short for C-S single bonds [Sections I.2.3(a)-(b)].

I.2.3(i). Crystal Structure of 2-Chloro-1,3,2-benzothiazarsole, 2h.

Crystals of **2h** were grown by slow evaporation of CH_2Cl_2. The structure was determined by Dr. John F. Richardson of the University of Louisville, Louisville, Kentucky. **2h** is isostructural with **2g(Cl)** and **2g(Br)**. Illustrations of the monomer and the unit cell are given in Figure I.2.3(i) and selected bond lengths and angles are provided in Table I.2.3(i).

As with **2g(Cl), g(Br)**, the dimeric interaction between two monomers of **2h** results in two unequal As-Cl interactions. The shorter [As-Cl, 239.3 (1) pm] is significantly longer than the As-Cl bond distances determined for related heterocycles, *e.g.* 223.6 (3) pm in **2d**[67]; 234.5 (1) pm $Me_2Si(tBuN)_2AsCl$.[133] The longer As---Cl contact

FIGURE I.2.3(i). Diagrams of the Molecular Unit and Unit Cell of 2-Chloro-1,3,2-benzothiazarsole, 2h



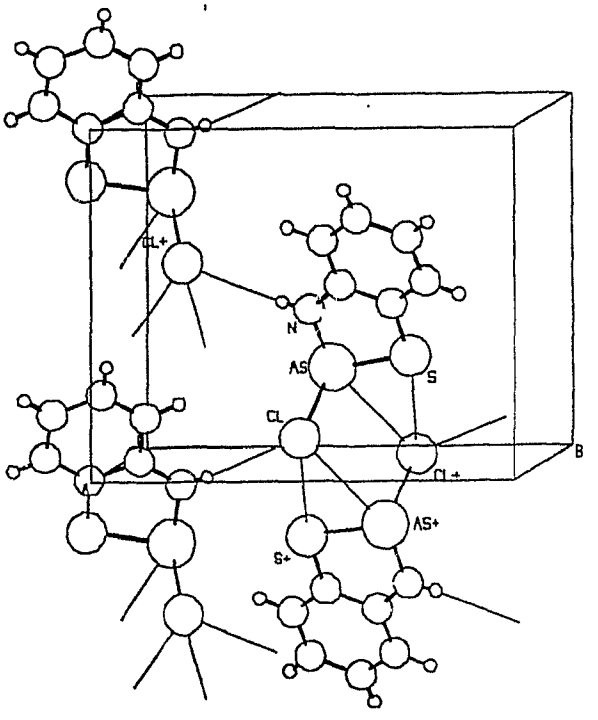


TABLE I.2.3(i). Selected Bond Lengths (pm) and Angles (°) for 2-Chloro-1,3,2-benzothiazarsole, 2h

As-S	219.91 (8)	As-N	179.5 (1)
As-Cl	239.3 (1)	As-Cl'	338.4 (1)
S-C(1)	175.5 (3)	N-C(6)	138.8 (4)
C(1)-C(6)	139.4 (5)	As-S'	342.8 (1)
S-Cl'	343.6 (1)		

Cl-S-As	98.65 (3)	Cl-N-As	101.28 (9)
As-S-C(1)	96.4 (2)	As-N-C(6)	121.4 (3)
S-C(1)-C(6)	116.2 (2)	N-C(6)-C(1)	116.6 (3)
Cl-As-Cl'	89.76 (3)	As-Cl-As'	90.24 (3)

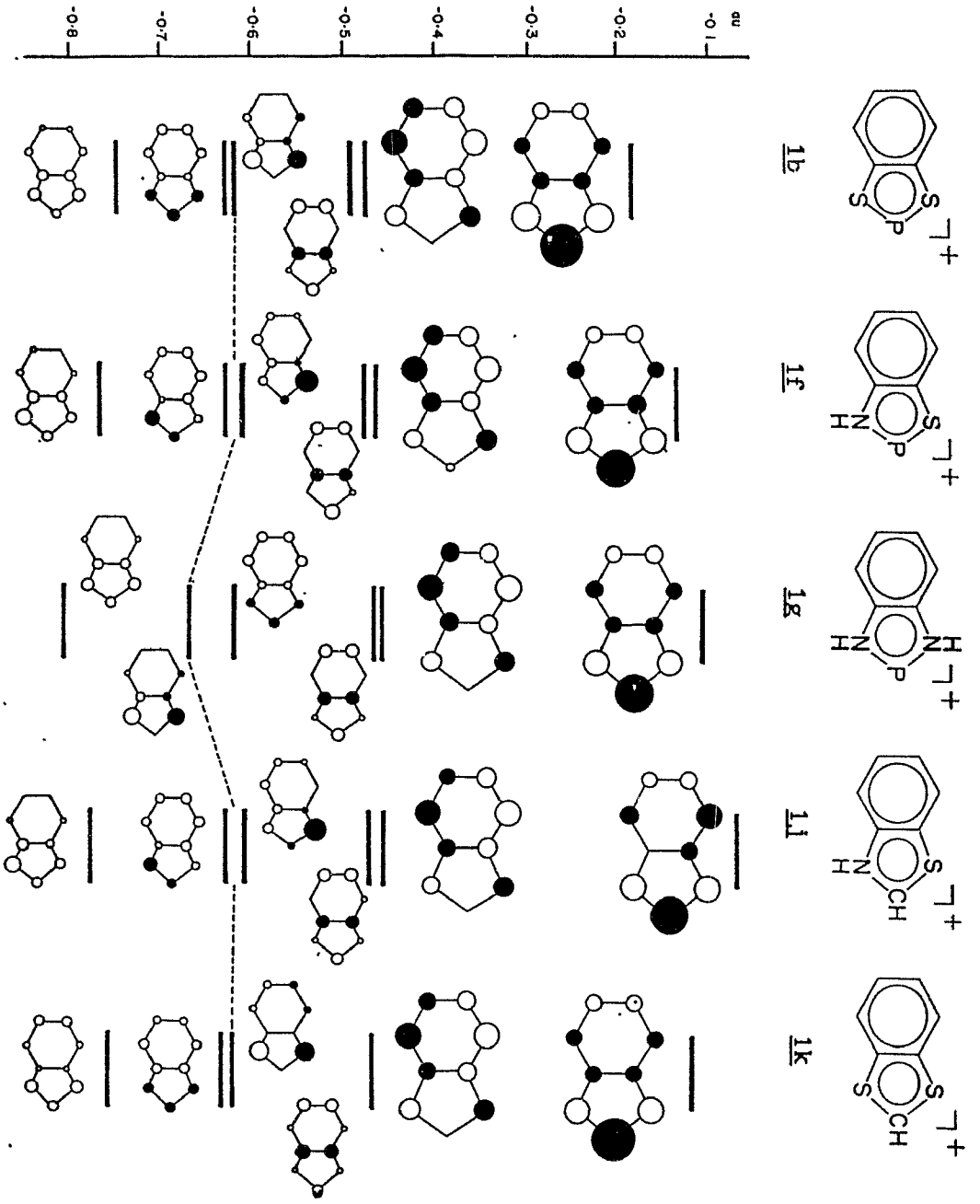
[338.4 (1) pm] is within the sum of the van der Waals radii of As and Cl[137] and may be related to interactions reported for the adduct of 1,3-dimethyl-2(3H)-imidazolethione and $AsCl_3$ [As---Cl, 312 pm],[150(a)] and $As_2Cl_8^{2-}$ [As---Cl, 306.3 (1) pm].[150(b)] Long contacts are also present between the chlorine of one monomer and the sulfur of the other [Cl---S, 343.6 (1) pm], so that the secondary interactions observed for **2h** are similar to the cation-anion contacts found in **1h**$AlCl_4$ [Section I.2.3(g)]

The monomeric unit is almost planar (maximum deviation occurs at As [14.5 pm]). The As-S and As-N bond lengths [219.91 (8) and 179.5 (3) pm, respectively] are both somewhat longer than the analogous distances determined for **1h** [215.36 (15) and 177.6 (4) pm, respectively], while the S-C and C-N bonds [175.5 (3) and 138.8 (4) pm, respectively] are essentially the same length as their counterparts in **1h**. The angles determined for the heterocyclic unit [Table I.2.3(i)] are also very close to those found in **1h**.

I.2.4 Molecular Orbital Calculations

Single point *ab initio* molecular orbital calculations have been performed on cations **1b,f** (N-H derivative),**g** at the STO-3G[151] level using the GAMESS set of programs,[152] on the Dalhousie University VAX 8800 computer. *d*-Orbitals were not included in the basis set. The imput geometries correspond to the experimentally determined values. Calculations were also performed on the 1,3-benzodithiolium **1j** and 1,3-benzothiazolium **1k** cations to allow a direct comparison. Figure I.2.4. provides a pictorial representation of the valence π-orbitals calculated for these systems.

FIGURE I.2.4. Energy Levels and Eigenvectors for the π-Molecular Orbitals of 1b, 1f, 1g, 1i and 1k (Molecular orbitals are viewed from above and the diameters of the circles represent the eigenvector coefficients (1 a.u. = 4.36×10^{-18} J)



The results agree well with those obtained using the π-electron Parsier, Parr, Pople method [Section I.2.2(d)].[91] Allowing for the asymmetry present in **1g,k**, the π-framework remains remarkably constant throughout the series. Consistent with a naphthalenic electronic structure, the π-manifolds closely resemble that reported for the indenyl anion.[123] Comparable results have recently been determined for **1a**.[59(c)]

The π-LUMO's are essentially identical in form and are based primarily on the apical (2-)position. This is in contrast to the dithiazolium derivative, **1a**, in which the π-LUMO is evenly distributed over the sulphur and nitrogen centres[59(c)] Consequently, the chemistry of **1a** is anticipated to be different from that of its heavier cogeners.

The HOMO-LUMO separation is smaller for **1b** (0.2894 a.u.) than for the hybrid **1g** (0.3252 a.u.) which, in turn, has a smaller HOMO-LUMO gap than **1f** (0.3524 a.u.). This is consistent with the observed colours of the three salts (**1b**: bright orange/yellow; **1g**: pale yellow; **1f** colourless). The consequences of the small energy differences for the two highest occupied orbitals and the large energy differences for the two lowest unoccupied orbitals have already been discussed in detail [Section I.2.2(d): MCD].

The HOMO-2 orbitals of the phospholium cations, **1b,f,g**, are not of π-symmetry, being composed primarily of the phosphorus 3*s* and $3p_{x,y}$ AO's, and are believed to represent the phosphorus lone pairs. The high energy of these orbitals indicates that **1b,f,g** are potential electron donors. In fact, Transition metal coordination complexes formed through phosphorus lone pair donation have been reported for

several dicoordinate aminophosphenium cations.[126,127] As discussed in Section I.2.2(c), interactions between the lone pair orbitals and the π-LUMO's may have a considerable effect on the NMR chemical shifts of the phosphorus nuclei. While transition energies derived in this manner are extremely unreliable, the changes in the energy difference between the HOMO-2 and the LUMO of the three phospholium cations (1b: 0.4215; 1g: 0.4649; 1f: 0.4842 a.u.) do reflect the differences in ^{31}P chemical shifts observed for these species (408, 306, 212 ppm, respectively).

I.2.5. Reactivity Studies

Unless otherwise stated, all reactions were performed using equimolar quantities of reagents and CH_2Cl_2 as solvent. Full details are provided in the experimental section (Part III).

I.2.5(a). The Reaction of 2c with Sodium Tetraphenylboron.

^{31}P NMR studies of the heterogeneous reaction of a solution of 2c with solid sodium tetraphenylboron reveals that there is a slow, but almost quantitative (>90%) formation of 3. The source of the phenyl group is confirmed as BPh_4^- by ^{11}B NMR, which shows the replacement of the sharp signal at -6 ppm (BPh_4) by a much broader resonance centred at *ca.* 60 ppm (BPh_3).[153] The reaction most likely involves a form of electrophilic aromatic substitution. Clearly, the mixture of 3 and BPh_3 is thermodynamically preferable to the formation of 1cBPh_4. The slow reaction rate is attributed to the poor solubility of $NaBPh_4$ in CH_2Cl_2.

I.2.5(b). Air Sensitivity of 1c$AlCl_4$

Exposure to the atmosphere of a CH_2Cl_2 solution of 1c$AlCl_4$ results in the almost instantaneous dissipation of its bright orange colour and

the precipitation of a white gel. The ^{31}P NMR spectrum of the mixture shows 2c to be the major phosphorus containing component while the white gel is thought to be mostly Al_2O_3 (a consequence of the thermodynamic strength of the Al-O bond).

I.2.5(c). The Reaction of 1c$AlCl_4$ with Ph_3PO

The reaction of 1c$AlCl_4$ and Ph_3PO leads quantitatively (^{31}P NMR) to 2c and $Ph_3PO.AlCl_3$. The latter product has been identified by comparison of its IR and ^{31}P NMR spectra with those of a pure sample synthesised by the direct reaction of Ph_3PO and $AlCl_3$. Consistently, other research groups have noted similar results when tetrachloroaluminate salts of aminophosphenium cations are reacted with strong Lewis bases.[154,155] It has been proposed that the initial step of such reactions is the coordination of the base to the electrophilic phosphorus centre.[154(a)] Similar mechanisms may account for the reaction of 1c$AlCl_4$ with atmospheric O_2/H_2O.

I.2.5(d). The Reaction of 1c$AlCl_4$ with Ph_3P

The room temperature ^{31}P spectrum of the reaction mixture containing 1c$AlCl_4$ and Ph_3P displays an AB pattern of two doublets, although the resonances are broad and the coupling poorly resolved. However, at lower temperatures the spectrum is much sharper (A: 49.4, B: 6.6 ppm. J_{PP} = 431 Hz). The coupling constant is consistent with a one bond phosphorus-phosphorus coupling[86] and suggests that the compound present in solution is [1c.PPh_3][$AlCl_4$], with the more deshielded chemical shift assigned to the phosphorus(III) centre.

The temperature dependence of the ^{31}P spectrum indicates that the complex is somewhat labile in solution and this is confirmed by ^{31}P NMR

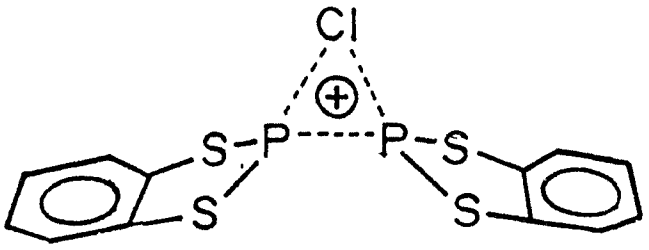
studies on a reaction mixture of **1c**$AlCl_4$ and excess (*ca.* 2 equivs.) Ph_3P. The room temperature spectrum consists of two broad resonances at *ca.* 51 and 1 ppm with an integration ratio of approximately 2:3. The signals coalesce separately at *ca.* -70°C. At -90°C two broad doublets due to [**1c**.PPh_3][$AlCl_4$], and a broad singlet at -8 ppm due to PPh_3, in an approximate ratio of 1:1:1, are observed.

Again, similar reactivity has been observed for the $AlCl_4^-$ salts of aminophosphenium cations.[154(a),155,156,157] However, there is a very fine energetic balance between chloride ion displacement and the formation of a stable phosphorus based adduct. For example, both the work reported here and studies by Parry[154(a)] show that Ph_3P forms a complex with the dicoordinate phosphorus centre. However, Niecke's group has demonstrated that Ph_3P displaces Cl^- from [Cp^*(NH*t*Bu)P][$AlCl_4$] to give $Ph_3P.AlCl_3$ ($Cp^* = C_5Me_5$).[155] Moreover, they prove that the reaction of PEt_3 with the same salt results in {[Cp^*(NH*t*Bu)P].PEt_3}[$AlCl_4$].[155]

I.2.5(e). The Reaction of 1cAlCl$_4$ with 2c

The room temperature ^{31}P spectrum of a **1c**$AlCl_4$/**2c** reaction mixture reveals labile adduct formation through the presence of a broad signal between 400 and 160 ppm. Variable temperature studies show that the system reaches coalescence at approximately -50°C and at -80°C two broad resonances attributable to **1c** and **2c** are observed. The adduct is most likely of form **12**.

It is believed that the existence of **12**, and other adduct species possible at higher concentrations of **2c**, is responsible for the reduced yields of **1c**$AlCl_4$ at high reactant concentrations. $AlCl_3$ is only



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sparingly soluble in the reaction solvent, CH_2Cl_2. Consequently, at first the reaction is mostly heterogeneous and the unreacted 2c complexes to the initially formed cationic centres. The resulting adducts are more reluctant to release a chloride ion than the neutral 2c due to the positive charge. Under such circumstances, alternative reaction pathways, such as electrophilic attack of the benzo unit, become competitive with chloride ion abstraction. Increased dilution of the reagents reduces adduct formation, decreases side reactions and allows easier isolation and a higher yield of the desired salt.

The broad ^{31}P signals observed at room temperature for pure solutions of 1c$AlCl_4$ may be due to a process in which the cation reabstracts chloride from the anion and this, in turn, leads to adduct formation [Section I.2.2(c)].

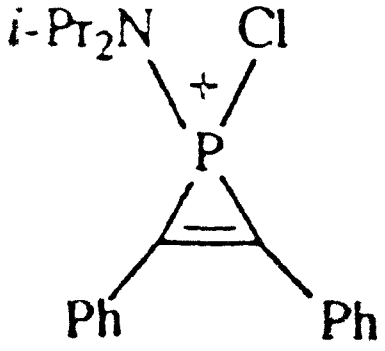
I.2.5(f). The Reaction of 1c$AlCl_4$ and Ph_3N

The ^{31}P NMR of the reaction mixture of Ph_3N and 1c$AlCl_4$ in CH_2Cl_2 indicates that displacement of chloride ion occurs to give 2c. However,

the initial colour of the reaction solution is a bright green, similar to that observed for the reaction of equimolar quantities of $AlCl_3$ and Ph_3N in CH_2Cl_2. As noted in Section I.2.1(b), $AlCl_3/CH_2Cl_2$ can function as an oxidising agent and the green colour is caused by the radical cation of Ph_3N and its dimerisation product, the tetraphenylbenzidene dication.[158] Therefore, the appearence of the green colour in the **1c**$AlCl_4/Ph_3N$ reaction provides evidence for chloride ion reabstraction by **1c** and the formation of trace amounts of $AlCl_3$.

I.2.5(g). The Reaction of **1c**$AlCl_4$ with Alkynes

Aminophosphenium cations have been shown to react with electron rich organic molecules such as dienes, olefins and alkynes and, as such, represent a useful synthetic methodology in the production of heterocyclic phosphorus compounds.[159] However, preliminary reactions of **1c** with *t*BuCCH and PhCCPh gave a mixture of products (^{31}P NMR). One of the ^{31}P NMR resonances obtained in the former reaction which occurs at -73 ppm is close to the signal assigned to the cation **13** at -75 ppm.[160] Therefore, it is possible that a phosphirenium ion is formed in the reaction of **1c** with alkynes. However, the reaction is not quantitative and the project was not pursued further.



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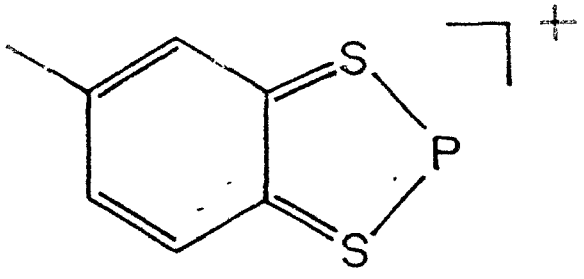
I.2.6. *pπ*-Bonding and the Heteronaphthalenic Framework

The experimental and theoretical evidence [Sections I.2.2 - 5] clearly indicates *pπ*-*pπ* bonding between the heteroatomic centres of **1**. The new bonding arrangements are stabilised by the combination of charge, weakly basic counterions and a Hueckel electron count. As outlined for the Group 16/17 homo- and hetero-polyatomic cations [Section I.1], the positive charge promotes thermodynamic stability by enhancing *pπ*-overlap. In contrast to salts of **1a**, in which the greater strength of N-S *pπ*-bonds allow the co-existence of relatively basic anions (Cl^-, Br^-, Br_3^-) and framework **1**,[59] the weaker *pπ*-bonds formed by the heavier non-metals require a weakly basic complex anion, such as $AlCl_4^-$, to stabilise the ionic environment and avoid pnictogen-halogen covalent bond formation.

The aromatic character of **1** is well established, in particular through MCD spectroscopy studies [Section I.2.2(d)]. Preliminary low temperature X-ray diffraction studies by Drs. Cameron and Linden on **1c**$AlCl_4$ suggest that the quinoid resonance structure **1c'** may make an important contribution to the overall structure.[161] Consistently, a larger three bond (*ortho*) proton-proton coupling constant is observed



1c'

for **1c** in comparison to **2c** [Table I.2.2(c)i], due to an increase in π-electron density for the ring C-C bond. However, a comparable difference is found between the proton NMR spectra of naphthalene and benzene, and is indicative of a change from a 6π- to a 10π-electron system.[81] Therefore, the evidence of quinoid character for **1c** at low temperature is not contradictory to a fully delocalised, aromatic electronic structure but complimentary, as it emphasises the relationship between **1c** and naphthalene. The importance of the Hueckel electron count to the stability of **1** is returned to in Section I.2.7.

The structural studies on the halobenzothiazapnictoles, **2g(Cl),g(Br),h** [Section I.2.3(h,i)], demonstrate near planarity, short heteroatom bond lengths and partial ionic character, and thereby emphasise the inherent thermodynamic stability of heteronaphthalenic framework of **1**. Derivatives of **1,2** and **3** can be catagorised as a series of Lewis acid/base adducts of varying strength. In this respect, **3**, which exhibits a standard covalent P-C bond [182.7 (4) pm], can be viewed as the most strongly bound adduct of **1**, as Ph^- is an extremely strong base [pK_a (benzene) = 43].[162] The halide derivatives **2g(Cl),g(Br),h** exhibit intermediate covalent character, consistent with the moderate basicity of Cl^- [pK_a (HCl) = -6] and Br^- [pK_a (HBr) = -8],[163] so that the solid state monomer units may be considered as ion pairs in which the long polar covalent P-X bond represents a donation of intermediate strength from the halide anion into the LUMO of the cation. The weakest solid state interactions are found in the cation-anion contacts between the derivatives of **1** and the $AlCl_4^-$ counterions. The complex anion is considerably less basic than the halides and

consequently the donor/acceptor interactions are substantially weaker. The secondary P---X interactions of **2g(Cl),g(Br),h** also fall into this category, as the majority of the halide electron density is tied up in the bond to the closer phosphorus atom, thereby considerably reducing basicity of the halide to other acidic centres.

The above observations and conclusions are based mainly on crystallographic data. However, **2g(Cl),g(Br)** have solution ^{31}P chemical shifts typical of tricoordinate phosphorus centres.[86] Furthermore, the solution electronic absorption spectra of **2g(Cl),2g(Br),2h** are clearly different from those of **1g,h**$AlCl_4$ [Section I.2.2(d)]. Therefore, the increased crystal lattice energy of the partially ionic form observed in the solid state, over that of a purely covalent form, may have an important influence in deciding the structure. Of course, the crystal lattice energies of **1**$AlCl_4$ must also be greater than those of the alternative covalent adduct structures (**2**.$AlCl_3$). Indeed, the apparent equilibrium processes observed by ^{31}P NMR for **1b,c**, the broader ^{27}Al NMR resonances obtained for **1b,c,d** $AlCl_4$ and the solution-phase instability of **1e**$AlCl_4/GaCl_4$ suggest that this extra lattice energy may be critical to the solid state stability of the dithia- derivatives of **1**.

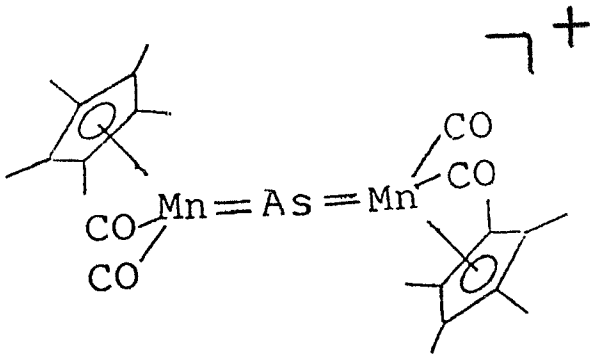
The unique stabilising features of **1** have also allowed the structural characterisation of a genuine dicoordinate cationic arsenic centre $p\pi$-bonded to other Main Group elements. Coincident to this work, the synthesis and structure of a dimanganese complex, **14**, with a cationic arsenic centre and linear two-fold coordination was reported, but this contains multiple arsenic-manganese $p\pi$-$d\pi$ bonding.[164] Jutzi's group determined the crystal structure of the bis(pentamethylcyclopenta-

dienyl)arsenium cation, **15**.[165] However, in agreement with spectroscopic and theoretical studies, the cyclopentadiene rings are bound in an η-3 configuration,[165,166] and the arsenic centre is not truely dicoordinate.

I.2.7. Studies on Non-Aromatic Analogues of 1

The role of the heteronaphthalenic electronic structure in the stabilisation of the novel bonding arrangements of **1** is of great interest.[+] ^{31}P NMR and structural studies demonstrate that aminophosphenium cations maintain a dicoordinate geometry at phosphorus and π-bonding between the phosphorus and nitrogen centres, both in solution and the solid state.[18(d)] For example, the reaction of the saturated 2-fluoro-N,N'-dimethyl-1,3,2-diazaphosphacyclopentane with BF_3 proceeds smoothly to give the N,N'-dimethyl-1,3,2-diazaphospholidinium cation, **16**, quantitatively.[18(d),168] The work reported in Sections I.2.2-6 shows that derivatives of **1** behave similarly. However, the preparation of the dithia- analogues (phosphorus, arsenic) of **16**, has not been reported. Therefore, the reactions of fully saturated 2-chloro-1,3,2-dithiaphospha- and arsa-cyclopentanes, and 2-chloro-1,3,2-diazarsacyclopentanes with $AlCl_3$ and/or $GaCl_3$ have been investigated to

[+] Aromaticity is a subject which continues to fascinate and, often, confuse chemists. The term has a magical aura, a consequence of the "special" stability it infers, and this had led to many, sometimes conflicting, definitions.[167] For the purposes of this work, aromaticity is defined as a planar, delocalised cyclic system which contains a Hueckel $(4n+2)$ number of π-electrons.



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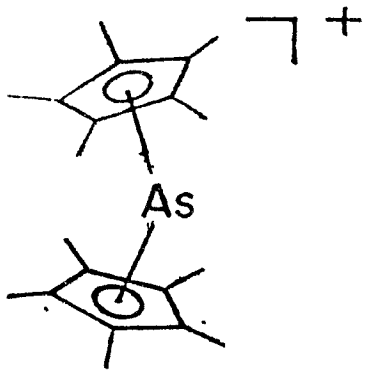

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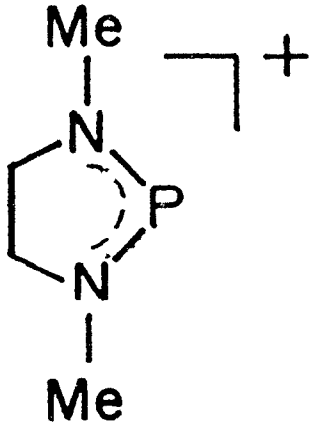

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determine the importance of the additional stabilisation provided by the 10π-electron count to the thermodynamic stability of the heavy element derivatives of **1**.

I.2.7(a) Reaction of 2-Chloro-1,3,2-dithiaphosphacyclopentane, 6, with ECl_3 (E = Al, Ga)

A ^{31}P NMR study of the reaction of **6**[169] with $GaCl_3$ reveals a complex solution behaviour [Figure I.2.7(a)i] which includes the formation of PCl_3. Over a period of minutes, precipitation of a yellow solid is observed. Multiple recrystallisations of the solid with CH_2Cl_2 allows the isolation, in low yield (25%), of the tetrachlorogallate salt of the spirocyclic 1,4,6,9-tetrathio-5-phosphonia-spiro(4,4)nonane cation, **17**. **17**$GaCl_4$ has been characterised by multinuclear NMR, elemental analysis [Table I.2.7(a)i] and X-ray crystallography. The spectral parameters are essentially identical to those of the tetrachloroborate salt prepared by Binder *et al.* from $[PCl_4][BCl_4]$.[170] The ^{31}P signal (154 ppm) identifies **17** as a major (phosphorus containing) component of the reaction mixture.

The crystal structure was determined by Dr. Robin D. Rogers of Northern Illinois University. Relevant bond lengths and angles are listed in Table I.2.7(a)ii, and a unit cell diagram of **17**$GaCl_4$ and an illustration of cation **17** are provided in Figure I.2.7(b)ii.[103] Crystallographic details are given in Appendix 1. The structure is isostructural to that **17**BCl_4.[170] The P-S bond lengths [mean 204.4 (5) pm] are short [Section I.2.3(a,b)], indicative of some $p\pi$-$d\pi$ interaction between the sulphur and phosphorus centres. The geometry at the phosphorus centre is distorted tetrahedral and the rings are non-planar.

FIGURE I.2.7(a)i. ^{31}P NMR Study of the Reaction of 2-Chloro-1,3,2-dithiaphosphacyclopentane, 8, with $GaCl_3$

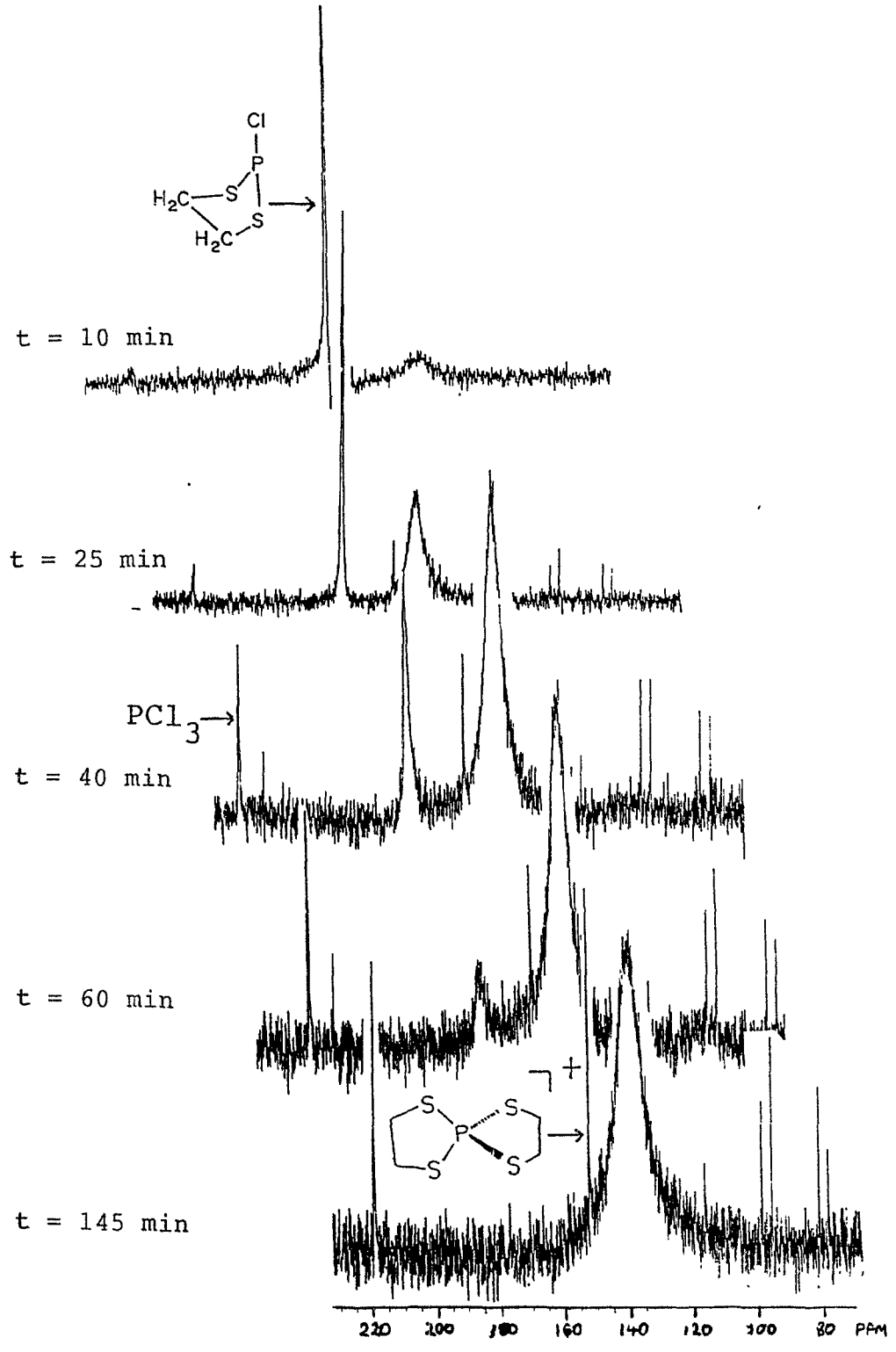


TABLE I.2.7(a)i. Characterisation Data for 1,4,6,9 Tetrathio-5-phosphoniaspiro(4,4)nonane 17 Tetrachlorogallate

^{31}P (CH_2Cl_2): 154.0 (nonet), $^{3}J_{H}$ = 22.2 Hz

^{1}H ($CDCl_3$): 3.94 (doublet), $^{3}J_{HP}$ = 22.7 Hz

^{13}C (CH_2Cl_2): 44.3 (singlet)

IR (ν_{max}, cm^{-1}): 600, 370 ($GaCl_4^-$)[75]

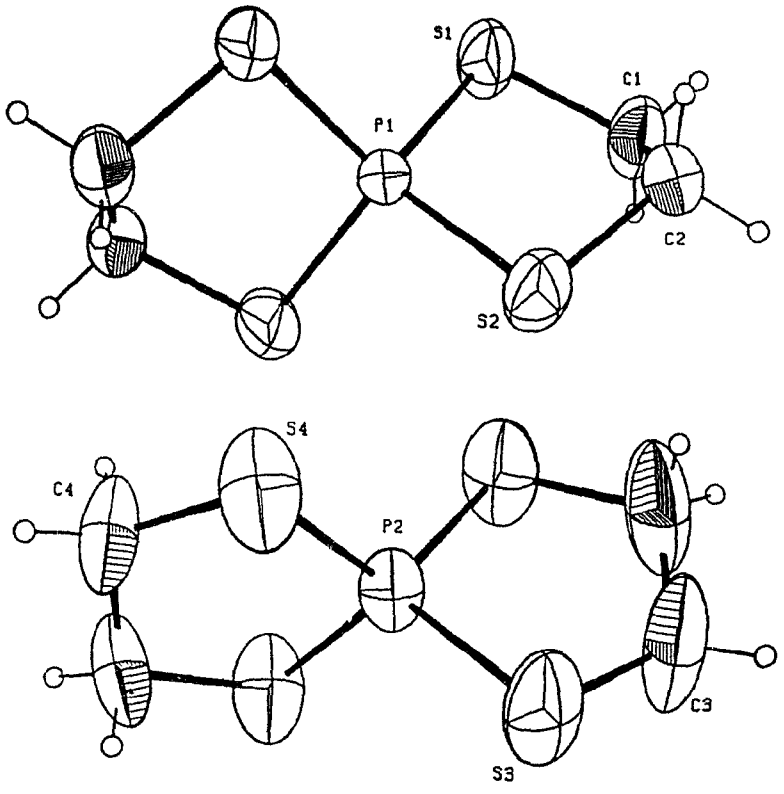
Elemental Analyses

Calcd: C, 11.25; H, 1.89; P, 7.25; S, 30.95 %.

Found: C, 10.98; H, 1.89; P, 7.26; S, 29.14 %.

Dpt. *ca.* 120°C

FIGURE I.2.7(a)ii. Diagrams of the 1,4,6,9-Tetrathio-5-phosphonia-spiro(4,4)nonane Cation, 17, and the Unit Cell of 17$GaCl_4$



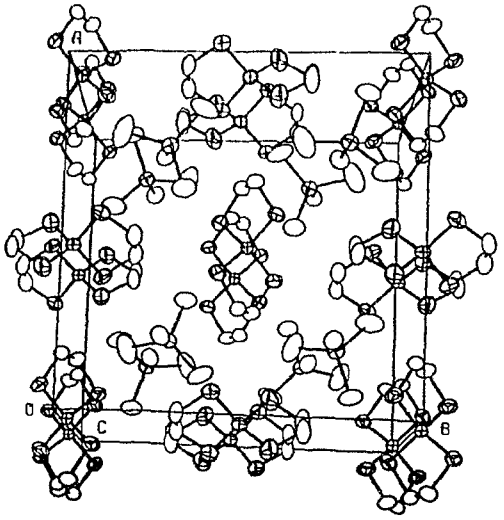


TABLE I.2.7(a)ii. Selected Bond Lengths (pm) and Angles (°) from 1,4,6,9-Tetrathio-5-phosphonia-spiro(4,4)nonane, 17, Tetrachlorogallate.

P(1)-S(1)	204.3 (4)	P(1)-S(2)	205.0 (4)
P(2)-S(3)	205.0 (5)	P(2)-S(4)	203.4 (5)
S(1)-C(1)	181 (1)	S(2)-C(2)	181 (1)
S(3)-C(3)	179 (1)	S(4)-C(4)	178 (1)
C(1)-C(2)	150 (1)	C(3)-C(3)a	140 (3)
C(4)-C(4)a	145 (2)		

S(1)-P(1)-S(2)	103.1 (1)	S(1)-P(1)-S(1)a	105.1 (3)
S(1)-P(1)-S(2)a	121.4 (2)	S(2)-P(1)-S(2)a	104.2 (3)
S(3)-P(2)-S(4)	107.5 (2)	S(3)-P(2)-S(3)a	101.8 (3)
S(4)-P(2)-S(4)a	102.7 (3)	S(3)-P(2)-S(4)a	119.1 (2)
P(1)-S(1)-C(1)	96.2 (4)	P(1)-S(2)-C(2)	96.2 (4)
P(2)-S(3)-C(3)	96.4 (4)	P(2)-S(4)-C(4)	96.2 (4)
S(1)-C(1)-C(2)	111.4 (9)	S(2)-C(2)-C(1)	111.6 (8)
S(3)-C(3)-C(3)a	115.0 (8)	S(4)-C(4)-C(4)a	113.4 (7)

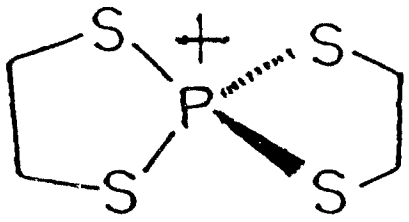
Ga-Cl	range	214.9 (4) - 216.5 (3)	mean	215.7 (4)
Cl-Ga-Cl	range	106.9 (1) - 113.6 (2)	mean	109.7 (2)

The equivalence of the proton and carbon nuclei on the NMR time scale is presumably due to rapid ring flips in solution. The closest cation-anion contacts occur at the sulphur centres [S(1)---Cl(3), 371.5 (6); S(2)-Cl(3), 343.1 (6); S(4)-Cl(3), 366.0 (6) pm] and are similar in length to those found in **1b,c,g**$AlCl_4$. The geometry of the tetrachlorogallate anion is standard.[171]

The mechanism for the formation of **17**$GaCl_4$ is uncertain. However, the reaction of **6** with $AlCl_3$ in the presence of 2,3-dimethylbutadiene leads to the quantitative formation of the bicyclic phospholenium cation **18** [Table I.2.7(a)iii], indicating the intermediate existence of the 1,3,2-dithiaphospholidinium cation, **19**.[159,160,172] ^{31}P NMR studies demonstrate that the reaction of **6** with $AlCl_3$ in the presence of a deactivated diene such as hexachlorocyclobutadiene does not result in a phospholenium cation. Instead, the reaction mixture is identical to that obtained in the absence of the diene.

A single point calculation at the STO-3G level[151,152] was performed on **19**. The geometry of the cation was taken to be planar and the bond lengths were set at 201.0 (P-S), 181.0 (C-S), 150.0 (C-C) and 110.0 (C-H). The results are consistent with both the calculations performed on **1** (Section I.2.4) and other molecular orbital studies on dicoordinate phosphorus cations.[18(d)] A pictorial representation of the π-manifolds of the frontier molecular orbitals (FMO's) is provided in Figure I.2.7(a)iii.

The nodal properties of the LUMO readily explain the rapid and quantitative reaction of **19** with 2,3-dimethylbutadiene,[72,172] although the LUMO cannot be low enough in energy to allow reaction with



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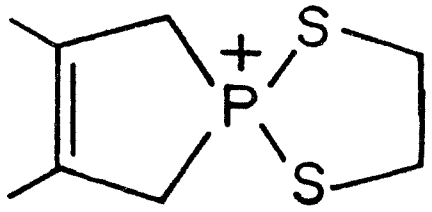

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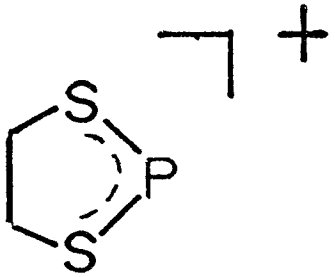

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TABLE I.2.7(a)iii. Multinuclear NMR Characterisation of the Phospholenium Salt, 18$AlCl_4$

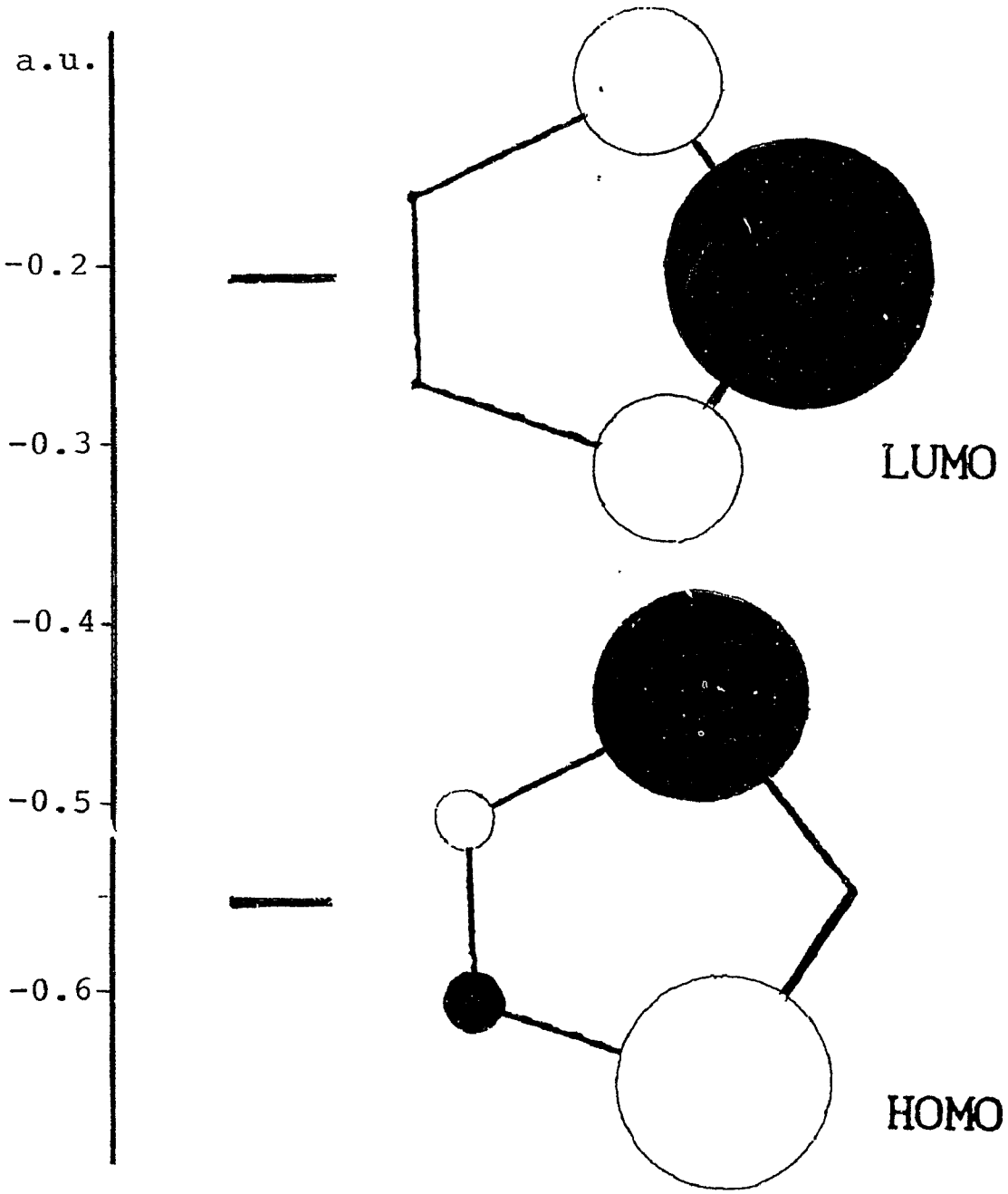
^{31}P {^{1}H} (CH_2Cl_2): 111 ppm

^{27}Al (CH_2Cl_2): 102 ppm ($\Delta\nu_{1/2}$ < 20 Hz, $AlCl_4^-$)

^{1}H ($CDCl_3$): 3.95 (SCH_2, doublet, $^{3}J_{PH}$ = 15.8 Hz), 3.58 (PCH_2, doublet, $^{2}J_{PH}$ = 9.7 Hz), 1.88 (singlet, CH_3) ppm.

^{13}C (CH_2Cl_2): 129 (alkene, doublet, $^{2}J_{CP}$ = 9.7 Hz), 43.4 (singlet, SCH_2), 41.2 (PCH_2, doublet, $^{1}J_{CP}$ = 42.6 Hz), 16.0 (CH_3, doublet, $^{3}J_{CP}$ = 14.6 Hz)

FIGURE I.2.7(a)iii. Energy Levels and Eigenvectors for the Frontier Molecular Orbitals of 19 (Molecular orbitals are viewed from above and the diameters of the circles represent the eigenvector coeffecients)



hexachlorocyclopentadiene. However, a comparison of the LUMO of **19** with those of stable dicoordinate phosphorus cations [Table I.2.7(a)iv] shows that it is the lowest in energy and thus **19** is expected to be, kinetically, the most reactive of these species, especially at the phosphorus centre. Therefore, although FMO analysis does not directly explain the mechanism of formation of **17**, the very low energy of the LUMO suggests that reactions which are not observed for other dicoordinate phosphorus cations, for example, reaction with solvent (CH_2Cl_2), may be possible for **19**.

I.2.7(b) Reaction of 2-Chloro-1,3,2-dithiarsacyclopentane, 20, with $GaCl_3$

The heterogeneous reaction of 2-chloro-1,3,2-dithiarsacyclopentane, **20**,[173] with $GaCl_3$ in CH_2Cl_2 results in a yellow precipitate, which can be recrystallised from CH_2Cl_2 to give pale yellow, air-sensitive crystals of *bis*-1,3,2-dithiarsolidinium, **21**, tetrachlorogallate in 35% yield. **21**$[GaCl_4]_2$ has been characterised by ^1H and ^{13}C NMR, and infrared spectroscopy, mass spectrometry, elemental analysis [Table I.2.7(b)i] and X-ray crystallography.

The crystal structure of **21**$[GaCl_4]_2$ has been determined by Dr. John F. Richardson of the University of Louisville, Kentucky. Relevant bond lengths and angles are reported in Table I.2.7(b)ii and illustrations of **21** and the unit cell of **21**$[GaCl_4]_2$ are provided in Figure I.2.7(b)i.[103] Crystallographic details are given in Appendix 1.

The cationic unit, **21**, can be viewed as a dimer of the 1,3,2-dithiarsolidinium cation, **22**, bound together by means of a planar As_2S_2 ring, and related by a crystallographic inversion centre. A similar dimeric interaction has been reported for neutral 1,2-thiastiba-

TABLE I.2.7(a)iv. STO-3G Single Point LUMO Energies (atomic units) for Selected Dicoordinate Phosphorus Cations.

1,3,2-dithiaphospholidinium, **19**	-0.2012
N,N'-Dimethyl-1,3,2-diaminophospholidinium, **16**	-0.1121
N,N'-Dimethyl,1,3,2-benzodiazaphospholium, **1f**	-0.1031
1,3,2-Benzothiazaphospholium, **1g**	-0.1356
1,3,2-Benzodithiaphospholium, **1b**	-0.1841

$$1 \text{ a.u.} = 4.36 \times 10^{-18} \text{ J}$$

TABLE I.2.7(b)i. Characterisation Data for *bis*-1,3,2-dithiarsolidinium, 21, Tetrachlorogallate

^{1}H ($CDCl_3$): 4.08 ppm

^{13}C (CH_2Cl_2): 45.4 ppm

IR (ν_{max}, cm^{-1}): 375 ($GaCl_4^-$)^{75}

Mass Spectrum [m/z (rel. int.)] 204 (21) $C_2H_4S_2As^{37}Cl^{+\cdot}$; 202 (52) $C_2H_4S_2As^{35}Cl^{+\cdot}$; 167 (100), $C_2H_4S_2As^{+}$; 139 (18), AsS_2^{+}; 107 (56), AsS^{+}.

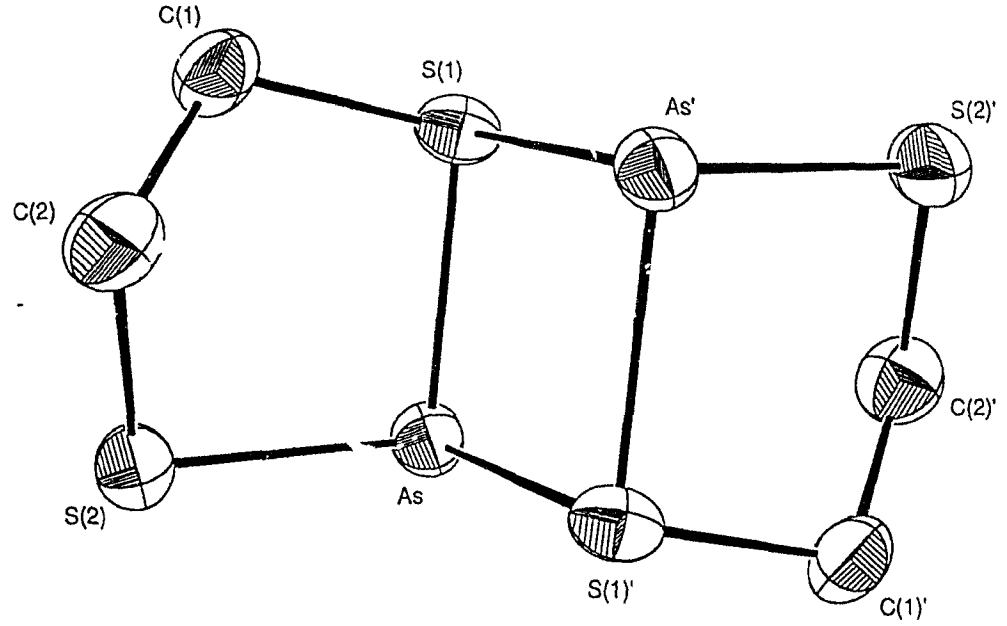
Elemental Analyses

Calcd. C, 6.34; H, 1.07; S, 16.94; As, 19.79 %

Found. C, 6.37; H, 1.16; S, 17.10; As, 19.65 %

Mpt. 88 - 91°C

FIGURE I.2.7(b)i. Diagrams of the *Bis*-1,3,2-Dithiarsolidinium Cation, 21, and the Unit Cell of 21$[GaCl_4]_2$



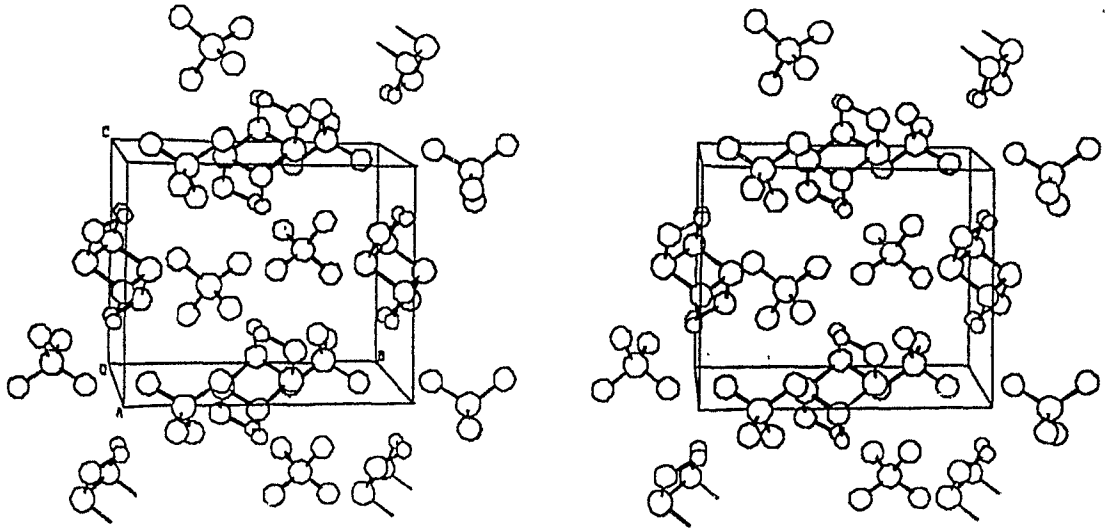
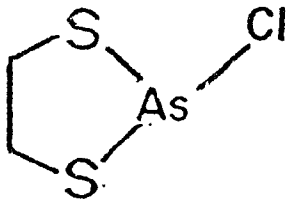


TABLE I.2.7(b)ii. **Selected Bond Lengths (pm) and Angles (°) for *Bis*-1,3,2-Dithiarsolidinium, 21, Tetrachlorogallate**

As-S(1)	232.6 (2)	As-S(2)	218.1 (1)
As-S(1)'	242.3 (2)	S(1)-C(1)	182.6 (6)
S(2)-C(2)	182.6 (7)	C(1)-C(2)	154 (2)

S(1)-As-S(2)	93.14 (6)	As-S(1)-As'	93.12 (6)
S(1)-As-S(1)'	86.88 (6)	As-S(1)-C(1)	98.7 (2)
As-S(2)-C(2)	100.6 (2)	S(1)-C(1)-C(2)	112.7 (5)
S(2)-C(2)-C(1)	111.7 (4)		

Ga-Cl	range	215.8 (2) - 222.2 (1)	mean	218.4 (2)
Cl-Ga-Cl	range	105.80 (6) - 113.45 (7)	mean	109.48 (7)



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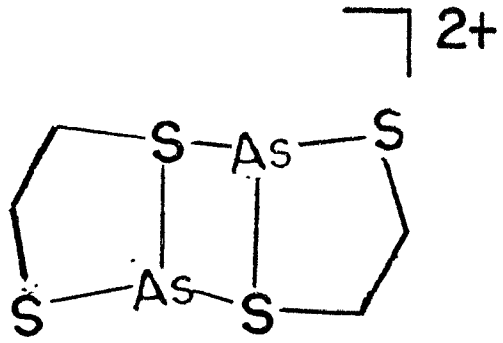

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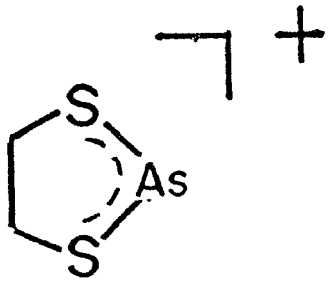


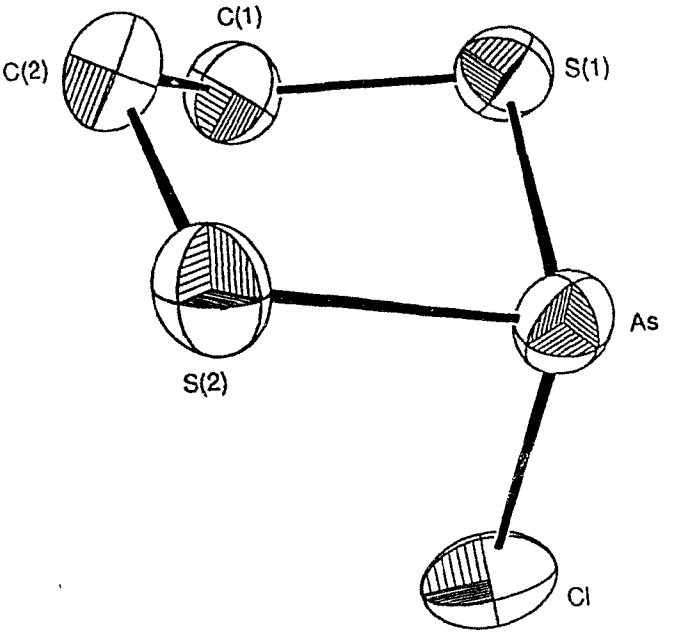
22

cyclopentanes.[174] There are three sets of As-S bonds. The longest [As-S(1)', 242.3 (2) pm], which links the monomeric units, is significantly longer than a standard As-S single bond *e.g.* 224.3 (1) in $(PhS)_3As$.[112] Within the five-membered heterocycle, the bond associated with the dimeric interaction [As-S(1), 232.6 (2) pm] is, again, somewhat longer than typical As-S single bonds. In contrast, the neighbouring bond [As-S(2), 281.1 (1) pm] is one of the shortest yet reported,[131] and is indicative of some degree of localised π-bonding. Close cation-anion contacts exist [*e.g.* As-Cl(1)b, 318.1; As-Cl(3)c, 347.8; As-Cl(4)c, 343.8 pm. S(1)-Cl(3)m, 336.2; S(1)-Cl(1)b, 346.2; S(2)-Cl(2)i, 340.3 pm] and are currently under investigation. However, the structure of the anion is unexceptional.[171]

The five-membered rings are not planar, C(2) lying 66.1 (6) pm out of the best plane through the remaining four atoms. Therefore, the ^1H and ^{13}C NMR spectra are consistent with monomerisation of **21** to **22**, in solution. The S(1)-As-S(2) [93.14 (6)°] and As-S-C [98.7 (2)° and 100.6 (2)°] angles are comparable to those determined for **2d** [S-As-S, 92.62 (9)°. As-S-C, 99.43 (10), 100.34 (10)°].[67] The four membered ring is planar [sum of angles = 360.0 (2)°], and, as expected, the angle at the heavier element is the smaller of the two [S(1)-As-S(1)', 86.88 (2); As-S(1)-As', 93.12 (2)°].

For direct comparison, the crystal structure of **20** has been determined by Dr. Richardson. Colourless crystals are grown by cooling a saturated CCl_4 solution to 0°C for several hours. Selected bond lengths and angles are listed in Table I.2.7(b)iii and diagrams of the heterocycle and the unit cell are given in Figure I.2.7(b)ii.[103]

FIGURE I.2.7(b)ii. Diagrams of the Molecular Unit and the Unit Cell of 2-Chloro-1,3,2-dithiarsacyclopentane, 20



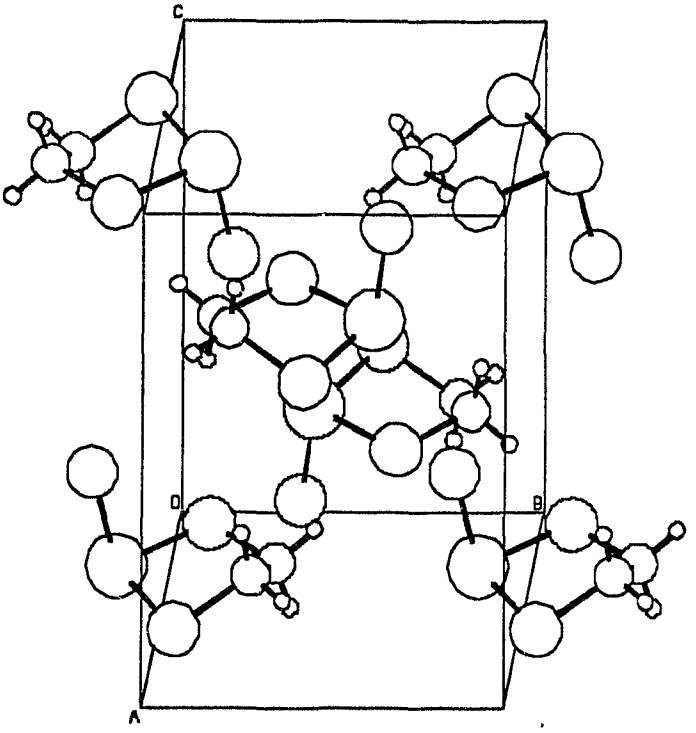


TABLE I.2.7(b)iii. Selected Bond Lengths (pm) and Angles (°) for 2-Chloro-1,3,2-dithiarsacyclopentane, 20

As-Cl	225.25 (8)	As-S(1)	219.42 (9)
As-S(2)	222.5 (1)	S(1)-C(1)	181.9 (4)
S(2)-C(2)	182.2 (4)	C(1)-C(2)	150.1 (5)
Cl-As-S(1)	99.51 (3)	Cl-As-S(2)	98.21 (3)
S(1)-As-S(2)	93.50 (3)	As-S(1)-C(1)	97.1 (1)
As-S(2)-C(2)	100.8 (1)	S(1)-C(1)-C(2)	110.2 (3)
S(2)-C(2)-C(1)	111.2 (2)		

Crystallographic details are provided in Appendix 1.

20 is also non-planar, C(1) being 81.2 (3) pm out of the best plane through the other four atoms. The As-S bond lengths [As-S(1), 2.1942 (9); As-S(2), 222.5 (1) pm] are slightly shorter than a standard As-S single bond,[112] most likely a consequence of the electronegative chlorine attached to the arsenic centre. The S-C bond lengths are standard and identical to those of **21** [**21**, 182.6 (7); 182.6 (6) pm. **20**, 181.9 (4); 182.2 (4) pm]. The As-Cl bond length [225.25 (8) pm] is comparable to that of **2d** [223.6 (3) pm][67] but considerably shorter than those determined for $Me_2Si(tBuN)_2AsCl$ and **2h** [234.5 (1) and 239.3 (1) pm, respectively].[133] In common with the above haloazarsines [Sections I.2.3(h,i)], **20** exhibits a secondary As---Cl contact [364.9 (1) pm]. However, this aspect of the structure is still under investigation.

The angles at arsenic and sulphur [S(1)-As-S(2), 93.50 (3); As-S(1)-C(1), 97.1 (1); As-S(2)-C(2), 100.8 (1) pm] are comparable to those exhibited by **21**. The Cl-As-S angles [Cl-As-S(1), 99.51 (3); Cl-As-S(2), 98.21 (3)^{o}] are also similar to those of **2d** [99.43 (10), 100.34 (10)^{o}][67] and **2h** [98.65 (3)^{o}].

As with **17**, the mechanism of formation of **21** is uncertain. Assuming similar molecular orbital pictures for **21** and **19**, [Figure I.2.7(a)iii], examination of the FMO's shows that a concerted [2+2] cycloaddition would be thermally forbidden, but a photochemically induced reaction may be allowed by orbital symmetry considerations.[72] However, a preliminary multinuclear NMR investigation of the reaction of **20** with $AlCl_3$ in the presence of 2,3-dimethylbutadiene did not indicate the formation of an arsolenium salt. Therefore, the reaction of **20** with

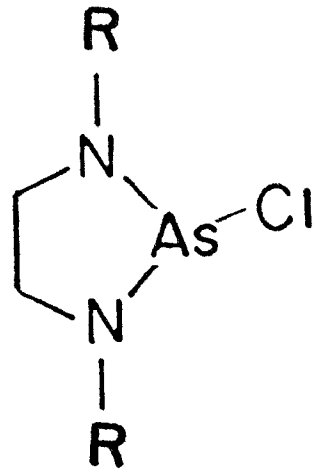
$GaCl_3/AlCl_3$ may follow a different pathway to that of **6** with $GaCl_3/AlCl_3$.

I.2.7(c). Reaction of 2-Chloro-N,N'-Dimethyl-1,3,2-diazarsacyclopentane, 23(Me), with $AlCl_3$

Recently, Wolf and co-workers reported the spectroscopic characterisation of arsenium cations derived from the reactions of 2-chloro-N,N'-diethyl-1,3,2-diazarsacyclopentane, **23(Et)**, and $(Et_2N)_2AsCl$ with $CF_3SO_3SiMe_3$ (or $AgSO_3CF_3$) and $AlCl_3$.[175] The triflate salt of the cyclic cation was obtained as a crystalline solid, while the remaining compounds were characterised either as oils or by spectroscopic study of the reaction mixture. In this laboratory, the reactions of several arsines [$(Et_2N)_2AsCl$, *i*PrNAsCl_2, Cl$As(t$BuN$)_2AsCl$, $\{(Me_3Si)_2N\}_2AsCl$, $(n$Bu$_2$N$)_2AsCl$, and **23(Me)**] with $AlCl_3$, $GaCl_3$ and/or $CF_3SO_3SiMe_3$ in CH_2Cl_2 have proved irreproducible. However, on one occasion, a low yield of a yellow, air sensitive, crystalline material (<5%) was obtained from the reaction of **23(Me)**[176] with $AlCl_3$, and characterised by X-ray crystallography as the tetrachloroaluminate salt of the *bis*-1,3,2-diazarsolidinium cation, **24**. Presumably **24**$[AlCl_4]_2$ is formed by a mechanism analogous to that responsible for the formation of **21**$[GaCl_4]_2$.

The structure was solved by Drs. Rosemary Hynes and Eric J. Gabe of the National Research Council in Ottawa. Relevant bond lengths and angles are listed in Table I.2.7(c) and diagrams of cation **24** and the unit cell of **24**$[AlCl_4]_2$ are given in Figure I.2.7(c).[103,104] Crystallographic details are provided in Appendix 1.

The structure of **24** is closely related to that of **21**. The



23(Me): R = Me

23(Et): R = Et

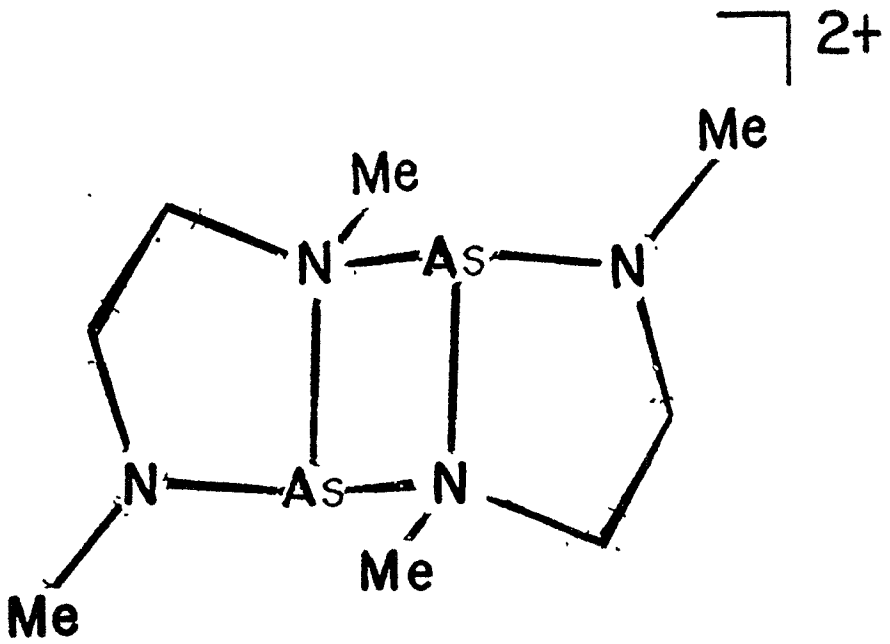


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FIGURE 1.2.7(c). Diagrams of the *Bis*-1,3,2-diazarsolidinium Cation, 24, and the Unit Cell of $24[AlCl_4]_2$

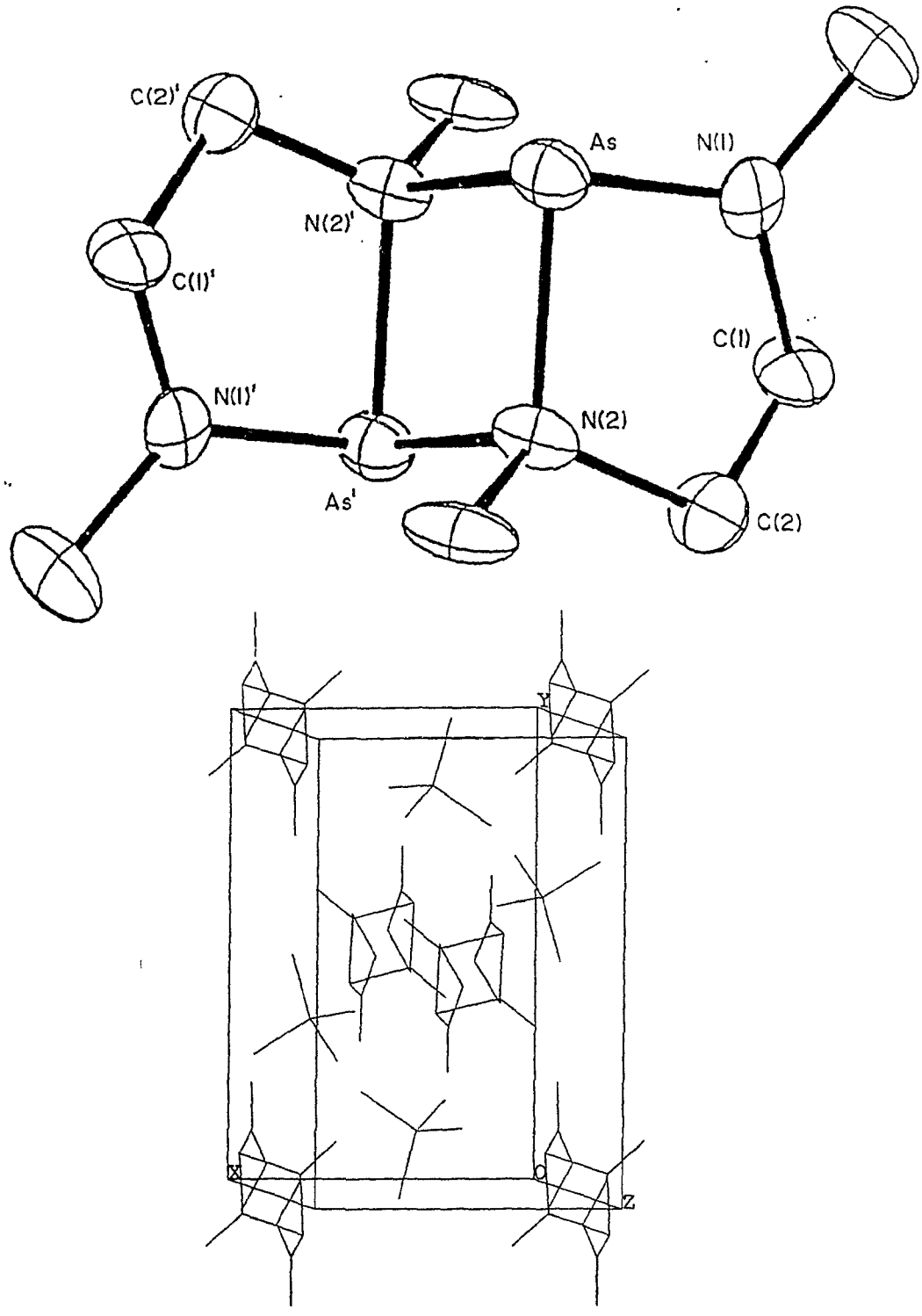


TABLE I.2.7(c). **Selected Bond Lengths (pm) and Angles (°) for *Bis*-1,3,2-diazarsolidinium, 24, Tetrachloroaluminate**

As-N(1)	176.3 (8)	As-N(2)	195.5 (7)
As-N(2)'	210.3 (8)	N(1)-C(1)	147.0 (14)
N(1)-C(3)	146.4 (14)	N(2)-C(2)	150.7 (14)
N(2)-C(4)	152.0 (12)	C(1)-C(2)	154.2 (16)

N(1)-As-N(2)	86.7 (4)	N(1)-As-N(2)'	102.0 (3)
N(2)-As-N(2)'	80.7 (3)	As-N(1)-C(1)	117.4 (7)
As-N(1)-C(3)	125.7 (8)	C(1)-N(1)-C(3)	116.8 (9)
As-N(2)-As'	99.3 (3)	As-N(2)-C(2)	109.1 (6)
As-N(2)-C(4)	113.9 (5)	As'-N(2)-C(2)	111.3 (6)
As'-N(2)-C(4)	112.2 (6)	C(2)-N(2)-C(4)	110.5 (8)
N(1)-C(1)-C(2)	105.7 (8)		

Al-Cl	Range	210.7 (4) - 212.9 (4)	Mean	212.2 (5)
Cl-Al-Cl	Range	106.2 (2) - 111.6 (2)	Mean	109.4 (2)

monomeric units are linked by long As-N bonds [As-N(2)', 210.3 (8) pm] and a crystallographic inversion centre. The heterocyclic bond of the five-membered ring associated with the dimer contact [As-N(2), 195.5 (2) pm] is somewhat longer than a standard As(III)-N bond [*e.g.* 188.9 (6) pm in $Cr(CO)_5(Ph_2AsNSO)$; 184.3 (3) pm in $Me_2Si(tBuN)_2AsCl$],[133,177] whereas the other As-N bond [As-N(1), 176.3 (8) pm is identical, within experimental error, to that determined for **1h** [As-N, 177.6 (4) ppm] and is indicative of multiple bond character. Moreover, the N(1) centre is planar [sum of angles = 359.9 (8)°]. In contrast, the bridgehead nitrogen, N(2), has a distorted tetrahedral geometry. The exocyclic [C(3)-N(1), 146.4 (14) pm] and endocyclic [C(1)-N(1), 147.0 (14); C(2)-N(2), 150.7 (14) pm] C-N bond lengths are crystallographically indistinguishable and are similar to those found for the exocyclic C-N bonds of **1f**, [C-N *exo*: 147.7 (10), 147.4 (10) pm. See Section I.2.3(d)].

As with **21**, the five membered ring exhibits an envelope conformation while the four-membered ring is planar. The angles within the five-membered ring reflect the different geometries of the nitrogen centres, as the angle at N(1) [117.4 (7)°] is much larger than that at N(2) [109.1 (6)°]. However, both angles are considerably greater than the corresponding sulphur angles in **21** [100.6 (2) and 98.7 (2)°, respectively], a reflection of the higher atomic number of sulphur. Consistently, the N(1)-As-N(2) angle of **24** [86.7 (4)°] is narrower than the S(1)-As-S(2) angle of **21** [93.14 (6)°], compensating for the large angles at nitrogen.

Cation-anion contacts are observed from the chlorines to the

arsenic centre (*e.g.* As-Cl(3)b, 344.1; As-Cla, 332.9 pm), however the steric presence of the methyl groups appear to shield the nitrogen centres from such interactions [see also, Section I.2.3(g)]. The anion geometry is comparable to those determined for $\underline{1}AlCl_4$ [Section I.2.3(g)].

I.3 CONCLUSION AND FUTURE WORK

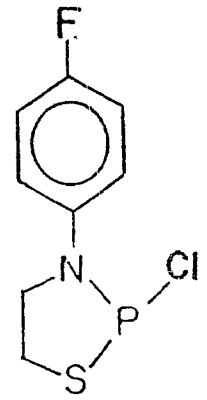
Use of the heteronaphthalenic framework, **1b-i**, has allowed the isolation and characterisation of compounds containing the first stable $p\pi$-$p\pi$ bonds between the heavier elements of Groups 15 and 16. The π-bonding, induced by the dicoordinate, electron deficient pnictogen centre, is stabilised by a combination of charge, a weakly basic counterion and a Hueckel electron count. The inherent thermodynamic stability of framework **1** has been demonstrated by the partially ionic solid state structures of **2g(Cl),g(Br),h**. Attempts to prepare non-aromatic derivatives of **1** have led, unexpectedly, to the formation of the previously reported spirocyclic cation **17**,[170] and the novel heterocyclic dications, **21** and **24**. The transient existence of the unstable $p\pi$-bonded **19** has been demonstrated by a trapping experiment. The instability of species such as **19** proves the pivotal role of the Hueckel electron count in stabilising heavy element derivatives of **1**.

As always, even after three years, much work remains unfinished. In particular, **1i**$AlCl_4$ and **24**$[AlCl_4]_2$ are not yet fully characterised, while the mechanisms for the formation of **17**, **21** and **24** are, at best, poorly understood. A preliminary ^{31}P NMR study on a reaction mixture of 2-chloro-N-*p*-fluorophenyl-1,3,2-thiazaphosphacyclopentane, **25**, with $AlCl_3$ shows a sharp peak at 407 ppm, indicative of a stable dicoordinate phosphorus centre. Therefore, it may be possible to stabilise $p\pi$-bonding between phosphorus and sulphur in a cationic environment without the supplemental stabilising influence of a 10π-electron count if an amine centre is also adjacent to the phosphorus. Certainly, the reactions of cyclic and acyclic halothiazaphosphines, such as **25**, with

$AlCl_3/GaCl_3$ should be subject to further study.

Other potentially fruitful avenues of research include further demonstration of the general applicability of **1** to the preparation of compounds containing new $p\pi$-bonds. For example, the dicoordinate sulphur (selenium) centres could be replaced by dicoordinate tellurium or tricoordinate phosphorus. Compounds such as **26** represent ideal precursors for such studies.[178] It should also be possible to prepare the 6π-analogues of **1** from reagents such as 2-chloro-1,3,2-dithiaphosphole, **27**.[179]

Derivatives of **1** may exhibit a rich coordination chemistry. It is known that diaminohalophosphines (*e.g.* 2-halo-N,N'-dimethyl-1,3,2-diazacyclopentane, **28**) react with transition metal anions [*e.g.* $C_5H_5Mo(CO)_3^-$] to give metallophosphenium complexes with a metal-phosphorus π-bond (*e.g.* **29**) accompanied by the spontaneous loss of CO.[126,127] In contrast, the reaction of **20** with $C_5H_5Mo(CO)_3^-$ does not lead to spontaneous CO evolution. However, photochemical ejection of CO from the intially σ-bonded complex results in another complex, **30**, without a Mo-As π-bond, but containing a novel η-2 coordination mode for the heterocycle.[180] A preliminary study in this laboratory indicates that the reaction of **6** with $C_5H_5Mo(CO)_3^-$ causes the spontaneous evolution of CO, although it has not been possible to isolate, or detect spectroscopically, the anticipated metallophosphenium complex. The coordination of **1** through donation of pnictogen lone pair electron density to the Transition metal centre should be possible and research of this kind will provide useful information on the thermodynamic balance between π- and σ-bonding for heavier pnictogens and sulphur.



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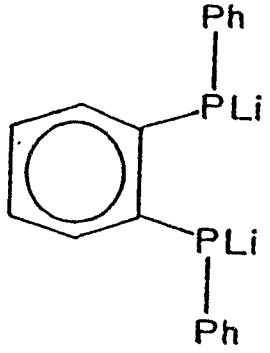

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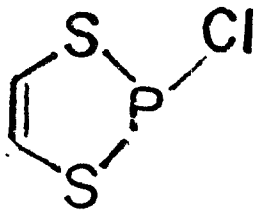

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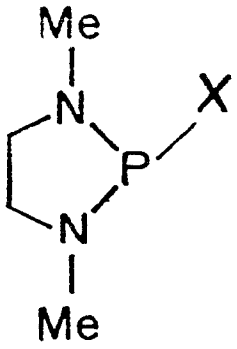

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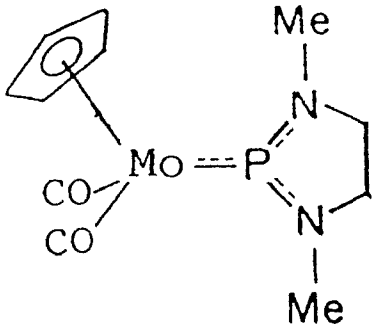

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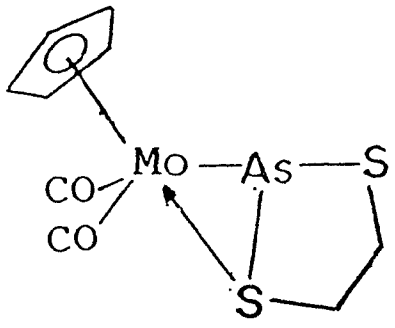

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PART II: AN INVESTIGATION OF THE TRIPHENYLPHOSPHINE CHALCOGENIDE-TRICHLOROALUMINIUM(III) ADDUCT SYSTEMS.

II.1 INTRODUCTION

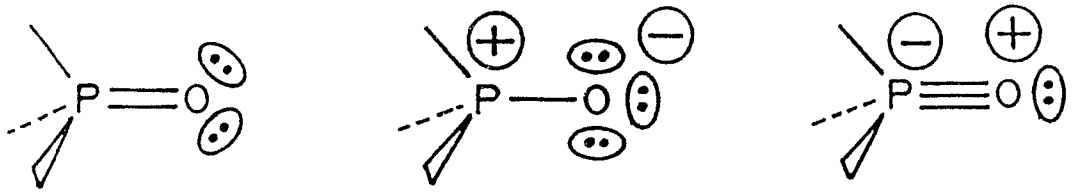
Part II of the thesis details the author's contribution to a project performed in collaboration with another researcher from this laboratory, Rupert Spence. As demonstrated by Part I and other work published by this group,[55,181] a key synthetic pathway to many new Main Group bonding arrangements relies on halide ion abstraction by a strong Lewis acid, in particular aluminium(III) chloride and gallium(III) chloride. Such a process is an extreme example of adduct formation. However, alternative reaction pathways exist which may be energetically competitive with chloride ion abstraction, in particular, adduct formation between the electron deficient Lewis acid and the electron rich low coordinate Main Group pnictogen, chalcogen or halogen.[55,181]

One area of the Group 13 Lewis acid adduct chemistry which has been studied in some detail concerns the behaviour of the acids towards phosphoryl and, to a lesser extent, thiophosphoryl units. This work has resulted in important developments to the chemistries of both adduct components and has contributed much to the present understanding of the bonding regime of phosphine chalcogenides.[182] However, although intensively investigated during the 1960's, such adducts remain incompletely characterised by modern day standards. In particular, they have not been subject to detailed examination by multinuclear NMR spectroscopy or X-ray diffraction techniques.

Recent theoretical advances have clarified the confusion surrounding the exact nature of the phosphoryl bond. In particular, the commonly held view of the linkage as a $p\pi$-$d\pi$ double bond, **31(a)**, has

been demonstrated to be invalid, as the axial symmetry of a symmetrically substituted phosphine oxide (R_3PO) requires that the oxygen centre employ two degenerate *p* orbitals for π-bonding to the phosphorus centre. A more correct model is a combination of resonance structures **31(b)** and **31(c)** [the contribution of **31(c)** to the overall resonance structure is theorised to diminish when oxygen is replaced by the heavier chalcogens].[5(a),183,184] Therefore, the oxygen centre can be regarded as isolobal[140] with, for example, CO, NO^+, CN^- and acetylides, having the ability to adopt an axial mode of coordination to acid centres.[185] However, no concrete experimental evidence for this is available.

In this context, a comprehensive study of the Lewis acid/base adducts formed by the reaction of the triphenylphosphine chalcogenides, Ph_3PCh (Ch = O, S, Se) with $AlCl_3$ was undertaken to develop a better understanding of the adduct chemistry of $AlCl_3$ and the bonding schemes of the phosphine chalcogenides.



31(a) **31(b)** **31(c)**

II.2 RESULTS AND DISCUSSION

II.2.1. Preparation of Adducts

The adducts $Ph_3PCh.AlCl_3$ are prepared in quantitative yield by the reaction of equimolar quantities of the phosphine chalcogenide and $AlCl_3$ in CH_2Cl_2. They are isolated as crystalline solids either by slow evaporation of solvent ($Ph_3PO.AlCl_3$) or by cooling a concentrated, *ca.* 1:1 CH_2Cl_2/CS_2 solution to 0^oC. All adducts are air and/or moisture sensitive and must be handled under inert conditions. Full experimental details are provided in Part III. $Ph_3PO.AlCl_3$ and $Ph_3PS.AlCl_3$ have been prepared previously,[182] but no information is available on their NMR spectra or X-ray crystal structures. $Ph_3PSe.AlCl_3$ is a new compound.

II.2.2. Spectroscopic Characterisation

II.2.2(a). Infrared Spectroscopy

The infrared spectra of $Ph_3PO.AlCl_3$ and $Ph_3PS.AlCl_3$ are identical to those reported in the literature.[182] The spectrum of $Ph_3PSe.AlCl_3$ exhibits an intense band at 545 cm^{-1} which is assigned to the P-Se linkage by comparison to similar bands observed in the spectra of $Ph_3PSe.HgX_2$ (X = Cl, 543; X = Br, 542; X = I, 542 cm^{-1}).[186] The positions of the P-Ch stretches of the three adducts are consistent with considerable disruption of the multiple bond character of the P-Ch bonds in comparison to those of the free bases (*c.f.* Ph_3PSe, 564 cm^{-1}).[187]

II.2.2(b). Mass Spectrometry

The mass spectrum of $Ph_3PO.AlCl_3$ provides a molecular ion peak at m/z = 310, whereas the spectra of the other two adducts exhibit highest

mass peaks corresponding to the respective free bases, indicating that the oxygen-aluminium bond is stronger than those between aluminium and the heavier chalcogens.

II.2.2(c). Multinuclear NMR Spectroscopic Data

The NMR data obtained for $Ph_3PCh.AlCl_3$ (^{13}C, ^{31}P, ^{27}Al and ^{77}Se) are reported in Table II.2.2(c), together with the corresponding data for the respective free bases and their conjugate acids, (Ph_3PChH^+).[188,189] The ^{31}P NMR spectra provide an interesting contrast between the Ph_3PO complexes and their heavier cogeners. Adduct formation results in a substantial (15.6 ppm) deshielding at the phosphorus centre of the oxide compound. The effect is most dramatic in Ph_3POH^+ (27.9 ppm). However, the ^{31}P chemical shifts of the sulphide and selenide complexes are apparently independent of the acid ($AlCl_3$ or H^+) and essentially identical to those of the free bases. This anomaly has been noted, but without explanation.[188,189] It appears that adduct formation leads to a loss in electron density at the phosphorus centre of the oxide complex which is not observed for the sulphide and selenide analogues. Therefore, the ^{31}P NMR data indicate a fundamental difference in the nature of the phosphorus-chalcogen interactions of the oxide and its heavier relatives.

In contrast, the ^{13}C NMR spectra of $Ph_3PCh.AlCl_3$ are very similar. Adduct formation leads to noticeable shielding of the *ipso* (*ca.* 8 ppm) and somewhat lesser deshielding of the *para* (*ca.* 3 ppm) carbon centres of the phenyl rings with respect to those of the free bases. However, the *ortho* and *meta* shifts remain basically unchanged on complexation. Analogous, but again more dramatic, adjustments are found for the

TABLE II.2.2(c). NMR Data for $Ph_3PCh.AlCl_3$ (Ch = O, S, Se) and Related Compounds. Chemical Shifts in ppm, Coupling Constants (Hz) in Parentheses

	^{13}C				^{31}P	^{27}Al	^{77}Se
	ipso	ortho	meta	para			
Ph_3PO	132.8	132.1	128.5	131.8	29.3		
	(103.5)	(9.8)	(17.7)	(2.4)			
Ph_3PS	133.0	132.2	128.5	131.3	43.2		
	(85.0)	(10.6)	(12.7)	(2.8)			
Ph_3PSe	131.9	132.7	128.5	131.5	35.8		-275
	(70.8)	(9.8)	(12.2)	(3.7)	($^1J_{PSe}$=730)		
$Ph_3PO.AlCl_3$	124.7	132.5	129.3	134.5	44.9	90	
	(109.4)	(12.2)	(12.6)	-		($\Delta\nu_{1/2}$=40)	
$Ph_3PS.AlCl_3$	124.4	133.2	129.4	134.1	42.8	107	
	(81.7)	(10.9)	(13.3)	-		($\Delta\nu_{1/2}$=200)	
						102	
						($\Delta\nu_{1/2}$<20)	
$Ph_3PSe.AlCl_3$	124.1	133.5	129.5	134.0	33.7	106	-190
	(79.9)	(10.2)	(13.2)	-		($\Delta\nu_{1/2}$=200)	
					($^1J_{PSe}$=540)	102	
						($\Delta\nu_{1/2}$<20)	
Ph_3POH^+	120.0	131.1	129.0	132.8	57.2		
$[H_2SO_4]$	(107.4)	(9.8)	(12.2)	-			
Ph_3PSH^+	119.3	132.6	129.8	135.2	42.6		
$[H_2SO_4]$	(85.4)	(11.8)	(14.6)	-			
Ph_3PSeH^+	116	130.8	133.8	137.0	37.6		
					($^1J_{PSe}$=414)		

conjugate acids [Table II.2.2(c)]. The changes in the phenyl ring chemical shifts have been rationalised in terms of simple resonance considerations and used to provide evidence for a π-type interaction between the phenyl groups and the heteroatoms.[188] Therefore, although the phosphorus centre of the oxide adduct is affected quite differently by complex formation than those of the sulphide and selenide, the phenyl groups of all three systems display identical behaviour on complexation.

The data suggest that the phosphorus-chalcogen interaction of the free bases is divided into σ and π components. The coordination of Ph_3PO to acids such as $AlCl_3$ causes a change in the nature of both components. The σ-frameworks of Ph_3PS and Ph_3PSe are relatively unaffected by adduct formation, as demonstrated by the negligble adjustments in ^{31}P chemical shifts. However, the ^{13}C resonances of the phenyl rings reflect a substantial disruption of the π-interactions.

The selenium centre of $Ph_3PSe.AlCl_3$ allows direct study of the acid/base interaction at the donor centre by NMR spectroscopy (^{77}Se, I = 1/2; natural abundance = 7.6%). The ^{77}Se NMR was obtained from a saturated CH_2Cl_2 solution of $Ph_3PSe.AlCl_3$ and is listed in Table II.2.2(c). The Se centre (-190 ppm) is noticeably deshielded from that of Ph_3PSe (-275 ppm),[188,189] consistent with donation of electron density from the selenium atom to the acid molecule. However, selenium demonstrates a huge chemical shift range and large chemical shift differences are observed even in structurally and/or electronically related molecules (*e.g.* Ph_3PSe, -275; Me_3PSe, -235; $(MeO)_3PSe$, -396 ppm).[190] The phosphcrus-selenium one-bond coupling constant ($^1J_{PSe}$ = 540 Hz) is intermediate to that of Ph_3PSe ($^1J_{PSe}$ = 730Hz)[188,189] and

those of compounds which contain P-Se single bonds ($[(NEt_2)_2PSe]_2^{2+}$, $^1J_{PSe}$ = 360 Hz;[55] $Me_2P(S)SeMe$, $^1J_{PSe}$ = 341 Hz[190]) and is in the range of those reported for some cadmium and mercury complexes of phosphine selenides [$Cd(Ph_3PSe)_4$, 542; $Cd(Ph_3PSe)_4$, 585; $HgX_2(Bu_3PSe)_2$ X = Cl, 512, 522; X = Br, 542, 531 Hz].[191] $^1J_{PSe}$ determined for the conjugate acid, Ph_3PSeH^+, is still smaller (414 Hz) than those of the Lewis adducts.[188,189] Variations in coupling constants are frequently analysed in terms of the degree of *s* character at the nuclei involved.[88,89] High *s* character, which corresponds to large coupling constants, is usually induced either by steric strain or by significant π-contributions to the bonding.[88,89] As steric considerations are not a factor here, the decrease in $^1J_{PSe}$ from Ph_3PSe to $Ph_3PSe.AlCl_3$ to Ph_3PSeH^+ may reflect diminishing π character in the phosphorus-selenium bonds. Therefore, the π-disruption of the selenophosphoryl bond is greater when the donor molecule behaves as a Brønsted base. The deshielded ^{31}P NMR chemical shift of Ph_3POH^+ also indicates a more dramatic electronic adjustment on the formation of a Brønsted adduct.

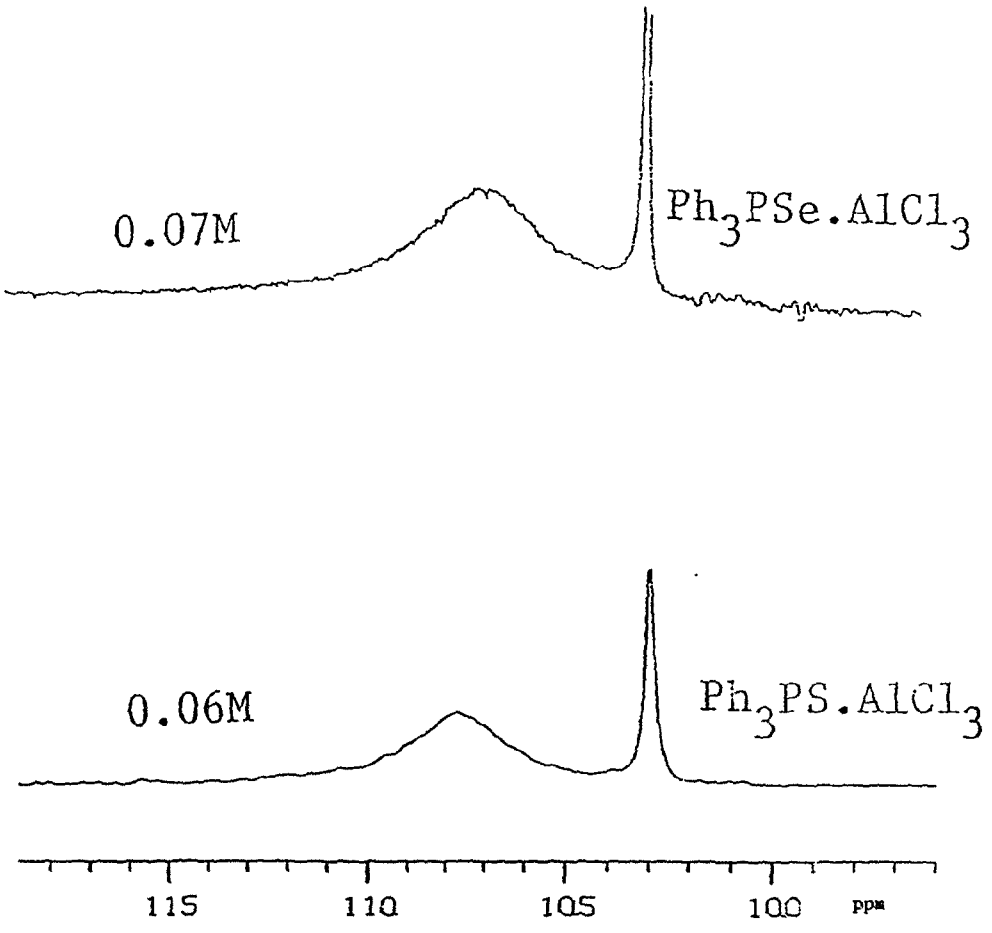
The quadrupolar nature of the aluminium nucleus, with the attendant broad resonances, is often considered a severe handicap to ^{27}Al NMR spectroscopy.[90] However, this feature can provide access to information on solution molecular structure which may otherwise be very difficult, or impossible, to obtain. Aluminium nuclei in symmetric environments often give sharp resonances while those in surroundings of lower symmetry exhibit significantly broader signals.[90] Usually, octahedral and tetrahedral symmetries at the aluminium centres are required to obtain narrow resonances. For example, $Al(NCPh)_6^{3+}$ gives a resonance

which has a linewidth of only 20 Hz while that of $Al(NCPh)_5Cl^{2+}$ is *ca.* 150 Hz wide.[192] However, "*psuedo*"-octahedral or "*psuedo*"-tetrahedral molecules, which mimic octahedral or tetrahedral symmetry, can also exhibit narrow resonances.[90,193] Therefore, although line widths depend on many variables, in particular chemical exchange processes, line broadening in ^{27}Al NMR can be a useful probe of molecular geometry in solution.[90,193]

The ^{27}Al NMR spectrum of $Ph_3PO.AlCl_3$ exhibits a single resonance at 90 ppm [with respect to $Al(H_2O)_6^{3+}$] with a line width of only 40 Hz, indicative of a "*psuedo*"-tetrahedral symmetry at the aluminium nucleus. This is consistent with a very wide P-O-Al angle for $Ph_3PO.AlCl_3$ in solution. In contrast, both the sulphide and selenide compounds give a broad ($\Delta\nu_{1/2}$ *ca.* 200 Hz) peak centred at approximately 107 ppm with a minor sharp resonance ($\Delta\nu_{1/2}$ < 40 Hz) at 102 ppm ($AlCl_4^-$) [Figure II.2.2(c)].[90,193] The broad signals, assigned to the adducts, are indicative of asymmetric environments for the aluminium centres.

The adduct/$AlCl_4$ intergration ratios of $Ph_3PS/Se.AlCl_3$ vary with concentration from *ca.* 10:1 (0.06 M, Ch = S; 0.07 M, Ch = Se) to *ca* 5:1 (0.018 M, Ch = S, Se). The spectra obtained at low concentration (0.018 M) show increased amounts of $AlCl_4^-$ relative to adduct and some evidence for the presence of $AlCl_3$ (*ca.* 90ppm). This is consistent with the ^{31}P NMR spectra obtained at the same concentration which demonstrate significant amounts of free base in solution. The ^{31}P spectrum of the selenide adduct also has a third, unidentified peak at 38.7 ppm. ^{31}P spectra obtained at higher concentrations do not indicate the presence of free base. Consequently, it appears that the complexes are labile

FIGURE II.2.2(c). ^{27}Al NMR Spectra of $Ph_3PSe.AlCl_3$ (0.07M) and $Ph_3PS.AlCl_3$ (0.06M)



and dissociate at low concentrations. The weak character of the S-Al and Se-Al linkages is further illustrated by the ^{27}Al spectra obtained for $Ph_3PS/Se.AlCl_3$ in tetrahydrofuran (THF) which display only one signal, assigned to $AlCl_3(THF)_2$.[194] Therefore, it is possible that some of the line broadening observed for the ^{27}Al signals of $Ph_3PS.AlCl_3$ and $Ph_3PSe.AlCl_3$ may be due to chemical exchange. However, the rates of such processes are relatively slow as the $^1J_{PSe}$ coupling is well resolved in the ^{77}Se spectrum of $Ph_3PSe.AlCl_3$.

II.2.3 X-Ray Crystallographic Studies on $Ph_3PCh.AlCl_3$

The solid state structures of all three adducts have been investigated by X-ray diffraction techniques. The crystal structure of $Ph_3PO.AlCl_3$ has been determined by Drs. Cameron and Linden of Dalhousie University. The structures of the sulphide and selenide complexes were solved by Dr. Rogers at Northern Illinois. Crystallographic details are provided in Appendix 1.

II.2.3(a). Crystal Structure of $Ph_3PO.AlCl_3$

Crystal are grown by the slow evaporation of CH_2Cl_2. The structure consists of discrete molecules with no unusual intermolecular contacts. Selected bond lengths (pm) and angles (^{o}) are provided in Table II.2.3(a)i. An illustration of the molecule and a diagram of the crystal packing are presented in Figure II.2.3(a).

The most striking feature of the molecule is the linear geometry observed at oxygen, the P-O-Al molecular backbone residing on a crystallographic C_3 axis. The possibility of a bent P-O-Al unit with a disordered oxygen atom lying off the three-fold axis has been

FIGURE II.2.3(a). Diagrams of the Molecular Structure and Unit Cell of Triphenylphosphine Oxide-Trichloroaluminium(III), $Ph_3PO.AlCl_3$

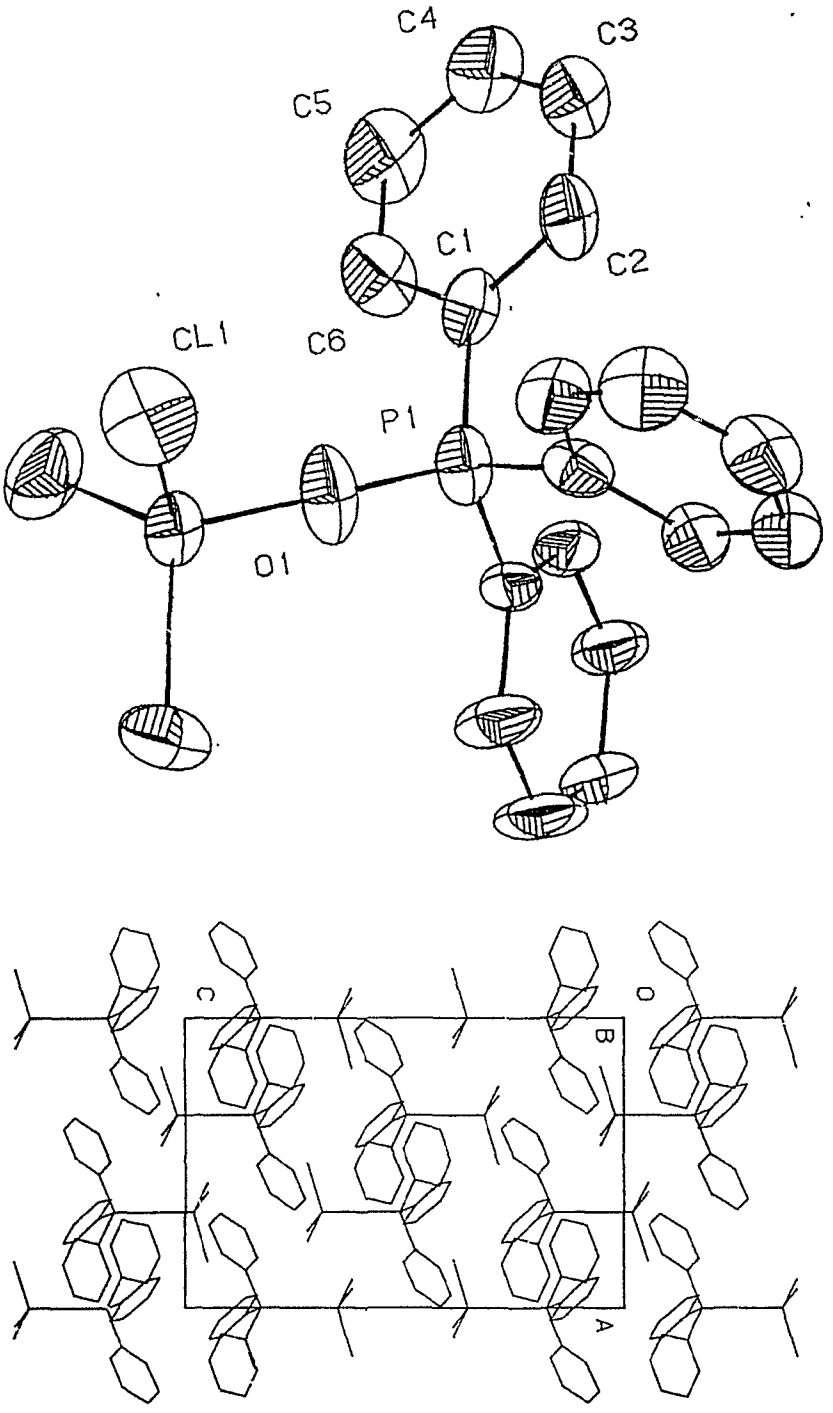


TABLE II.2.3(a)i. Selected Bond Lengths (pm) and Angles (°) for Triphenylphosphine Oxide-Trichloroaluminium(III) Adduct, $Ph_3PO.AlCl_3$

$C_{18}H_{15}AlCl_3OP$

P-O	151.9 (4)	Al-Cl	209.9 (2)
O-Al	173.3 (4)	P-C	178.4 (5)
P-O-Al	180	O-Al-Cl	106.9 (1)
Cl-Al-Cla	111.89 (9)	O-P-C(1)	110.2 (2)
C(1)-P-C(1)a	108.8 (2)		

considered, as the thermal parameters of the phosphorus, aluminium and oxygen atoms give rather oblate ellipsoids, with the minor axis along the three-fold axis. However, any oxygen atom disorder is barely detectable. Studies by Drs. Cameron and Linden,[195] in which the *x*-fractional coordinate of the oxygen atom was displaced from the 3-fold axis and the atom's thermal parameters allowed to refine, revealed that the R factor is not particularly sensitive to small displacements (< 26 pm) but rises rapidly with larger displacements. The thermal parameters of the oxygen atom are also observed to fall rapidly beyond this displacement. Therefore, the position of the oxygen atom exactly on the three-fold axis may be the result of thermal averaging of rotational or vibrational motion. A similar phenomenon has been reported for pyrophosphate anions, which appear to possess linear P-O-P backbones.[196] However, the data obtained for $Ph_3PO.AlCl_3$ suggest that the centre of such a libration lies at most 6 pm from the crystallographic C_3 axis and this results in a minimum P-O-Al angle of 175.8°.[195] Consequently, the solid state structure contains an essentially linear skeleton and is consistent with the solution structure deduced from ^{27}Al NMR [Section II.2.3(c)].

$Ph_3PO.AlCl_3$ represents a rare example of a structurally characterised compound containing a P-O-Al framework.[197] The P-O-Al angles found for other such compounds, $[\{AlPO_4)(HCl)(EtOH)_4\}_4]$; 146.4 (5), 166.3 (5) and 148.1 (5)°,[197(a)] $(AlMe)(Ph_2COPPh_2)_2(AlMe_2)$; < 180°,[197(b)] $(AlCl_3)_2[(Ph_2PO)_2CH_2]$; 164.3 (3)°,[197(c)] $AlPO_4$; 145°,[197(d)] $C_{45}H_{83}O_{13}Si_7PO.AlCl_3$; 160.4 (4)°,[197(e)] $C_{12}H_{26}N_3PO.AlCl_3$; 152.95 (9)°, $Cl_3Al.OP(C_{12}H_{26}N_4)PO.AlCl_3$; 155.1 (1),[197(f)] are all substantially less

than 180°.

To the best of the author's knowledge, $Ph_3PO.AlCl_3$ contains the first example of a linear phosphoryl-Lewis acid adduct. However, a large number of related complexes have unexpectedly wide angles at oxygen [Table II.2.3(a)ii].[198,199] Molecules with relatively narrow P-O-E angles (<140°) are either sterically constrained, *e.g.* cyclic,[199(m)] or do not have accessible empty *d*-orbitals on the Lewis acid centre, *e.g.* boron.[199(a)]

The P-O bond distances of the complexes [Table II.2.3(a)ii] change very little [150 (+/- 6) pm], although those with electronegative elements, such as chlorine, attached to the phosphorus are consistently shorter than those of other derivatives. The P-O bond distance in $Ph_3PO.AlCl_3$ [151.9 (4) pm] is typical and longer than that of Ph_3PO [148.3 (2);[200(a)] 146 (1)[200(b)]]. However, it is still shorter than a standard P-O single bond [*e.g.* 160.4 (3) pm in P_4O_{10}].[201] Therefore the structural data agree with the conclusions drawn from infra-red studies,[182] in that adduct formation partially interrupts the phosphorus-oxygen interaction of Ph_3PO. The P-C bonds of $Ph_3PO.AlCl_3$ [178.4 (5) pm] are identical to those determined for the free base [178.7 (3) - 179.6 (3) pm][200(a)] and are somewhat less than observed for Ph_3P [182.2 (5) - 183.1 (5) pm],[117] consistent with either some degree of $d\pi$-$p\pi$ bonding between the phosphorus(V) centre and the phenyl ring or bond contraction due to the electronegative oxygen. The O-P-C [110.2 (2)°], C-P-C [108.8 (2)°] and P-C-C [119.4 (4); 121.3 (4)°] angles are also similar to those found for Ph_3PO.[200(a)] The aromatic rings adopt a staggered conformation with respect to the chlorine atoms of the acid

TABLE II.2.3(a)ii. Comparison of the P-O Bond Lengths (pm) and P-O-E (°) Bond Angles of some Phosphine Oxide Complexes

Compound	P-O	P-O-E	Ref.
$Ph_3O.AlCl_3$	151.9 (4)	180	
$Ph_3O.BF_3$	152.2 (3)	134.5 (2)	199(a)
$[Ph_3PO.SeOCl_2]_2$	152.0 (8)	123.0 (4)	199(b)
	149.7 (9)	142.5 (4)	
		143.4 (5)	
$(Ph_3PO)_2.MnCl_2$	148.8 (6)	156.0 (4)	199(c)
$[NpO_2(Ph_3PO)_2]^{2-}$	150.2 (9)	159.1 (4)	199(d)
$[UO_2(Ph_3PO)_2]^{2-}$	150.5 (9)	160.0 (4)	199(d)
$NpO_2Cl_2(Ph_3PO)_2$	150 (1)	167 (1)	199(d)
	155 (2)	153 (1)	
$[\{ReCl_2(O)Me(Ph_3PO)\}O]$	152.4 (4)	171.7 (3)	199(e)
cis-$[\{Sm(C_5H_5)_2(Ph_3PO)\}_2(C_2H_2O_2)]$	150.1 (10)	167.6 (6)	199(f)
	149.6 (11)	168.8 (7)	
trans- " " "	151.4 (7)	163.0 (5)	199(f)
$TlCl(Br)I(Ph_3PO)_2]$	149.1 (4)	149.0 (2)	199(g)
	148.5 (4)	148.5 (2)	
$Cu_2(MeCHClCO_2)_4(Ph_3PO)_2$	150.7 (6)	146.7 (4)	199(h)
$Cu_2(ClCH_2CH_2CO_2)_4(Ph_3PO)_2$	147.7 (3)	149.0 (2)	199(i)
$Os(oep)(Ph_3PO)_2$	148.3 (8)	152.4 (5)	199(j)
$La\{N(SiMe_3)_2\}_3(Ph_3PO)_2$	152 (2)	174.6 (9)	199(k)
$La(O_2)\{N(SiMe_3)_2\}_4(Ph_3PO)$	151 (1)	172.6 (14)	199(k)
		138.5 (14)	
$Co(NO_3)_2(Ph_3PO)_2$	148 (1)	158.5 (8)	199(l)

TABLE II.2.3(a)ii. Comparison of the P-O Bond Lengths (pm) and P-O-E Bond Angles (°) of some Phosphine Oxide Complexes (Continued)

Compound	P-O	P-O-E	Ref.
$Ph(Me_3EtClSn)PO.(SnMe_2EtCl)$	150.1 (6)	113.4 (3)	199(m)
$Cl_3PO.MoNCl_4(C_2Cl_5)$	142.6 (9)	160.3 (6)	199(n)
$[Cl_2PO.Mo(NO)Cl_3]_2$	143.9 (5)	149.8 (4)	199(o)
$Cl_3PO.WCl_4(C_{10}H_{18})$	145.6 (12)	146.1 (8)	199(p)
$(Cl_3PO.WNCl_3)_4$	139.3 (5)	152.4 (1)	199(q)
	153.0 (3)	146.9 (1)	
	153.4 (3)	146.6 (1)	
	151.7 (4)	157.9 (3)	
$Cl_3PO.ReCl_5$	145 (1)	143.2 (8)	199(r)
$Cl_3PO.ReNCl_4(C_2Cl_5)$	143.4 (11)	158.6 (6)	199(s)
$Cl_3PO.TiCl_4$	144 (2)	151.8 (13)	199(t)
$[SnCl_5(Cl_3PO)]^-$	146 (1)	147.3 (6)	199(u)

oep = octaethylporphinato

unit.

The bond lengths of the $AlCl_3$ moiety [209.9 (2) pm] are slightly greater than those determined by electron diffraction for the terminal Al-Cl bonds of Al_2Cl_6 [206 (4) pm][202] and close to those found for the $Ph_2NH.AlCl_3$ adduct [209.0 (2), 213.0 (3) pm].[203] The Al-O distance [173.3 (4) pm] is significantly shorter than standard Al-O bonds, which are typically 178 - 180 pm,[204] and is indicative of a bonding interaction between the phosphorus and aluminium centres over and above that of a regular σ-bond.

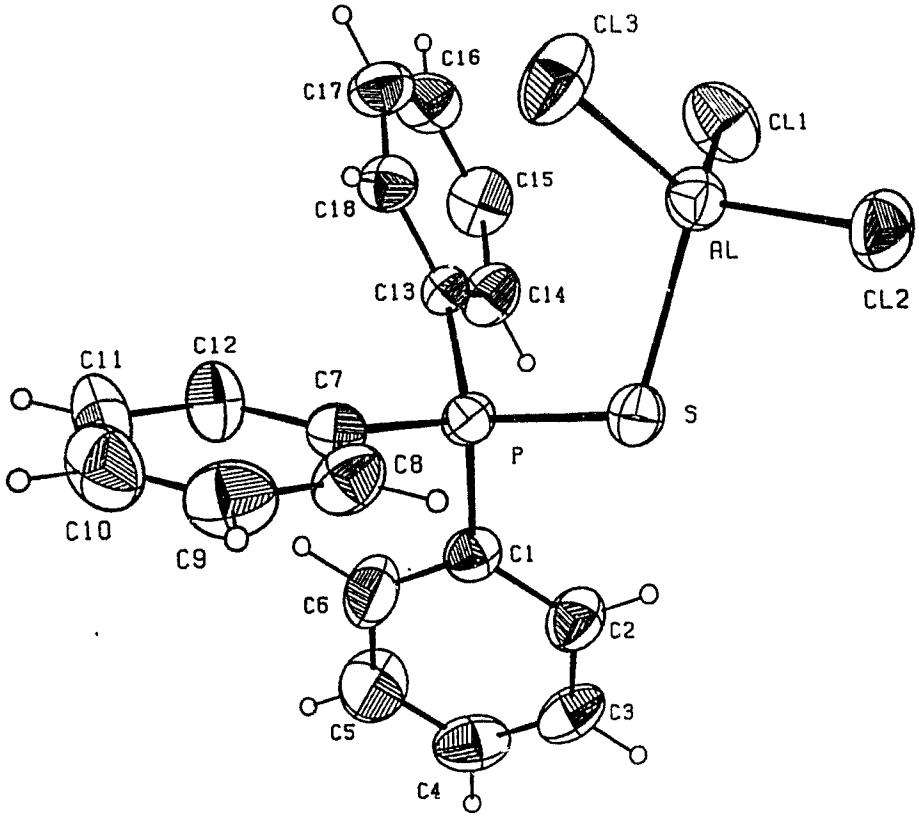
The aluminium centre has a distorted tetrahedral geometry. The O-Al-Cl angle [106.9 (1)°] is narrower than the Cl-Al-Cl' angles [111.89 (9)°], so that the aluminium is forced towards the plane defined by the chlorine atoms. This distortion minimises intramolecular lone pair-lone pair repulsions between the chlorine atoms.[203]

II.2.3(b). The Crystal Structures of $Ph_3PS.AlCl_3$ and $Ph_3PSe.AlCl_3$

Crystals of both adducts are grown by cooling a CH_2Cl_2/CS_2 (1:1) solution to 0°C. Both structures consist of discrete molecular units with no unusual intermolecular contacts. In contrast to the free bases,[205,206] which are isostructural, $Ph_3PS.AlCl_3$ and $Ph_3PSe.AlCl_3$ assume different crystal classes. The sulphide complex crystallizes in the monoclinic system, while the selenide is triclinic and has two molecules in the asymmetric unit. Relevant bond lengths (pm) and angles (°) are presented in Table II.2.3(b)i while illustrations of the molecular units and packing diagrams of the two adducts are provided in Figures II.2.3(b)i and II.2.(b)ii.

In contrast to $Ph_3PO.AlCl_3$, both $Ph_3PS.AlCl_3$ and $Ph_3PSe.AlCl_3$ have

FIGURE II.2.3(b)i. Diagrams of the Molecular Structure and Unit Cell of Triphenylphosphine Sulphide-Trichloroaluminium(III), $Ph_3PS.AlCl_3$



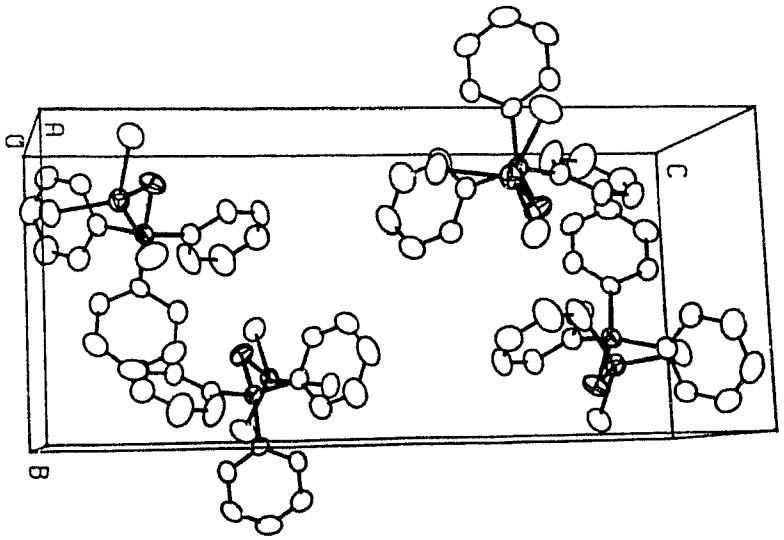


FIGURE II.2.3(b)ii. Diagrams of the Molecular Structure and Unit Cell of Triphenylphosphine Selenide-Trichloroaluminium(III), $Ph_3PSe.AlCl_3$

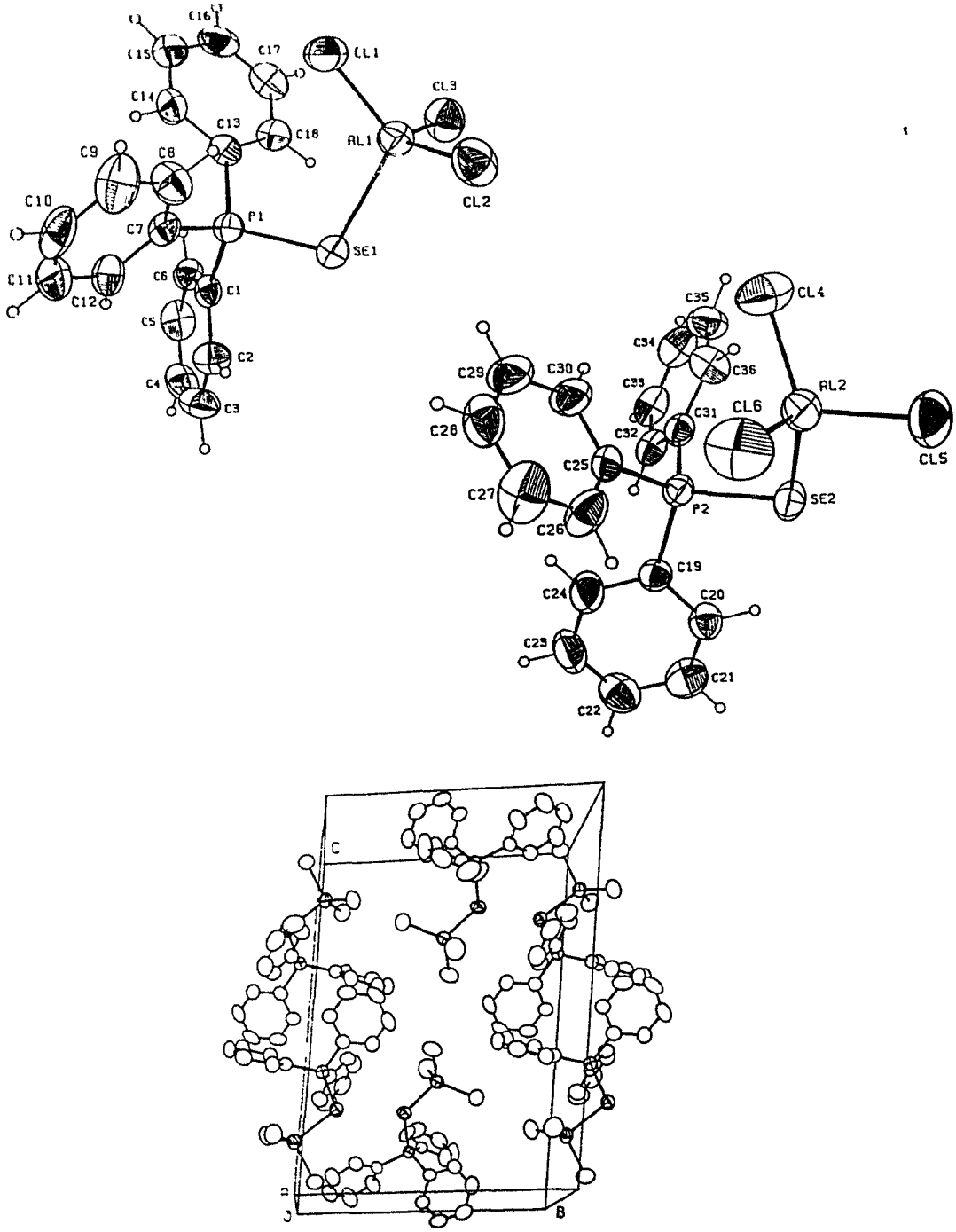


TABLE II.2.3(b)i. Selected Bond Lengths (pm) and Angles (°) for Triphenylphosphine Sulphide-Trichloroaluminium(III), $Ph_3PS.AlCl_3$, and Triphenylphosphine Selenide-Trichloroaluminium(III), $Ph_3PSe.AlCl_3$, Adducts

$C_{18}H_{15}AlCl_3PS$		$C_{18}H_{15}AlCl_3PSe$	
P-S	202.8 (2)	P(1)-Se(1)	218.2 (2)
		P(2)-Se(2)	218.1 (2)
S-Al	229.7 (2)	Se(1)-Al(2)	245.2 (2)
		Se(2)-Al(2)	242.1 (2)
P-C(1)	180.1 (5)	P(1)-C(1)	180.0 (7)
P-C(7)	179.5 (5)	P(1)-C(7)	181.2 (6)
P-C(13)	179.3 (5)	P(1)-C(13)	179.3 (5)
		P(2)-C(19)	178.9 (7)
		P(2)-C(25)	180.7 (6)
		P(2)-C(31)	178.1 (7)
Al-Cl(1)	210.7 (2)	Al(1)-Cl(1)	211.7 (3)
Al-Cl(2)	212.0 (2)	Al(1)-Cl(2)	211.9 (3)
Al-Cl(3)	211.5 (2)	Al(1)-Cl(3)	211.3 (3)
		Al(2)-Cl(4)	211.1 (3)
		Al(2)-Cl(5)	211.8 (3)
		Al(2)-Cl(6)	210.6 (3)
P-S-Al	109.62 (8)	P(1)-Se(1)-Al(1)	106.95 (7)
		P(2)-Se(2)-Al(2)	107.15 (7)
Cl(1)-Al-Cl(2)	112.2 (1)	Cl(1)-Al(1)-Cl(2)	111.0 (1)
		Cl(4)-Al(2)-Cl(5)	112.5 (1)

TABLE II.2.3(b)i. Selected Bond Lengths (pm) and Bond Angles (°) for $Ph_3PS.AlCl_3$ and $Ph_3PSe.AlCl_3$ (continued).

$C_{18}H_{15}PS.AlCl_3$		$C_{18}H_{15}PSe.AlCl_3$	
Cl(1)-Al-Cl(3)	111.2 (1)	Cl(1)-Al(1)-Cl(3)	113.0 (1)
		Cl(4)-Al(2)-Cl(6)	110.2 (1)
Cl(2)-Al-Cl(3)	112.37 (9)	Cl(2)-Al(1)-Cl(3)	111.8 (1)
		Cl(5)-Al(2)-Cl(6)	110.3 (1)
Cl(1)-Al-S	111.17 (9)	Cl(1)-Al(1)-Se(1)	112.3 (1)
		Cl(4)-Al(2)-Se(2)	110.3 (1)
Cl(2)-Al-S	97.42 (8)	Cl(2)-Al(1)-Se(1)	100.2 (1)
		Cl(5)-Al(2)-Se(2)	96.2 (1)
Cl(3)-Al-S	111.80 (9)	Cl(3)-Al(1)-Se(1)	107.9 (1)
		Cl(6)-Al(2)-Se(2)	114.3 (1)
S-P-C(1)	106.7 (2)	Se(1)-P(1)-C(1)	106.3 (2)
		Se(2)-P(2)-C(19)	108.3 (2)
S-P-C(7)	110.4 (2)	Se(1)-P(1)-C(7)	110.5 (2)
		Se(2)-P(2)-C(25)	113.0 (2)
S-P-C(13)	113.5 (2)	Se(1)-P(1)-C(13)	113.5 (2)
		Se(2)-P(2)-C(31)	111.0 (2)
C(1)-P-C(7)	109.2 (2)	C(1)-P(1)-C(7)	108.2 (3)
		C(19)-P(2)-C(25)	107.3 (3)
C(7)-P-C(13)	108.6 (2)	C(7)-P(1)-C(13)	109.7 (3)
		C(25)-P(2)-C(31)	109.1 (3)
C(1)-P-C(13)	108.4 (2)	C(1)-P(1)-C(13)	108.5 (3)
		C(19)-P(2)-C(31)	107.9 (3)

bent geometries at the chalcogen centres. The observed angles [P-S-Al = 109.62 (8)°; P-Se-Al (mean) = 107.0 (1)°] are comparable to those determined for other neutral dicoordinate sulphur [*c.f.* α-S_8 (mean), 108.0 (7); S_2Cl_2, 103 (2)°][207,208] and selenium [e.g. γ-Se_8 (mean), 106.0 (12), 105.7 (14); Se_2Br_2, 104.51 (5), 103.86 (5)°][209,210] moieties.

Structurally characterised examples of thiophosphoryl and selenophosphoryl adducts are rare. Table II.2.3(b)ii provides P-Ch-M (Ch = S, Se; M = Lewis Acid) angles of a few such compounds.[211,212] The angles at the chalcogen centres are consistently narrow (<120°) and occur within a relatively restricted range (91 - 117°).

The P-S bond length of $Ph_3PS.AlCl_3$ [202.8 (2) pm] is intermediate to that of a P-S single bond [*e.g.* 211.2 (1) pm in $(PhS)_3P$, Section I.2.3(a)] and that of Ph_3PS [195.0 (3) pm].[205] The Al-S bond [229.7 (2) pm] is similar to the Al-S distances found in aluminium sulphides [*e.g.* α-$ZnAl_2S_4$, Al-S = 236 (3); $Ce_6Al_{10/3}S_{14}$, Al-S (tetrahedral) = 209, 229, Al-S (octahedral) = 242, 265; α-Al_2S_3, Al-S = 226 pm][213,214] and is believed to represent a standard Al-S σ-bond, as the sum of the respective covalent radii (Al = 126, S = 104 pm) is 230 pm.[78] Apparently, the literature contains no structurally characterised examples of what might be termed "molecular" or "organo" compounds with covalent Al-S bonds, so the bond length reported here may provide a useful benchmark for other workers.

The lengths of the P-Se bonds of the two molecules in the asymmetric unit of $Ph_3PSe.AlCl_3$ are not significantly different [218.2 (2) and 218.1 (2) pm] and fall between those of typical P-Se single

TABLE II.2.3(b)ii Comparison of the P-Ch (Ch = S, Se) Bond Lengths (pm) and the P-Ch-E Bond Angles (°) for some Phosphine Chalcogenide Complexes

	P-Ch	P-Ch-E	Ref.
$Ph_3PS.AlCl_3$	202.8 (2)	109.62 (2)	
$2Ph_3PS.3I_2$	200.7 (3)	107.0 (1)	211(a)
$Ph_3PS.MoOCl_3$	204.1 (1)	111.31 (4)	118
$Ph_3PS.NbSCl_3$	202.8 (5)	116.6 (2)	119
	202.6 (6)	111.5 (2)	
$\{Ph_2P(S)CH_2P(S)Ph_2\}CuCl$	197.0 (2)	91.52 (8)	211(b)
	197.4 (3)	95.68 (8)	
$(Me_3PSCuCl)_3$	202.4 (2)	104.72 (5)	211(c)
	202.6 (1)	103.88 (6)	
		104.58 (4)	
$(Me_3PS)_3CuClO_4$	200.7 (6)	107.2 (3)	211(d)
	200.9 (7)	104.3 (3)	
	196.7 (7)	110.3 (3)	
$(Me_4P_2S_2)CuCl_2$	197.3 (2)	100.71 (7)	211(e)
	199.5 (2)	110.87 (7)	
$[(Me_4P_2S_2)CuCl]_2$	199.5 (9)	113.1 (3)	211(f)
	199.1 (9)	109.5 (3)	
$Me_3PSCr(CO)_5$	199.0 (3)	112.5 (1)	211(g)
$Ph_3PSe.AlCl_3$	218.2 (2)	106.95 (7)	
	218.1 (2)	107.15 (7)	
$Ph_3PSe.HgCl_2$	216.9 (6)	98.1 (1)	212(a)
$Ph_3PSe.AuCl$	218.7 (5)	100.1 (1)	212(b)
$\{Ph_2PCH_2P(Se)Ph_2\}Pd(CN)(SeCN)$	245.0 (2)	98.8 (1)	212(c)

bonds [*e.g.* P_4Se_3, 224 (1) pm][215] and that determined for the free base [210.6 (1) pm].[206] Structural information on the Se-Al bond is even scarcer than for its S-Al analogue. The Se-Al distances in $Ph_3PSe.AlCl_3$ [245.2 (2) and 242.1 (2) pm] are somewhat longer than those of Al_2Se_3 [Al-Se (mean) = 237 pm][216] but are close to the sum of the covalent radii (242 pm)[78] and therefore probably represent standard σ-bonds.

Therefore, the P-Ch and Ch-Al bond lengths determined for $Ph_3PS.AlCl_3$ and $Ph_3PSe.AlCl_3$ are consistent with partial disruption of the P-Ch π-interactions found in the free bases, and with standard donor-acceptor σ-bonds between the chalocogen and aluminium centres.

The Al-Cl and P-C bond lengths of both compounds [$Ph_3PS.AlCl_3$, Al-Cl (mean) = 211.4 (2), P-C (mean) 179.6 (5) pm; $Ph_3PSe.AlCl_3$, Al-Cl (mean) = 211.4 (3), P-C (mean) = 179.7 (7) pm] are similar to those determined for $Ph_3PO.AlCl_3$ [Al-Cl = 209.9 (2), P-C = 178.4 (5) pm].

The phosphorus and aluminium centres of both adducts have distorted tetrahedral geometries. The Cl-Al-Cl angles are similar to those of $Ph_3PO.AlCl_3$ [Cl-Al-Cl' 111.89 (9)°]. However, the steric requirements introduced by the narrow chalcogen angles cause a significant variation in the angles at the acid centre as both complexes display one Ch-Al-Cl angle which is noticeably narrower than the other two [Ch = S: 97.42 (8) vs 111.17 (9) and 111.80 (9)°. Ch = Se: 100.2 (1) vs 112.3 (1) and 107.9 (1)°; 96.2 (1) vs 112.7 (1) and 114.3 (1)°]. The analogous angles in $Ph_3PO.AlCl_3$ [O-Al-Cl = 106.9 (1)°] fall in the middle of the range defined by the S(Se)-Al-Cl angles. The constricted chalcogen angles force the phenyl rings of the base and the chlorine atoms of the acid together, so that the closest C---Cl contacts [Ch = S: C(18)---Cl(13) =

359.8 (5), C(17)---Cl(3), 365.0 (6) pm. Ch = Se: C(8)---Cl(1) = 376.2 (8), C(26)---Cl(6) 352.0 (8) pm] are near to the sum of the van der Waals' radii (355 pm).[137] Consequently, the Ch-Al-Cl angles of the chlorines facing the phenyl rings are forced open so that phosphorus and aluminium centres are also brought into contact with each other [Ch = S: P---Al = 353.8 (2) pm. Ch = Se: P---Al = 372.7 (3), 370.6 (3) pm].

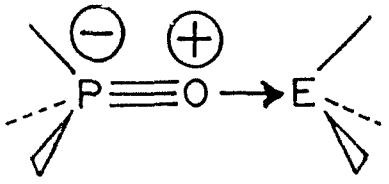
II.2.4 Structure and Bonding in $Ph_3PCh.AlCl_3$

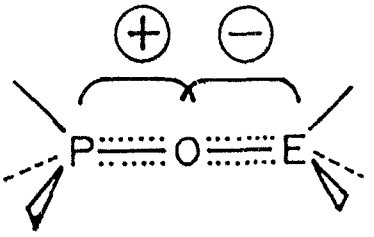
The linear bonding at oxygen in $Ph_3PO.AlCl_3$ (confirmed in related studies on $Ph_3PO.AlBr_3$ and $Ph_3PO.GaCl_3$)[195] and the general observation of wide angles at oxygen in other phosphine oxide Lewis acid-base adducts [Table II.2.3(a)ii] is perhaps at first unexpected. However, molecules which are isoelectronic to R_3PO display similar coordination properties. For example, F_3SN forms complexes, $[M(NSF_3)_4(AsF_6)_2]$, with several transition metals which exhibit wide angles at the centre of donation [*e.g.* Mn-N-S = 161.1 (4), 162.0 (3)°].[217] Also, coordination compounds of phosphinimine anions (R_3PN^-) contain a wide range of angles at the nitrogen, some close to 180°.[218] In both systems, the wide angles can be attributed to coincident σ- and π-donation from the base to the metal centre.[218] The siloxanes, the Si-O-Si units of which are isoelectronic to the P-O-Al unit, and pyrophosphates, the P-O-P units of which are isolobal to $Ph_3PO.AlCl_3$, contain linear or close to linear backbones.[137,196,219] Furthermore, reports exist of compounds containing Al-O units with wide angles at oxygen. The pentacoordinate aluminium compound, $Al_2O(C_{10}H_8NO)_4$ has an essentially linear [178.0 (3)° Al-O-Al skeleton.[220] Steric effects may play a role in enforcing such a

large angle at the oxygen. However, the short Al-O bonds [167.6 (4) and 167.8 (4) pm] suggest electronic control of the geometry, and a π-interaction between the oxygen lone pairs and the empty aluminium *d*-orbitals has been proposed.[220] Barron has reported phenolate complexes of aluminium which also possess wide angles at the oxygen centres and relatively short Al-O bonds [*e.g.* $AlMe_2(OC_6H_2Me\text{-}4\text{-}t\text{-}Bu_2\text{-}2,6)(PMe_2)$: Al-O-C = 164.5 (4)°, Al-O = 173.6 (5) pm. $[AlMeCl_2(OC_6H_2Me\text{-}4\text{-}t\text{-}Bu_2\text{-}2,6)]^-$: Al-O-C = 164.0 (3)°, Al-O = 171.3 (4) pm].[221] Although steric constraints of the bulky phenolate group must be influential in determining the C-O-Al geometry, Barron suggests that electronic effects are also important. He points out the very high energy of unoccupied aluminium *d*-orbitals and believes that Al-O π-bonding is achieved by the donation of oxygen lone pair electron density into Al-X σ^*-orbitals.[221]

Steric effects are not responsible for the linear geometry at the oxygen of $Ph_3PO.AlCl_3$, as is made evident by the P-O-B angle [134.5 (2)°] in $Ph_3PO.BF_3$.[199(a)] Therefore, the angle at oxygen is a function of the electronic structure of the adduct. It is proposed that this is best described by a σ-donation from the oxygen lone pair not involved in back-bonding with the phosphorus *d*-orbitals, as illustrated by **32(a)**. However, the short Al-O bond, similar in length to those of the phenolate complexes,[221] implies some auxiliary bonding. Consequently, the acid centre must act as an acceptor in both σ and π-senses, receiving π-electron density either into empty *d*-orbitals or σ^*-hybrid orbitals, so that there is a delocalisation of electrons along the P-O-Al framework and the axial symmetry present in the free base is maintained, as pictured in **32(b)**. Therefore, the linearity of

$Ph_3PO.AlCl_3$ represents experimental evidence for the importance of **31(c)** the overall electronic structure of the phosphoryl bond.



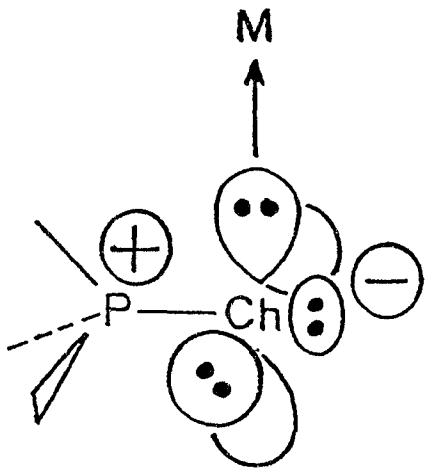


32(a) **32(b)**

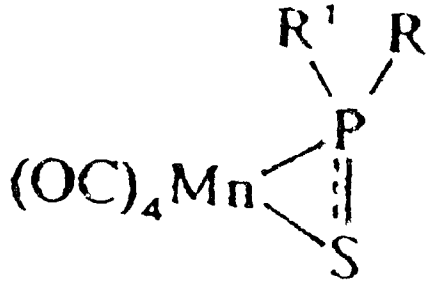
In contrast, the bent structures of the sulphide and selenide complexes demand a very different bonding model. The angles at the chalcogen centres are compatible with a simple σ-donation from a chalcogen lone pair of resonance structure **31(b)** to give an adduct with a "sp^3" hybridised chalcogen centre exhibiting a geometry predicted by VSEPR rules.[222] However, the P-S and P-Se bonds are markedly shorter than those of standard single bonds and indicate that there is some retention of the π-bonding present in the free bases. In addition, the aluminium centres are as close to the phosphorus centres [Ch = S: Al---P, 353.8 (2) pm. Ch = Se: Al---P, 372.7 (3) pm] as the steric requirements of the chlorines and the phenyl rings allow.

Similar interactions between the phosphorus and acid centres have been reported for the severely bent phosphine selenide complexes

$Ph_3PSe.HgCl_2$ (Hg---P, 353 pm) and $Ph_3PSe.AuCl$ (Au---P 49.7 pm),[212(a,b)] and have been rationalised in terms of repulsions between non-bonding electrons on the selenium centre. However, the results from this laboratory suggest that the thio- and selenophosphoryl bonds behave as extremely distorted or polarised π-bonds[16,223] and can be classified as "side-on" or π-donors. It is proposed that the π-electrons involved in back-bonding to the phosphorus *d*-orbitals are more available to donate into the acid centre as such back-bonding is weaker (less effective) in the heavier chalcogenide adducts.[183] This donation leads to the formation of a "π-complex", 33, analogous to those formed by alkenes to transition metal centres.[224] As in the organometallic[224] and non-



33



34

metal[16,223] counterparts, a degree of π-bonding is maintained by the donor system.

The proposed bonding scheme for $Ph_3PS.AlCl_3$ and $Ph_3PSe.AlCl_3$ is again perhaps somewhat foreign. However, there is some precedence for the π-complexation of thiophosphoryl bonds to transition metal centres. Lindner's group has prepared and structurally characterised several examples of complexed thioxophosphorus(V) cations, where the ligand is a cationic derivative of a neutral phosphine sulphide.[225] The complexes have the general structure **34**, and the similarities of these compounds to $Ph_3PS.AlCl_3$ are obvious. Moreover, the P-S bond lengths [*e.g.* $(C_6H_{11})_2PS.Mn(CO)_4$, P-S 200.6 (2) pm][225] are similar to that in $Ph_3PS.AlCl_3$ [202.8 (2) pm]. The most important difference is that the vacant coordination site at the phosphorus allows the formation of a full bond between the phosphorus and transition metal centres and a genuine π-complex.

II.3 CONCLUSION

In summary, the nature of a dative contact between an acid centre and phosphine chalcogenide is dependent on both the chalcogen and the Lewis acid. Effective back-bonding from the oxygen to the phosphorus, [31(c)], lowers the energy of the lone pairs in the π-type orbitals on the oxygen centre and makes the σ-type non-bonding electrons available for donation. The wide range of coordination angles observed for the phosphoryl bonds [Table II.2.3(a)ii] suggest that the three oxygen lone pairs are very close in energy and that the mode of coordination, to give either σ- or π-complexation, is influenced by many variables. $Ph_3PO.AlCl_3$ represents an extreme example of σ-coordination. The reduced effectiveness of back-donation in the heavier phosphine chalcogenides raises the energies of the π-type lone pairs and makes them a target for electrophilic reagents. However, the short adduct P-S/Se bonds and the close contacts between the phosphorus and aluminium centres suggest that the dative contacts are not simple Lewis acid-base interactions, like *e.g.* $Me_3N.AlCl_3$,[226] but rather "π-complexes" of very polarised π-bonds.

The proposed differences in electronic structures of the adducts account not only for their different molecular geometries, providing experimental evidence for the importance of resonance structure 31(c) to the phosphoryl bond, but may also provide insight into as yet unexplained differences in their NMR properties [Section II.2.2(c)].

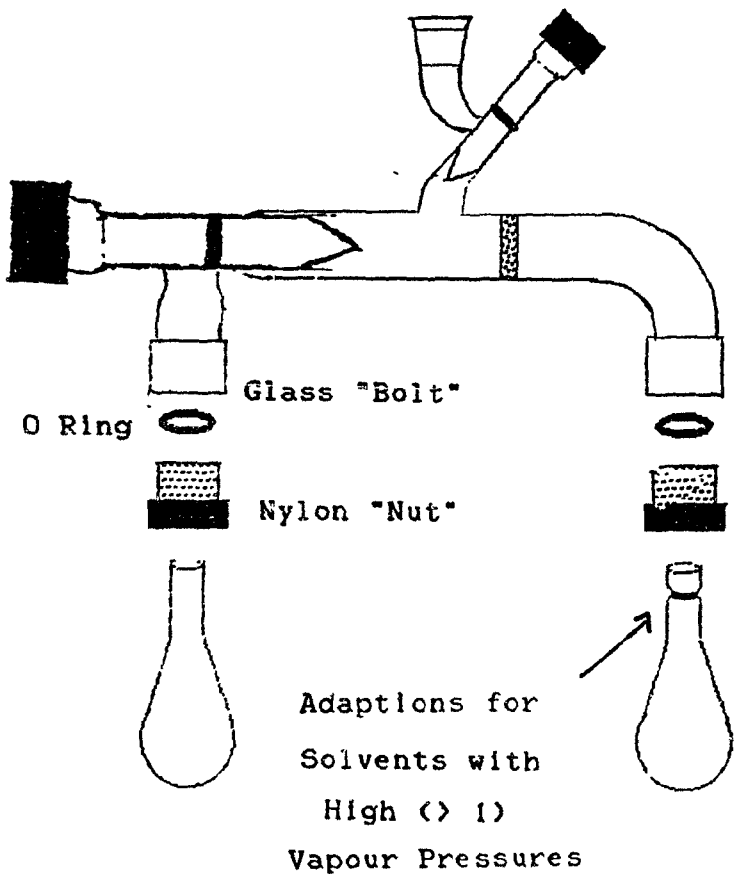
PART III: EXPERIMENTAL

III.1 GENERAL PROCEDURES

Specialised techniques and equipment are required to allow the preparation and handling of the many extremely air- and moisture-sensitive compounds reported in this thesis. Standard vacuum line techniques were used throughout[227] and air- and moisture-sensitive solids were manipulated in a Vacuum Atmospheres HE-243-2, N_2-filled dry box. Standard Schlenk techniques[227] were occasionally used in the preparation of some of the halo-phosphines and -arsines, *e.g.* **23(Me)**. However, the majority of the synthetic work was performed in specially designed reaction vessels,[228] an example of which is illustrated in Figure III(i). Solvents were scrupulously dried before use. Chlorinated solvents, CS_2 and alkanes were dried once over P_2O_5 and twice over CaH_2. Ethers were dried over either Na/benzophenone or CaH_2. For some experiments involving **1**, the solvent was also predried by storage over samples of the compounds under study.

IR spectra were recorded as Nujol mulls or liquid films on CsI plates using a Perkin-Elmer 283B spectrophotometer and referenced internally. The accuracy of the internal calibration was checked regularly against polystyrene. Mass spectra were obtained using a CEC Model 21-104 mass spectrometer. NMR spectra were recorded on a Nicolet NT-360 spectrometer. Spectra were referenced either internally against the residual protio-solvent resonance (^1H) or the solvent carbon resonance (^{13}C), both relative to tetramethylsilane (TMS), or externally against 85% H_3PO_4 (^{31}P), $Al(H_2O)_6^{3+}$ (^{27}Al), $Et_2O.BF_3$ (^{11}B), or H_2SeO_3, relative to Me_2Se (^{77}Se). Melting/decomposition points were

FIGURE III(i). Reaction Vessel used for the Manipulation of Air-Sensitive Compounds



recorded on a Fishers-Johns apparatus and are uncorrected. Electronic absorption and MCD spectra were recorded at the University of Texas at Austin, on a Varian 2300 spectrophotometer and a JASCO J-600 spectropolarimeter (equipped with a 16kG electromagnet), respectively. Characterisation data for new derivatives of **1** and **2** are given in Tables I.2.1(a,b), I.2.2., I.2.2(c)i, and Table I.2.2(d), and Figures I.2.2(c), I.2.2(d)i-v, and I.2.2(e)i,ii. Characterisation data for **17**$GaCl_4$, **18**$AlCl_4$, **21**$[GaCl_4]_2$ and $Ph_3PCh.AlCl_3$ are provided in Tables I.2.7(a)i,iii, I.2.7(b)i and II.2.2(c) respectively. Infra-red and mass spectral data for all new compounds are listed in Tables III(i,ii). Samples for crystallographic analyses were mounted in pyrex capillaries under N_2 and flame-sealed. Crystallographic details are provided in Appendix 1. Elemental analyses were performed by Beller laboratories in Gottingen, Federal Republic of Germany.

$AlCl_3$ (Aldrich), $GaCl_3$ (Aldrich/AESAR) and $SbCl_3$ (BDH) were sublimed *in vacuo* and stored in N_2-filled glass tubes. PCl_3 (Aldrich), $AsCl_3$ (AESAR), 1,2-benzenedithiol, 3,4-toluenedithiol, Et_3N, iPr_2NH, nBu_2NH, Et_2NH, hexachlorocyclopentadiene (all Aldrich) were distilled before use. *o*-Aminothiophenol, *o*-phenylenediamine, thiophenol, $PhPCl_2$, $AlBr_3$, PBr_3, sodium tetraphenylboron, Ph_3P, PhCCPh, *t*BuCCH, ethane-1,2-dithiol, N,N'-dimethylethylenediamine, hexamethyldisilazene, 2,3-dimethylbutadiene, Ph_3PO, Ph_3PSe (all Aldrich) and Ph_3PS (P&B) were used as received from suppliers. 2-Chloro-1,3,2-benzodithiapnictoles, **2b-e**,[66,67] 2-chloro-N,N'-dimethyl-1,3,2-benzodiazaphosphole, **2f**,[68] and 2-chloro-1,3,2-dithia- and diazapnictacyclopentanes[169,173,176] were prepared by literature methods or minor adaptations thereof.

III.2. PREPARATION OF THE NEW DERIVATIVES OF 2

III.2.1. Preparation of 2-Chloro-1,3,2-benzazathiaphosphole, 2g(Cl)

Following a reaction scheme outlined by Pudovik,[69] a solution of phosphorus trichloride (1.3 g, 0.8 mL, 9.4 mmol) in Et_2O (*ca.* 15 mL) was added to a stirred suspension of *o*-aminothiophenol (1.2 g, 1.0 mL, 9.4 mmol) and Et_3N (1.0 g, 2.6 mL, 9.4 mmol) in Et_2O (*ca.* 15 mL) over a period of 0.5 h. A white precipitate of triethylammonium hydrochloride formed immediately. The reaction was stirred overnight and the solution decanted. The solvent was removed from the filtrate by evacuation to leave a beige solid characterised as 2-chloro-1,3,2-benzazathiaphosphole [1.5 g, 8.0 mmol, 85% (crude yield)]. Analytically pure crystals (mpt. 83-84°C) were obtained by recrystallisation from CH_2Cl_2. Crystals suitable for X-ray diffraction studies were obtained from a dilute ether solution by slow evaporation to produce a beige oil, which crystallised overnight while under vacuum.

III.2.2. Preparation of 2-Bromo-1,3,2-benzazathiaphosphole, 2g(Br)

A solution of Et_3N (1.9 g, 2.6 mL, 19mmol) in CH_2Cl_2/Et_2O (*ca.* 1:1, 15 mL) was combined with *o*-aminothiophenol (1.2 g, 9.4 mmol) in CH_2Cl_2/ether (*ca.* 1:1, 15 mL). On stirring at room temperature, the yellow solution produced a pale white precipitate of triethylammonium chloride. A solution of phosphorus tribromide (2.5 g, 0.9 mL, 9.4 mmol) in CH_2Cl_2/Et_2O (*ca.* 1:1, 15 mL) was added and the mixture was stirred for 3 h at room temperature, enhancing precipitation. The pale yellow solution was decanted from the precipitate and the solvent was slowly

removed by evaporation under vacuum to leave yellow crystals, which were characterised as 2-bromo-1,3,2-benzazathiaphosphole, **2g(Br)**, (1.0 g, 4.4 mmol, 47%), mpt 139-142°C.

III.2.3. Preparation of 2-chloro-1,3,2-benzothiazarsole, 2h

A solution of $AsCl_3$ (1.08 g, 6.0 mmol) in Et_2O (*ca.* 15 mL) was added to a stirred mixture of *o*-aminothiophenol (0.75 g, 6.0 mmol) and Et_3N (1.21 g, 12.0 mmol) in Et_2O (*ca.* 20 mL). The resulting mixture was stirred a room temperature for *ca.* 3 h. The yellow solution was decanted from the resulting precipitate and the solvent removed *in vacuo* to give a bright yellow solid. The crude product was recrystallised from CH_2Cl_2 to give yellow/orange crystals of 2-chloro-1,3,2-benzothiazarsole, **2h**, (0.92 g, 3.9 mmol, 65%) mpt 135-137°C.

III.2.4. Preparation of 2-Chloro-1,3,2-benzodiselenaphosphole, 2i[229]

A 500-mL, three-necked round-bottomed flask, equipped with a 40 mm teflon stirring bar and fitted with two rubber septa, was purged with Ar for 20 min. THF (300 mL) was then added to the flask. The flask was cooled to -40°C and purged again for a further 10 minutes. *o*-Dilithiobenzene[230] (<18 mmol) in Et_2O (*ca.* 100 mL) was transferred from an evacuated Schlenk tube into the rapidly stirred THF-selenium mixture using Cannula techniques. The resulting suspension was allowed to warm to room temperature and stirred for 20 h. The mixture was filtered into a 500 mL Schlenk tube, and purged with Ar. The tube was then cooled to -40°C and PCl_3 (3.9 g, 28.4 mmol) rapidly added by syringe. A white precipitate formed immediately. The reaction mixture was then allowed

to warm to room temperature and stirred for 10 h. The precipitate was removed by filtration and the solvent removed *in vacuo* to give a brown oil. The oil was extracted with Et_2O, leaving behind a dark solid, and the extract fractions concentrated to give an amber oil. This oil was distilled under reduced pressure (<0.1 mmHg). Three fractions were obtained (80-100, 134, 140-200°C). The fractions were combined and shown by ^{31}P NMR to have only one phosphorus containing molecule, characterised spectroscopically as **2i**. This material was used without further purification in the *in situ* preparation of **1i**$AlCl_4$.

III.3. PREPARATION OF SALTS CONTAINING THE NEW HETERONAPHTHALENIC CATIONS, 1

III.3.1. Preparation of 1,3,2-Benzodithiaphospholium, 1a, Tetrachloroaluminate.

A solution of 2-chloro-1,3,2-benzodithiaphosphole, 2a,[66] (1.30 g, 6.3 mmol) in CH_2Cl_2 (*ca.* 20 mL) was poured in small portions onto a suspension of $AlCl_3$ (0.84 g, 6.3 mmol) in CH_2Cl_2 (*ca.* 20 mL), maintaining maximum dilution of the reaction mixture with vigorous stirring. A bright yellow precipitate formed immediately under an orange solution. The mixture was stirred overnight at room temperature. The solution was filtered and solid then recrystallised by several back-distillations of the solvent, to give a yellow crystalline solid. In this way, the initial yellow precipitate was quantitatively recrystallised as a pure material. The sample was washed once and isolated by filtration. The solvent was removed *in vacuo*, and the yellow crystals were characterised as 1,3,2-benzodithiaphospholium, 1b, tetrachloroaluminate (2.0 g, 5.8 mmol, 93%), dec pt *ca.* 80°C.

III.3.2. Preparation of 5-Methyl-1,3,2-benzodithiaphospholium, 1c, Tetrachloroaluminate.

A solution of 2-chloro-5-methyl-1,3,2-benzodithiaphosphole, 2c,[66] (0.55 g, 2.5 mmol) in CH_2Cl_2 (*ca.* 20 mL) was poured in small portions onto a suspension $AlCl_3$ (0.36 g, 2.7 mmol) in CH_2Cl_2 (*ca.* 20 mL) with vigorous mixing. An orange solution formed immediately, and the $AlCl_3$ was taken into solution. The solution was stirred at room temperature

overnight, and then approximately 70% of the solvent was removed. When the resulting solution was cooled to -10°C, orange needle-like crystals formed These were filtered and characterised as 5-methyl-1,3,2-benzodithiaphospholium, 1c, tetrachloroaluminate (0.74 g, 2.1 mmol, 84%), dec pt *ca.* 106-108°C.

III.3.3. Preparation of 5-Methyl-1,3,2-benzodithiaphospholium, 1c, nChloro(4-n)bromoaluminate.

A solution of 2-chloro-5-methyl-1,3,2-benzodithiaphosphole, 2c (1.00 g, 4.5 mmol) in CH_2Cl_2 (*ca.* 20 mL) was poured in small portions onto a solution of $AlBr_3$ (1.21 g, 4.5 mmol) in CH_2Cl_2 (*ca.* 20 mL) to give an orange solution, which was stirred at room temperature for *ca.* 2 h. Most of the solvent was removed *in vacuo*, and a small quantity of *n*-hexane was added. The solution was then cooled to -10°C and gave an orange microcrystalline precipitate of 5-methyl-1,3,2-benzodithiaphospholium, 1c, *n*chloro(4-*n*)bromoaluminate (1.03g), dec pt *ca.* 75-78°C.

III.3.4. Reaction of 2-Chloro-5-methyl-1,3,2-benzodithiaphosphole, 2c, with Pentachloromolybdenum(V).

A solution 2c (0.15 g, 0.68 mmol) in CH_2Cl_2 (*ca.* 30 mL) was added to solid $MoCl_5$ (0.19 g, 0.68 mmol) and a bright purple reaction mixture resulted. The majority of the solvent was removed *in vacuo* and the remainder by decanting to give a dark purple solid, mpt > 320°C. Attempts to recrystallise the material were unsucessful.

III.3.5. Preparation of 5-Methyl-1,3,2-benzodithiarsolium, 1d, Tetrachloroaluminate.

5-Methyl-1,3,2-benzodithiarsole, 2d,[67] (0.497 g, 1.88 mmol in CH_2Cl_2 (*ca.* 25 mL) was added dropwise over *ca.* 3 hours to a vigorously stirred suspension of $AlCl_3$ (0.250 g, 1.88 mmol) in CH_2Cl_2 (*ca.* 25 mL). Initial addition of 2d resulted in a pale orange coloration to the reaction mixture. As the addition progressed, the reaction mixture colour darkened, so that on completion the reaction solution was a bright orange/red. The mixture was stirred for 14 h and the solvent was slowly evaporated until preliminary crystallisation was observed. This solid was redissolved and the reaction vessel cooled in a ice water/NaCl bath. The bright orange solid which resulted was isolated and characterised as 5-methyl-1,3,2-benzodithiarsolium, 1d, tetrachloroaluminate (0.262 g, 0.66 mmol, 35%), mpt 121-123°C.

III.3.6. Preparation of 5-Methyl-1,3,2-benzodithiastibolium, 1e, Tetrachloroaluminate.

5-Methyl-1,3,2-benzodithiastibole, 2e,[67] (0.854 g, 2.77 mmol) in a CH_2Cl_2 (*ca.* 20 mL) suspension/solution was added in small portions to a stirred suspension of $AlCl_3$ (0.420 g, 3.15 mmol). A dark red solution resulted, from which large quantities of an orange solid precipitated after several minutes. The sparingly soluble precipitate was washed several times with solvent, isolated by filtration, and characterised as impure 5-methyl-1,3,2-benzodithiastibolium, 1e, tetrachloroaluminate (0.618 g, 1.39 mmol, 50%), mpt. 166-168°C.

III.3.7. Preparation of 5-Methyl-1,3,2-benzodithiastibolium, 1e, Tetrachlorogallate.

5-Methyl-1,3,2-benzodithiastibole, 2e,[67] (0.302 g, 0.97 mmol) in CH_2Cl_2 (*ca.* 25 mL) was added dropwise to a vigorously stirred solution of $GaCl_3$ (0.171 g, 0.97 mmol) in CH_2Cl_2 (*ca.* 10 mL). The reaction solution immediately turned orange. By completion of the addition, this colour had changed to a dark red. The reaction solution was then stirred at room temperature for 2 h. Slow removal of solvent resulted in some precipitation and a red oil. Re-addition of a small amount of solvent resulted in more precipitation. The reaction mixture was then vigorously stirred for several hours, but very little precipitate redissolved. The mixture was allowed to settle, and the solvent decanted. The bright orange/red solid thus isolated was characterised as 5-methyl-1,3,2-benzodithiastibolium, 1e, tetrachlorogallate (0.18 g 0.37 mmol, 38%), dpt *ca.* 130°C.

III.3.8. Preparation of N,N'-Dimethyl-1,3,2-benzodiazaphospholium, 1f, Tetrachloroaluminate.

A solution of 2-chloro-1,3-dimethyl-1,3,2-benzodiazaphosphole, 2f[68] (0.104 g, 0.52 mmol) in CH_2Cl_2 (*ca.* 20 mL) was added in small portions to a stirred suspension of $AlCl_3$ (0.075 g, 0.56 mmol) in CH_2Cl_2 (*ca.* 20 mL). The resulting colourless reaction solution was stirred 60 h at room temperature. Slow removal of the majority of the solvent followed by cooling of reaction solution to -10°C gave a small amount of very pale pink crystals. These were isolated by filtration and characterised as N,N'-dimethyl-1,3,2-benzodiazaphospholium, 1f, tetrachloroaluminate

(0.043 g, 0.13 mmol, 23%), mpt 126-128°C.

III.3.9. Preparation of 1,3,2-Benzazathiaphospholium, 1g, Tetrachloroaluminate.

A solution of 1,3,2-benzazathiaphosphole (0.8 g, 4.1 mmol) in CH_2Cl_2 (*ca.* 10 mL) was poured in small portions onto a vigorously stirred suspension of $AlCl_3$ (0.6 g, 4.1 mmol) in CH_2Cl_2 (*ca.* 10 mL). A bright orange solution formed immediately and the reaction mixture was stirred at room temperature for 3 h. Slow evaporation of *ca.* 80% of the solvent and cooling of the concentrated reaction solution provided bright yellow crystals. These were separated from the reaction mixture by filtration and characterised as 1,3,2-benzazathiaphospholium, 1g, tetrachloroaluminate (0.8 g, 2.2 mmol, 53%), mpt 123-125°C.

III.3.10 Reaction of 2-Bromo-1,3,2-benzazathiaphosphole, 2g(Br), with $AlCl_3$

2-Bromo-1,3,2-benzazathiaphosphole, 2g(Br), (0.091 g, 0.39 mmol) and $AlCl_3$ (0.052 g, 0.39 mmol) were combined in a bulb of a vacuum vessel equipped with a 10 mm (o.d.) NMR tube. CH_2Cl_2 (*ca.* 15 mL) was distilled onto the mixture and the resulting green/yellow solution was stirred at room temperature for 1 h. A $^{31}P/^{27}Al$ NMR study demonstrated the formation of the 1,3,2-benzazathiaphospholium cation.

III.3.11. Preparation of 1,3,2-Benzothiazarsolium, 1h, Tetrachloroaluminate.

A solution of 2-chloro-1,3,2-benzothiazarsole, 2h, (0.365 g, 1.54

mmol) in CH_2Cl_2 (ca. 20 mL) was added dropwise to a stirred suspension of $AlCl_3$ (0.205 g, 1.54 mmol) in CH_2Cl_2 (ca. 20 mL). The resulting red solution was stirred at room temperature for 4h. Slow removal of solvent resulted in the formation of orange crystals, which were isolated by decanting residual solvent and characterised as 1,3,2-benzothiazarsolium, **1h**, tetrachloroaluminate (0.329 g, 0.90 mmol, 58%), mpt 125-128°C.

III.3.12. in situ Preparation of 1,3,2-Benzodiselenaphospholium, 1i, Tetrachloroaluminate.

2-Chloro-1,3,2-benzodiselenaphosphole, **2i**, (<1.11 g, 3.7 mmol) and $AlCl_3$ (0.5 g, 3.7 mmol) were placed in a 10 mm (o.d.) NMR tube. The generation of a deep red colour indicated an immediate heterogeneous reaction. CH_2Cl_2 (3 mL) was distilled into the tube and the resulting dark red solution was shown by ^{31}P and ^{27}Al NMR to contain **1i**$AlCl_4$.

III.4. PREPARATION OF TRIS(PHENYLTHIO)PHOSPHINE AND 5-METHYL-2-PHENYL-1,3,2-BENZODITHIAPHOSPHOLE, 3.

III.4.1. Preparation of tris(Phenylthio)phosphine, $(PhS)_3P$

Thiophenol (7.7 g, 0.07 mol) in Et_2O (100 mL) was added dropwise under N_2 to a stirred solution of $PhSPCl_2$[231] (14.8 g, 0.07 mol) in Et_2O (250 mL). The reaction mixture was stirred at reflux for 4 h and then at room temperature for a further 12 h. Excess solvent was removed to give crude $(PhS)_3P$ (10.7 g, 0.03 mol, 43 %) as a creamy white solid. This product was recrystallised from CCl_4 to give colourless crystals of $(PhS)_3P$, mpt. 76-78°C (lit. 74-77°C).[232]

III.4.2. Preparation of 5-Methyl-2-phenyl-1,3,2-benzodithiaphosphole, 3.

3 was prepared using a modified literature procedure.[114] Toluene-3,4-dithiol (2.09 g, 13.3 mmol) in Et_2O (10 mL) was added dropwise under nitrogen to a stirred solution of dichlorophenylphosphine (2.40 g, 13.3 mmol) in Et_2O (30 mL). A reaction occurred immediately with evolution of HCl, and the mixture was stirred at room temperature for 1h. The solvent was removed *in vacuo* to give a pale brown viscous oil, which dissolved in boiling *n*-hexane. On cooling, the mixture separated into two layers. The mixture was allowed to stand overnight at room temperature, during which time clusters of lustrous white needle-like crystals formed at the junction of the layers and eventually all of the lower layer crystallised. The relatively air-stable crystals were characterised as 5-methyl-2-phenyl-1,3,2-benzodithiaphosphole, 3 (3.3 g,

12.3 mmol, 94%), mpt 55-58°C.

III.5. REACTIVITY STUDIES ON 5-METHYL-1,3,2-BENZODITHIAPHOSPHOLIUM, 1c, TETRACHLOROALUMINATE

III.5.1. Reaction of 2-Chloro-5-methyl-1,3,2-benzodithiaphosphole, 2c, with Sodium Tetraphenylboron.

2c, (0.080 g, 0.36 mmol), $NaBPh_4$ (0.125 g, 0.36 mmol) and CH_2Cl_2 (4 mL) were combined in a 10 mm (o.d.) NMR tube. An NMR study revealed the slow transformation (>72 h) of 2c into 5-methyl-2-phenyl-1,3,2-benzodithiaphosphole, 3.

III.5.2. Exposure of 5-Methyl-1,3,2-benzodithiaphospholium, 1c, Tetrachloroaluminate to the Atmosphere.

Stirred CH_2Cl_2 solutions of 1c$AlCl_4$ immediately changed in colour from yellow to colourless, when exposed to the atmosphere. The colour change was accompanied by the precipitation of white solid. The soluble reaction products were shown by ^{31}P NMR to consist of mostly 2c.

III.5.3. Reaction of 5-Methyl-1,3,2-benzodithiaphospholium, 1c, Tetrachloroaluminate with Triphenylphosphine Oxide

1c$AlCl_4$ (0.135 g, 0.38 mmol) in CH_2Cl_2 was added in small portions to a stirred CH_2Cl_2 solution of Ph_3PO (0.106 g, 0.38 mmol). An immediate discharge of the yellow colour of the salt solution was observed. Complete addition resulted in a pale yellow solution which was stirred a room temperature for several hours. ^{31}P NMR revealed the

presence of two phosphorus containing compounds, one of which was identified as 2-chloro-5-methyl-1,3,2-benzodithiaphosphole, 2c. Removal of solvent gave a white solid which was recrystallised from CH_2Cl_2 to give triphenylphosphine oxide-trichloroaluminium(III) adduct, identified by comparison of its spectral properties to a sample prepared by direct combination of Ph_3PO and $AlCl_3$.

III.5.4. Reaction of 5-Methyl-1,3,2-benzodithiaphospholium, 1c, Tetrachloroaluminate with Triphenylphosphine.

(a) Equimolar quantities: CH_2Cl_2 (*ca.* 10 mL) was distilled onto a mixture of 1c$AlCl_4$ (0.173 g, 0.49 mmol) and Ph_3P (0.126 g, 0.48 mmol). The initial bright colour of the solution rapidly faded to a pale yellow.

(b) Excess Ph_3P: CH_2Cl_2 (*ca.* 10 mL) was distilled onto a mixture of 1b$AlCl_4$ (0.089 g, 0.25 mmol) and Ph_3P (0.121 g, 0.46 mmol). Again the initial red colour of the reaction solution faded rapidly to a pale yellow.

The results of variable temperature ^{31}P NMR studies on the above solutions are reported in Section I.2.5(d).

III.5.5. Reaction of 5-Methyl-1,3,2-benzodithiaphospholium, 1c, Tetrachloroaluminate with 2-Chloro-5-methyl-1,3,2-benzodithiaphosphole, 2c

CH_2Cl_2 (*ca.* 10 mL) was distilled onto a mixture of 2 (0.060g, 0.29 mmol) and $AlCl_3$ (0.019 g, 0.14 mmol) to give a bright orange/yellow solution. The results of variable temperature ^{31}P NMR studies on this

solution are reported in Section I.2.5(e).

III.5.6. Reaction of 5-Methyl-1,3,2-benzodithiaphospholium, 1c, Tetrachloroaluminate with Triphenylamine

Ph_3N (0.082 g, 0.33 mmol) in CH_2Cl_2 was added dropwise to a CH_2Cl_2 solution of **1c**$AlCl_4$. The reaction solution immediately turned bright green. Removal of the solvent gave a bright green residue. ^{31}P NMR demonstrated the presence of 2-chloro-5-methyl-1,3,2-benzodithiaphosphole, **2c**. The origin of the green colour is discussed in Section I.2.5(f).

III.5.7. Reaction of 5-Methyl-1,3,2-benzodithiaphospholium, 1c, Tetrachloroaluminate with Acetylenes

(a) PhCCPh: A solution of **1c**$AlCl_4$ (0.194 g, 0.55 mmol) in CH_2Cl_2 (*ca.* 10 mL) was added in small portions to an agitated solution of PhCCPh (0.098 g, 0.55 mmol) in CH_2Cl_2 (*ca.* 10 mL). The reaction mixture turned from yellow to orange to deep red as the solution of **1c**$AlCl_4$ was added. The reaction mixture was then stirred for several hours at room temperature. An attempt to grow crystals by slow evaporation of solvent was unsuccessful.

(b) *t*-BuCCH: *t*BuCCH (0.025 g, 0.305 mmol) in CH_2Cl_2 (*ca.* 10 mL) was added to solid **1c**$AlCl_4$. The salt was rapidly taken into solution and the colour of the reaction mixture changed from orange to yellow. Slow removal of solvent resulted in a red oil. The ^{31}P NMR spectra of the above reaction mixtures are discussed in Section I.2.5(g).

III.6. PREPARATION OF NON-AROMATIC DERIVATIVES OF 1

III.6.1. Preparation of 1,4,6,9-Tetrathio-5-phosphonia-spiro (4,4)nonane, 17, Tetrachlorogallate.

2-Chloro-1,3,2-dithiaphosphacyclopentane, 6,[189] (1.74 g, 0.011 mol) in CH_2Cl_2 (*ca.* 1-2 mL) was added to a stirred solution of $GaCl_3$ (1.94 g, 0.011 mol) in CH_2Cl_2 (*ca.* 4 mL). A bright yellow solution immediately resulted in the reaction bulb, and a thick yellow oil coated other parts of the reaction vessel. Over a period of 1.5 h, the oil spontaneously crystallised into an orange solid. The reaction solution was stirred for this time with the gradual precipitation of an orange semi-solid. The reaction mixture was stirred vigorously at room temperature for 14 h and the pale orange/yellow solution above the solid was decanted and *ca.* 80% of the solvent removed. The remaining solution was cooled in an ice bath and yellow crystals were deposited. These crystals were washed several times with CH_2Cl_2 and then isolated. CH_2Cl_2 was re-distilled onto the orange semi-solid and the above extraction process repeated three more times to give a total of four crops of pale yellow crystals, characterised as 1,4,6,9-Tetrathio-5-phosphonia-spiro(4,4)nonane, 17, tetrachlorogallate (combined yield: 0.585, 1.4 mmol, 25%), dpt *ca.* 120°C.

III.6.2. Reaction of 2-Chloro-1,3,2-dithiaphosphacyclopentane, 6, with $AlCl_3$ in the Presence of 2,3-Dimethylbutadiene

A solution of 2,3-dimethyl-1,3,2-butadiene and 2-chloro-1,3,2-dithiaphosphacyclopentane, 6, in CH_2Cl_2 (*ca.* 15 mL) was added to a

stirred suspension of $AlCl_3$ in CH_2Cl_2 (*ca.* 10 mL). After *ca.* 1/2 h, all the $AlCl_3$ had been taken into solution. The pale yellow reaction solution was stirred for 22 h at room temperature, and the major (>90%) species present in solution was characterised by multinuclear NMR as **18**$AlCl_4$.

III.6.3. Reaction of 2-Chloro-1,3,2-dithiaphosphacyclopentane, 6, with $AlCl_3$ in the Presence of Hexachlorocyclopentadiene.

Hexachlorocyclopentadiene (3.55 g, 0.013 mol) and 2-chloro-1,3,2-dithiaphosphacyclopentane, **6**, (2.06 g, 0.013 mol) in CH_2Cl_2 (*ca.* 20 mL) were added to a stirred suspension/solution of $AlCl_3$ (1.74 g, 0.013 mol) in CH_2Cl_2 (*ca.* 10 mL) The reaction mixture immediately turned bright red. It was then stirred at room temperature for 72 h, by which time all the $AlCl_3$ had been taken into solution. The results of NMR analysis of the reaction solution are discussed in Section I.2.7(a).

III.6.4. Preparation of bis-1,3,2-dithiarsolidinium, 21, Tetrachlorogallate.

CH_2Cl_2 (total *ca.* 10 mL) was distilled onto solid $GaCl_3$ (0.750 g, 4.25 mmol) and 2-chloro-1,3,2-dithiarsacyclopentane, **20**,[173] (0.860 g, 4.25 mmol). Neither reagent completely dissolved ($GaCl_3$, *ca.* 2 mL of CH_2Cl_2: **20**, *ca.* 8 mL of CH_2Cl_2). Sufficient solvent was distilled over from the suspension of **20** onto the $GaCl_3$ to completely dissolve the latter, and this solution was then added to the vigorously agitated CH_2Cl_2 suspension/solution of **20**. The reaction mixture settled to give a yellow solution above a white precipitate. This solution was decanted

and the solvent slowly removed to give a yellow crystalline solid. Solvent was then distilled onto this solid and the resulting suspension vigorously stirred. The yellow solution thus obtained was decanted and cooled in a ice/water/salt bath to give pale yellow crystals, which were then isolated by filtration. CH_2Cl_2 was then redistilled onto the white precipitate and the double extraction process repeated to give a second crop of yellow crystals. The combined product was then characterised as *bis*-1,3,2-dithiarsolidinium, 21, tetrachlorogallinate (0.560 g, 1.48 mmol, 35%), mpt 88-91°C.

III.6.5. The Reactions of $(R_2N)_2AsCl$ (R = Et, Me_3Si, nBu), $ClAs(tBuN)_2AsCl$ and iPr_2NAsCl_2 with ECl_3 (E = Al, Ga) and/or Trimethylsilyltriflate.

When equimolar quantities of a chloroaminoarsine and chloride abstracting agent ($AlCl_3$, $GaCl_3$ or $CF_3SO_3SiMe_3$) were combined in CH_2Cl_2 (*ca.* 15 mL), the reaction solution turned orange/brown. Stirring of the reaction solutions at room temperature either led to somewhat darker solutions or the precipitation of a brown powder. In the cases where $AlCl_3$ was used, most or all of the Lewis acid was taken into solution. Removal of solvent from the orange/brown solutions led to brown oils/powders. Similar results were obtained for reactions performed in *n*-hexane, except that brown precipitates were obtained directly over periods of several hours and the *n*-hexane remained colourless.

III.6.6. Preparation of *bis*-N,N'-Dimethyl-1,3,2-diazarsolidinium, 24, Tetrachloroaluminate.

In an irreproducible reaction, 2-chloro-N,N'-dimethyl-1,3,2-diazarsacyclopentane (0.51 g, 2.6 mmol) in CH_2Cl_2 (*ca.* 25 mL) was added over a period of 10 min to a stirred suspension of $AlCl_3$ in CH_2Cl_2 (*ca.* 25 mL). The reaction suspension turned greenish yellow and was stirred at room temperature for 2h. Even after this time, some $AlCl_3$ remained undissolved. The mixture was allowed to settle and the solution decanted. The solvent was rapidly removed to give a brown oil. The oil was then redissolved in CH_2Cl_2 and the solvent removed more slowly. The resulting residue was held at $-25^{o}C$ for 72 h and this led to the formation of a small amount of yellow crystals in a brown oil. The oil was removed by washing with CH_2Cl_2. The crystals were then isolated and characterised crystallographically as *bis*-1,3,2-N,N'-dimethyl-1,3,2-diazarsolidinium, **24**, tetrachloroaluminate (0.04 g, 4.7%).

III.7. PREPARATION OF TRIPHENYLPHOSPHINE CHALCOGENIDE-TRICHLORO-ALUMINIUM(III) ADDUCTS

III.7.1. Preparation of Triphenylphosphine Oxide-Trichloro-aluminium(III) Adduct.

Ph_3PO (0.121 g, 0.44 mmol) in CH_2Cl_2 (*ca.* 7 mL) was added to $AlCl_3$ (0.058 g, 0.44 mmol). The resulting reaction mixture for 14 h at room temperature. Slow removal of solvent gave a quantitiative yield of slightly off-white crystals characterised as triphenylphosphine oxide-trichloroaluminium(III) adduct, mpt 168-170°C.

III.7.2. Preparation of Triphenylphosphine Sulphide-Trichloro-aluminium(III) Adduct.

Ph_3PS (0.725 g, 2.46 mmol) in CH_2Cl_2 (*ca.* 15 mL) was added to a stirred suspension of $AlCl_3$ (0.328 g, 2.46 mmol) in CH_2Cl_2 (*ca.* 5 mL). The $AlCl_3$ was taken into solution and the reaction mixture stirred at room temperature for several hours. Slow evaporation of gave only an oil. The oil was redissolved in CS_2 the mixed solvent slowly evaporated and the resulting oil cooled in an ice water bath for 1 week to give an essentially quantitative yield of crystallographic quality crystals of triphenylphosphine sulphide-trichloroaluminium(III) adduct, mpt 137-140°C.

III.7.3. Preparation of Triphenylphosphine Selenide-Trichloro-aluminium(III) Adduct.

Ph_3PSe (1.44 g, 4.22 mmol) in CH_2Cl_2 (*ca.* 10 mL) was added dropwise

to a stirred suspension of $AlCl_3$ (0.56 g, 4.22 mmol) in CH_2Cl_2 (*ca.* 10mL). The reaction mixture turned yellow and the $AlCl_3$ was rapidly taken into solution. The reaction mixture was then stirred at room temperature for 2 h. Slow evaporation of solvent gave a viscous brown oil. CS_2 (*ca.* 20 mL) was distilled onto the oil and the oil redissolved. Slow removal of solvent followed by cooling in an ice water bath gave a quantitative yield of bright yellow crystals, characterised as triphenylphosphine selenide-trichloroaluminium(III) adduct, mpt 107-109°C.

TABLE III(i). Infra-red Listings (ν_{max}; cm^{-1}) for All New Compounds

2b*	2c*	2g(Cl)	2g(Br)	2h	2i
3100-2500 (m)	1585 (m)	3300 (m)	3330 (m)	3290 (m,br)	3070 (s)
3060 (m)	1450 (s)	1580 (m)	1575 (m)	1450 (s)	1580 (m)
1450 (s)	1375 (m)	1370 (s)	1365 (s)	1355 (m)	1560 (s)
1430 (s)	1260 (m)	1305 (s)	1300 (s)	1300 (m)	1480 (m)
1260 (s)	1145 (m)	1255 (s)	1250 (m)	1250 (m)	1455 (vs)
1120 (m)	1120 (m)	1130 (m)	1020 (m)	1020 (m)	1445 (vs)
1040 (m)	1030 (m)	1030 (m)	900 (vs)	850 (m)	1425 (vs)
1030 (m)	870 (s)	910 (s)	840 (m)	740 (vs)	1260 (s)
940 (m)	865 (m, sh)	750 (vs)	815 (m)	580 (m)	1100 (m)
745 (vs)	800 (s)	730 (m, sh)	750 (vs)	555 (m,br)	1030 (m)
665 (s)	690 (m)	715 (m, sh)	620 (s)	460 (m)	940 (m)
500 (vs)	680 (s)	610 (m)	610 (s)	420 (s)	855 (m)
440 (s)	630 (m)	580 (s, br)	500 (vs)	290 (m)	745 (vs)
420 (vs)	535 (vs)	500 (vs)	575 (m)	230 (vs)	690 (m)
350 (s)	490 (vs)	485 (m)	535 (m)		645 (m)
285 (s)	360 (s)	350 (s)	340 (s)		420 (vs)
	330 (s)	290 (s, br)	245 (vs)		250 (s)

* Known compounds, but infra-red spectra not reported

2b,c,i recorded as liquid films. Remaining spectra with samples obtained as nujol mulls.

vs, very strong; s, strong; m, medium; br, broad; sh, shoulder.

TABLE III(i). Infra-red Listings (ν_{max}; cm^{-1}) for All New Compounds

(Continued)

1b$AlCl_4$	**1c**$AlCl_4$	**1d**$AlCl_4$	**1e**$AlCl_4$	**1e**$GaCl_4$	**1f**$AlCl_4$	**1g**$AlCl_4$	**1h**$AlCl_4$
1100 (m)	815 (s)	820 (s)	810 (s)	810 (s)	1345 (m)	3020 (m)	3230 (m)
760 (s)	520 (m)	540 (m)	520 (s)	395 (s)	1290 (m)	1580 (s)	1555 (m)
670 (m)	505 (vs)	510 (m)	480 (s)	370 (s)	1205 (m)	1240 (s)	760 (s)
565 (m)	485 (vs)	485 (vs)	450 (s)	350 (s)	1145 (m)	1175 (m)	720 (m)
555 (m)	465 (vs)	435 (m)	310 (m)	330 (m)	1135 (m)	920 (s)	710 (m)
525 (m)	430 (m)			320 (m)	1050 (s)	835 (m)	540 (m)
480 (vs)	425 (m)			300 (s)	720 (vs)	770 (vs)	530 (s)
460 (s)					515 (m)	740 (m)	505 (vs)
430 (m)					505 (s)	725 (s)	475 (vs)
					485 (vs)	550 (s)	450 (s)
					400 (m)	510 (vs)	290 (m)
						485 (vs)	
						445 (m)	

vs, very strong; s, strong; m, medium.

All spectra recorded with samples as nujol mulls

TABLE III(i). Infra-red Listings (ν_{max}; cm^{-1}) for All New Compounds (Continued)

17$GaCl_4$	**21**$[GaCl_4]_2$	$Ph_3PSe.AlCl_3$
940 (m)	1150 (m)	1100 (s)
840 (m)	830 (m)	1000 (m)
720 (m)	720 (m)	755 (m, sh)
660 (m)	390 (vs)	745 (s)
590 (s)	375 (vs)	720 (s)
540 (m)	355 (vs)	685 (s)
370 (vs)	320 (s)	550 (s)
		515 (vs)
		500 (vs, sh)
		395 (s)
		280 (s)

vs, very strong; s, strong; m, medium.

All spectra recorded with samples in nujol mulls.

TABLE III(ii). Mass Spectral Data [m/z (rel. int.)] for All New Compounds.

2b*	2c*	2d*	2e*	2g(Cl)	2g(Br)	2h
208 (12)	222 (12)	266 (9)	314 (16)	155 (5)	235 (0.6)	235 (2)
207 (3)	221 (3)	265 (2)	312 (54)	154 (9)	233 (0.5)	233 (7)
206 (28)	220 (29)	264 (21)	310 (48)	153 (100)	154 (14)	199 (6)
173 (10)	187 (10)	231 (10)	278 (12)	63 (28)	153 (100)	198 (26)
172 (10)	186 (10)	230 (10)	277 (90)		82 (22)	197 (100)
171 (100)	185 (100)	229 (100)	276 (18)		80 (21)	107 (33)
108 (11)	121 (11)	121 (8)	275 (100)			
70 (11)		107 (5)	155 (2)			
64 (12)			153 (33)			
			121 (30)			

* Known compound but mass spectral data not previously reported

TABLE III(ii). Mass Spectral Data [m/z (rel. int.)] for All New Compounds (Continued).

1b$AlCl_4$	**1c**$AlCl_4$	**1c**$AlCl_xBr_{4-x}$	**1d**$AlCl_4$	**1e**$AlCl_4$	**1e**$GaCl_4$
208 (12)	222 (12)	266 (1)	266 (10)	314 (17)	314 (15)
207 (3)	221 (3)	264 (1)	265 (3)	312 (57)	312 (50)
206 (28)	220 (29)	222 (11)	264 (25)	310 (47)	310 (44)
173 (10)	187 (10)	223 (3)	231 (10)	277 (85)	277 (68)
172 (9)	186 (10)	220 (26)	230 (10)	276 (13)	276 (9)
171 (100)	185 (100)	187 (10)	229 (100)	275 (100)	275 (81)
108 (11)	121 (11)	186 (10)	121 (9)	155 (10)	195 (42)
70 (10)		185 (100)	107 (7)	153 (16)	193 (100)
64 (10)		121 (10)		121 (15)	191 (72)
					155 (10)
					153 (15)
					122 (23)

1g$AlCl_4$	**1h**$AlCl_4$
155 (5)	235 (1)
154 (9)	233 (3)
153 (100)	199 (6)
128 (10)	198 (19)
64 (7)	197 (100)
	107 (44)

TABLE III(ii). Mass Spectral Data [m/z (rel. int.)] for All New Compounds (Continued).

21$[GaCl_4]_2$	$Ph_3PO.AlCl_3$*	$Ph_3PS.AlCl_3$*	$Ph_3PSe.AlCl_3$
204 (21)	412 (1)	296 (6)	344 (16)
202 (52)	410 (1)	295 (22)	343 (18)
167 (100)	379 (6)	294 (100)	342 (83)
139 (18)	377 (9)	293 (59)	341 (15)
107 (56)	279 (11)	185 (49)	340 (43)
	278 (63)	183 (49)	339 (19)
	277 (100)	139 (12)	338 (17)
	203 (17)		262 (36)
	201 (13)		185 (100)
	185 (12)		184 (16)
	81 (16)		183 (94)
			152 (10)
			109 (13)
			108 (18)

* Known compound but mass spectral data not previously reported.

APPENDIX 1: TABLES OF CRYSTALLOGRAPHIC DATA

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

TABLE A1. Tris(phenylthio)phosphine, $(PhS)_3P^+$ and 5-Methyl-2-phenyl-1,3,2-benzodithiaphosphole, 3*

Formula	$C_{18}H_{15}PS_3$	$C_{13}H_{11}PS_2$
fw	358.47	262.32
crystal class	hexagonal	monoclinic
space group	$R\bar{3}$	$P2_1/n$
a, pm	1267.60 (12)	1469.1 (3)
b, pm	-	629.1 (1)
c, pm	1889.21 (20)	1488.2 (3)
β, °	-	114.56 (2)
Z	6	4
R	0.031	0.037
R_w	0.045	0.037

+ Structure determined by Dr. P. S. White, University of New Brunswick (Present address: University of North Carolina, Chapel Hill, NC)

* Structure determined by Drs. T. S. Cameron and A. Linden, Dalhousie University

TABLE A2. The Tetrachloroaluminate Salts of the 1,3,2-Benzodithiaphospholium, 1b,* 5-Methyl-1,3,2-benzodithiaphospholium, 1c,* and N,N'-Dimethyl-1,3,2-benzodiazaphospholium, 1f+, Cations.

Formula	$C_6H_4S_2PAlCl_4$	$C_7H_6S_2PAlCl_4$	$C_8H_{10}N_2PAlCl_4$
fw	339.98	354.01	333.93
crystal class	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	Pbca
a, pm	660.5 (3)	803.0 (1)	1106.90 (5)
b, pm	2337.7 (4)	934.6 (3)	1846.66 (17)
c, pm	866.6 (3)	1875.8 (3)	1409.75 (12)
β, °	100.28 (3)	96.47 (1)	90
Z	4	4	8
R	0.036	0.042	0.055
R_w	0.037	---	0.059

* Structures determined by Drs. Cameron and Linden.

\+ Structure determined by Dr. White.

TABLE A3. 1,3,2-Benzazathiaphospholium, 1g, Tetrachloroaluminate and 1,3,2-Benzothaizarsolium, 1f, Tetrachloroaluminate

Formula	$C_6H_5NPSAlCl_4$	$C_6H_5AsNSAlCl_4$
fw	322.83	366.89
crystal class	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, pm	647.73 (6)	642.59 (5)
b, pm	2354.24 (21)	2365.4 (3)
c, pm	851.01 (7)	858.59 (7)
β, ^{o}	98.048 (7)	98.203 (6)
Z	4	4
R	0.035	0.054
R_w	0.047	0.042

Structures determined by Dr. White.

TABLE A4. 2-Chloro-1,3,2-benzazathiaphosphole, 2g(Cl),[+] 2-Bromo-1,3,2-benzazathiaphosphole, 2g(Br),[+] and 2-Chloro-1,3,2-benzothiazarsole, 2h[#]

Formula	C_6H_5ClNPS	C_6H_5BrNPS	$C_6H_5NSAsCl$
fw	189.60	234.05	233.55
crystal class	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, pm	856.07 (10)	853.45 (12)	837.0 (3)
b, pm	1069.48 (10)	1069.90 (14)	1082.9 (3)
c, pm	859.94 (13)	882.13 (7)	875.6 (2)
β, ^{o}	95.516 (11)	94.705 (8)	95.99 (2)
Z	4	4	4
R	0.035	0.056	0.025
R_w	0.044	0.066	0.026

[+] Structures determined by Dr. White

[#] Structure determined by Dr. J. F. Richardson, University of Louisville, Louisville, Kentucky, USA.

TABLE A5. 1,4,6,9-Tetrathia-5-phosphonia-spiro(4,4)nonane, 17, Tetrachlorogallate[$] and 2-Chloro-1,3,2-dithiarsacyclopentane, 20[#]

Formula	$C_4H_8S_4PGaCl_4$	$C_2H_4S_2AsCl$
fw	426.89	202.56
Crystal class	orthorhombic	monoclinic
space group	Pbcn	$P2_1/c$
a, pm	1554.9 (3)	993.0 (2)
b, pm	1528.7 (2)	714.1 (1)
c, pm	1294.2 (2)	943.2 (2)
β, ^{o}	90	112.23 (1)
Z	8	4
R	0.048	0.026
R_w	0.045	0.025

[$] Structure determined by Dr. R. D. Rogers, Northern Illinois University, DeKalb, Illinois.

[#] Structure determined by Dr. Richardson

TABLE A6. bis-1,3,2-Dithiarsolidinium, 21, Tetrachlorogallate[#] and bis-1,3,2-Diazarsolidinium, 24, Tetrachloroaluminate[@]

Formula	$C_2H_4S_2AsGaCl_4$	$C_4H_{10}N_2AsAlCl_4$
fw	378.64	329.85
crystal class	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, pm	645.4 (2)	935.54 (7)
b, pm	1436.0 (3)	1374.25 (8)
c, pm	1153.6 (2)	971.91 (4)
β, ^{o}C	104.62 (2)	101.939 (4)
Z	4	4
R	0.033	0.055
R_w	0.037	0.030

[@] Structure determined by Drs. E. J. Gabe and R. Hynes of the National Research Council, Chemistry Division, Ottawa, Ontario.

[#] Structure determined by Dr. Richardson.

TABLE A7. Triphenylphosphine Oxide,* Sulphide$ and Selenide$/ Trichloroaluminium(III) Adducts

Formula	$C_{18}H_{15}POAlCl_3$	$C_{18}H_{15}PSAlCl_3$	$C_{18}H_{15}PSeAlCl_3$
fw	411.63	427.70	474.59
crystal class	hexagonal	monoclinic	triclinic
space group	$R\bar{3}$	$P2_1/c$	$P\bar{1}$
a, pm	1366.3 (2)	971.0 (2)	896.7 (2)
b, pm	-	946.4 (1)	1262.6 (4)
c, pm	1825.8 (2)	2189.3 (5)	1824.2 (4)
α, ^{o}	-	-	84.83 (2)
β, ^{o}	-	95.15 (2)	89.02 (2)
γ, ^{o}	-	-	85.67 (2)
Z	6	4	4
R	0.062	0.042	0.044
R_w	0.060	0.043	0.044

* Structure determined at -60^{o}C by Drs. Cameron and Linden. Cell parameters at room temperature: *a*, 1371.6 (2); *c*, 1836.9 (2).

$ Structure determined by Dr. Rogers.

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