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Pnicogylidenes

by

Trenton M. Parks

Submitted in partial fulfilment of the requirements

for the degree of Doctor of Philosophy

at

Dalhousie University

Halifax, Nova Scotia

July 1994

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Abstract

The preparation and characterization of various cationic species containing arsenic and antimony in low-coordinate environments are reported. These species, known as *arsylidenes* and *stibylidenes*, may be viewed as *carbene* analogues and consequently are of general interest to many chemists. Stabilization techniques involving inclusion of the low-coordinate pnictogen atom in a heteronaphthalenic framework result in monomeric species. Attempts to isolate monomers without a heteronaphthalenic framework, instead using charge repulsion or steric effects as methods of stabilization, have been less successful. Investigations indicate that such reactions produce monomeric systems in solution and dimeric species in the solid state, however this dimerization does not involve As=As or Sb=Sb double bonds akin to carbene dimerizations, but rather a weak coordination from the electron-rich atom adjacent to the pnictogen is observed. Amino- or thia-chloroarsolidines, when reacted with the chloride ion abstractors GaCl₃ or AlCl₃, produce either dicationic dimers or monocationic complexes dependent upon the stoichiometry of the addition. Similar reactivity is observed with chloroarsenanes. Preliminary studies indicate that the thia-chlorostibolidine reacts in a similar manner, however the systems are complex and are not yet fully understood. Investigations into the chemistry of these compounds have revealed new and unexpected traits. Cycloaddition reactions in particular have produced surprising results that differ significantly from those observed in the associated carbenes or well-known *phosphyliidenes*.

List of Abbreviations Used

amu	atomic mass unit
avg.	average
bp.	boiling point
CP	cross polarization
EI-MS	electron impact mass spectrum
e.s.d.	estimated standard deviation
ESMS	electrospray mass spectrum
eV	electron-volt
FAB	fast atom bombardment
HOMO	highest occupied molecular orbital
i.d.	inside diameter
IR	infrared
LC	liquid chromatography
LUMO	lowest unoccupied molecular orbital
MAS	magic angle spinning
MHz	megahertz
mp.	melting point
NMR	nuclear magnetic resonance
o.d.	outside diameter
ppm	parts per million
VT	variable temperature
w.r.t.	with respect to

Acknowledgements

Many people have been involved in this body of work and without their contributions it would not have been possible.

I would like to thank Dr. T.S. Cameron, Dr. B. Borecka, Mr. P.K. Bakshi (Dalhousie University), and Dr. Richardson (University of Louisville) for performing the crystal structures in such a timely and efficient manner, and without complaint. Dr. D. Hooper and, especially, Dr. G. Wu, of the Atlantic Regional Magnetic Resonance Centre have been invaluable in the collection and interpretation of NMR spectra. Thanks to Dr. J. Curtis (Institute of Marine Biosciences) for performing the mass spectrometry and for his patience when the electrospray setup was under development. Jürgen Müller's expertise has been indispensable to my work in the form of designing and crafting the many pieces of unique glassware required; without him, it could not have happened. Thanks also go to Mr. D. Gates and Miss S. Sikka (Dalhousie University) for preparing some of the starting materials used in this study. Very great thanks go to J. Clyburne and P. Losier for their opinions and discussions. Thanks to L. Parks for putting up with me.

I appreciate the financial support provided me by Dalhousie University, the Walter C. Sumner Foundation, and the Natural Sciences and Engineering Research Council of Canada.

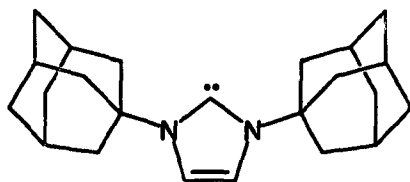
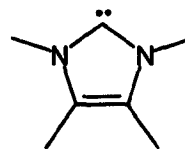
Finally, thanks to Neil Burford, my supervisor, and my friend.

1.0 Introduction

Electron deficient, coordinatively unsaturated atomic centres are of interest to the chemist due to their structural, electronic, and reactive novelty. Systems of this type have been recognized as important synthetic fragments, or “molecular building-blocks”, in that they are structurally and electronically simple units. Ylidene centres (*carbenes*) consist of a carbon atom which has two covalent bonds to other groups and two non-bonding orbitals containing two electrons between them. Long recognized as reaction intermediates,¹ carbenes have defied isolation as stable products until very recently.^{2,3,4} Previous attempts at isolation had been unsuccessful and usually resulted in a dimeric product containing a C=C double bond.⁵ In contrast to this, isovalent analogues of the carbenes, such as germylenes⁶ and stannylenes⁷ are well known as stable species.

The most commonly used techniques for generating ylidenes are elimination and abstraction. This leaves electrons distributed between two orbitals which, in the starting material, were both bonding orbitals. Such an elimination may involve two groups attached to a tetravalent carbon which simultaneously form a bond to each other and break their bonds to carbon, or they may be lost simultaneously through some other method. Another related technique involves homolysis of a double bond to the carbon. An example of this is the well-known decomposition of ketene to give methylene and carbon monoxide.⁸

A stable, crystalline carbene was first isolated by Arduengo and coworkers in 1991,⁴ and was prepared using a proton abstraction technique. The deprotonation was carried out using either sodium hydride in the presence of a catalytic amount of dimethyl anion [$\text{CH}_3(\text{O})\text{SCH}_2^-$], or potassium *tert*-butoxide in THF at room temperature. Yields of 96% crystalline carbene **1** have been reported. The marked stability of this species results from the presence of several types of electronic stabilization effects, operating in both the σ - and π -frameworks. In the π -framework, electron donation into the carbene out-of-plane *p*-

**1****2**

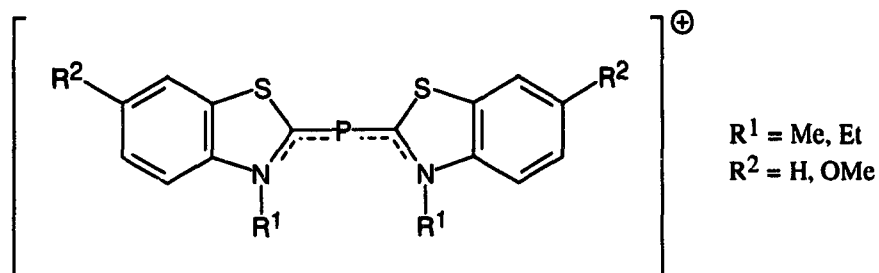
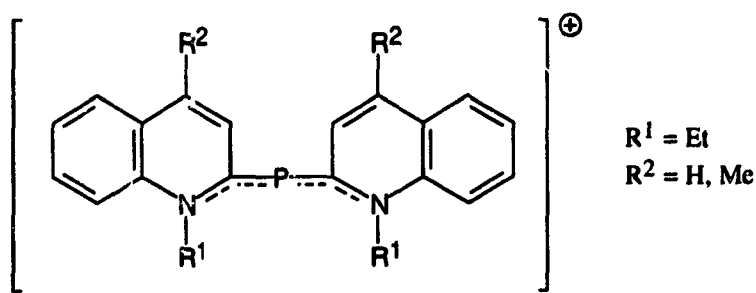
orbital by the electron rich π -system of the ring (:N-C=C-N:) leads to a moderation of the typical electrophilic behaviour of carbenes, while in the σ -framework, additional stability for the carbene lone pair is gained from the σ -electron-withdrawing effects of the highly electronegative nitrogen atoms, producing the same effect. Additional stability is afforded through the steric shielding of the ylidene centre by the surrounding adamantyl groups. Although important, it was thought that these electronic factors were insufficient to allow the isolation of nucleophilic carbenes without the assistance of additional steric protection,⁹ however more recent work has resulted in the isolation of non-sterically protected stable crystalline carbenes,¹⁰ including the remarkable 1,3,4,5-tetramethylimidazol-2-ylidene **2**, and has shown that the imidazol-2-ylidene framework itself is sufficient to produce stable species.

Although carbenes themselves are generally unstable, analogous isoelectronic phosphorus cations exhibit a sufficient degree of stability to have long been isolable as monomeric species. In analogy to the stabilities demonstrated by the germylenes and stannylenes, which are heavier congeners of carbenes, compounds containing the heavier pnictogen arsenic in a cationic "carbenic" environment might also be expected, however examples are extremely rare. The work performed in this laboratory has traditionally been associated with the study of low coordinate environments for the pnictogen species, especially phosphorus, and with the firm establishment of carbenic environments for phosphorus (*vide infra*), attention has now turned to the isolation of arsenic, as well as the other heavier pnictogens, in a carbenic type environment.

1.1 Phosphylidene Species

The usual system of nomenclature for cationic low-coordinate phosphorus systems follows the organic chemistry convention suggested by Olah.¹¹ Cations with lower coordination number are given the suffix *enium*, while those of higher coordination number are given the suffix *onium*. Consequently, dicoordinate phosphorus cations are commonly known as *phosphenium* ions, or *phospharyliums* in IUPAC terminology. In keeping with the analogous nature of these species to carbon ylidenes systems these phosphenium ions will also be referred to here as *phosphylidenes*.

Much has been written about the synthesis and chemistry of stable phosphylidene systems. The last major review in this area was published in 1985,¹² and a comprehensive book on low coordination phosphorus chemistry, including phosphylidenes, in 1990.¹³ The first dicoordinate phosphorus cations were reported by Dimroth and Hoffmann¹⁴ in 1964, however the ³¹P NMR chemical shifts and patterns of reactivity of these cationic phosphamethine cyanine dyes **3** and **4** suggest the presence of extensive charge

**3****4**

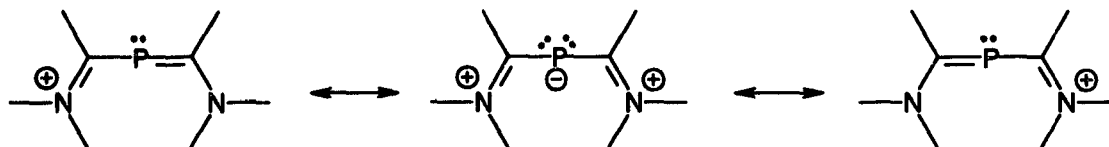


Figure 1.1: Resonance structures for cations **3** and **4**.

delocalization. Lewis resonance diagrams of these species do not include a structure in which the positive charge is localized on the phosphorus centre (Figure 1.1). Generally, when the term phosphylidene is used, it is implied that there is a large degree of positive charge accumulation at the two-coordinate phosphorus centre, and as a result these phosphamethacyanine species are usually not included in discussions of phosphylidene compounds.

Phosphenium ions may be considered as constituting one member of an isoelectronic series extending from silicenium¹⁵ to chlorenium¹⁶ ions (Figure 1.2). Alternatively, one may recognize the parallel between the singlet states of phosphenium ions (phosphylidenes) and those of the carbenes and silylenes. This focuses attention on

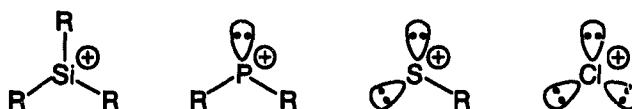


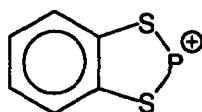
Figure 1.2: The series of silicenium to chlorenium ions.



Figure 1.3: Analogous ylidene species.

the lone pair of electrons and the formally vacant $3p$ orbital at phosphorus (Figure 1.3). This analogy may also be extended to the corresponding *arsylidenes* species, as well as the *stibylidenes* and *bismylidenes*.

With a very few exceptions all isolable phosphylidene compounds contain at least one amido substituent attached to the phosphorus. This observation highlights the necessity for the thermodynamic stabilization of these species through the means of ligand (R) to P^+ π -bonding or donation (*vide infra*). The ferrocenyl substituents in $[(Fc)_2P]^+$ effect stabilization through the dispersion of the positive charge.¹⁷ The marginal stability of $[Cp^*(tBu)P]^+$ is attributable to the multihapto bonding occurring between the Cp^* ligand (pentamethylcyclopentadienyl) and the P^+ centre, and the concomitant delocalization of positive charge.¹⁸ The stability of the novel dithiaphosphylidene **5** results from the

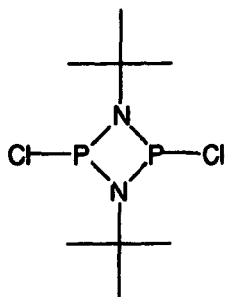
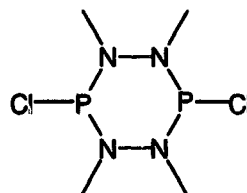


5

inclusion of the phosphylidene centre in a Hückel 10π -electron system and the resultant delocalization attained.¹⁹

In principle at least, substituents such as halogens²⁰ and alkoxy groups should be capable of conjugatively stabilizing phosphylidenes. It seems, however that these species possess insufficient π -donor character to provide the necessary thermodynamic stabilization. Because of this, reactions combining PX_3 ($X = F, Cl$) with Al_2Cl_6 , which is a commonly used chloride ion acceptor (*vide infra*), result in acid-base donor-acceptor complexes of the type $X_3P \rightarrow AlCl_3$, rather than the ionic phosphylidene alternative.²¹

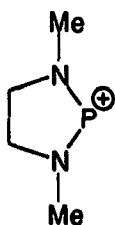
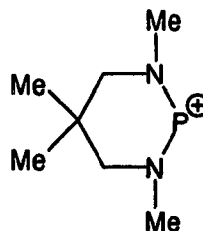
Attempts to prepare polyphosphylidene systems have also demonstrated the requirement for a certain minimum of electron donation. As an example, treatment of **6** with an excess of Al_2Cl_6 results in the abstraction of only one chloride ion and the

**6****7**

formation of the mono-phosphylidene.²² However, when a similar reaction is performed starting with **7**, a bis AlCl_3 adduct is formed.²³ This species may be regarded as the AlCl_4^- salt of the corresponding bis-phosphylidene. Evidently, at least four nitrogen atoms are necessary to satisfy the conjugative requirements of two cationic phosphylidene centres in the same molecule.

1.1.1 Synthesis

The first example of a stabilized phosphylidene species **8** was reported by Fleming, Jekot, and Lupton in 1972.²⁴ This was closely followed by a paper by Maryanoff and Hutchins describing a second stabilized cation **9**.²⁵ Both of these cyclic phosphylidene species were prepared by halide ion abstraction from the precursor diaminohalophosphines. The first examples of acyclic phosphylidenes, $[(\text{Me}_2\text{N})_2\text{P}]^+$ and $[(\text{Me}_2\text{N})(\text{Cl})\text{P}]^+$, were prepared in 1976 using the same technique.^{26,27} Chloride ion abstraction by Al_2Cl_6 has

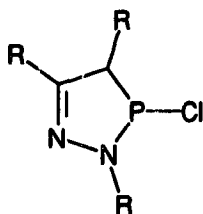
**8****9**

proven to be a most versatile approach, however there are instances when other chloride ion acceptors such as GaCl_3 ,^{26,27} FeCl_3 ,²⁰ and PCl_5 ²⁵ have been successfully employed.

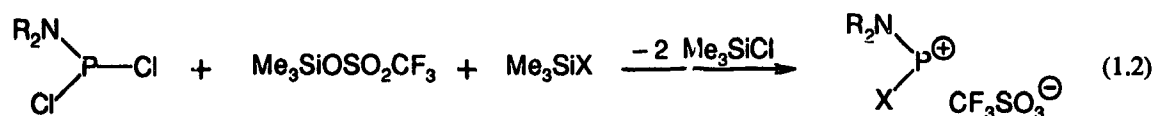
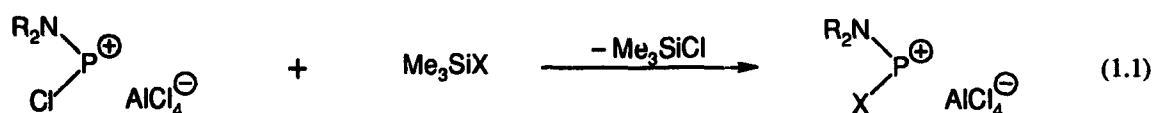
In general, the preparation of phosphylidenes is effected by allowing a mixture of the appropriate phosphorus chloride and a stoichiometric quantity of Al_2Cl_6 in dichloromethane solution to warm slowly from -78°C to room temperature, however in many cases it has been determined that the reactions are complete at -78°C . The progress of the reaction may be conveniently monitored through the use of ^{31}P NMR spectroscopy. Dichloromethane is the preferred solvent for these reactions since it is noncoordinating yet is sufficiently polar to permit solubilization of the ionic phosphylidene salts.

Another commonly employed synthetic technique is based on the ability of chlorophosphine starting materials to react with silylated compounds containing Si–O, Si–S, Si–N, or similar bonds.²⁸ Reacting a monochlorophosphine with $\text{Me}_3\text{SiOSO}_2\text{CF}_3$ (trimethylsilyltriflate) in solution results in the production of a proposed covalent intermediate possessing a P–O single bond with the resultant elimination of Me_3SiCl . Successive heterolytic cleavage of the P–O bond to produce the cationic phosphylidene species is a result of the stability of the triflate anion as well as its low nucleophilicity. Homogeneous solutions and the easy elimination of Me_3SiCl are the major points which make this technique favourable for these syntheses.^{29,30}

In rare cases, heterolysis of a P–Cl bond may occur even without the assistance of a chloride ion abstractor.^{31,32} In such a case, a chloride ion is extruded in a spontaneous fashion from a cyclic chlorophosphine precursor **10**. This precursor is formed through the reaction of the hydrazone $\text{R}^1\text{--NH--N=C(R}^3\text{)--CH}_2\text{--R}^2$ with PCl_3 , with the resultant elimination of two equivalents of hydrogen chloride. Crystal structural data indicate that these compounds are ionic in nature.³² The stability of this system evidently stems from the inclusion of the cationic phosphylidene centre in a 6π -electron system exhibiting aromatic stabilization.

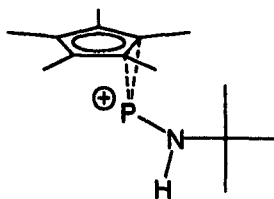
**10**

There are at least two other synthetic techniques commonly employed for phosphylidene formation. The first of these takes advantage of the great reactivity of the P(III)–Cl bond towards silylated reagents [Eqn. (1.1)].²⁸ The same results may be obtained by a one-pot synthesis under mild conditions [Eqn. (1.2)], and in such a case the



counter ion is CF_3SO_3^- . The mixing of the two reagents gives, as reactive intermediates, the chlorophosphenium cation $\text{R}_2\text{N}-\text{P}^+-\text{Cl}$, which spontaneously reacts with the silylated compound Me_3SiX .^{29,30}

The second technique begins with iminophosphine starting materials ($\text{R}^1-\text{P}=\text{N}-\text{R}^2$). An electrophilic attack on the polar $\text{P}=\text{N}$ double bond leads to the corresponding phosphylidene. This technique has enabled the synthesis and stabilization of the first phosphylidene possessing a secondary amino group **11** AlCl_4^- .³³ Its stability results from the multihapto bonding which occurs between the Cp^* ligand and the



11

phosphorus atom, producing a delocalization of the positive charge throughout the cluster structure.^{18,34} A similar result has been obtained through the protonation of a similar phosphalkene, producing the phosphylidene $[\text{Cp}^*-\text{P}^+-\text{CH}(\text{SiMe}_3)_2] [\text{CF}_3\text{SO}_3^-]$.³⁵

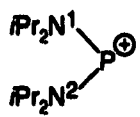
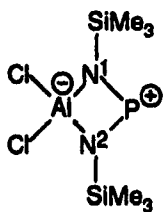
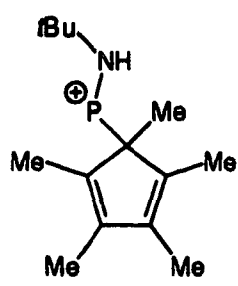
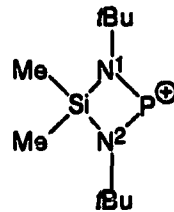
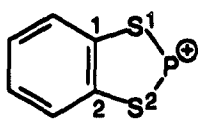
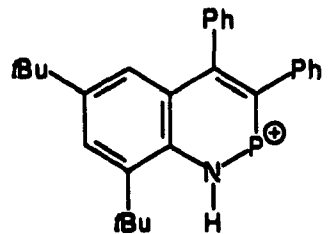
1.1.2 Structural and Spectroscopic Properties

X-ray crystallography has been a very useful tool in studying phosphylidene systems. Table 1.1³⁶ contains some pertinent structural parameters for six different crystallographically characterized phosphylidenes. These species exhibit common traits which confirm the expected structural properties of dicoordinated phosphorus cations if they are to be considered as carbene analogues.

The first of the common traits occurs in the geometry of the backbone of these systems. The observed geometry is consistent with a central sp^2 -hybridized phosphorus atom, exhibiting planar geometry and, discounting the actual nature of the substituents, being approximately trilaterally symmetric, with the lone pair of electrons acting as one of the three substituents.

Secondly, the bond angles at the phosphorus atom are smaller than the idealized geometry of 120° . The N–P–N and N–P–C bond angles for the acyclic phosphylidenes **1** and **3** are 114.8° and 105.1° respectively, the decrease believed to be due to the repulsive interactions which occur between the lone pair of electrons on the phosphorus atom and the P–N bonds.^{33,37} *Ab initio* calculations on the virtually strain-free model system $[(\text{H}_2\text{N})_2\text{P}]^+$ reveal a similarly decreased N–P–N bond angle.³⁸ In the cyclic compounds **2**,

Table 1.1: Important bond lengths and angles for six phosphylidenes (anion = AlCl_4^- or GaCl_4^-).

	Phosphylidene	Bond Lengths (Å)	Bond Angles (°)
1		P-N ¹ = 1.611(4) P-N ² = 1.615(4)	N ¹ -P-N ² = 114.8(2)
2		P-N = 1.614(6) N-Si = 1.758(6) N-Al = 1.890(6)	N ¹ -P-N ² = 97.4(4) N ¹ -Al-N ² = 79.9(3) P-N ¹ -Al = 91.4(3)
3		P-N = 1.620(2) P-C = 1.990(2)	P-N-C = 127.7(3) N-P-C = 105.1(1)
4		P-N ¹ = 1.619(7) P-N ² = 1.638(8) N-Si = 1.797	N ¹ -P-N ² = 90.0(4) N ¹ -Si-N ² = 79.7(3) P-N ¹ -Si = 95.8(4)
5		P-S ¹ = 2.016(3) P-S ² = 2.015(3) S ¹ -C ¹ = 1.728(5) S ² -C ² = 1.711(6)	S ¹ -P-S ² = 97.59(10) P-S ¹ -C ¹ = 102.6(2) P-S ² -C ² = 102.5(2)
6		P-C = 1.720(9) P-N = 1.651(8)	N-P-C = 99.5(4) P-N-C = 131.6(6)

4, **5**, and **6** the N–P–N and S–P–S bond angles are 97.4°, 90.0°, 97.6°, and 99.5° respectively. These angles, which are considerably smaller than the idealized sp^2 geometry, are further reduced by the constrained nature of the small four- and five-membered rings.

A third notable feature is that the P–N bond lengths in **1** to **4** are roughly 5% shorter than those of dialkylaminophosphines,³⁹ indicative of the presence of partial double bond character, possibly a result of conjugation between the $2p\pi$ lone pair of the adjacent coplanar nitrogen atoms and the formally vacant $3p\pi$ orbital of the phosphorus atom. This results in dative bonding occurring between these atoms. Cation **6** also exhibits shortening, although to a slightly lesser degree.

The cyclic phosphylidene salt **5** is the first example of a cation containing P–S bonds.¹⁹ The P–S bond length (2.016 Å) is approximately 4% shorter than that found in P_4S_3 (2.090 Å),⁴⁰ analogous to the above cases involving P–N bonding. This is among the shortest P–S bond lengths known, with the exception of the thiophosphoryl bonds P=S (1.86 Å).⁴¹ The planarity of the two rings in this system implies that the heteroatoms are involved in a Hückel heteronaphthalenic framework containing 10π electrons and affording an effective delocalization of the positive charge. Such π -bonding stabilizes the phosphorus ions and provides a good explanation for the observed planarity.¹⁹

Phosphorus-31 nuclear magnetic resonance spectroscopy is a very useful technique for the identification and characterization of phosphorus containing compounds, and of the numerous compilations of NMR data published, at least three deal with phosphylidenes.^{12,42} The values for the chemical shifts of the N–P⁺–N ions, which are the most numerous stable systems, are spread between $\delta = 220$ and 380 ppm¹³ as referenced to 85% H_3PO_4 , and are generally about 100 ppm downfield from the precursor halophosphines. A greater localization of the positive charge on the phosphorus atom in the cations results in less shielding and a larger chemical shift. This effect increases when

one of the ligands is Cl,²⁰ which has inferior conjugating ability, and becomes dominant with R = *t*Bu,²² which has no π -donor character. Conversely, when the ligands work to delocalize the positive charge of the cation, smaller chemical shifts are encountered. This effect is very important for the Cp* group whose multihapto bonds afford great dispersion of the positive charge.^{17(a)} The lowest values are encountered when one of the ligands is the cyano group, which has a rather weak donor effect.^{29,30} The observed large displacement of the ³¹P chemical shift is due to the anisotropic shielding effect of this group. Such an effect has also been observed in other families of phosphorus compounds.⁴³

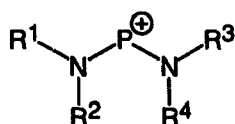
Steric effects also have a role to play in determining ³¹P chemical shift values. In Table 1.2⁴⁴ note that the chemical shifts of the bis(amido)-substituted phosphylidenes increase with increasing ligand size. This trend has been interpreted on the basis of progressive twisting of the R₂N groups with increasing ligand bulk reducing the 2p-3p N-P orbital overlap. Such an effect reduces the charge delocalization ability of these ligands and hence the chemical shift increases.

²⁷Al NMR spectroscopy can also play a role in characterizing phosphylidene species when their preparation has been carried out through the use of Al₂Cl₆ promoted chloride abstraction techniques.⁴⁵ In such cases phosphylidene formation is accompanied by production of the highly symmetrical AlCl₄⁻ anion. ²⁷Al chemical shifts and line width

Table 1.2: ³¹P NMR chemical shifts for some bis(amido) substituted phosphylidenes (referenced to 85% H₃PO₄).	
Phosphylidene	³¹P Chemical Shift
[(Me ₂ N) ₂ P] ⁺	264
[(Et ₂ N) ₂ P] ⁺	263
[(<i>i</i> Pr ₂ N) ₂ P] ⁺	313
[((Me ₃ Si) ₂ N) ₂ P] ⁺	450
[(Me ₂ N)(<i>t</i> Bu)P] ⁺	513

data of aluminium complexes in solution allow one to discuss symmetry and structure. For the AlCl_4^- ion the resonance signal of a $^{27}\text{Al}\{^1\text{H}\}$ NMR spectrum exhibits a sharp singlet between 102 and 104 ppm downfield relative to $\text{Al}(\text{H}_2\text{O})_6^{3+}$, and a half-height line-width of between 6 and 15 Hz. These data are consistent with a symmetric structure for the AlCl_4^- anion.⁴⁶ Al_2Cl_6 itself exhibits a very broad signal (half-height line-width of 260 Hz) at a chemical shift of 105 ppm in chloroform solution.⁴⁶

Variable temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR have provided important information on the static and dynamic stereochemistry of acyclic bis(dialkylamino)phosphenium cations **12**.^{31,38} At higher temperatures R^1 and R^2 , and R^3 and R^4 are averaged and give only a single signal. Typically, however, anisochronous R groups are detectable at lower

**12**

- a:** $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{Me}$
- b:** $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = i\text{Pr}$
- c:** $\text{R}^1 = \text{R}^2 = \text{Me}; \text{R}^3 = \text{R}^4 = i\text{Pr}$
- d:** $\text{R}^1 = \text{R}^2 = \text{Me}; \text{R}^3 = \text{R}^4 = \text{Me}_3\text{Si}$

temperatures.^{20,22,37} The averaging of the R^1 and R^2 environments (as well as that of the R^3 and R^4 environments) could arise from P–N bond rotation, inversion at the P^+ centre, or a combination of the two, becoming rapid on the NMR timescale. Investigations performed on $[(\text{Me}_2\text{N})(i\text{Pr}_2\text{N})\text{P}]^+$ **12c**³⁷ reveal separate coalescence phenomena for the Me_2N and $i\text{Pr}_2\text{N}$ groups, thus indicating that P–N bond rotation, and not inversion at the P^+ centre, is the rate determining process. Furthermore, it appears that as rotation about any given P–N bond occurs, the rest of the cation remains fixed in order to minimize the loss of $p\pi$ - $p\pi$ conjugation. These conclusions agree with theoretical studies performed on $[(\text{H}_2\text{N})_2\text{P}]^+$ and $[(\text{H}_2\text{N})(\text{H})\text{P}]^+$ which indicate that the barrier to inversion at the phosphorus centre is significantly higher than the barrier to P–N bond rotation.^{38,47}

1.1.3 Chemical Properties

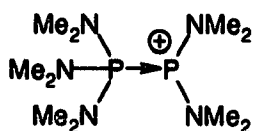
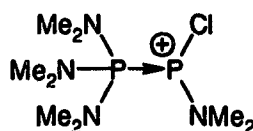
Phosphyridene systems possess a rich and varied chemical reactivity. Since these species are electron deficient, possessing only six valence electrons, they should be expected to perform as electrophiles, however, the presence of the non-bonding electron pair should also allow exhibition of nucleophilic behaviour. There are many examples of both types of reactivity resulting from this dual nature.

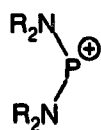
1.1.3.1 Lewis Acidity

Phosphyridenes are six electron species bearing a formal positive charge and hence would be expected to exhibit the properties of Lewis acids. Reactions with Lewis bases have in fact been observed for these compounds, most notably when the Lewis base is a phosphine.²⁷ The acid base reaction, resulting in the formation of a $(B \rightarrow PR_2)^+$ adduct, depends upon the strength of the base. Additionally, when the anion in the system is $AlCl_4^-$, the system may be perturbed as a result of side reactions which produce a chloride ion and $AlCl_3$.⁴⁸

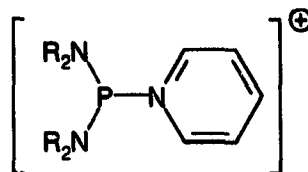
It is well known that phosphines display donor properties towards transition metals or main group acceptors. Since phosphyridenes are Lewis acids the formation of stable $(R_3P \rightarrow PR_2)^+$ adducts is very easy. The structures of the first of these adduct compounds **13** and **14** were assigned in 1976.²⁷

Studies of the Lewis acidity of the bis(dialkylamino)phosphyridene **15a-c** triflates, and their formation of pyridine adducts **16a-c** have been carried out.⁴⁹ The adducts are

**13****14**

**15**

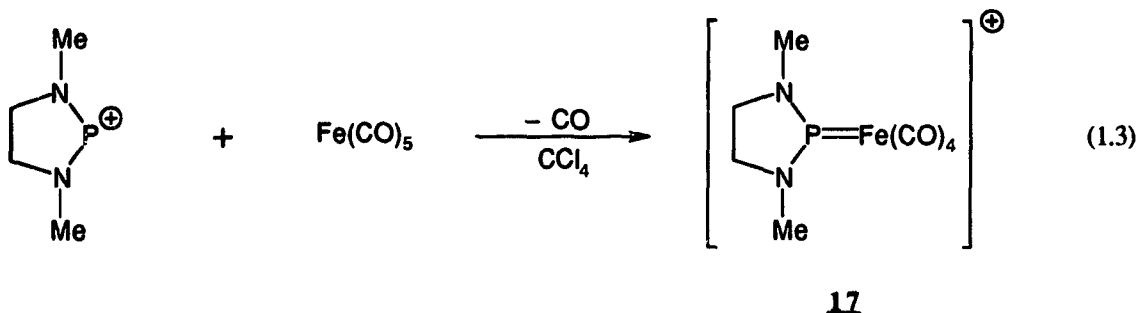
a: R = Me
b: R = Et
c: R = *i*Pr

**16**

characterized by large (>100 ppm) ^{31}P NMR chemical shifts towards high field as a result of the change of coordination number at the phosphorus centre. In ^{13}C NMR, formation of the adduct deshields the C_4 atom of the pyridine ring and changes the chemical shift by 6.56 to 8.35 ppm. This provides a measure of the relative acidity of these phosphylidenes **15**. By comparison with the boron derivatives⁵⁰ of the adducts **16** it appears that **15** should have a Lewis acidity comparable with that of BF_3 , which changes the C_4 chemical shift by 7.72 ppm. It is interesting to note that when the counter ion of these systems **15** is AlCl_4^- , it competes with pyridine and the reaction proceeds via a chloride ion transfer to the phosphylidene, yielding the chlorophosphine and the stable $(\text{Py} \rightarrow \text{AlCl}_3)$ adduct.⁵¹ Similar results have been observed with the bases 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN).⁵²

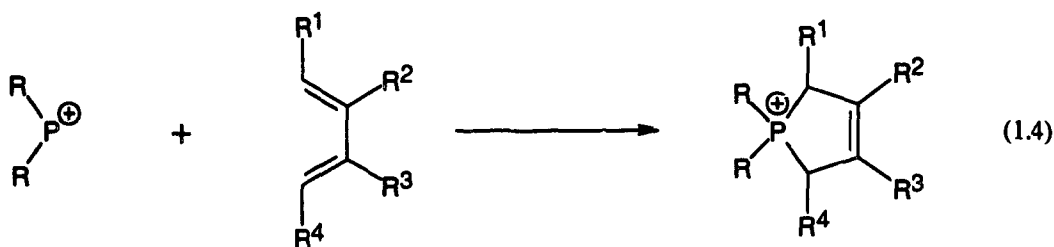
1.1.3.2 Phosphylidene Coordination

Phosphylidenes have been shown to exhibit the features of a Lewis base in the presence of electron deficient transition metal fragments. In such a case the lone electron pair of the phosphylidene is used to form a coordination bond to a 16-electron transition metal fragment. This results in the production of a tricoordinate phosphonium centre, such as is observed in **17**. In the first observed production of such complexes, the cyclic phosphonium cation slowly displaces CO from $\text{Fe}(\text{CO})_5$ [or $\text{Fe}_2(\text{CO})_9$] according to Eqn. (1.3).⁵³



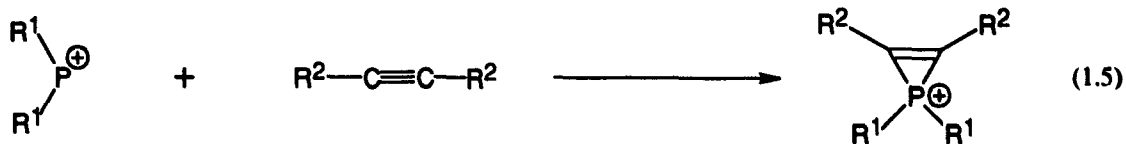
1.1.3.3 Cycloadditions

Phosphylidene species act like dienophiles towards 1,3-dienes. The reaction products in such a case are phospholenium cations, resulting from a 1,4-addition [Eqn. (1.4)]. This reaction is generally characterized by short reaction times, much shorter than

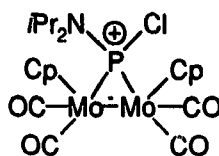


the McCormack reaction,⁵⁴ which involves the analogous reactions of dihalophosphines on 1,3-dienes and occurs slowly over a period of several days. The time required for completion of the reaction with phosphylidenes depends upon the steric and electronic effects of both the diene and the phosphylidene. Phosphylidenes are also known to react with 1,4-dienes, and in this regard behave in a manner similar to an electrophilic carbene centre.⁵⁵

Reactions of phosphylidenes with alkynes produce three-membered ring phosphirenium cations [Eqn. (1.5)],⁵⁶ exactly analogous to the reactions observed when silylenes ($\text{R}_2\text{Si}:$) are reacted with alkynes.⁵⁷ Recognizing the isolobal relationship of alkynes to compounds containing metal=metal triple bonds, has led to the exploration of the reactivity of the phosphylidene ($i\text{Pr}_2\text{NPCI}^+$) towards $\text{Cp(CO)}_2\text{Mo}\equiv\text{Mo(CO)}_2\text{Cp}$.⁵⁸

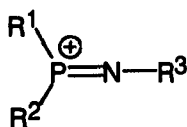
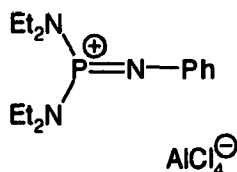
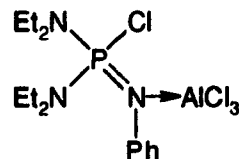


Spectroscopic evidence indicates that such a reaction produces the dimetallaphosphirenium cation **18**.

**18**

1.1.3.4 Staudinger Reactions⁵⁹

On the basis of solution ^{31}P NMR studies, in 1982 it was suggested that, in an interesting extension of the Staudinger reaction, phosphylidenes react readily with organic azides to form iminophosphonium salts **19**.⁶⁰ Attempts to perform an X-ray crystal structural analysis of the iminophosphonium salt **20** resulted in the characterization of the $AlCl_3$ complex of the chloroiminophosphane **21**,⁶¹ a result of displacement of a chloride

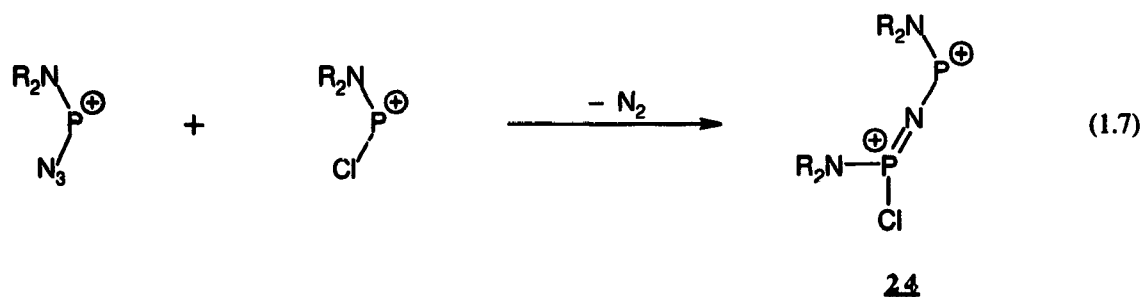
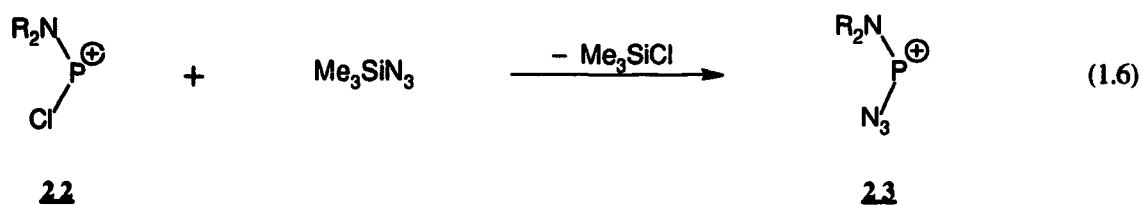
**19****20****21**

ion from the $AlCl_4^-$ anion. More recent work has revealed, however, that **20** is not in fact produced and what was characterized in solution by ^{31}P NMR was the hydrolysis product of **21**. Repetition of the reaction with more careful control of the reaction conditions revealed a quantitative production of **21**.⁶² Current investigations in this area are utilizing

azides possessing substituents with more steric bulk than a phenyl ring, as well as AlX_3 type Lewis acids (X = bulky groups), to prevent formation of the coordination complex.⁶³

1.1.3.5 Polymers

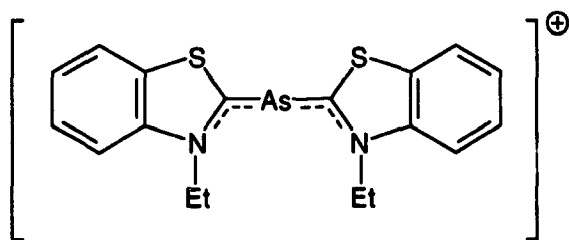
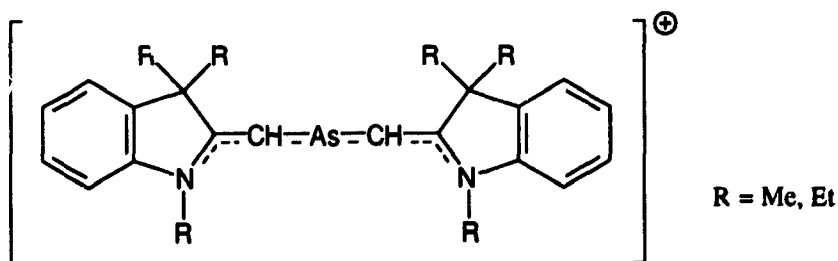
When chloro(amido)phosphylidenes **22** are treated with trimethylsilylazide (Me_3SiN_3) a second reaction pathway, differing from the standard Staudinger reaction (*vide supra*) seems to occur. The first step of this reaction is believed to be a metathesis which results in the formation of an azidophosphylidene **23** [Eqn. (1.6)].⁶⁴ This species, itself an azide, reacts with the chlorophosphylidene **22** to produce novel phosphonium-iminophosphonium dications **24** [Eqn. (1.7)]. It has also been established that the azidophosphylidenes **23** will self-condense to afford polymers and bis(cations) analogous to **24**.⁶⁴ In light of the results obtained with previous Staudinger type reactions (*vide supra*), one should approach these results with caution since it is possible that adduct type products are also formed in these cases.



1.2 Arsylidene Species

The body of knowledge about arsenium ions or *arsylidenes* is much smaller than that of the analogous phosphylidene systems and much less work has been published in the area. The lack of a readily accessible NMR probe has likely proven to be an effective deterrent to such studies in a number of cases. With the exception of the relatively common four coordinate arsonium centres there are few cationic arsenic species which have been isolated, and even fewer of these are arsylidenes.

The first examples of cationic compounds containing a dicoordinate arsenic centre were reported in 1967.⁶⁵ These arsa-monomethinecyanine dyes **25**⁶⁵ and **26**⁶⁶ are the arsenic analogues of the phosphamethine cyanine species¹⁴ discussed in Section 1.1. Compound **25** is not an arsylidene for the same reasons that the phosphamethines **3** and **4** are not phosphylidenes. Cation **26** however, does possess a Lewis resonance structure in which the positive charge is localized on the arsenic centre (Figure 1.4). The presence of another structure which localizes a negative charge on the same atom indicates that the

**25****26**

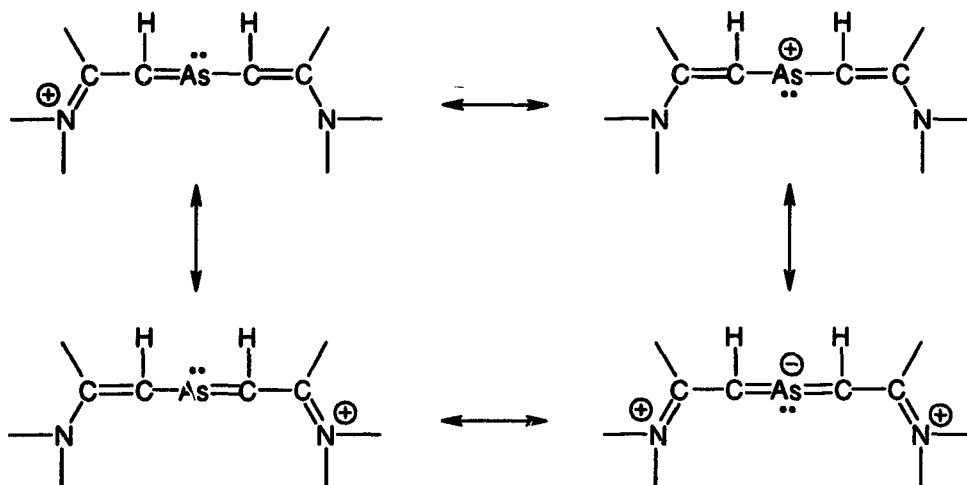
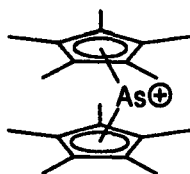


Figure 1.4: Lewis resonance structures for cation **26**.

majority of the positive charge in this molecule does not lie on the arsenic. The lack of positive charge accumulation at the two-coordinate arsenic centre implies that **26** is not an arsyliene.

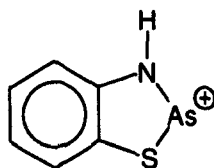
The number of isolated and structurally characterized arsyliene species is very small. To date there are only two distinct sets of compounds which might fall into this category. The first of these species was reported by Jutzi and coworkers in 1983.⁶⁷ This metallocene type cation **27** possesses a dynamic structure in solution, as evidenced by ¹H and ¹³C NMR studies. An X-ray structural analysis of the compound reveals that the ligands are not ideally *pentahapto*-bonded to the central atom in the cation, but rather exhibit a distortion in the sense of a *dihapto*- and *trihapto*-coordination. This results in the



27

pentamethylcyclopentadienyl rings being non-coplanar, with an angle of 36.5° between them. The stability of this species results from the multihapto bonding between the Cp^* ligands and the As^+ centre and the concomitant delocalization of the positive charge. In the case of a phosphylidene centre, isolation of a stable species is possible with the inclusion of a single Cp^* ligand,^{18(b)} however it is necessary to include two Me_5C_5 ligands in order to stabilize the more reactive arsylidene species. Due to the multihapto nature of the bonding between the Cp^* ligands and the As^+ centre, it is possible to present the argument that **27** is in fact pentacoordinated and does not possess a true dicoordinate arsenic centre.

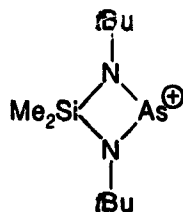
The first, and to date only, structurally characterized compound which unambiguously contains an arsylidene type centre was reported in 1989.^{68,69} 1,3,2-Benzothiazarsolium **28** tetrachloroaluminate relies upon two features for its stability. The



28

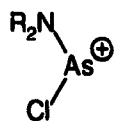
first of these, and the most important, is the Hückel nature of the 10π -electron ring system, which provides a substantial resonance stabilization energy. The second is the presence of the positive charge on the arsenic atom, which results in a decrease in the diffuse nature of the π -orbitals and enhances π -bonding in the hetero-atom ring. In addition, charge repulsion inhibits multimolecular rearrangement to an oligomeric σ -bonded alternative.⁷⁰ A second, and closely related species, 5-methyl-1,3,2-benzodithiarsolium tetrachloroaluminate, has also been isolated⁶⁹ but has not been crystallographically characterized.

The only other example of an arsylidene species in the literature was reported in 1988. 1,3-Diazo-2-sila-4-arsaetidines **29** were prepared with aluminate, gallate, and indate

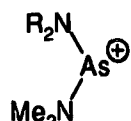
**29**

counterions.⁷¹ The phosphorus, arsenic, antimony, and bismuth derivatives of this molecule have all been synthesized and spectroscopically characterized, however, of the four, only the arsenic analogue could not be isolated as a crystalline solid. The stability of this system to the presence of the positive charge on the Group 15 atom results, in the case of the phosphorus derivative, from intramolecular back-bonding from the adjacent nitrogen atoms, as is common for phosphylidene systems (*vide supra*). In the case of the antimony and bismuth derivatives, the stability results through coordination of the chlorine atoms of the ECl_4^- anions to the unsaturated antimony or bismuth centre in an intermolecular manner.⁷¹ The lack of stability of the arsyliidene species was not addressed. These comments on the stability of the heavier analogues were also supported by Burford and coworkers with regard to the synthesis of systems similar to **28** but with different pnictogens in the place of arsenic.⁷²

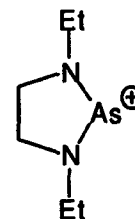
A number of other arsyliidene salts have been reported recently in the literature,



R = Me, Et, *i*Pr

30

R = Me, Et

31**32**

including **30**CF₃SO₃,⁷³ **31**CF₃SO₃,⁷³ and **32**CF₃SO₃,⁷⁴ however these species are reported as viscous brown or dark yellow oils and have been incompletely characterized.

1.2.1 Synthesis

The only technique which has been successfully used to produce arsyldiene centres is that of halide ion abstraction. Of the three types of arsyldienes synthesized, two utilize chloride ion abstraction and the third utilizes fluoride ion abstraction.

Compound **27** was synthesized by allowing the fluorinated precursor (Cp*)₂AsF to react with the fluoride abstracting reagent boron trifluoride.⁶⁷ Similarly, slow addition of 2-chlorobenzo-1,3,2-thiazarsole to a suspension of aluminum trichloride resulted in a microcrystalline precipitate of compound **28**.⁶⁹ The same technique was also successful in producing the related compound 5-methyl-1,3,2-benzodithiarsolium tetrachloroaluminate.⁶⁹ Chloride ion abstraction using AlCl₃, GaCl₃, or InCl₃ enabled the production of cation **29** from the precursor N,N'-bis(*tert*-butyl)-1,3-diaza-2-sila-4-chloroarsane,⁷¹ however recrystallization did not result in crystals of crystallographic quality.

1.2.2 Structural and Spectroscopic Properties

Due to the fact that the arsenic nucleus possesses very poor properties for study utilizing NMR techniques, a very large role in the identification of arsyldiene systems has fallen to X-ray crystallography. Table 1.3⁶⁸ contains the pertinent structural parameters for **28**, the only crystallographically characterized species which is unambiguously an arsyldiene system. In this cation, as was encountered for the various phosphylidenes, one observes traits which support comparisons between arsyldienes and carbenes.

The geometry of the ring of this system is consistent with an *sp*²-hybridized arsenic atom. This centre exhibits planar geometry with a S–As–N bond angle of 89.3°. This is

Table 1.3: Selected bond lengths and angles for the cationic unit of the arsyliene species **C₆H₅AlAsCl₄NS 28**.

Bond Lengths (Å)	Bond Angles (°)
As–S = 2.1536(15)	S–As–N = 89.27(14)
As–N = 1.776(4)	C–S–As = 96.95(18)
C–N = 1.382(7)	C–N–As = 121.6(3)
C–S = 1.736(5)	

considerably smaller than the ideal for an sp^2 -hybridized atom (120°), and is likely a result of the constrained nature of its small five-membered ring. The larger size of the arsenic atom in the ring also results in it necessarily being

at a greater distance from the other atoms, further reducing the S–As–N bond angle.⁷⁵

The As–S bond observed in the ring is the shortest yet reported (2.154 Å) with the exception of the arsenic(V) sulfides (2.075 Å).⁷⁶ A normal As–S single bond [such as for (PhS)₃As] is expected to be around 2.243 Å in length.⁷⁷ Additionally the As–N bond is the shortest yet reported (1.776 Å), considerably shorter than those observed in (CH₃)₂Si(*t*BuN)₂AsCl (1.832 Å),⁷⁸ Fe₂(CO)₆[μ-*t*BuAs(NSN)As*t*Bu] (1.843 Å),⁷⁹ and Cr(CO)₅(Ph₂AsNSO) (1.889 Å).⁸⁰ The shortness of these bonds, together with the shorter than usual C–S (1.736 Å) and C–N (1.382 Å) bonds (normal single bond lengths are 1.82 Å and 1.47 Å respectively)⁴¹ are indicative of a delocalized heteronaphthalenic framework for this molecule. This necessitates the presence of some degree of As–S $4p\pi$ - $3p\pi$ and As–N $4p\pi$ - $2p\pi$ bonding.⁶⁸ Since there is no indication of As–N π -localization, likewise absent in the case of the phosphorus analogue,⁸¹ the authors have concluded that, within the heteronaphthalenic environment, $4p\pi$ - $3p\pi$ bonding can coexist with, and is energetically comparable to, $4p\pi$ - $2p\pi$ bonding.⁶⁹

The very short As–S bond length exhibited by cation **28** (2.1536 Å), is dramatically shorter than that of the chloroarsine starting material **33** (2.1991 Å).⁶⁹ This bond length comparison is also related to the relative planarity of the bicyclic unit in each compound (**33** and **28**), and indicates that an enhancement of the heterocyclic π -structure takes place in the cation, a rationale which is also supported by the ¹H and ¹³C NMR spectroscopic results (*vide infra*).

X-ray structural analysis has determined that **28** is isostructural with other similar structurally characterized AlCl_4^- salts.^{19,82,83} While discrete cationic and anionic units are evident, there are significant cation-anion interactions (Table 1.4, Figure 1.5)⁶⁹ which possess distances shorter than the sums of the respective van der Waals radii (As, 2.0; S,

Table 1.4: Intermolecular contacts possessing distances within the sums of the van der Waals radii between the cationic and anionic units of the arsyliene species $\text{C}_6\text{H}_5\text{AlAsCl}_4\text{NS}$ **28**.

Contact Distances (Å)	
As—Cl(2)	= 3.399(2)
As—Cl(2)'	= 3.345(1)
As—Cl(4)	= 3.637(2)
As—Cl(4)'	= 3.390(2)
S—Cl(4)'	= 3.583(2)
NH—Cl(3)	= 2.389(2)
NH—Cl(2)'	= 2.913(2)

1.85; N, 1.5; Cl, 1.80 Å).⁸⁴ This is consistent with the contact array observed for the isostructural series of phosphylidene species.^{70,81} The contacts are similar in length and array to those reported for many main group cations which have been investigated theoretically, such as the series Ch_4^{2+} (Ch = S, Se, Te),⁸⁵ and are viewed as

nucleophilic charge transfer interactions.⁸⁶ It is believed that the magnitude of these interactions is small and their effect on the electronic structure of the cation is therefore negligible.⁶⁹ Identical structural features are observed within the cationic units of the tetrachloroaluminate salts of 1,3,2-benzodithiaphospholium⁷⁰ and 5-methyl-1,3,2-benzodithiaphospholium⁸⁷ despite their very different packing arrangements. This is corroborated by the regular tetrahedral geometry of the anion, which can be severely distorted in the presence of transition metal/arene cationic complexes⁸⁸ and small polarizing cations, such as Li^+ .⁸⁹

The number of nuclear magnetic resonance studies performed on the ^{75}As nucleus is very limited. The fact that this nucleus is of 100% abundance and possesses a receptivity 2.5% that of the proton would seem to indicate that it is an ideal nucleus for such studies. Unfortunately, however, the high spin quantum number ($I = 3/2$) and the associated large quadrupole moment leads to short relaxation times, broad NMR lines, and difficulties of

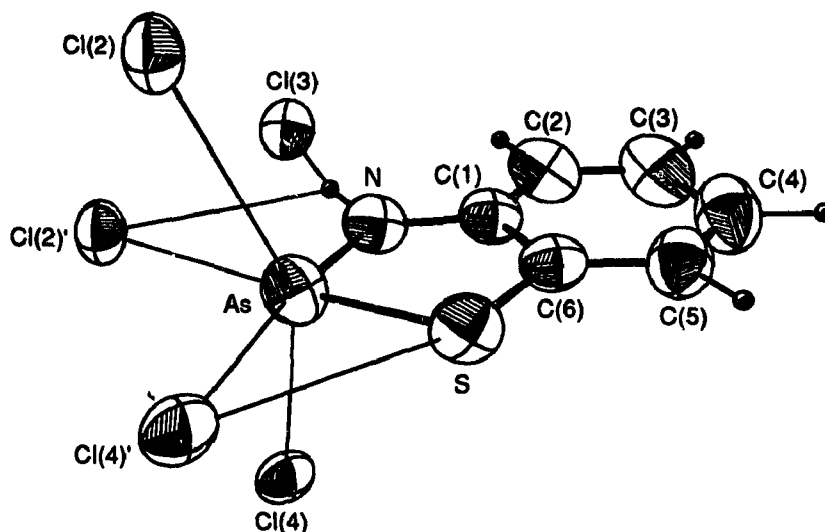


Figure 1.5: ORTEP view of the cation **28** showing the cation-anion interactions involving the chlorine atoms of the AlCl_4^- units.

observation with all but the most symmetrical molecules.⁹⁰ This effectively excludes compounds containing trivalent arsenic atoms from these types of NMR investigations. All of the compounds which have been studied to date by ^{75}As NMR contain an arsenic centre of the tetra- or hexa-coordinated pentavalent type.⁹¹

NMR studies of the arsyliene species utilizing NMR active nuclei within the molecule other than arsenic have been performed. Examination of the metallocene type arsenic compound **27** involved ^1H and ^{13}C NMR of the cation and ^{11}B and ^{19}F NMR of the accompanying BF_4^- anion.⁶⁴ These spectra indicated the existence of a dynamic structure in solution with all of the protons being equivalent and exhibiting a single peak in the ^1H NMR spectrum. The ^{13}C spectrum also revealed the equivalence on the NMR timescale of all of the methyl carbons ($\delta = 9.8$) and all of the ring carbons in the cyclopentadienyl rings ($\delta = 129.8$). The fluorine NMR likewise indicated the equivalence of all fluorine atoms in the anion.

^1H and ^{13}C NMR studies of compound **28** show a dramatic deshielding of the respective nuclei in the benzo unit of the cation with respect to the precursor chloroarsoles.⁶⁹ This is consistent with the values reported for the similar cationic species

benzo-1,3-dithiolium,⁹² benzo-1,3-thiazolium,⁹³ and benzo-1,3,2-dithiazolium.⁹⁴ This effect has been attributed to the effective delocalization of the positive charge throughout the bicyclic framework.⁶⁹ A similar effect is also observed for the chemical shift of the amine proton in **28**. ²⁷Al NMR has been used to characterize this species and exhibits a singlet at $\delta = 102$ ppm,⁶⁸ indicative of the AlCl_4^- anion.⁴⁶

The cyclic arsyliene species **29** has also been examined by ¹H NMR, however the resulting data is reported only as structural characterization information and is not interpreted.⁷¹ The chemical shifts for the Si-CH₃ and C-CH₃ protons were found to move slightly downfield as the associated anion increased in size from AlCl_4^- to InCl_4^- , possibly as a result of less effective anionic shielding as the size of the anion increases.

1.2.3 Chemical Properties

Very little is known about the chemistry of arsyliene centres. Of the species identified to date (*vide supra*) only three reports of their reactivity have been presented. Of these, two have examined the Lewis acidity of several arsylienes,^{74,95} and the third dealt with substitution reactions of the chlorodialkylaminoarsenium **30** species with silylated reagents.⁷³ The results of the Lewis acidity studies are interesting and seem to indicate that arsylienes do possess significant acidic character, albeit much less than that of the corresponding phosphylidenes, however the authors indicate that additional work is required.

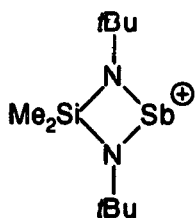
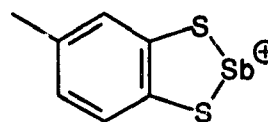
1.3 Stibylidene Species

Like arsenic, antimony is not readily amenable to NMR studies and as a result, work in the area of stibenium ions, or *stibylidenes*, has been limited. There are a number of reports in the literature dealing with anionic species containing antimony in low coordinate environments,⁹⁶ and several dealing with neutral species,⁹⁷ however there are

only two reports dealing with cationic dicoordinate antimony compounds.

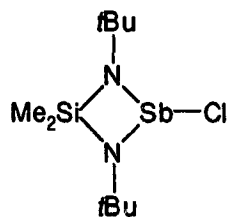
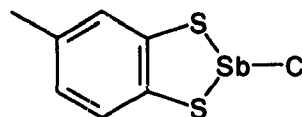
The first example of a cationic compound containing antimony in a dicoordinate environment was reported in 1988.⁷¹ This cyclic bis(amino)stibine **34** was made as the tetrachloroaluminate, tetrachlorogallate, and tetrachloroindate salts. In benzene solution, cryoscopic determination of molar masses indicates that dissociation of the species into discrete anions and cations does not occur, inferring the presence of either close ion pairs or chlorine bridged coordination complexes. The crystal structure of the AlCl_4^- salt has been determined and indicates that the cation is stabilized by donation of electron density from the lone pairs of the anions.

5-methyl-1,3,2-benzodithiastibolium **35** tetrachloroaluminate has been isolated and spectroscopically characterized,⁷² however crystallographic characterization was not possible. As is the case in the comparable arsyliene **28**,⁶⁸ the stibylidene centre is part of a Hückel 10π -electron system with the concomitant delocalization of the positive charge and resonance stabilization energy. Interestingly, this compound is only stable in the solid state and disproportionates in solution, which seems to indicate that stibylidene species rely more on intermolecular interactions and less on π -bonding to stabilize their low coordinate environments. This is consistent with the observations made for **34**, which adopts an anion-cation-anion-cation polymer structure in the solid state to satisfy the coordinative requirements of the antimony atom.

**34****35**

1.3.1 Synthesis

The only technique which has been found to be successful in forming cationic antimony species is that of halide ion abstraction. Cation **34** is formed through removal of a chloride ion from the chlorinated precursor **36** by reaction with AlCl_3 , GaCl_3 , or InCl_3 .⁷⁸ Reacting N,N'-bis(*tert*-butyl)-1,3-diaza-2-sila-4-chlorostibane **36** with AlCl_3 , GaCl_3 , or InCl_3 in solution or suspension produces from 60% (InCl_4^-) to 95% (GaCl_4^-) yields of **34**. Cation **35** is formed by reacting **37** with AlCl_3 , giving a 50% yield of **35** AlCl_4 .⁷²

**36****37**

1.3.2 Structural and Spectroscopic Properties

Neither of the two isotopes of antimony possesses favourable NMR qualities. As a result of this, characterization of stibylidene species is difficult and emphasis is placed on X-ray crystallography. Of the two reported stibylidene species, **34** AlCl_4 is the only one to have been crystallographically characterized.⁷¹ In the anion-cation-anion-cation arrangement which is observed (*vide supra*), the mean Sb---Cl distance is 3.05 Å, which is well within the sum of the van der Waals radii for antimony and chlorine (Sb, 2.2 Å; Cl, 1.80 Å),⁸⁴ but still much longer than a typical Sb—Cl bond as encountered in **36** [2.472(3) Å],⁷⁸ and so should be viewed as contacts and not bonds.

Although **35** has not been crystallographically characterized, it has been studied in the solid state to some degree by IR spectroscopy.⁷² The IR spectrum of **35** AlCl_4 exhibits bands for the AlCl_4^- anion (622 and 320 cm^{-1}) and none for Sb—Cl (*ca.* 275 cm^{-1}),

indicating that an ionic species does exist in the solid state. It is likely that close contacts between Sb and Cl occur, much as they do in the case of **34**, especially since close As---Cl contacts are observed in the closely analogous arsyliene species **28**.⁶⁸

Antimony possesses two NMR active nuclei, ^{121}Sb and ^{123}Sb , with natural abundances of 57% and 43%, respectively. Unfortunately however, these atoms are both quadrupolar, with spin quantum numbers of $I = 5/2$ and $I = 7/2$, and produce broad lines with little informational content. As a result, NMR studies of **34** and **35** have involved examination only of the protons present. ^{13}C NMR data was not reported for **34**, and could not be obtained for **35** due to its low solubility.

On going from the neutral species N,N'-bis(*tert*-butyl)-1,3-diaza-2-sila-4-chorostibane **36** to the cationic species **34**, changes in the ^1H NMR chemical shifts are minimal. Due to the remoteness of the protons from the Sb centre, the environments about the protons are little affected by ionization. An obvious change is apparent, however, in the number of signals present in the spectrum. The chorostibane **36** exhibits separate signals for the two inequivalent Si-CH₃ groups (toluene; $\delta = 0.24$ and 0.46 ppm; 1:1),⁷⁸ a result of the chlorine atom being nearer to one face of the ring than the other, whereas in the spectrum of **34**, only a single Si-CH₃ signal is observed (AlCl_4^- salt; benzene; $\delta = 0.13$ ppm),⁷¹ a good indication that the chlorine atom has been removed.

The ^1H NMR spectrum of a CD_2Cl_2 solution of **35** indicates that it is only a minor component of a mixture, with the dominant species in solution being its chlorostibine precursor **37**, formed as a result of disproportionation. The ^{27}Al NMR spectrum is likewise complex, containing signals for AlCl_4^- as well as two additional peaks.⁷²

1.3.3 Chemical Properties

There is no published data on the chemical properties of stibylidene systems. However it is expected that stibylidenes will possess a fair degree of Lewis acidity as a

result of the molecular positive charge and the electron deficiency at the antimony centre.

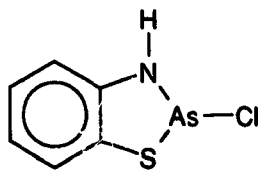
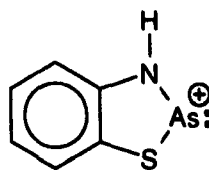
2.0 Arsylienes

While species containing dicoordinate arsenic centres (dicoordinate arsine) are known to exist, the arsenic centre is invariably contained within a Hückel framework or protected by sterically bulky ligands (see Section **1.2**). Species containing an unprotected arsyliene centre (cationic arsenium) are unknown and as a result, a whole area of chemistry is virtually uninvestigated. The vast majority of the work described in this report focuses on examinations of compounds containing “naked” arsyliene centres. Stability is imbued on these systems through the presence of π -electron donation from adjacent electron rich centres, such as nitrogen or sulfur atoms, into the formally vacant *p*-orbital of the arsenic centre. Additional stability is conferred through the presence of the cationic charge on the arsenic. Charge repulsion is partially responsible for preventing intermolecular interactions and the concomitant oligomerizations expected in these systems.

As mentioned previously, the halide ion abstraction reaction is a known quantity, having been widely used in inorganic synthesis and widely exploited in the development of nonmetal cations, and so this was to be the method of choice for the creation of the arsylienes. Such reactions generally proceed cleanly to give crystalline salts with a minimum number of byproducts.

2.1 Benzothiazarsolium Cations

Preliminary observations⁶⁸ had shown that the reaction of 2-chloro-1,3,2-benzothiazarsole **33** with aluminium trichloride, in dichloromethane, gives the ionic arsyliene species 1,3,2-benzothiazarsolium **28** tetrachloroaluminate. This was the first confirmed example of a compound containing an arsyliene centre (see Section **1.2**). It had been characterized by IR and ¹H, ¹³C, and ²⁷Al NMR spectroscopy in solution, as well as by elemental analysis. An X-ray crystal structural analysis revealed features indicative of a π -delocalized dicoordinate arsenic centre. Comparison with the structural

**33****28**

features of the chloroarsole **33** indicated the presence of N–As–S π -bonding, the first example of $4p\pi$ - $3p\pi$ bonding.

The synthesis of **28**AlCl₄ was difficult to reproduce. Compounds of this type are generally very onerous to handle as a result of their extreme sensitivity to moisture and air. Additionally, they are very difficult to study in solution since they lack a useful NMR probe. The creation of a reproducible, reliable, and routine technique for the synthesis of **28**AlCl₄ necessitated the development of techniques and procedures for the effective handling of such reactive compounds.⁹⁸ The most important factors ensuring reproducibility are the rigorous exclusion of air and water from the reaction mixture and the slow and controlled combination of the reagents.

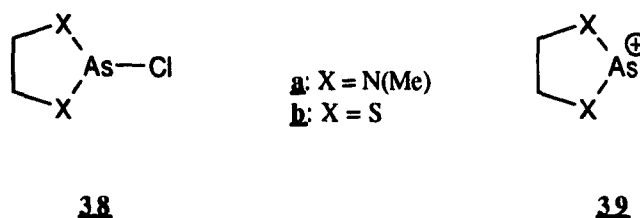
Low solution concentrations are employed and the addition of the chloroarsole **33** is carried out at a slow and controlled rate. The colour of the reaction mixture and the isolated yield vary considerably with the addition procedure. Performed properly, immediate reaction results in the production of a deep yellow solution which produces a bright yellow microcrystalline precipitate after stirring overnight. Initial characterization by IR spectroscopy indicates that the product is **28**AlCl₄ (75% yield, mp. 135-137°C). X-ray diffraction of a single crystal selected from the microcrystalline precipitate gives cell parameters identical to those reported in the preliminary study.⁶⁸

Good yields and easy isolation of salts are usually only possible if the concentration of the chloroarsole is kept low with respect to that of the acid during the course of the reaction. This prevents aromatic substitution of the benzo ring by the solvent, consistent

with the case of the phosphylidene analogue.⁷⁰ Halide ion abstracting reagents other than aluminium trichloride have been found to react with the chloroarsolidines, however the products have proven difficult to isolate and characterize.

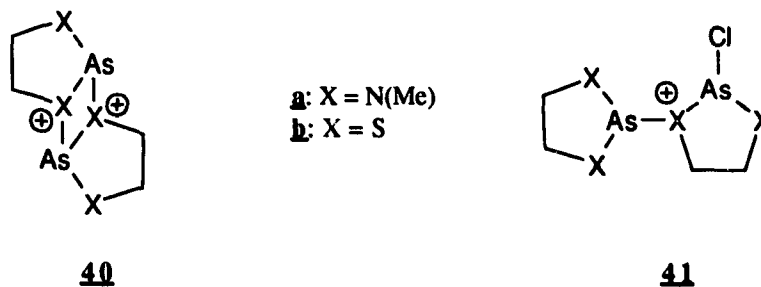
2.2 Arsolidinium Cations

The slow addition of dichloromethane solutions of 2-chloro-1,3-dimethyl-1,3-diaza-2-arsolidine **38a** or 2-chloro-1,3-dithia-2-arsolidine **38b** to equimolar suspensions of AlCl_3 or solutions of GaCl_3 in the same solvent, consistently proceed rapidly to give bright yellow solutions from which crystalline materials are isolable. If an excess of the chloride ion abstractor is maintained at all times the reaction is found to be quantitative. The ionic nature of these crystalline compounds is evident from the IR spectra, which



display very strong characteristic absorptions at 495 cm^{-1} or 370 cm^{-1} for the AlCl_4^- and GaCl_4^- anions, respectively.⁹⁹ Crystallographic examination reveals that the arsolidinium cations **39** exist as dimeric dicationic species **40** in the solid state.¹⁰⁰ If addition of **38** is discontinued while a 2:1 excess of the chloride ion abstractor exists, the resulting product is the heptachlorodigallate (Ga_2Cl_7^-) salt of **40**. These species may be viewed as formal arsyliene systems that exist without the benefit of steric or Hückel features, but are stabilized through the formation of weak dimers.

The slow, controlled addition of one half molar equivalent of GaCl_3 to a solution of chloroarsolidine **38** (resulting in a 2:1 excess of the chloroarsolidine), while at all times maintaining an excess of the chloroarsolidine, produces GaCl_4^- salts of the novel bicyclic



monocation **41**. This species may be viewed as a Lewis complex of the chloroarsolidine starting material **38**, which acts as the base, and the arsolidinium cation **39**, which acts as the acid. The structure of **41b** has been confirmed by X-ray crystallographic studies and IR spectroscopy (ν_3 stretch apparent for both GaCl_4^- , 375 cm^{-1} , and As-Cl , 310 cm^{-1}). The low temperature solution ^1H NMR spectrum of **41a** is consistent with the solid state structure of **41b** (*vide infra*).

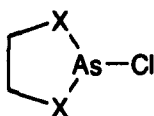
The monocations **41** were also obtained from the dicationic species **40** by reaction with one equivalent of triphenylphosphine oxide (Ph_3PO), which is a better base towards GaCl_3 than is Cl^- . The reaction can be conceived as proceeding through the release of Cl^- from GaCl_4^- which is then available for coordination to the cationic arsenic centre, giving **38**, which subsequently coordinates with a molecule of the arsyldiene species **39** to form **41**. Interestingly, the reverse reaction (**41** + $\text{GaCl}_3 \rightarrow \textbf{40}$) does not occur for the sulfur derivatives, implying thermodynamic stability for **41b** and GaCl_3 over **40b**, but does occur in the case of the nitrogen derivatives (see Section **2.2.3.1**).

A preliminary study attempting to form salts of **40b** through the reaction of **38b** with a number of other halide abstracting reagents was unsuccessful in producing isolable salts. No visible reaction occurred with ethyl acetate, NaBF_4 , AgPF_6 , AgCN , Ag_2CO_3 , or Ag_2SO_4 , as evidenced by no apparent change in the colour of the reaction suspension or solution. Some reaction did occur with NaBPh_4 , AgAsF_6 , silver tosylate, silver triflate, AgNO_3 , AgCNO , AgClO_4 , and LiTCNQ , apparent by the formation of a large quantity of colourless precipitate, but no colour change was observed. A small number of agents,

AgBF₄, CF₃COOAg, CF₃CF₂CF₂COOAg, and CH₃COOAg, resulted in the initial formation and immediate decomposition of the cationic species, apparent by the immediate formation of the distinctive bright yellow colour of **40b**, rapidly followed by fading of the solution to colourless. In no case was an isolable material recovered from any of the reaction mixtures, which instead resulted in the production of intractable oils or unidentifiable colourless precipitates.

2.2.1 Chloroarsolidines: Arsolidinium Precursors

The chloroarsolidine framework **38** represents an ideal candidate from which to form unprotected arsyldene systems through removal of a chloride ion. For this purpose, four previously known derivatives of **38** have been prepared, as well as two new derivatives. Chloroarsolidine **38a**, 2-chloro-1,3-dimethyl-1,3-diaza-2-arsolidine, is a highly air sensitive, thermally unstable colourless liquid which has been known since 1964.¹⁰¹ At room temperature it quickly decomposes over a period of a few hours, however it may be stored as a colourless crystalline solid for many months in the refrigerator. Chloroarsolidine **38b**, 2-chloro-1,3-dithia-2-arsolidine, is a slightly air sensitive white crystalline solid, first isolated in 1946.¹⁰² Compounds **38c-f** are all extremely air sensitive oily yellow liquids. 2-chloro-1,3-diisopropyl-1,3-diaza-2-arsolidine **38c**, and 2-chloro-1,3-dibenzyl-1,3-diaza-2-arsolidine **38d**, a very viscous liquid, are new derivatives. 2-chloro-1,3-dioxa-2-arsolidine **38e** and 2-chloro-1-methyl-1-aza-3-oxa-2-arsolidine **38f**, first reported in 1954¹⁰³ and 1976,¹⁰⁴ respectively, exhibit melting



38

- a:** X = N(Me)
- b:** X = S
- c:** X = N(*i*Pr)
- d:** X = N(Bz)
- e:** X = O
- f:** X = N(Me), O

points close to room temperature and exist as both a liquid and a solid unless warmed or cooled. It was not possible to isolate products from reactions of **38c-f** with GaCl₃. However, NMR studies were performed on the reaction mixtures and have produced some interesting results (*vide infra*).

The crystal structure of **38a** (m.p. $\approx 19^\circ\text{C}$) was determined at low temperature (-60°C). The compound is purified by distillation into sample tubes which are sealed under vacuum. These tubes are stored at 4°C in the refrigerator and, over the course of several months, large colourless crystals of **38a** sublime onto the walls of the tube (the largest crystal produced in this manner is approximately $1 \times 1 \times 2 \text{ cm!}$). These crystals are prepared for crystallography within a nitrogen filled glove bag and under a stream of cold nitrogen (boil-off).

The structure of **38a** is shown in Figure 2.1 and selected bond lengths and angles are given in Tables 2.1 and 2.2, respectively.¹⁰⁵ All C–N bonds are crystallographically identical in length and are consistent with the value expected for a single C–N bond ($1.47 \text{ \AA}$).⁴¹ The C–C bond is also typical of a single bond ($1.54 \text{ \AA}$).⁴¹ Published values for As–N bonds are limited, but are typically in the range of 1.82 to $1.88 \text{ \AA}$.¹⁰⁶ While one of the As–N bonds in the structure is within this range, the other [As(1) to N(1)] is

Table 2.1: Selected bond lengths (Å) for 38a .	
As(1)-Cl(1)	2.390(5)
As(1)-N(1)	1.77(1)
As(1)-N(2)	1.830(8)
N(2)-C(4)	1.47(1)
N(2)-C(2)	1.46(1)
N(1)-C(3)	1.44(1)
N(1)-C(1)	1.43(1)
C(1)-C(2)	1.50(2)
As(1)-N(2)'	2.84(1)

significantly shorter and indicates the presence of some π -bonding, which is also supported by the planarity exhibited at N(1) (sum of the angles is 359.3°). The pyramidal geometry of N(2) (sum of the angles is 339.4°) is a result of the presence of short intermolecular contacts which occur between the As atom of each molecule of **38a** and the N(2) atom of

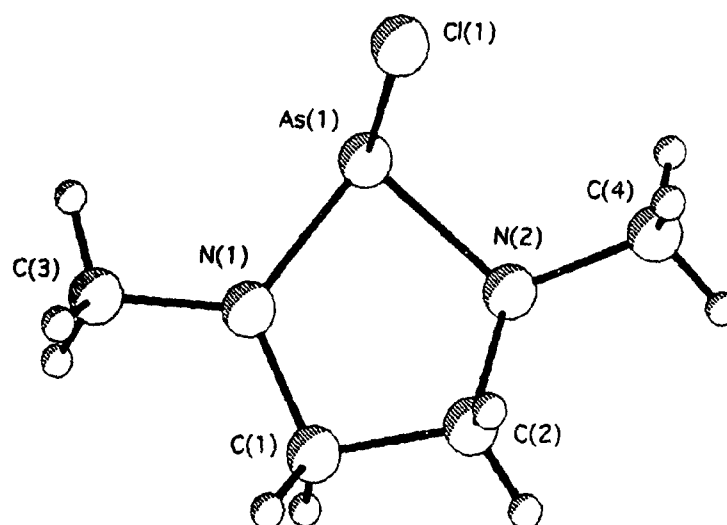


Figure 2.1: PLUTO view of the chloroarsolidine **38a**.

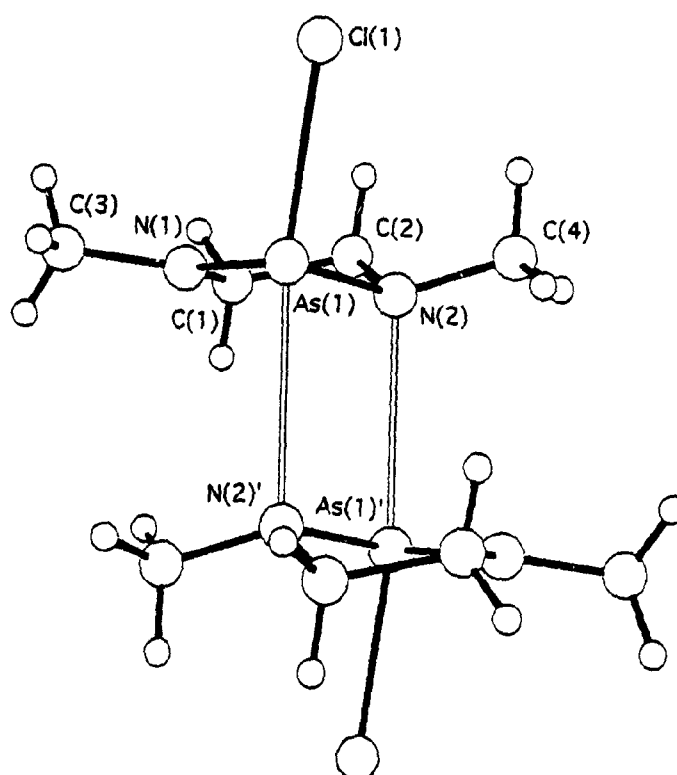


Figure 2.2: PLUTO view of a portion of the unit cell of the chloroarsolidine **38a** showing the incipient dimer contacts between two molecules.

Table 2.2: Selected bond angles (°) for **38a**.

Cl(1)-As(1)-N(1)	100.8(3)
Cl(1)-As(1)-N(2)	97.8(3)
N(1)-As(1)-N(2)	87.8(4)
As(1)-N(2)-C(2)	108.7(7)
As(1)-N(2)-C(4)	116.8(7)
C(2)-N(2)-C(4)	113.9(9)
As(1)-N(1)-C(1)	115.9(7)
As(1)-N(1)-C(3)	124.4(8)
C(1)-N(1)-C(3)	119(1)
N(1)-C(1)-C(2)	107.4(9)
N(2)-C(2)-C(1)	107.4(9)

another (Figure 2.2). These interactions are within the sum of the van der Waals radii for As and N (As, 2.0 Å; N, 1.5 Å),⁸⁴ and involve the donation of a lone pair of electrons from the nitrogen atom of one molecule into a vacant orbital of the arsenic atom of another molecule. This donation effectively results in N(2) becoming tetracoordinate, inhibiting π -bonding to arsenic. The As–Cl bond in **38a** is longer than a conventional As–Cl bond (2.161 Å),⁴¹ probably a result of the electron donation to the arsenic centre from both N(2) of a neighbouring molecule and the incipient intramolecular π -interaction occurring between N(1) and As. The long As–Cl bond implies the onset of arsyldene formation. Consistently, the observed ν_3 As–Cl stretching frequency in the IR spectrum of **38a** is observed at the lower wavenumber of 280 cm⁻¹ (*c.f.* arsenic trichloride, 370 cm⁻¹).

The crystal structure of **38b** (previously described)¹⁰⁷ provides a useful comparison with **38a**. Selected bond lengths and angles for **38b** are given in Tables 2.3 and 2.4, respectively, while the structure is shown in Figure 2.3.¹⁰⁸ Both C–S bond

Table 2.3: Selected bond lengths (Å) for **38b**.

As(1)-Cl(1)	2.2525(8)
As(1)-S(1)	2.1942(9)
As(1)-S(2)	2.225(1)
S(1)-C(1)	1.819(4)
S(2)-C(2)	1.822(4)
C(1)-C(2)	1.501(5)
As(1)-S(2)'	3.430(1)

lengths are typical of single bonds (1.82 Å),⁴¹ as is the C–C bond.⁴¹ The two As–S bonds are likewise within this range (2.20 to 2.27 Å).¹⁰⁹ As in the case of **38a**, two molecules of **38b** adopt a dimeric arrangement (Figure 2.4) with inter-ring contacts occurring between As

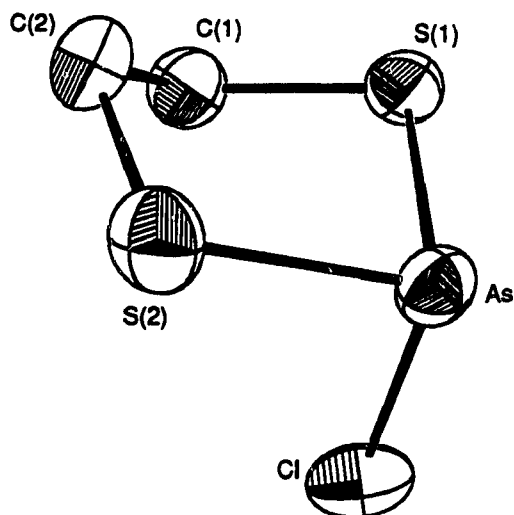


Figure 2.3: ORTEP view of the chloroarsolidine **38h** (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity.

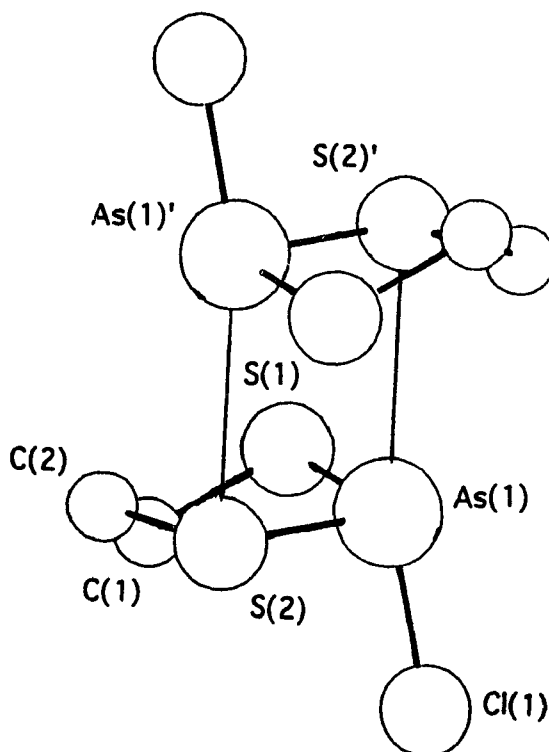


Figure 2.4: PLUTO view of a portion of the unit cell of the chloroarsolidine **38h** showing the incipient dimer contacts between two molecules. The hydrogen atoms have been omitted for clarity.

Table 2.4: Selected bond angles (°) for **38b**.

Cl(1)-As(1)-S(1)	99.51(3)
Cl(1)-As(1)-S(2)	98.21(3)
S(1)-As(1)-S(2)	93.50(3)
As(1)-S(2)-C(2)	100.8(1)
As(1)-S(1)-C(1)	97.1(1)
N(1)-C(1)-C(2)	110.2(3)
S(2)-C(2)-C(1)	111.2(2)

of one molecule and S(2) of the other [3.430(1) Å]. This distance lies within the sum of the van der Waals radii for As and S (As, 2.0 Å; S, 1.85 Å).⁸⁴ The shorter of the two intra-ring As–S bonds is to the S(1) sulfur atom which is not involved in the intermolecular

interactions. The difference in the As–S bond lengths occurs for reasons similar to those in the case of the As–N bonds in **38a**, but is less extreme since sulfur is less effective than nitrogen at π -bonding with arsenic, and so the disruption of this effect affects the distances to a lesser degree. The reduced incidence of π -bonding results in less electron density on the arsenic atom and hence less arsyldene character is present in the compound. This is apparent when examining the length of the As–Cl bond. Although approximately 4% longer than a typical As–Cl bond, it is approximately 6% shorter than the As–Cl bond observed in **38a**, a species exhibiting a significant amount of arsyldene character. The IR spectrum of **38b** exhibits a ν_3 As–Cl stretching frequency at 310 cm⁻¹, approximately midway between that of AsCl₃ and the much longer As–Cl bond of **38a**, consistent with the observed bond lengths.

In an effort to further characterize the chloroarsolidines, a dichloromethane solution of 2-chloro-1,3-dithia-2-arsolidine **38b** was examined by electrospray mass spectrometry (ESMS). Although technical difficulties were encountered (see Section 2.2.3.2), some interesting results were obtained. No evidence for the presence of **38b** itself is seen in the positive ion ESMS (Figure 2.5). The large peak at $m/z = 167$ is assigned to **39b**, which is formed as a result of loss of a chloride ion from **38b**. Because ESMS involves a very gentle ionization technique, minimal fragmentation is encountered, and it is likely that some quantity of **39b** is present in the dichloromethane solution of **38b**. The presence of **39b**

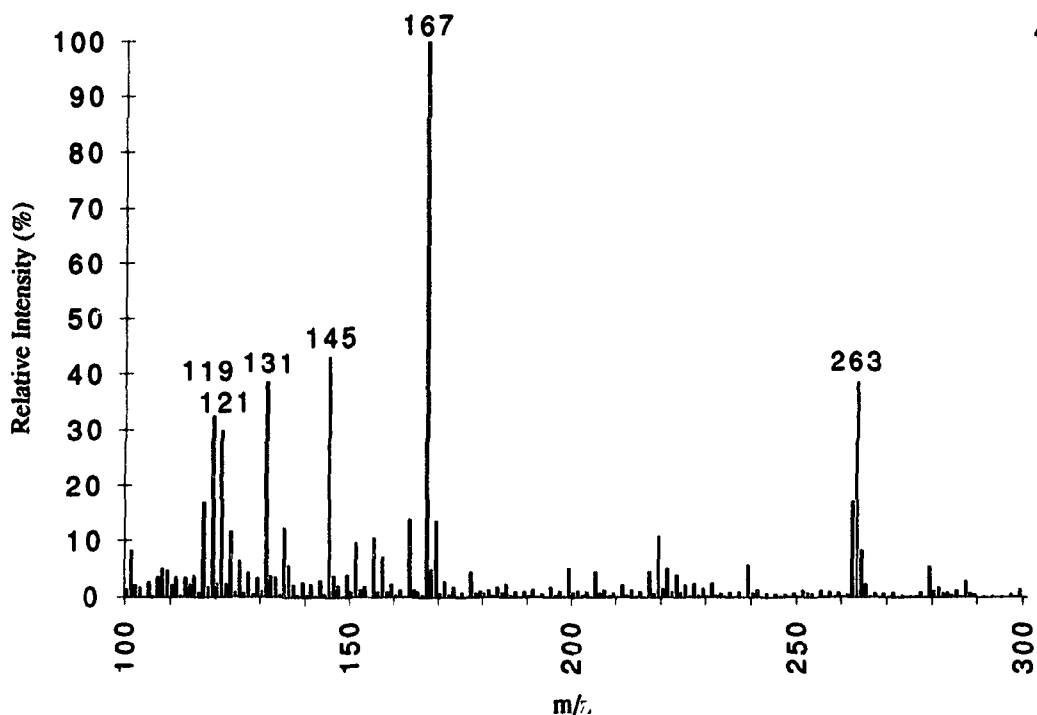


Figure 2.5: Positive ion electrospray mass spectrum of an approximately one millimolar solution of **38b** in CH₂Cl₂.

indicates that **38b** is autoionizing to some degree, a not completely unexpected phenomenon due to the presence of some arsyldiene character in the chloroarsolidine (*vide supra*). Unfortunately, it is impossible to tell to what extent this autoionization occurs since the technique used is not a quantitative one. The absence of **38b** in the spectrum is not surprising since the technique is sensitive only to the presence of charged species. Neutral compounds are typically acidified by the addition of a weak acid to the solution to promote protonation, however since it was desired to observe the species already present in a typical dichloromethane solution, acidification was not an option in this case. The remainder of the stronger peaks in the spectrum remain unassigned and may result from the presence of small quantities of oxidation products of **38b**, or from fragmentation of the dichloromethane solvent which is known to form clusters and fragments under these conditions (see Section 2.2.3.2). MS/MS scans of $m/z = 167$ (**39b**) reveal the fragmentation species $\text{As}=\text{S}^+$ and $\text{S}=\text{As}^+=\text{S}$, which are identifiable at $m/z = 107$ and 139

respectively.

Owing to the large anisotropic effect of the chlorine atom attached to the arsenic, the chloroarsolidines are expected to exhibit complex AA'BB' splitting patterns in the solution NMR. Such a pattern implies that interconversion of the compounds occurs at a rate which is large on the NMR timescale.¹¹⁰ This is consistent with the pyramidal stability of arsines. The spectrum of **38b** does exhibit the expected AA'BB' pattern, however the spectrum of **38a** exhibits only two singlets in a 3:2 integration ratio (Table 2.5).

Obviously **38a** is fluxional at room temperature to a sufficient degree to render all methylene protons equivalent and all methyl protons equivalent on the NMR timescale, despite the presence of the anisotropic chlorine atom. This fluxionality may involve either inversion of the arsenic centre, resulting in placement of the chlorine atom on the opposite side of the ring, an intermolecular exchange of chlorine atoms between two molecules of the chloroarsolidine,¹¹⁰ or both. If inversion is the pathway, it is likely to occur via edge-inversion processes.¹¹¹

The chloroarsolidines 2-chloro-1,3-diisopropyl-1,3-diaza-2-arsolidine **38c**, 2-

Table 2.5: Solution ¹H and ¹³C NMR chemical shifts (δ, ppm, CD₂Cl₂) of the chloroarsolidines **38** (referenced to TMS and calibrated to the internal solvent signal).

Compound	Assignment	¹ H (mult. integration)	¹³ C
38a	CH ₂	3.29 (s, 4H)	56.9
	CH ₃	2.82 (s, 6H)	36.0
38b	CH ₂	3.74 (m)	44.6
38c	CH ₂	3.30 (s, 4H)	51.5
	CH	3.30 (sept, 2H)	50.7
	CH ₃	1.24 (d, 12H)	23.2
38d	C ₆ H ₅	6.85 (m, 10H)	<i>i</i> -138.6, <i>m</i> -128.7, <i>o</i> -128.5, <i>p</i> -127.6
	CH ₂ (benzyl)	3.71 (s, 4H)	54.1
	CH ₂ (ring)	2.82 (s, 4H)	53.9
38e	CH ₂	4.20 (m), 4.04 (m)	68.0
38f	CH ₂ O	4.34 (t, 2H)	71.9
	CH ₂ N	3.24 (t, 2H)	55.6
	CH ₃	2.84 (s, 3H)	34.1

chloro-1,3-dibenzyl-1,3-diaza-2-arsolidine **38d**, 2-chloro-1,3-dioxa-2-arsolidine **38e**, and 2-chloro-1-methyl-1-aza-3-oxa-2-arsolidine **38f** were also examined by solution NMR and IR techniques. A summary of their NMR data is presented, along with that of compounds **38a** and **38b**, in Table 2.5.

In the ^1H NMR spectra of the chloroarsolidines **38**, the four nitrogen containing species, **38a**, **38c**, **38d**, and **38f**, are all fluxional, exhibiting equivalent ring protons on the NMR timescale. A simple A_4 spin system is observed for the four ring protons of **38a**, **38c**, and **38d**, and a simple A_2X_2 spin pattern for **38f**. Compound **38e** presents a more complex situation with the spin pattern exhibiting dependency on both the temperature and concentration. The splitting pattern changes from $AA'BB'$ at low concentration or low temperature to A_4 at high concentration or high temperature. This indicates the presence of both intermolecular exchange and rapid intramolecular conformational averaging depending on the solution conditions.¹¹²

The ν_3 As–Cl stretching frequencies for the chloroarsolidines range from 255 cm^{-1} to 310 cm^{-1} (*c.f.* AsCl_3 at 370 cm^{-1}). These values are listed in Table 2.6. With the increased π -electron density on the arsenic centre as a result of the intermolecular contacts and π -donation from the adjacent atoms, the onset of a degree of ionization occurs and the chlorine atom moves to a greater distance. The more effective the contacts and the π -

Table 2.6: As–Cl ν_3 stretching frequencies.	
Compound	Wavenumber (cm^{-1})
38a	280
38b	310
38c	260
38d	255
38e	255
38f	275
AsCl_3	370

bonding are at increasing the electron density at the As centre, the greater this distance. As this distance increases the As–Cl bond weakens and the resulting signal in the IR spectrum moves to a lower wavenumber. Compounds containing atoms which can effectively π -bond with arsenic, such as nitrogen and oxygen, consequently exhibit lower As–Cl stretching frequencies than do compounds containing

atoms less effective in π -bonding, such as sulfur. This trend is apparent in the IR stretching frequencies of the chloroarsolidines.

2.2.2 Solid State Structural Features

2.2.2.1 X-Ray Crystallography

Spectroscopic and analytical data for the derivatives of the arsolidinium cations **39** are of little value in assessing their physical structures. The X-ray crystal structures of salts **40a**(AlCl₄)₂,¹⁰⁷ **40a**(GaCl₄)₂, **40b**(GaCl₄)₂,¹⁰⁷ **40b**(Ga₂Cl₇)₂, and **41b**GaCl₄, as well as that of the two neutral chloroarsolidines **38a** and **38b**,¹⁰⁷ have been determined. Crystals suitable for X-ray crystallography were obtained for each of the materials as described in Section 6.4 or in the original reference,¹⁰⁷ and were selected and mounted in pyrex capillary tubes in a drybox. The cations of the tetrachloroaluminate and tetrachlorogallate salts of **40a** are isostructural, as are the cations of the tetrachlorogallate and heptachlorodigallate salts of **40b**, with the exception of slightly wider inter-ring bond angles at As and S(1) of **40b**(Ga₂Cl₇)₂ (only one of which is significantly different). Selected bond lengths and bond angles for the nitrogen containing compounds are compared in Tables 2.7 and 2.8, and the sulfur containing compounds are compared in

Tables 2.9 and 2.10.

Table 2.7: Selected bond lengths (Å) for compounds 38a , 40a (AlCl ₄) ₂ , and 40a (GaCl ₄) ₂ .			
	C ₄ H ₁₀ AsClN ₂	C ₈ H ₂₀ Al ₂ As ₂ Cl ₈ N ₄	C ₈ H ₂₀ As ₂ Cl ₈ Ga ₂ N ₄
As-N(2)	1.830(8)	1.955(7)	1.949(4)
As-N(1)	1.77(1)	1.763(8)	1.752(5)
As-N(2)'	2.84(1)	2.103(8)	2.103(4)
C(2)-N(2)	1.46(1)	1.507(14)	1.462(8)
C(1)-N(1)	1.43(1)	1.470(14)	1.487(8)
C(1)-C(2)	1.50(2)	1.542(16)	1.500(9)

The cationic units of **40** and **41** are all found to be composed of the arsolidinium species **39** in associated structural

Table 2.8: Selected bond angles ($^{\circ}$) for compounds **38a**, **40a**(AlCl₄)₂, and **40a**(GaCl₄)₂.

	<u>C₄H₁₀AsClN₂</u>	<u>C₈H₂₀Al₂As₂Cl₆N₄</u>	<u>C₈H₂₀As₂Cl₆Ga₂N₄</u>
As-N(2)-As'		99.3(3)	99.5(2)
N(1)-As-N(2)'		102.0(3)	100.9(2)
N(2)-As-N(2)'		80.7(3)	80.5(2)
N(1)-As-N(2)	87.8(4)	86.7(4)	87.2(2)
As-N(2)-C(2)	108.7(7)	109.1(6)	107.6(3)
As-N(1)-C(1)	115.9(7)	117.4(7)	116.2(4)
N(2)-C(2)-C(1)	107.4(9)	106.1(9)	107.2(5)
N(1)-C(1)-C(2)	107.4(9)	105.7(8)	106.0(5)

arrangements.

The novel

dicationic species

40 (**40a**: Figure

2.6, X = NMe;

40b: Figure 2.7,

X = S) are dimers

of **39** bound

together by a

four-membered As₂X₂ ring, the centre of which represents a crystallographic centre of symmetry. A step-like structure is observed with very long As–X bonds between the monomers, shorter As–X bonds for the adjacent sides of the As₂X₂ ring, and the shortest As–X bonds exocyclic to the As₂X₂ ring. The lack of structural data available for arsenic

Table 2.9: Selected bond lengths (Å) for compounds **40b**(GaCl₄)₂, **40b**(Ga₂Cl₇)₂, **41b**GaCl₄, and **38b**.

	<u>C₄H₈As₂Cl₈</u>	<u>C₄H₈As₂Cl₁₄</u>		<u>C₄H₈As₂Cl₅GaS₄</u>	<u>C₂H₄AsClS₂</u>
			As-Cl	2.226(2)	2.2525(8)
			As(1)-S(1)	2.318(2)	2.1942(9)
			As(1)-S(2)	2.195(3)	2.225(1)
As-S(1)	2.326(2)	2.35(1)	As(2)-S(3)	2.189(3)	
As-S(2)	2.181(1)	2.182(8)	As(2)-S(4)	2.175(3)	
As-S(1)'	2.422(6)	2.437(8)	As(2)-S(1)	2.523(2)	
C(1)-S(1)	1.826(6)	1.83(2)	C(3)-S(3)	1.77(1)	
C(2)-S(2)	1.826(7)	1.81(2)	C(4)-S(4)	1.80(1)	
C(1)-C(2)	1.493(9)	1.46(3)	C(3)-C(4)	1.36(2)	
			C(1)-S(1)	1.810(9)	1.819(4)
			C(2)-S(2)	1.833(9)	1.822(4)
			C(1)-C(2)	1.51(1)	1.501(5)

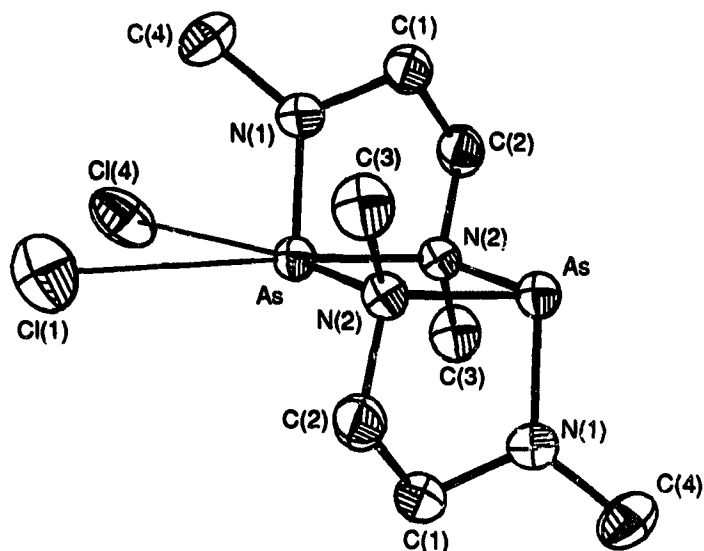


Figure 2.6: ORTEP view of the dication **40a** showing the cation-anion interactions involving the chlorine atoms of the GaCl_4^- units (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity.

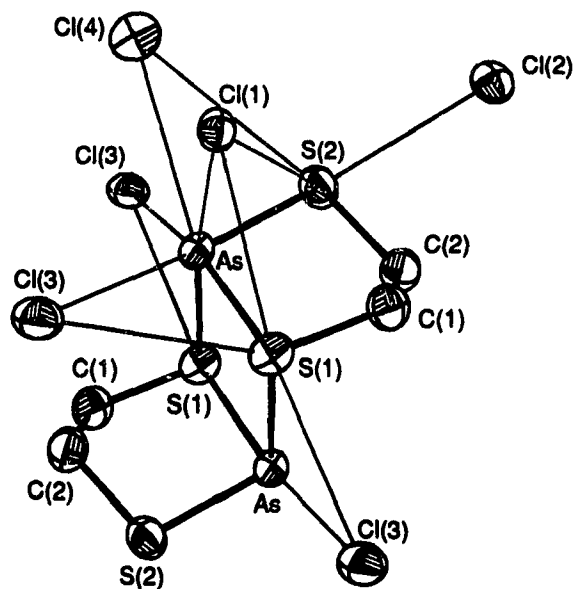


Figure 2.7: ORTEP view of the dication **40b** showing the cation-anion interactions involving the chlorine atoms of the GaCl_4^- units (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity.

Table 2.10: Selected bond angles (°) for compounds **40b**(GaCl₄)₂, **40b**(Ga₂Cl₇)₂, **41b**GaCl₄, and **38b**.

	$\frac{\text{C}_4\text{H}_8\text{As}_2\text{Cl}_8}{\text{Ga}_2\text{S}_4}$	$\frac{\text{C}_4\text{H}_8\text{As}_2\text{Cl}_{14}}{\text{Ga}_4\text{S}_4}$		$\frac{\text{C}_4\text{H}_8\text{As}_2\text{Cl}_5}{\text{GaS}_4}$	$\frac{\text{C}_2\text{H}_4\text{AsClS}_2}{\text{GaS}_4}$
			Cl-As(1)-S(1)	91.29(9)	99.51(3)
			Cl-As(1)-S(2)	101.1(2)	98.21(3)
			S(1)-As(1)-S(2)	91.08(9)	93.50(3)
As-S(1)-As'	93.13(6)	93.1(3)	As(1)-S(1)-C(1)	97.1(1)	106.4(3)
S(1)-As-S(1)'	86.87(6)	86.9(3)	As(1)-S(2)-C(2)	97.5(3)	100.8(1)
S(1)-As-S(2)	93.14(6)	92.3(3)	S(1)-C(1)-C(2)	110.7(6)	110.2(3)
As-S(1)-C(1)	98.7(2)	97.9(8)	S(2)-C(2)-C(1)	109.9(6)	111.2(2)
As-S(2)-C(2)	100.6(2)	100.7(8)	As(1)-S(2)-As(2)	101.16(8)	
S(1)-C(1)-C(2)	112.7(5)	114(2)	S(1)-As(2)-S(3)	99.04(9)	
S(2)-C(2)-C(1)	111.7(4)	112(2)	S(1)-As(2)-S(4)	102.1(2)	
S(1)-As-S(2)	96.96(6)	99.4(3)	S(3)-As(2)-S(4)	94.7(1)	
As'-S(1)-C(1)	98.7(2)	100.7(7)	As(2)-S(3)-C(3)	99.8(4)	
			As(2)-S(4)-C(4)	100.0(5)	
			(3)-C(3)-C(4)	119(2)	
			S(4)-C(4)-C(3)	117(1)	

systems makes it difficult to interpret the bond lengths reliably in terms of bond orders, nevertheless direct comparison with the chloroarsolidines **38**, published values for structures containing As–N bonds,¹⁰⁶ and the compilations of As–S bond lengths provided by Gillespie¹⁰⁹ and Dräger⁷⁶ point toward weak interactions between the five-member ring units **39** and typical or only slightly shortened As–X bonds within the arsolidinium rings themselves.

Cation **41b** (Figure 2.8) is a bicyclic system involving two five-membered rings bound together by a single inter-ring As–S connection. In contrast to **40**, in which the two rings adopt a step-like conformation, **41b** contains two rings which are almost eclipsed with respect to the inter-ring contact. The sulfur bound ring, ring 2, contains an exocyclic As–Cl bond and is structurally similar to, but not identical with, the free chloroarsolidine

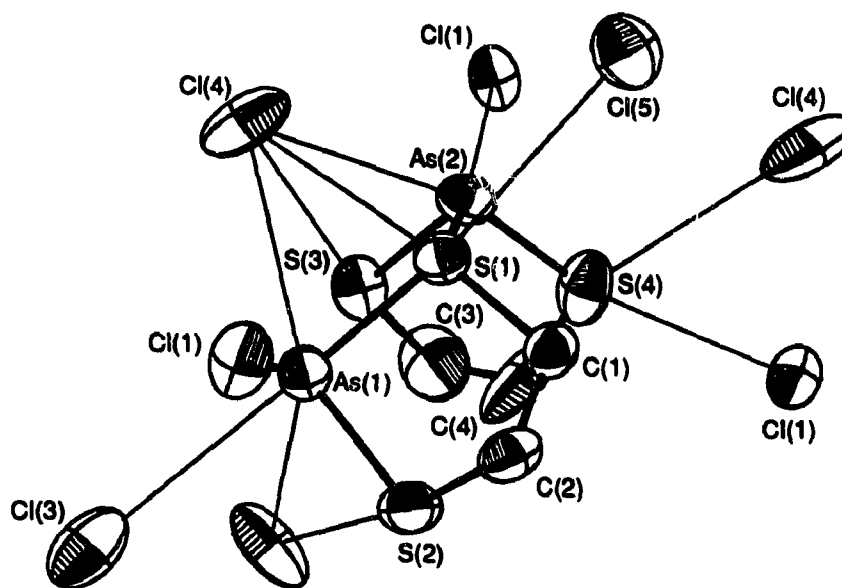


Figure 2.8: ORTEP view of the monocation **41b** looking down through the centres of both rings and showing the cation-anion interactions involving the chlorine atoms of the GaCl_4^- units (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity.

38b. The anomalous bond lengths and angles about C(3) and C(4) are a result of a slight disorder of these atoms, as indicated by the large thermal parameters in Figure 2.8

Interestingly, the As–S bond between the two rings of **41b** is substantially longer than the dimer interactions observed in **40b**, and is in fact the longest As–S covalent bond in the literature. Aside from this anomaly, the As–S bond lengths are comparable within the two structures. The three As–S bonds adjacent to tricoordinate arsenic centres [As(1)–S(2), As(2)–S(2), and As(2)–S(4)] are crystallographically identical in length and are slightly shorter than the average of the bonds in the neutral chloroarsolidine **38b** (2.210 Å). The As–S bond adjacent to the tricoordinate sulfur centre [As(1)–S(1)] is significantly longer than those encountered in **38b**.

The five-membered rings are distorted from planarity, as expected for cyclopentane derivatives, and the series of thia-derivatives illustrates some interesting features. All rings may be viewed as a [S(2)–As–S(1)–C(1)] “planar” unit with C(2) displaced from the plane

[**40b**(GaCl₄)₂, 0.661 Å; **40b**(Ga₂Cl₇)₂, 0.332 Å; **41b**GaCl₄ ring 1, 0.366 Å; ring 2, 0.787 Å; **38b**, 0.511 Å]. The maximum deviation from the best planes varies, ranging from 0.047 Å to 0.248 Å [**40b**(GaCl₄)₂, S(1) 0.047 Å; **40b**(Ga₂Cl₇)₂, C(1) 0.247 Å; **41b**GaCl₄ ring 1, S(3) 0.060 Å; ring 2, S(1) 0.049 Å; **38b**, S(1) 0.248 Å]. In all of the derivatives of **3** the out of plane carbon atom exhibits *endo*-displacement, that is, it is displaced towards the side of the dimer interaction. The greatest distortions from planarity of the four atom unit are observed for the neutral system **38b**, although the displacement of the C(4) atom of ring 2 in **41b** from the best plane is more pronounced. Ring 1 of **41b**, which is the analogue of **38b**, is the closest to planarity for all five atoms. The differences in planarity are not manifest in the endocyclic bond angles observed at the arsenic and sulfur centres.

Cation-anion interactions with interatomic distances less than the sum of the van der Waals radii of the two atoms involved occur between the chlorine atoms of the anions and the arsenic or sulfur centres of the cations in the salt structures **40b** and **41b**. Contacts to nitrogen are not observed in the salts of **40a**. In general, these interactions are similar [shortest contacts: **40a**(GaCl₄)₂, As---Cl(1), 3.296 Å; **40b**(GaCl₄)₂, As---Cl(1), 3.180 Å, S(2)---Cl(2), 3.404 Å; **40b**(Ga₂Cl₇)₂, As---Cl(6), 3.290 Å, S(1)---Cl(6), 3.555 Å; **41b**GaCl₄, As(2)---Cl(1), 3.325 Å, S(1)---Cl(4), 3.294 Å] to the intermolecular interactions evident in the structure of the neutral chloroarsolidine **38b** [shortest contacts: As---Cl', 3.650 Å, S(1)---Cl', 3.442 Å]. Such contacts also compare with those encountered in the benzothiazarsolium species **28** [shortest contacts: As---Cl(2)', 3.345 Å, S---Cl(4)', 3.583 Å]. Interactions between cations and anions are very common in non-metal salts,¹¹³ and are usually viewed as donations from the anion to the cation.⁶⁹ These interactions furnish additional stability to the arsyldene species by protecting the arsenic centres in solution from attack by nucleophiles such as solvent. This feature has been described as *anionic protection*.¹¹⁴ The interactions have little effect on the gross structural

features of either the anion or the cation, and at most effect minor distortion to the tetrahedral geometry of the GaCl_4^- or AlCl_4^- anion.¹¹⁵ Similar conclusions may be drawn from this work if one recognizes that despite the presence of more numerous and substantially shorter cation-anion contacts in cation **40b** than in **40a**, the structural arrangements of the cations are essentially identical.

2.2.2.2 Solid State ^{13}C NMR Spectroscopy

Solid state cross polarization magic angle spinning (CP MAS) ^{13}C NMR investigations of **38b** and the tetrachlorogallate salts of **40a**, **40b**, and **41b** are consistent with the solid state structures as determined by X-ray crystallography in terms of number

Table 2.11: Solid state CP MAS ^{13}C NMR chemical shifts (ppm) for compounds 38b , 40a (GaCl ₄) ₂ , 40b (GaCl ₄) ₂ , and 41b GaCl ₄ .		
Compound	Assignment	δ
38b	CH ₂	47.2
40a (GaCl ₄) ₂	CH ₂ N ⁺	62.9
	CH ₂ N	58.9
	2 x CH ₃	42.1
40b (GaCl ₄) ₂	CH ₂ S ⁺	54.0
	CH ₂ S	49.3
41b GaCl ₄	2 x CH ₂ (arsylidene ring)	50.9
	CH ₂ S ⁺	48.2
	CH ₂ S	45.1

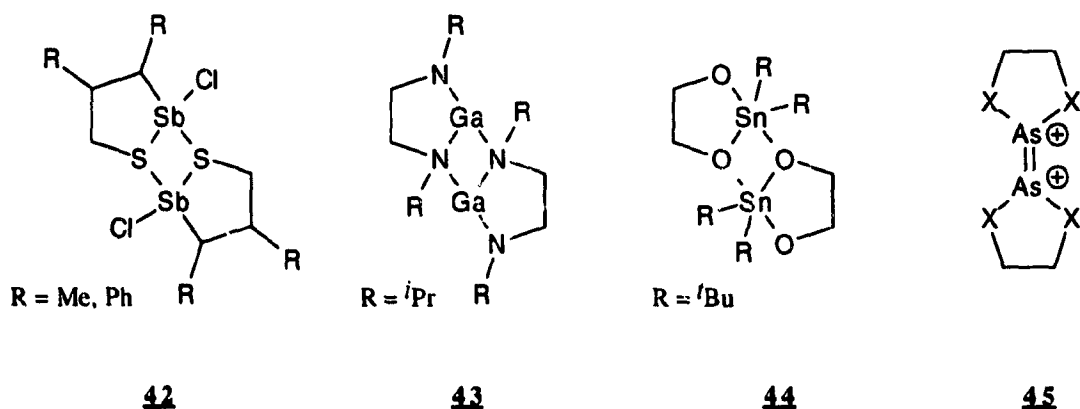
and approximate integration of the observed peaks (Table 2.11). Compound **38b** exhibits a single peak in the CP MAS ^{13}C spectrum, indicating the equivalent carbon atoms. Dications **40** exhibit two peaks (three peaks in the case of **40a**, the two methyl peaks overlapping), indicating the presence of two distinct types of methylene (and

methyl in **40a**) carbon atoms. Monocation **41b** exhibits three peaks, consistent with the observed structure assuming rapid rotation about the As(2)–S(1) bond in the solid state. Although the integration of peak areas in solid state CP MAS ^{13}C NMR is not a strict indicator of relative abundance of the number of carbon atoms giving the signal, the observed peak integration ratios are reasonable for the observed structures. The sulfur derivatives exhibit a slightly broader range of chemical shifts in the solid state (6.8 ppm) than in dichloromethane solution (1.2 ppm) (*vide infra*).

2.2.2.3 Simple Bonding Model

The nature of the dimer structure **40** is reminiscent of some novel neutral main group systems such as **42**,¹¹⁶ **43**,¹¹⁷ and **44**.¹¹⁸ However, in the context of the carbene analogy, the dimeric arsolidinium dication represents an alternative to the alkenic dimer arrangement **45**, which would require the formation of an energetically unfavourable $4p\pi$ - $4p\pi$ As=As double bond and the close proximity of two positive charges. Dimerization through formation of a double bond is to be expected if the HOMO of these systems is the orbital containing the σ -lone pair, as in the carbene case,¹¹⁹ however recent photoelectron spectroscopy work on the analogous silylene and germylene compounds indicates that the HOMO in these cases is principally of π -character,¹¹⁹ consistent with the observed dimers. The weakness of the inter-ring bonds in **40** is not clearly understood but may be an indication of a fine balance between a coordinatively saturated σ -bonded dimer system (Figure 2.9, top left structure) and two carbenic centres involving As-X π -interactions (Figure 2.9, bottom five structures). It is possible to interpret the observed structural features of the dimers using a simple Lewis resonance model, as illustrated in Figure 2.9 (lone pairs omitted for clarity). The calculated bond orders [As-S(1), 0.93; As-S(2), 1.28; As-S(1)', 0.50, labelling according to Figure 2.7] are consistent with the observed relative bond lengths in the solid state [2.326(2) Å, 2.181(1) Å, and 2.422(6) Å, respectively].

The structural features of the chloroarsolidine-arsolidinium complex **41** can be



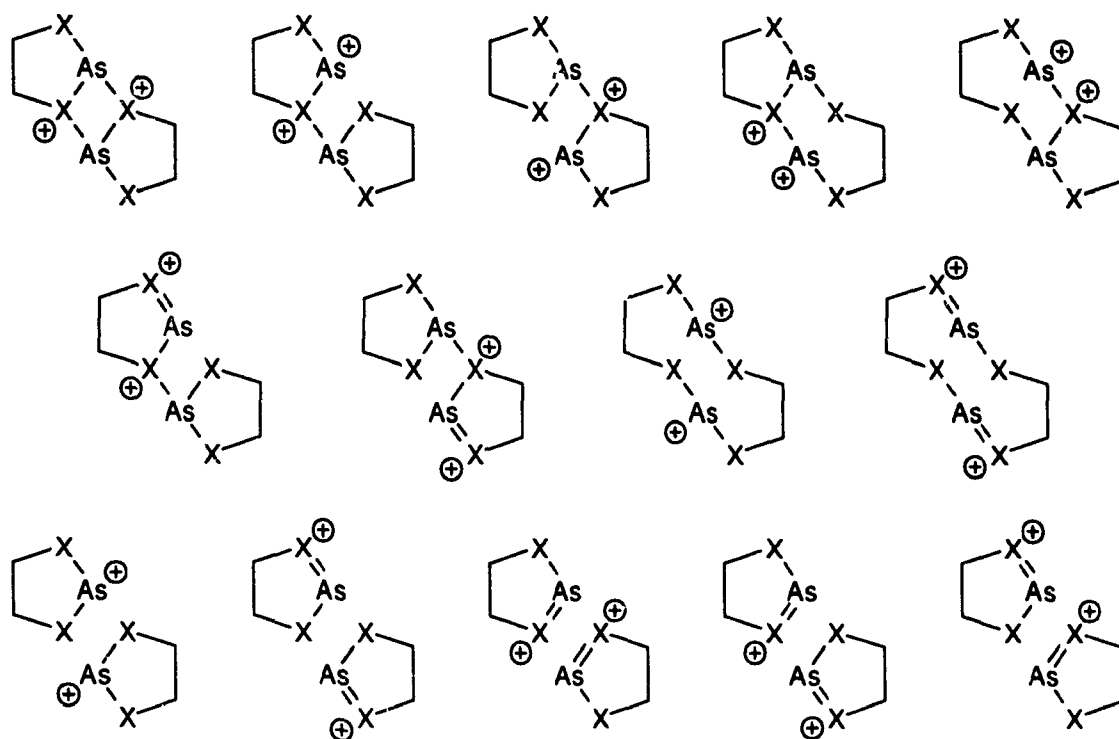


Figure 2.9: Principal resonance structures for the dication **40**. Lone pairs omitted for clarity.

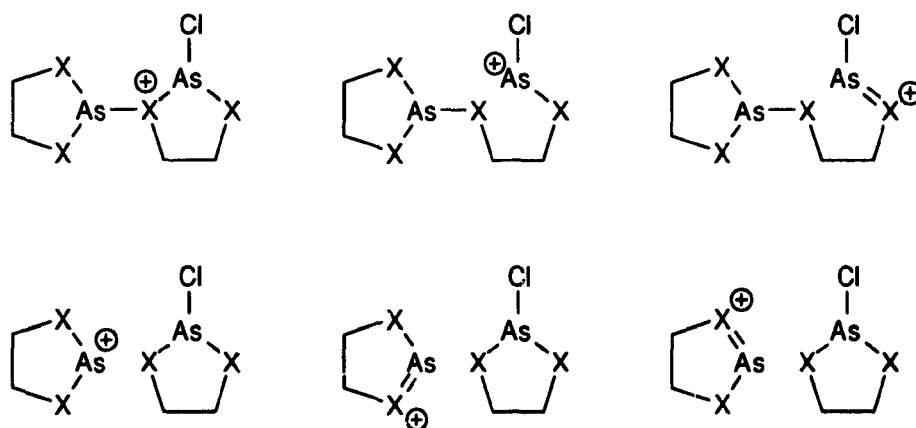


Figure 2.10: Principal resonance structures for the monocation **41**. Lone pairs omitted for clarity.

interpreted in a similar fashion to those of **40**. Using the Lewis structures shown in Figure 2.10 (lone pairs omitted for clarity), the calculated bond orders are As(1)–S(1), 0.67; As(2)–S(1), 0.50; As(1)–S(2), As(2)–S(3), and As(2)–S(4), 1.17. The observed bond lengths are 2.318(2) Å, 2.523(2) Å, 2.195(3) Å, 2.189(3) Å, and 2.175(3) Å, respectively. It is interesting to note that the inter-ring bonds in the complexes **41** are in contrast to the observed features of the analogous phosphine-phosphenium complexes which exhibit a P–P bond.^{12,17(b),22,27}

2.2.3 Solution Properties

2.2.3.1 Solution ¹H and ¹³C NMR Spectroscopy

The room temperature solution ¹H and ¹³C NMR spectra for salts of **40** and **41** reveal distinct downfield chemical shifts, relative to the corresponding neutral

Table 2.12. Solution ¹H and ¹³C NMR chemical shifts (δ, ppm, CD₂Cl₂) of the chloroarsolidines **38** and arylidenes **40** and **41** (referenced to TMS and calibrated to the internal solvent signal).

Compound	Assignment	¹ H	¹³ C
38a	CH ₂	3.29	56.9
	CH ₃	2.82	36.0
40a (GaCl ₄) ₂	CH ₂	3.83	57.8
	CH ₃	3.20	37.6
41a GaCl ₄	CH ₂	3.58	57.6
	CH ₃	3.03	37.1
38b	CH ₂	3.74	44.6
40b (GaCl ₄) ₂	CH ₂	4.06	45.8
41b GaCl ₄	CH ₂	3.90	45.0

chloroarsolidine **38**. A single line is observed for **40b** and **41b** with the ¹H chemical shifts ranging from 0.16 to 0.32 ppm downfield, and two lines, in a 3:2 integration ratio, for **40a** and **41a** which are 0.21 to 0.54 ppm downfield (Table 2.12). Similar shifts are observed in the ¹³C NMR spectra, ranging from 0.4 to 1.2 ppm for **40b** and **41b**, and 0.7 to 1.6 ppm for **40a**

and **41a**. In all cases the chemical shifts of the monocationic species **41** occur between those of the dications **40** and the chloroarsolidines **38**.

Peak broadening occurs below room temperature in the ¹H NMR spectra and, in the

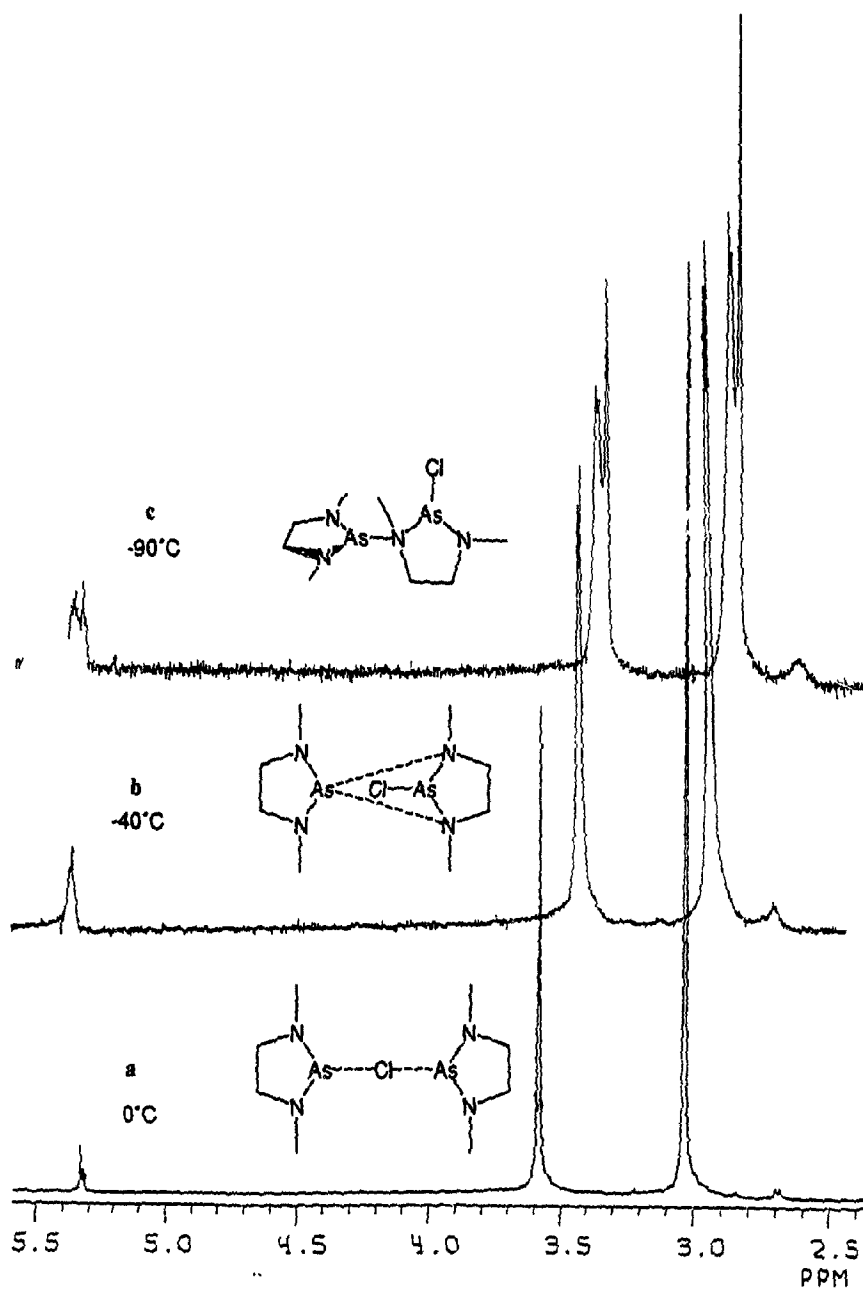


Figure 2.11: Variable temperature ^1H NMR spectra at 360 MHz of monocation **41a** at a concentration of approximately 60 millimolar in CD_2Cl_2 .

case of **41a**, two coalescence points are observed. For **41a** two separate structural manipulations are required to render all methylene substituents equivalent and all methyl substituents equivalent at room temperature. These represent transfer of the chlorine atom from one ring to another and the shift of the inter-ring connection to the neighbouring atoms on each ring (Figure 2.11a). Consistently, each of the two signals is split into two below -30°C , implying the retardation of the chloride ion exchange and thereby differentiating between the two rings (Figure 2.11b). At -85°C each of the lower field signals is again split into two (Figure 2.11c), implying a firm As–N association between the two rings consistent with that observed in the solid state structure of **41b**.¹²⁰

The coalescence temperatures are concentration dependent, however the solvent peaks from residual CH_2Cl_2 and CHDCl_2 in the CD_2Cl_2 exhibit broadening and coalescence at the same temperatures, implying that at least part of the concentration dependence is the result of interaction between the cation and the solvent. In the case of **41a**, the coalescence temperature increases as the concentration of the solution increases. Sixty millimolar solutions in CD_2Cl_2 exhibit the first coalescence point at -35°C , whereas at a concentration of approximately 30 millimolar, the coalescence occurs at -65°C . The onset of coalescence is apparent at -90°C for a saturated solution of **40a**, which is also very near the freezing point of the solvent (-96°C).¹²¹ Unfortunately these arsyldene species have low solubility in other solvents. Similar studies for the thia-derivatives **40b** and **41b** are precluded by their low solubility, even in dichloromethane.

The equivalence of the proton and carbon signals in the NMR spectra of **40** and **41** contradict the solid state structure and indicate fluxionality, the nature of which is unclear (whether inter- or intra-molecular) and is difficult to ascertain due to solvent interactions. In the usual case (in the absence of solvent interactions) independence of the coalescence temperature with solution concentration (concentration $\downarrow$, coalescence temperature unchanged) would point towards an intra-molecular fluxionality, while an increase in

coalescence temperature with decreasing solution concentration (concentration ↓, coalescence temperature ↑) would be suggestive of an inter-molecular mechanism. In fact, a decrease in the coalescence temperature with a decrease in solution concentration (concentration ↓, coalescence temperature ↓) is observed, suggestive of the presence of solvent interactions.¹²²

While assignment of the ^1H signals (CH_2 : 3.5 - 4.0 ppm; CH_3 : 2.8 - 3.2 ppm) is straightforward, reasons for equivalence at room temperature and non-equivalence at low temperatures are not so obvious. Equivalence of the protons in the dication **40** may result from a single step fluxional mechanism, such as a ring flip, or a dissociative process which produces free arsyldene species in solution (Figure 2.12). For **41** the signal equivalence implies transfer of the chlorine atom from one arsenic centre to the other and a subsequent shift of the inter-ring connection to the neighbouring atoms on each ring, as illustrated

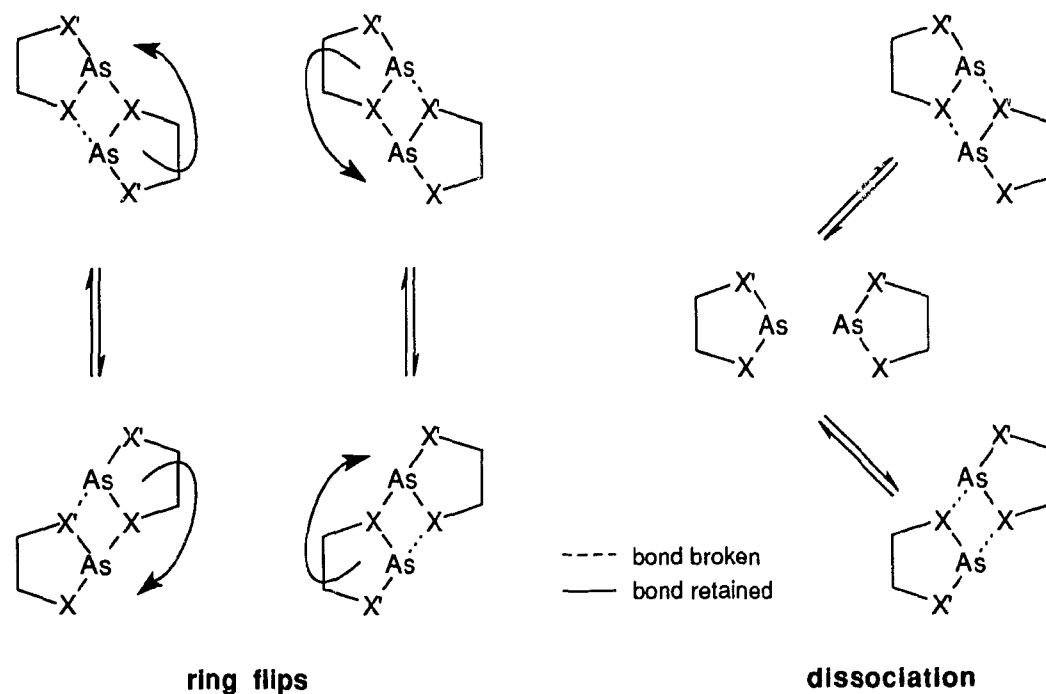


Figure 2.12: Fluxional processes resulting in X and X' equivalence for the dication **40**.

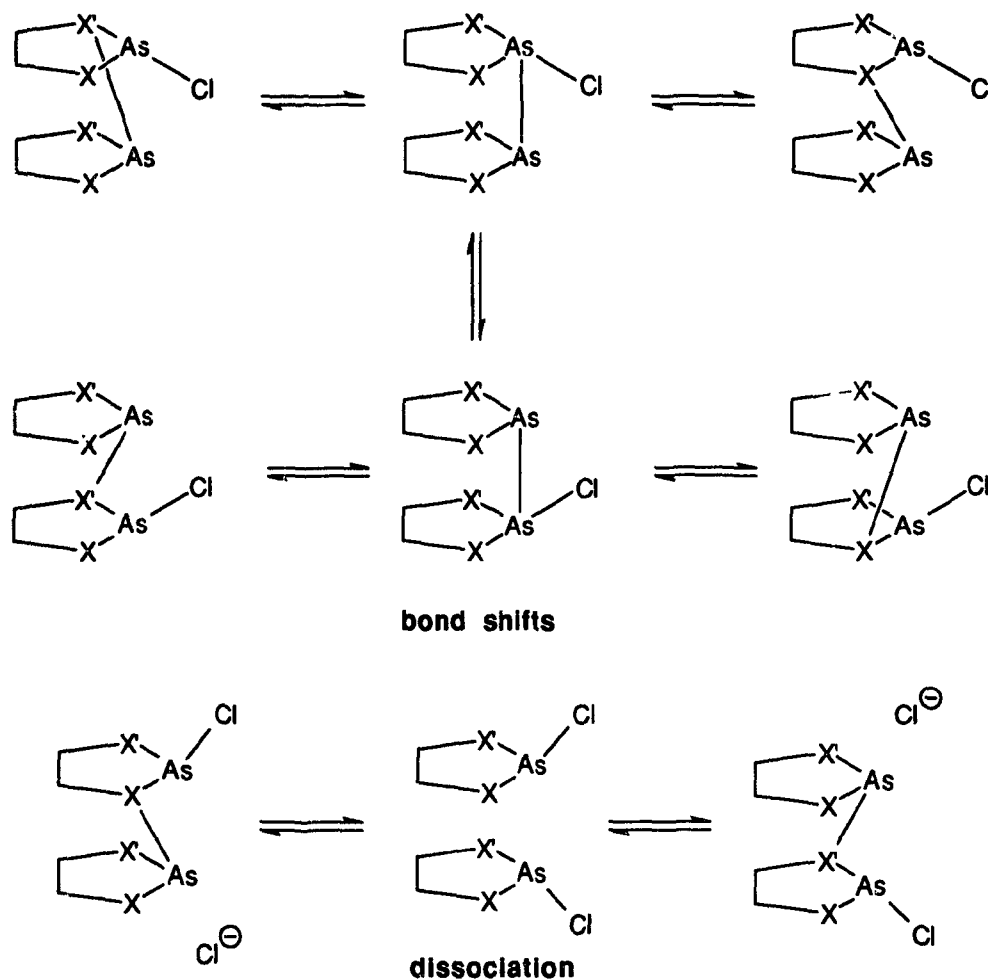


Figure 2.13: Fluctional processes resulting in X and X' equivalence for the monocations **41**.

topologically in Figure 2.11. An alternate mechanism involves a dissociative process resulting from the *exo*-attack of a free chloride ion (from GaCl_4^- ; *vide infra*) on the As of Ring 1 (arsylidene ring), resulting in the breakage of the weak inter-ring bond between As and the X atom in Ring 2 (chloroarsolidine ring). A new inter-ring bond then forms between As and X, causing cleavage of the As–Cl bond (Figure 2.13). The complexities inherent in the non-dissociative manipulations, together with the weakness of the inter-ring interactions as observed in the solid state, suggest that the dissociative processes may be most likely. Moreover, tetrachloroaluminate and tetrachlorogallate salts have been

suspected of readily exchanging chloride ions with non-metal cations and chlorinated solvents.⁷⁰ The two coalescence points observed in the VT spectra of **41a** may be viewed as a retardation of the chloride exchange, distinguishing Ring 1 from Ring 2, and as firm As–X association between the cation (Ring 1) and the chloroarsolidine (Ring 2), respectively.

Further evidence of the fluxional nature or exchange processes of compounds **40** is observed in the ¹H NMR of dichloromethane solutions of **40a** with **38a** at 10:1 or 1:10 stoichiometric ratios. The observed chemical shifts are very similar to those of the excess material, shifted only slightly in the direction of the minor component. Separate signals for either component of the mixture are not observed.

Relative downfield shifts (0.58 to 1.22 ppm for **38d**, 0.29 ppm for **38e**) in the ¹H NMR spectra of reaction mixtures containing chloroarsolidines **38d** and **38e** with equimolar quantities of GaCl₃ are also consistent with the formation of cationic arsylienes, presumably **40d** and **40e**, respectively (Table 2.13). In contrast, a multitude of signals are

Table 2.13: Solution ¹H NMR chemical shifts (δ, ppm, CD₂Cl₂) of reaction mixtures of chloroarsolidines **38d,e** and equimolar quantities of GaCl₃ (referenced to TMS and calibrated to the internal solvent signal).

Compound	Assignment	¹ H (mult., integration)
38d	C ₆ H ₅	6.85 (m, 10H)
	CH ₂ (benzyl)	3.71 (s, 4H)
	CH ₂ (ring)	2.82 (s, 4H)
40d	C ₆ H ₅	7.43 (m, 10H)
	CH ₂ (benzyl)	4.55 (s, 4H)
	CH ₂ (ring)	4.04 (s, 4H)
38e	CH ₂	4.20 (m), 4.04 (m)
40e	CH ₂	4.49 (m), 4.33 (m)

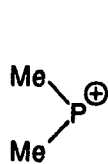
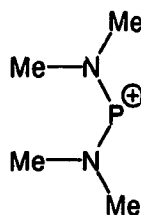
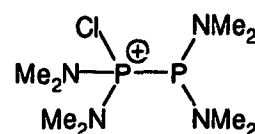
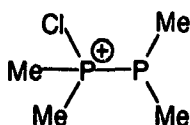
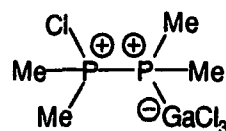
observed in the reaction of **38f** with GaCl₃. In the case of the reaction of **38e** a large quantity of a solid product is isolable (93% mass of starting materials), presumably **40e**(GaCl₄)₂, however the IR spectrum showed no evidence for the presence of the GaCl₄[–] anion and carbon and hydrogen elemental analyses gave

values very different from those calculated for **40e**(GaCl₄)₂. No solid material was isolated from reactions of **38d** or **38f**.

All isolated examples of phosphylidene systems possess significant degrees of π-

bonding between phosphorus and the adjacent atoms. Systems lacking this π -bonding have not been reported and attempts to form them commonly result in the production of covalent coordination complexes, such as $t\text{Bu}_2\text{CIP} \rightarrow \text{AlCl}_3$,¹²³ or cationic coordination complexes involving a phosphine and a phosphylidene centre (phosphinophosponium).¹²⁴ The presence of π -bonding is sufficient to stabilize phosphylidene centres, but the absence of this stabilizing feature results in the salt of the complex being thermodynamically favoured with respect to two phosphylidene units.¹²⁵ The free cation arsyldene systems **39a** and **39b** involve less effective π -overlap between the As 4p- and the S 3p- or N 2p-orbitals, and this is likely responsible for the observed dimers and complexes.

Slow addition of a GaCl_3 solution to a solution of the chloroarsolidine **38** results initially in the formation of a small amount of free arsyldene **39**, which immediately complexes with **38** to form a molecule of **41**. The sulfur derivative **41b** does not react with GaCl_3 , irrespective of the concentration. This indicates an energetic preference for **41bGaCl₄** and GaCl_3 over **40b(GaCl₄)₂** ($\Delta G = +ve$). In contrast, addition of GaCl_3 to

**46****47****48****49****50**

the nitrogen derivative **41a** gives **40a** quantitatively, indicating a preference for **40a**(GaCl₄)₂ over **41a**GaCl₄ and GaCl₃ ($\Delta G = -ve$). Further evidence of this is seen in reaction mixtures containing equimolar quantities of chloroarsolidines **38a** and **38b** with two equivalents of GaCl₃, where **40a**(GaCl₄)₂ is recoverable from solution but **40b**(GaCl₄)₂ is not. The production of complexes in these cases are related to reactions of the phosphylidene species dimethylphosphenium **46** and bisdimethylaminophosphenium **47**. Reactions of (Me₂N)₂PCl with limited amounts of GaCl₃ result in the formation of the P–P complex **48**, which breaks up into individual phosphonium cations **47** as additional GaCl₃ is added.^{20,27(a)} Reaction of Me₂PCl with limited amounts of GaCl₃ gives a similar complex **49**, however the phosphylidene **46** cannot be obtained by the addition of more GaCl₃. Instead, the novel complex **50** is formed¹²⁵ due to the absence of π -interactions at the phosphorus centre which would work to stabilize the phosphylidene. In this context, it seems logical to conclude that the relative stabilities of **40a**, **40b**, **41a**, and **41b** result from the effectiveness, or lack thereof, of the π -interactions between arsenic and nitrogen (better interaction) and arsenic and sulfur (poorer interaction).

2.2.3.2 Electrospray Mass Spectrometry

Electrospray mass spectrometry (ESMS) is a recently developed and powerful mass spectrometric technique which allows analysis of species as they exist in solution.¹²⁶ It is the mildest of all currently available mass spectrometric ionization methods and allows examination of thermally labile species which are typically not amenable to study using some of the more energetic ionization techniques such as electron impact (EI) or even fast atom bombardment (FAB). ESMS has been chiefly employed in the past to study proteins¹²⁷ and other large organic molecules such as the fullerenes,¹²⁸ but has also more recently been successfully used in the identification of inorganic ionic species in water¹²⁹ and in examining dimeric species bound together by very weak intermolecular contacts.¹³⁰

As such, ESMS is an excellent approach to apply towards the study of the arsolidinium cations. Although these species exhibit weak dimerization in the solid state, evidence points towards their being either dissociated monomers in solution or fluctuating. ESMS seemed a likely technique to answer this question.¹³¹

ESMS is a technique which provides a method of transferring preexisting ions from solution to the gas phase. It is a very gentle ionization technique which results in minimal fragmentation of ions. Typically, ESMS is performed on a solution sample in which the ionic species of interest are dissolved in a suitable solvent such as water, methanol, acetonitrile, or some mixture of the three, and mildly acidified to promote ionization. In a typical setup, a mobile phase solvent is passed through a LC pump and, via a silica capillary, into a stainless steel T-joint. Introduced into the second arm of the T-joint is the sample solution, the rate of which is controlled by means of an electric syringe driver. By adjustment of the rates of flow from the LC pump and the syringe driver it is possible to vary both the overall flow rates and the relative concentration of the sample solution. Exiting from the T-joint, the solutions again pass through a length of silica capillary and are introduced into the electrospray source.

Within the electrospray source is a stainless steel needle through which the silica capillary passes and extends by approximately 0.5 mm. Also introduced through the needle is a flow of an inert nebulizing gas, usually helium, nitrogen, or argon. As the sample solution flows through the capillary at rates of from 1 μ L to 1 mL per minute, small droplets form on the end of the capillary and are nebulized by the action of both the carrier gas and an electrical field which is applied to the needle. The electric field charges the droplets and the polarity of the droplets is determined by the sign of the potential. From the needle the sample is "electrosprayed" at 8 kV onto a grounded steel plate with a small hole in it approximately 2–4 cm away from the needle. The droplets move across the intervening distance between the needle and the plate through a sealed chamber which is

reduced in pressure to remove the nebulizing gas and solvent vapour. This reduced pressure results in the solvent of the droplet being slowly drawn off. As the droplet gets smaller, the ions of the sample are forced closer together and eventually, due to repulsion of the like charges, are popped out of the droplet altogether. This results in a stream of free ions moving towards the mass spectrometer. The ions pass through a stream of an inert curtain gas, again usually helium, nitrogen, or argon, then through a skimmer and into the vacuum of the mass spectrometer. The process is very gentle and will often result in minimal changes occurring to the ions which are present in the sample solution.

The pnicylidene compounds present a number of experimental difficulties. While water/methanol or water/acetonitrile mixtures are typically used as solvents for ESMS, the hydrolytical sensitivity of the cations **40** and **41** required the use of dichloromethane as a solvent for both the sample solution and as the mobile phase. Although dichloromethane has been used previously in ESMS studies,¹³² it has typically been only a minor component in a mixed solvent system with methanol. Additionally, the use of dichloromethane was necessitated by the extremely low solubilities of **40** and **41** in other solvents.

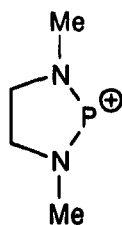
Unfortunately, the fittings used to connect the silica capillaries and the stainless steel components, such as the T-joint, degrade on contact with the dichloromethane and the resulting effluent rapidly blocks the capillaries. Additionally, a very noisy and unstable spectral background is obtained with this solvent, making background subtraction of the spectra very difficult. This is possibly a result of solvation of varying quantities of the degraded fitting material being introduced into the sample solution. Chief amongst the difficulties encountered, however, was the inability of dichloromethane to form an effective spray. The spray used in ESMS is formed electrostatically and is very dependent upon the dielectric properties of the solvent. Dichloromethane does not possess suitable properties and so sprayed poorly, often sputtering or dribbling out of the end of the capillary. In spite

of these difficulties, it was possible to obtain useful ESMS data for several compounds (*vide infra*).

To the best of the author's knowledge, this study is the first attempt to examine compounds of such extreme moisture sensitivity using ESMS, and so it was necessary to develop a working protocol. A nitrogen filled polyethylene glove bag housed a syringe driver and syringe, the sample solutions, and the fitting on one end of the silica capillary which was used to introduce samples into the mass spectrometer. All sample solution manipulations were performed within the dry nitrogen atmosphere and the sample solutions maintained their integrity after being exposed to the atmosphere for over 90 minutes.

Systems examined by ESMS include the arsylydene species **40a**(GaCl₄)₂ and **40b**(GaCl₄)₂, and, for comparison purposes, the related phosphylidene species **51**GaCl₄. Both of the arsylydene systems, though dimeric in the solid state, are fluxional and appear to be monomeric in solution, at least on the basis of ¹H and ¹³C NMR studies (*vide supra*), however, the nature of the fluxionality has not been determined (monomers, fluxional dimers or dissociative equilibria). The phosphylidene compound **51**, in contrast, is observed to be monomeric in the solid state¹³³ and solution ¹H and ¹³C NMR studies are consistent with this view.

Although the ESMS studies are difficult to reproduce, the spectra never being identical twice, certain spectral features are consistent and the observations are interesting¹³⁴ and worthy of comment. Typical positive ion ES mass spectra of



51

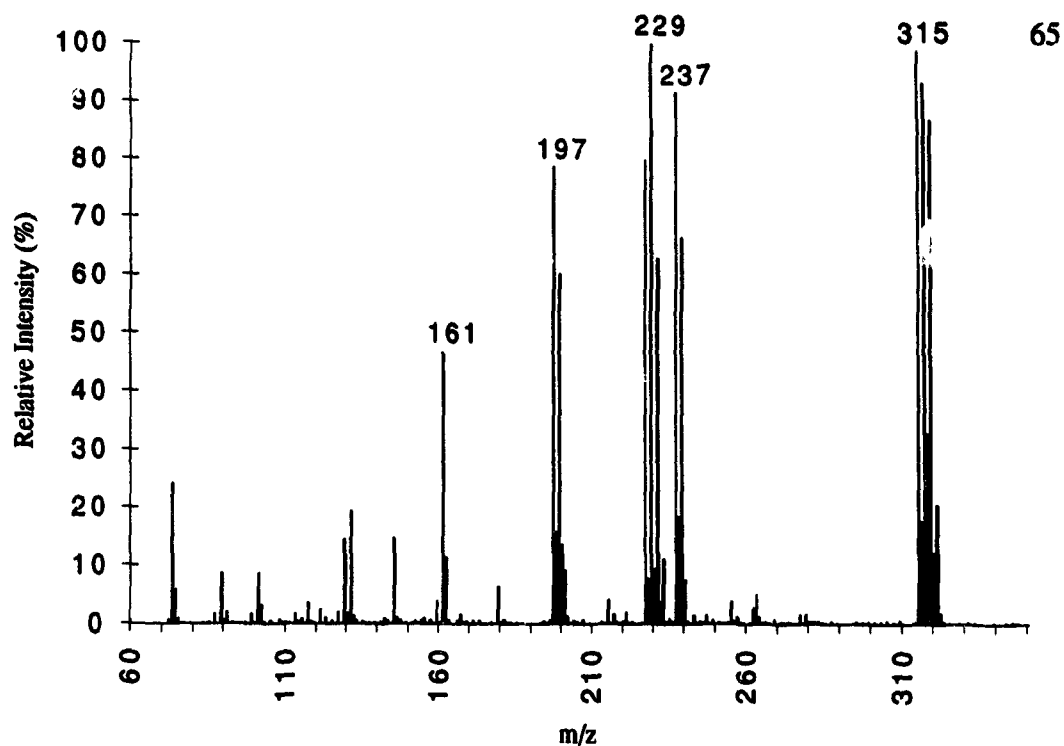


Figure 2.14: Positive ion electrospray mass spectrum of an approximately one millimolar solution of **40a** ($(\text{GaCl}_4)_2$) in CH_2Cl_2 .

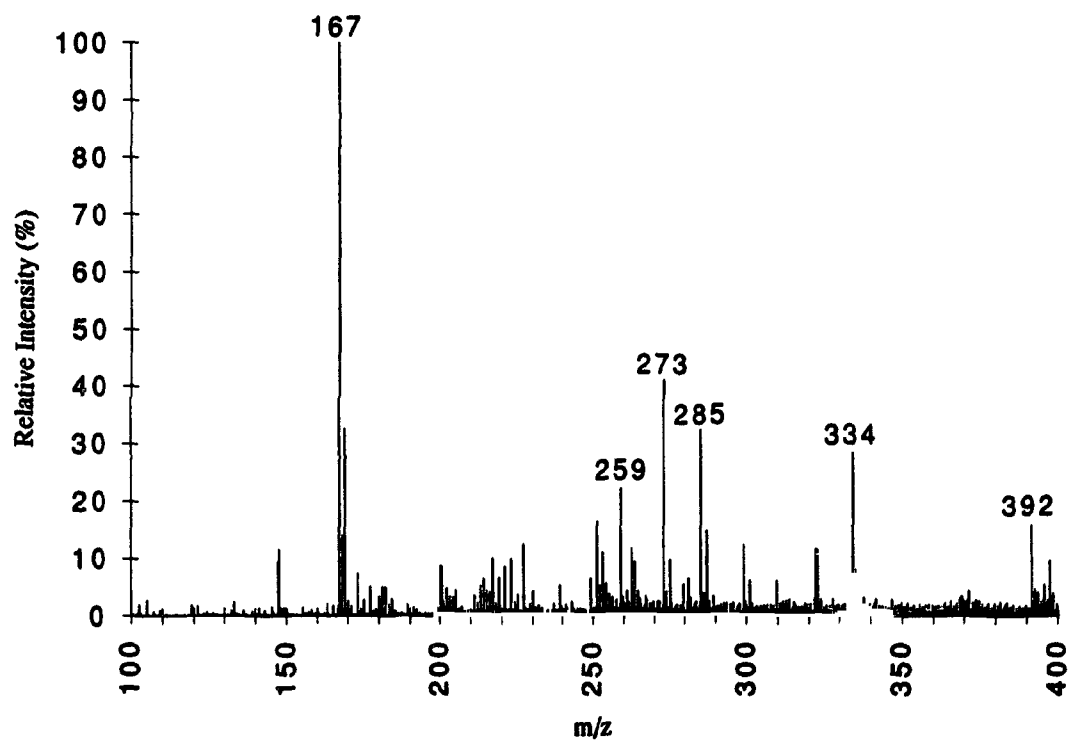


Figure 2.15: Positive ion electrospray mass spectrum of an approximately one millimolar solution of **40b** ($(\text{GaCl}_4)_2$) in CH_2Cl_2 .

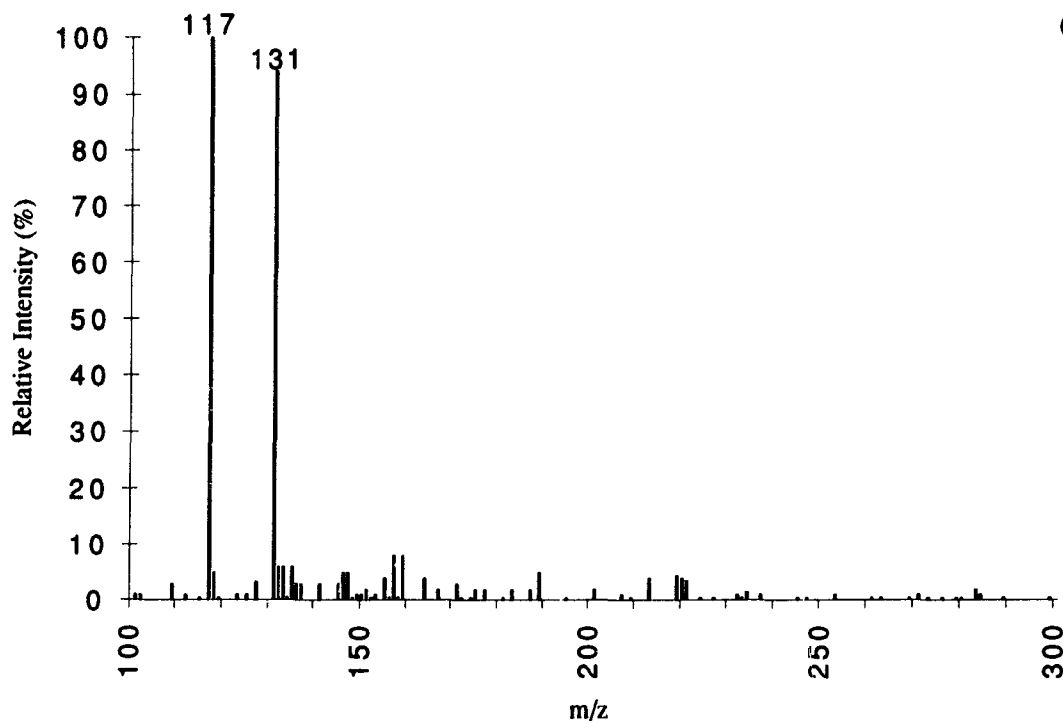


Figure 2.16: Positive ion electrospray mass spectrum of an approximately one millimolar solution of **51**GaCl₄ in CH₂Cl₂.

40a(GaCl₄)₂, **40b**(GaCl₄)₂, and **51**GaCl₄ are shown in Figures 2.14, 2.15, and 2.16, respectively. All the spectra exhibit a prominent peak corresponding to the monomeric cationic unit ($m/z = 161$, 167 , and 117 , respectively). For the arsenic derivatives, peaks at twice the m/z are evident (322 and 334 , respectively), corresponding to monocationic radical dimers, which likely result from either a reduction of the dicationic dimer or from loss of a chlorine atom from the known monocationic complex **41** which may be present in the equilibria. An analogous high molecular weight peak is not observed in the spectrum of the phosphorus derivative, consistent with the monomeric structure of the solid. If the dimeric dications were present in solution the spectra would include half integral isotope peaks at $m/z = 161.5$, 167.5 , and 117.5 , for **40b**, **40a**, and **51** respectively, however no such peaks are observed. The absence of such peaks implies that either the dimeric species are not present in solution, or that the sensitivity is low for that particular species.

In the positive ion ESMS spectrum of the diazarsolidinium **40a** (Figure 2.14), the

monomeric unit produces a strong peak at $m/z = 161$. The peak corresponding to the singly charged radical dimer, at $m/z = 322$, is present but very weak. This signal is the weakest and most massive peak in a cluster ranging from 315 to 322 amu. These signals correspond to species produced as a result of the loss of single protons from the dimeric cation. The pattern exhibited, in which every second peak is relatively large, indicates that the species resulting from loss of an odd number of protons are more stable than those which result from loss of an even number. Altogether there are four clusters of major peaks evident in the spectrum, including the one mentioned above. Other clusters occur around 237 amu, likely the result of loss of $\text{CH}_3\text{NCH}_2\text{CH}_2\text{NCH}_2$ from the dimer, and around 229 and 197 amu, both of which result from unidentified species. The medium strength peaks found below 150 amu are also observed in the spectrum of the dichloromethane background and are likely present as a result of inadequate background subtraction due to the instabilities inherent in using dichloromethane as an electrospray solvent.

The positive ion ESMS of the dithiarsolidinium **40b** (Figure 2.15) reveals a somewhat different pattern than that observed for **40a**. The base peak of this spectrum corresponds to the monomeric unit, which appears at 167 amu. Clusters of peaks are not evident, however there are a number of relatively strong peaks present. The peak assigned to the singly charged radical dimer species is apparent at $m/z = 334$. Other conspicuous peaks are situated at 273 amu, the result of loss of SCH_2CH_3 from the dimer, and at 259 amu, resulting from loss of an As atom from the dimer. An additional strong signal, at 285 amu, is unidentified. There are a large number of unidentified smaller peaks present, including some at higher m/z values than that of the dimer at 334. Prominent amongst these is a peak at 392, possibly due to addition of a C_4H_{10} fragment to the dimer. Such clustering is also apparent in spectra of the dichloromethane background, which often exhibit peaks of up to 448 amu (*c.f.* M.W. of $\text{CH}_2^{35}\text{Cl}_2 = 84$ amu).

The positive ion ES mass spectrum of the diazaphospholidinium species **51**GaCl₄ was also obtained (Figure 2.16), and is consistent with the solid state structure, with no evidence for the presence of a dimeric species (expected at $m/z = 234$). The base peak of the spectrum is at 117 amu and is attributable to the monomeric unit. Whereas the spectra for the arsyliene species **40a** and **40b** are quite complex, this compound exhibits a simple spectrum with only two major peaks, the base peak and a peak at 131 amu. This higher mass peak likely comes about as the result of the addition of a CH₂ unit to the monomer. The most plausible source of the CH₂ unit is the dichloromethane solvent. These types of ions are known to be notoriously reactive with CH₂Cl₂.¹³³

The negative ion ESMS of compounds **40a**(GaCl₄)₂, **40b**(GaCl₄)₂, and **51**GaCl₄ all exhibit a strong pattern of m/z peaks centred around 211 amu, distinctive of the isotope pattern of GaCl₄⁻. The negative ion scans are much less complex than are the positive ion scans; the large amount of fragmentation encountered in the positive ions seems to be absent. This indicates that, not surprisingly, the tetrachlorogallate anion is a much more stable species in dichloromethane solution than are the cations **40** and, to a lesser extent, **51**.

Using the procedures developed here, electrospray mass spectrometry can be a useful tool in the study of moisture sensitive materials. Though difficult, it is viable and offers a valuable new technique for the study of compounds that provide only limited data through spectroscopic study, however a more suitable solvent than dichloromethane is highly recommended. This study, although somewhat ambiguous, indicates that the dimeric arsolidinium cations **40** are dissociated in solution, supporting the conclusions developed from the solution state NMR studies (see Section **2.2.3.1**).

2.2.4 Investigations Into Reactivity

Arsylicenes are expected to possess a diverse reactivity, especially in light of recent

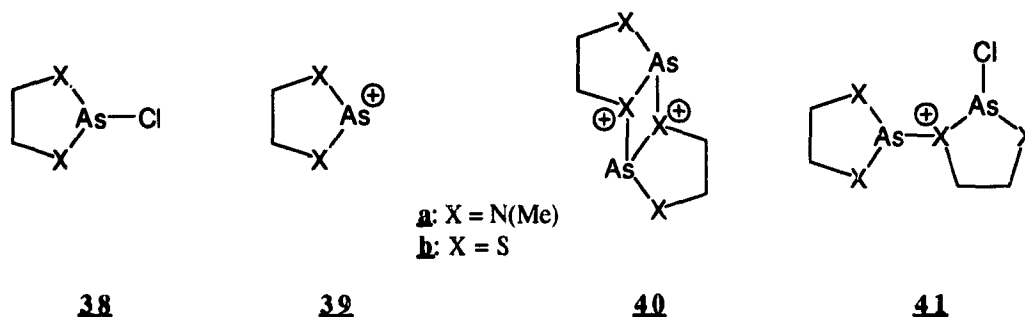
developments in the chemistry of carbenes.¹³⁵ As analogues of phosphylidenes (see Section **1.1.3**), their electron deficiency suggests activity as electrophiles, however the non-bonding electron pair should also allow for nucleophilic behaviour. While such behaviour is likely to be less prominent for cationic systems, the phosphylidenes are observed to have donor capabilities, particularly as ligands for transition metals⁵³ and by induction with other bases.¹²⁵

The arsyldene cations **40** are seemingly ideal units on which to carry out a systematic development of arsenic chemistry. They are simple, small molecules possessing minimal substitution (of little steric significance) and contain few sites at which reactions might be expected to take place. Their ionic nature causes them to assume the form of stable crystalline solids which are easily handled, preparable in large quantities, and can be stored indefinitely in inert environments.

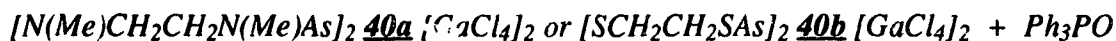
This study examines aspects of arsyldene Lewis acidity and basicity, and cycloaddition and Staudinger type reactions. The reactions carried out are chosen to provide direct comparison with related phosphylidene systems (Section **1.1.3**), and reveal that the reactivity of arsyldenes is very different from that of the analogous phosphylidenes. In addition, the reactivity of the diaza derivative **40a** is often found to differ considerably from that of the dithia derivative **40b**.

2.2.4.1 Lewis Acidity and Basicity

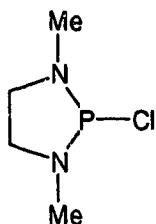
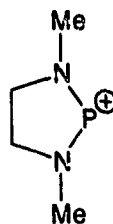
Just as some phosphylidenes have been shown to exhibit electrophilic features and behave as Lewis acids towards phosphines,^{49,124,136} the molecular positive charge and formal electron deficiency at arsenic provide an obvious means for the formation of bonds between arsenic and electron-rich centres (Lewis bases). Indeed **39** reacts with its chloroarsolidine precursor **38** in this fashion to form **41**. Although the nucleophilicity of the non-bonding electron pair in the σ -plane at arsenic is expected to be significantly



reduced with respect to that of the neutral arsine or an analogous carbene, it is possible that suitably strong Lewis acids may provide further potential for the formation of bonds. Such nucleophilic effects are likely to manifest themselves towards transition metal sites and possibly other non-metal cationic centres, as observed for phosphylidenes.^{53,125,137,138} Cation **39b** has been observed as a ligand on transition metals in several cases,^{139,140} however in all cases it has been formed *in situ* by reaction of **38b** with the sodium salts of transition metal anions.¹⁴⁰

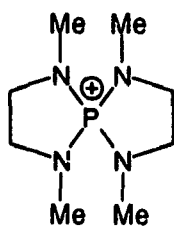
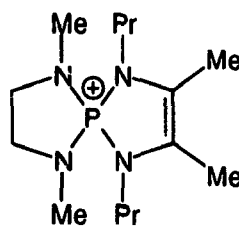
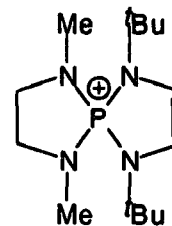


Combining triphenylphosphine oxide with an equimolar quantity of **40a**($GaCl_4$)₂ results in quantitative formation of $Ph_3PO \rightarrow GaCl_3$ as shown by the ³¹P NMR spectrum of the reaction mixture ($\delta = 47.5$ ppm). The ¹H and ¹³C NMR spectra of the mixture exhibit two peaks (the ¹H peaks revealing the familiar 3:2 ratio) with the chemical shifts occurring between those of **40a** and the corresponding chloroarsolidine **38a**, which are assigned to **41a**. Variable temperature ¹H NMR studies of dichloromethane solutions of this compound are consistent with the structure of **41a**. Clearly Ph_3PO is a better base towards $GaCl_3$ than is Cl^- , which is displaced and made available for reaction with **40a** to give **41a**. The reaction of **40b** with triphenylphosphine oxide proceeds in a similar fashion with the concomitant formation of **41b**, which is recoverable from the reaction mixture along with $Ph_3PO \rightarrow GaCl_3$ (82% combined mass of starting materials).

**52****51**

Reaction of 2-chloro-1,3-dimethyl-1,3-diaza-2-phospholidine **52** (phosphorus analogue of **38a**) with **40a**(GaCl₄)₂, in a 2:1 molar ratio, produces a solution which is noticeably duller yellow and results in the production of an uncharacterized brown precipitate. After ten days at room temperature, the ³¹P NMR spectrum reveals the presence of a single phosphorus containing species in the reaction mixture (δ = 43.1 ppm; *c.f.* **52**, δ = 169 ppm) which is within the range assigned to tetracoordinate phosphonium ions. The ¹H NMR spectrum shows two doublets, at 3.39 and 2.67 ppm, of 2:3 integration ratio and with H–P coupling of 9.6 and 10.8 Hz, respectively. A medium strength signal is apparent at 2.86 ppm. The ¹³C NMR spectrum exhibits two doublets, centred at 46.6 ppm (²J_{C-P} = 14.8 Hz) and 31.0 ppm (²J_{C-P} = 5.2 Hz). Similar observations are made if the reaction mixture is refluxed for two and a half hours.

The NMR data is interpretable as belonging to the spirocyclic phosphonium cation 1,4,6,9-tetramethyl-1,4,6,9-tetraaza-5λ⁵-phosphoniaspiro[4.4]nonane **53** tetrachlorogallate, which has not been previously reported. The related compounds 1,4-dipropyl-2,3,6,9-tetramethyl-1,4,6,9-tetraaza-5λ⁵-phosphoniaspiro[4.4]non-2-ene **54** triflate and 1,4-di-*tert*-butyl-6,9-dimethyl-1,4,6,9-tetraaza-5λ⁵-phosphoniaspiro[4.4]non-2-ene **55** triflate both exhibit similar chemical shifts and coupling constants for the methyl and methylene protons [**54**: CH₂, 3.4 ppm (10 Hz); CH₃, 2.4 ppm (10 Hz); **55**: CH₂, 3.4 ppm (9.3 Hz); CH₃, 2.6 ppm (10.9 Hz)] and carbons [**54**: CH₂, 45.3 ppm (15.6 Hz);

**53****54****55**

CH₃, 30.0 ppm (5.9 Hz); **55**: CH₂, 43.3 ppm (17.5 Hz); CH₃, 30.8 ppm (16.5 Hz)].¹⁴¹ Likewise, the chemical shifts in the ³¹P NMR are within the same range (**54**: 35.4 ppm; **55**: 29.6 ppm).¹⁴¹ Attempts to isolate **53**GaCl₄ from solution have not been successful.

The formation of **53** presumably occurs through an arsolidinium-chlorophospholidine complex similar in structure to **41** (Figure 2.17a).¹⁴² Assuming that this complex undergoes fluxional processes similar to those proposed for **41**, reversible rearrangement to the phospholidinium-chloroarsolidine complex is possible (Figure 2.17b),

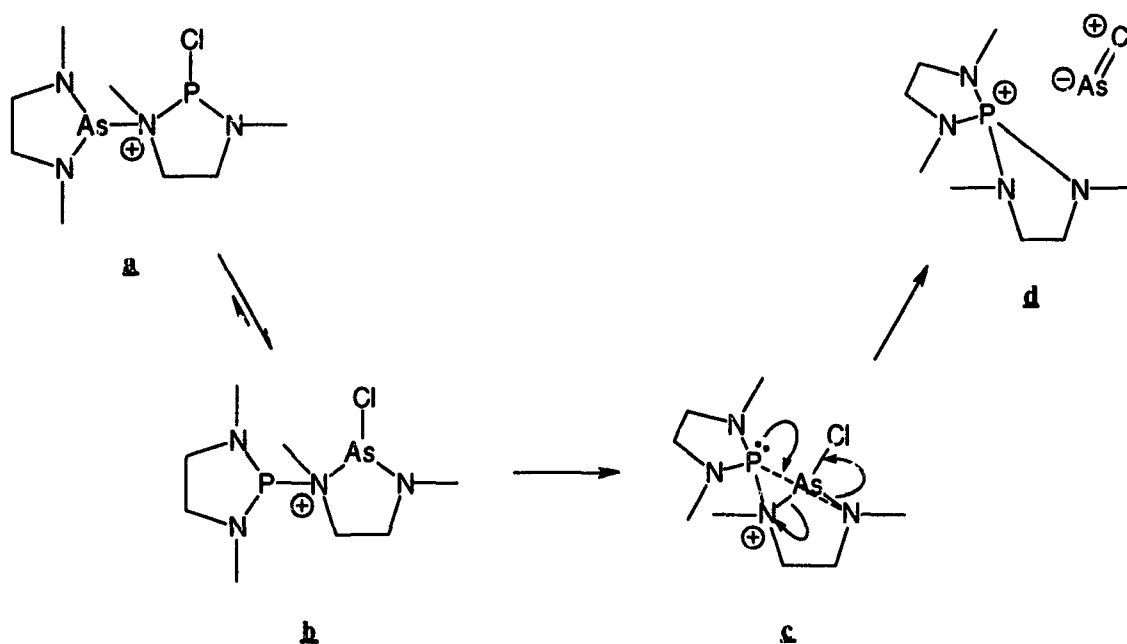
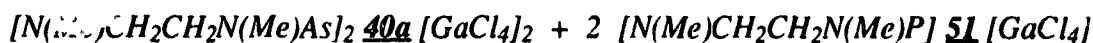
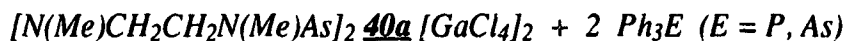


Figure 2.17: Proposed mechanism for the formation of **53**.

with exchange occurring between the nitrogen atoms on the chloroarsolidine ring. While in this form, cleavage of the less thermodynamically favourable As–N bonds occurs (Figure 2.17c), releasing As=Cl and producing **53** (Figure 2.17d). The As=Cl likely disproportionates to give As_(s) (brown precipitate) and AsCl₃.



In contrast to the above reaction, no reaction is observed between the phosphylidene salt 1,3-dimethyl-1,3-diaza-2-phosphenium **51** tetrachlorogallate (formed *in situ*) and one half molar equivalent of **40a**(GaCl₄)₂. The ¹H NMR spectrum of the reaction mixture shows distinct peaks for both of the starting compounds, although the peaks for the arsyldiene species are slightly broadened. This result supports the above mechanism for formation of **53** since the absence of **52** means that formation of the complex is not possible.



Addition of a solution of **3a**(GaCl₄)₂ to a 2:1 molar excess of triphenylphosphine produces an immediate reaction as evidenced by the fading of the colour of the solution and the production of a small amount of a pale precipitate. The ¹H NMR spectrum of the reaction mixture exhibits typical complex aromatic multiplet at 7.57 ppm and singlets at 3.35 and 2.88 ppm with integration ratios of 10:2:3, respectively. This ratio seems to indicate that a phenyl ring has been lost during the course of reaction. The ³¹P NMR exhibits signals at 66.4, 47.5, 28.0, and –5.6 ppm with an integration ratio of 1:9:13:32. The three higher field signals have been assigned to Ph₃PO→GaCl₃,¹⁴³ Ph₃PO,⁹⁰ and Ph₃P→GaCl₃ **56**,¹⁴⁴ respectively, while the downfield signal has not been assigned. The principal phosphorus containing product of this reaction is **56**, indicating that Ph₃P is a better base towards GaCl₃ than is Cl[–], much as in the case of Ph₃PO. The presence of

Ph_3PO in this reaction mixture is puzzling. Likely sources of oxygen atoms include wet solvent and the glass of the reaction vessel itself. The first source seems unlikely due to the rigorous procedures used in drying solvents and the latter seems unlikely due to the extreme strength of the Si–O bonds in glass. The ^{13}C spectrum shows a total of seven peaks, five of which are attributable to phenyl carbons (134.3, 134.1, 132.8, 130.1, and 130.0 ppm; *ipso* carbon not observed). The remaining two peaks are singlets situated at 57.3 and 36.3 ppm. Small colourless crystals of **56** have been isolated from reaction mixtures and crystallographically characterized.

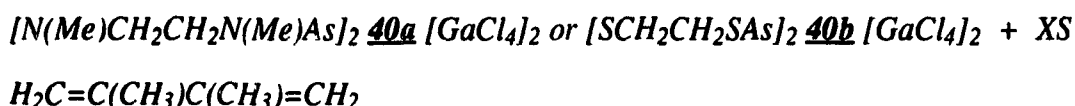
No reaction is observed between triphenylarsine and **40a**(GaCl₄)₂, and the majority of the arsyldene starting material (94%) is recoverable from the reaction mixture.

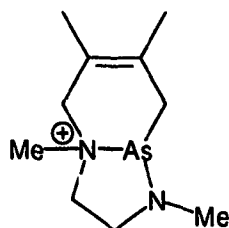
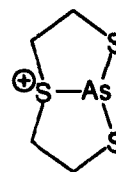
Other Reactions

No reaction is observed between **40b**(GaCl₄)₂ and benzene, in contrast to complexations which occur with phosphylidenes.¹⁴⁵ No reaction occurs between **40a**(GaCl₄)₂ and Fe₂(CO)₉, again in contrast to observations for phosphylidenes.⁵³

2.2.4.2 Cycloadditions

Addition to multiple bonds is a classical reaction of an electrophilic carbene.^{1(a)} While such reactivity is duplicated to some degree in the phosphylidene systems, the enhanced electrophilic nature imposed by the molecular positive charge stabilizes the frontier orbitals such that the cyclization reactions are more general and also occur with dienes and metal-metal multiple bonds.¹² Consequently, there is a potential for a systematic development of new arsenic heterocycles using analogous procedures.



**57****58**

The tetrachlorogallate salts of **40a** and **40b** each react rapidly with 2,3-dimethyl-1,3-butadiene in CH_2Cl_2 to give bicyclic cationic products. Reaction of **40a**(GaCl_4)₂ gives the ammonium salt 1,3,4,7-tetramethyl-1-azonia-7-aza-6-arsabicyclo[4.3.0]non-3-ene **57** tetrachlorogallate in essentially quantitative yield (as shown by ^1H NMR spectroscopy of the reaction mixture). Crystallographic characterization of **57** GaCl_4 confirms the bicyclic structure of the cation, and reveals an expected pyramidal geometry for arsenic (Figure 2.18). Selected bond lengths and angles are given in Tables 2.14 and 2.15, respectively. The cross-ring As(1)-N(2) bond is significantly longer [2.056(10) Å]

Table 2.14: Selected bond lengths (Å) for **57** GaCl_4 .

As(1)-N(1)	1.797(11)
As(1)-N(2)	2.056(10)
N(1)-C(1)	1.50(2)
N(1)-C(3)	1.49(2)
N(2)-C(2)	1.50(2)
N(2)-C(4)	1.53(2)
N(2)-C(5)	1.51(2)
C(1)-C(2)	1.54(2)
C(5)-C(6)	1.54(2)
C(6)-C(7)	1.33(2)
C(6)-C(9)	1.51(3)
C(7)-C(8)	1.48(2)
C(7)-C(10)	1.53(2)

than that of As(1)-N(1) [1.797(11) Å], and both are slightly longer than those observed in the dication **40a** [tetracoordinate-N, 1.949(4) Å; tricoordinate-N, 1.752(5) Å]. Published values for As-N bonds are limited, but single bonds are typically in the range of 1.82 to 1.88 Å.¹⁰⁶ The formation of **57** can be rationalized in terms of a Diels-Alder cycloaddition across the shorter As-N bond of **40a** with subsequent dissociation of the arsenium heterocycles. The shorter As-N bond, at 1.77 Å, lies within the range of published values for As=N double bonds (1.72 to 1.77 Å).¹⁴⁶

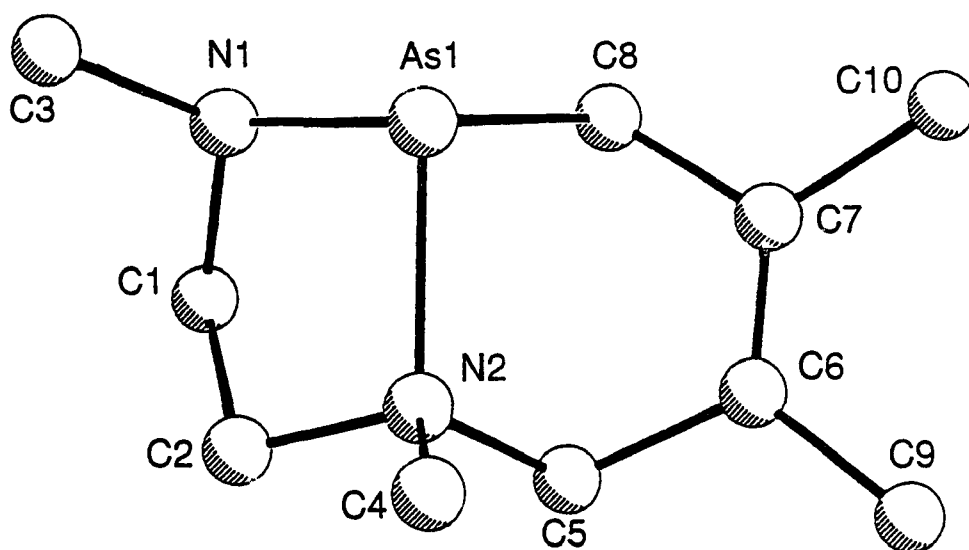


Figure 2.18: PLUTO view of **57**. The hydrogen atoms have been omitted for clarity.

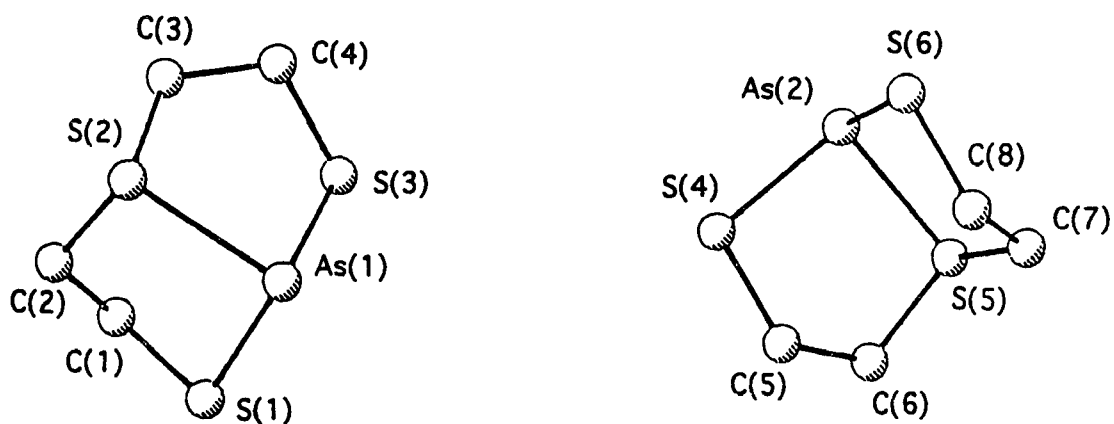


Figure 2.19: PLUTO view of **58** showing the two different molecules. The hydrogen atoms have been omitted for clarity.

2,3-Dimethylbutadiene reacts with **40b**(GaCl₄)₂ to give a complex mixture of unknown compounds (¹H and ¹³C NMR spectra exhibit a multitude of complex and broad signals) from which it is possible to isolate the GaCl₄⁻ salt of 1-thionia-4,6-dithia-5-arsabicyclo[3.3.0]octane **58**. Crystallographic characterization reveals a bicyclic structure for cation **58** with two different molecules in the unit cell (Figure 2.19). Selected bond lengths and angles are given in Tables 2.20 and 2.21 in Section 2.4. While all three of the As–S bonds are slightly different in length, the cross-ring bond is the longest [2.390(4) Å in one molecule, 2.347(4) Å in the other], consistent with the observations made in **57**. The unexpected structure of **58** can be considered in terms of an extrusion of an As–S⁺ moiety from the dimer **40b**, perhaps through an initial interaction with butadiene in a fashion similar to that of **40a**. Whereas dissociation of the two arsolidinium rings of **40a** results in formation of **57**, the two rings of **40b** stay attached to each other and the As–S⁺ unit is lost. It has proven possible to synthesize **58**GaCl₄ quantitatively (as shown by ¹H and ¹³C NMR of the reaction mixture) using a different technique (see Section 2.4). The long cross-ring bonds in both **57** and **58** allow a classification of these compounds as intramolecular base-stabilized arsenium cations (see Section 2.4).

Table 2.15: Selected bond angles (°) for 57 GaCl ₄ .			
N(1)-As(1)-N(2)	89.3(4)	C(4)-N(2)-C(5)	111.5(11)
N(1)-As(1)-C(8)	101.8(6)	N(1)-C(1)-C(2)	107.4(12)
N(2)-As(1)-C(8)	91.7(6)	N(2)-C(2)-C(1)	106.4(11)
As(1)-N(1)-C(1)	110.0(9)	N(2)-C(5)-C(6)	112.1(11)
As(1)-N(1)-C(3)	117.2(10)	C(5)-C(6)-C(7)	117.2(14)
C(1)-N(1)-C(3)	112.6(12)	C(5)-C(6)-C(9)	118.4(14)
As(1)-N(2)-C(2)	104.2(8)	C(7)-C(6)-C(9)	124(2)
As(1)-N(2)-C(4)	107.8(9)	C(6)-C(7)-C(8)	119.1(15)
As(1)-N(2)-C(5)	112.6(7)	C(6)-C(7)-C(10)	125(2)
C(2)-N(2)-C(4)	109.7(11)	C(8)-C(7)-C(10)	115.9(14)
C(2)-N(2)-C(5)	110.8(10)	As(1)-C(8)-C(7)	108.4(11)

Reactions of **40** with butadiene are in dramatic contrast to the corresponding established butadiene cycloaddition chemistry of the phosphonium cations, which produces spirocyclic phosphonium cations.^{55(a),147} Although the nature of the arsenium cations in solution is not clear (see Section 2.2.3), the quantitative formation of **57** implies a concerted process, possibly a Diels-Alder type cycloaddition involving the As–N bond of either the dimer or the monomer as the dienophile. From these results it is apparent that the electronic structure of the arsenium cations differs significantly from the phosphonium analogues in terms of the relative energy of the LUMO and of the non-bonding electron pair at the arsenic centre. However, it is possible that the reactivity of the arsenium cations is biased by the penchant for dimer formation, a feature not observed for the corresponding phosphonium cations.¹³³

*[N(Me)CH₂CH₂N(Me)As]₂ **40a** [GaCl₄]₂ or [SCH₂CH₂SAs]₂ **40b** [GaCl₄]₂ + Various Alkynes*

Preliminary investigations involving reactions of **40a**(GaCl₄)₂ or **40b**(GaCl₄)₂ with a variety of alkynes indicate a markedly different reactivity. Although isolable materials are not realized, ¹H NMR spectroscopy offers some useful information. Reaction with 2-butyne (dimethylacetylene, MeC≡CMe) results in a single unidentified product in the case of **40a** and a complex mixture in the case of **40b**. A few crystals of **41b**GaCl₄ are recoverable from the latter mixture. No reaction is observed between **40a** and diphenylacetylene (PhC≡CPh) but a complex mixture of products is observed with **40b**. The acetylene DMAD (dimethyl acetylenedicarboxylate, MeO₂CC≡CCO₂Me) produces complex mixtures when reacted with both derivatives of **40**. Finally, no reaction is observed between hexafluorobut-2-yne (F₃CC≡CCF₃) and either **40a** or **40b**.

These reactions may be rationalized if one considers the types of acetylenes used and their relative HOMO energies, as illustrated in Figure 2.20. The π-type LUMOs of the

arsylidenes are likely higher in energy than the π HOMOs of the acetylenes, with that of the dithia derivative **40b** being lower in energy than that of the diaza derivative **40a**, a result of the better π overlap of the As 4p orbital with the 2p orbital of nitrogen than the 3p orbital of sulfur. Since the interaction of orbitals of similar energy produces a lowering of energy in the transition state, and therefore makes reaction more favourable, increased reactivity of the arsylidenes is expected with the higher energy alkynes, as is observed. Neither arsyldiene reacts with the alkyne containing the lowest energy HOMO, hexafluorobut-2-yne, but both react with the higher HOMO energy species 2-butyne. Interestingly, **3a**(GaCl₄)₂ reacts with DMAD but not diphenylacetylene, probably through reaction with the COOMe group and not the triple bond. Consistent with this hypothesis are the ¹H

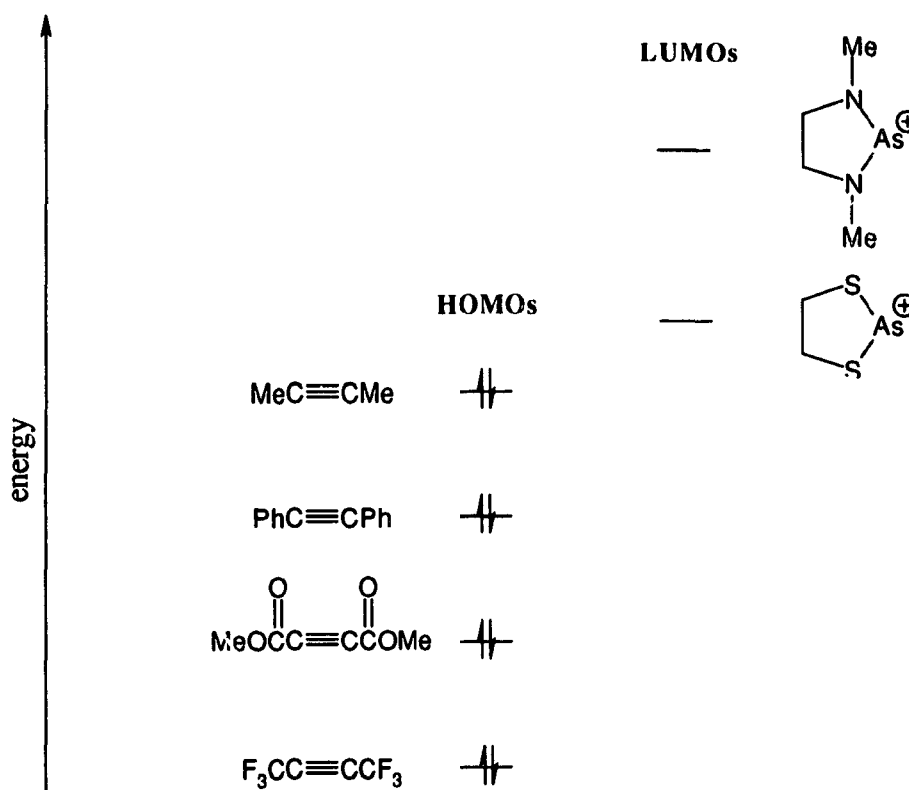


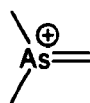
Figure 2.20: Relative energy levels of the HOMOs of various acetylenes and the LUMOs of the arsyldiene species **40**.

NMR spectra of reaction mixtures of the dithia derivative **40b** with the various acetylenes. Dimethylacetylene and diphenylacetylene produce spectra which, though complicated, share many similar features (*vide infra*). This indicates that they probably react in a similar fashion. The spectrum produced by reaction with DMAD, however, does not exhibit features observed in the spectra of the other two reactions.

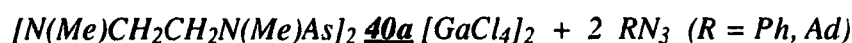
The ^1H NMR spectra of reaction mixtures of **40b**(GaCl₄)₂ with dimethylacetylene and diphenylacetylene exhibit some common features. Among the peaks present are four sets of doublets of doublets of doublets with integration ratios of 1:1:1:1 situated at 4.68, 4.24, 3.20, and 2.54 ppm for the reaction with MeC≡CMe, and at 4.78, 4.22, 3.51, and 2.82 ppm for the reaction with PhC≡CPh. Such a pattern is consistent with the arsolidine ring being locked into a single conformation, differentiating all four ring protons. The relatively large differences in chemical shifts indicate that the environment of each of the four protons is significantly different and could indicate that some type of cycloaddition reaction has taken place.

2.2.4.3 Staudinger Reactions

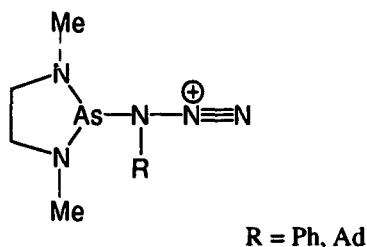
An extension of the Staudinger reaction has been implicated in the reactions of phosphylidene salts with organic azides and sulfur,⁶⁰ however, the results are inconclusive and the tricoordinate iminophosphonium cation has been shown to be unstable with respect to tetracoordinate covalent alternatives.⁶² Despite this, the isolation of phosphylidenes through the use of steric shielding seems to validate the use of such models in the development of phosphorus chemistry.^{148,149} In an analogous fashion, tricoordinate



arsonium cations **59** represent milestones in the development of arsenic chemistry, and the arsyliene cations **40** would seem to be ideal precursors. Arsenic seems to exhibit less of a preference for higher coordination numbers than does phosphorus and so might be expected to sustain the tricoordinate environment more readily. Additionally, as is found in the case of the phosphorus derivatives, the molecular positive charge might be expected to enhance reactions with electron-rich systems.



No reaction is observed in dichloromethane solution between **40a**(GaCl₄)₂ and either of the organic azides 1-azidoadamantane or phenyl azide. This indicates that formation of the adduct intermediate **60**, analogous to that encountered in the case of

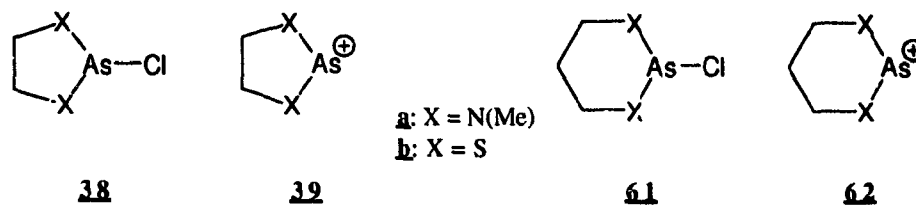


60

phosphylidenes¹⁵⁰ is unfavourable and does not take place, probably as a result of the higher energy As orbitals. Since the initial interaction cannot occur, no Staudinger type reaction is observed with the arsyliene. Alternatively, the reaction may be thermodynamically favourable, but does not occur for kinetic reasons. Too little is known at this stage to make definitive conclusions.

2.3 Arsenanium Cations

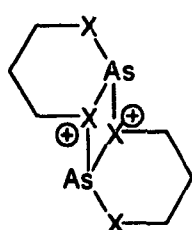
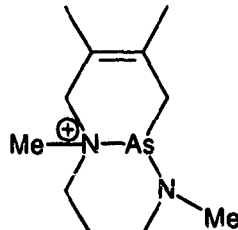
Preliminary investigations have begun on the chloroarsenanes **61**, compounds



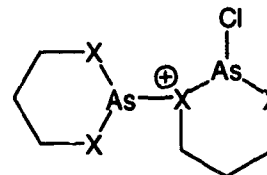
closely related to the chloroarsolidines **38**, with the goal of synthesizing arsenanium cations **62**. As for the chloroarsolidines **38**, slow addition of dichloromethane solutions of 2-chloro-1,3-diaza-1,3-dimethyl-2-arsenane **61a** or 2-chloro-1,3-dithia-2-arsenane **61b** to equimolar solutions of GaCl_3 consistently result in a rapid reaction. Reaction mixtures containing **61a** produce an immediate purplish red colour which turns bright yellow as the addition is completed. NMR data of the reaction mixture (*vide infra*) are consistent with formation of the arsenanium cation **62a**, exhibiting distinct downfield shifts. By analogy with the arsolidine systems, the arsenaniums are expected to exist as the dimer **63a** $(\text{GaCl}_4)_2$. Solid material is isolable from the reaction and exhibits a strong absorption at 390 cm^{-1} in the IR region, characteristic of the GaCl_4^- anion, however repeated attempts at crystallization have been unsuccessful. Mixtures of **61b** with GaCl_3 do not change colour and it has not been possible to isolate solid material from the reaction mixtures. ^1H and ^{13}C NMR spectra of reaction mixtures are consistent with the formation of **62b** or **63b**.

Further evidence of the formation of **62a** or **63a** is given by the *in situ* reaction with a slight excess of 2,3-dimethyl-1,3-butadiene. NMR studies of the reaction mixture, including COSY and inverse HETCOR scans, indicate quantitative formation of the ammonium salt 1-azonia-1,3,4,7-tetramethyl-7-aza-6-arsabicyclo[4.4.0]dec-3-ene **64** tetrachlorogallate, consistent with the formation of the arsolidine analogue **57**.

The slow controlled addition of one half molar equivalent of GaCl_3 to a solution of chloroarsenane **61** (resulting in a 2:1 excess of the chloroarsenane), while at all times

**63****64**

a: X = N(Me)
b: X = S

**65**

maintaining an excess of the chloroarsenane, results in pale yellow solutions. These reaction mixtures exhibit ^1H and ^{13}C NMR spectra compatible with the proposed bicyclic monocationic chloroarsenane-arsenanium complex **65**GaCl₄, which is comparable to the arsolidine structure **41**. As in the case of **41**, this species may be viewed as a Lewis complex of the chloroarsenane **61** and the arsenanium cation **62**. Unfortunately, isolation of solid reaction products has not been possible.

2.3.1 Chloroarsenanes: Arsenanium Precursors

Chloroarsenane **61** is a six-membered analogue of the chloroarsolidine **38**. The dithia derivative **61b** is a slightly moisture sensitive colourless crystalline solid first

reported in 1972.¹⁵¹ The dimethyldiaza derivative **61a** is reported here for the first time. Unlike the chloroarsolidine **38a**, which is an extremely moisture sensitive, thermally unstable liquid, **61a** is a moderately moisture sensitive colourless crystalline solid.

The crystal structures of **61a**

Table 2.16: Selected bond lengths (Å) for **61a** and **61b**.

	<u>C₅H₁₂AsClN₂</u>		<u>C₃H₆AsClS₂</u>
As(1)-Cl(1)	2.357(2)	As(1)-Cl(1)	2.223(2)
As(1)-N(1)	1.796(4)		
As(1)-N(2)	1.803(5)	As(1)-S(1)	2.208(2)
N(1)-C(3)	1.459(8)		
N(1)-C(5)	1.456(8)	S(1)-C(1)	1.827(4)
N(2)-C(1)	1.459(8)		
N(2)-C(4)	1.465(7)		
C(1)-C(2)	1.516(9)	C(1)-C(2)	1.504(5)
C(2)-C(3)	1.514(9)		

Table 2.17: Selected bond angles (°) for **61a** and **61b**.

	<u>C₅H₁₂AsClN₂</u>		<u>C₃H₆AsClS₂</u>
Cl(1)-As(1)-N(1)	99.8(2)	Cl(1)-As(1)-S(1)	98.69(5)
Cl(1)-As(1)-N(2)	99.1(2)		
N(1)-As(1)-N(2)	98.4(2)	S(1)-As(1)-S(1)'	102.23(1)
As(1)-N(1)-C(3)	121.9(4)	As(1)-S(1)-C(1)	104.5(1)
As(1)-N(1)-C(5)	113.7(4)		
C(3)-N(1)-C(5)	112.3(5)		
As(1)-N(2)-C(1)	121.1(4)		
As(1)-N(2)-C(4)	113.2(4)		
C(1)-N(2)-C(4)	112.6(5)		
N(2)-C(1)-C(2)	112.0(5)	S(1)-C(1)-C(2)	115.8(4)
C(1)-C(2)-C(3)	113.1(5)	C(1)-C(2)-C(1)'	115.52(1)
N(1)-C(3)-C(2)	111.3(5)		

and **61b** have been determined (**61b** was first crystallized by Dr. Bruce Royan of this laboratory and characterized by Dr. John Richardson in 1990 but has not been previously reported)¹⁰⁷ and are shown in Figures 2.21 and 2.22, respectively.

Selected bond lengths and angles for the two compounds are given in Tables 2.16 and 2.17, respectively. The arsenanes do not exhibit the incipient dimerization observed for the arsolidines **38**. An intermolecular contact within the sum of the van der Waals radii for As and N (As, 2.0 Å; N, 1.5 Å),⁸⁴ does occur in **61a** between As(1) and N(2) of another molecule, however at 3.250(5) Å this distance is much longer than the contact encountered in **38a** [2.84(1) Å] and has no effect on the shape of the molecule, as evidenced by the identical geometry about both nitrogen centres. A similar contact is observed in **61b** between As(1) of one molecule and S(1) of another, however at 3.84 Å it lies just barely within the sum of the van der Waals radii for As and S (As, 2.0 Å; S, 1.85 Å)⁸⁴ and also has no effect on the shape of the molecule.

The crystal structure of **61a** reveals that all C–N bonds are crystallographically indistinguishable and are consistent with the established lengths for a C–N single bond (1.47 Å).⁴¹ Likewise, both C–C bonds are crystallographically identical and are consistent with single bonds (1.54 Å).⁴¹ The two As–N bonds are also identical in length, in contrast to chloroarsolidine **38a**. In fact, the length of the As–N bonds in **61a** (1.80 Å) is exactly

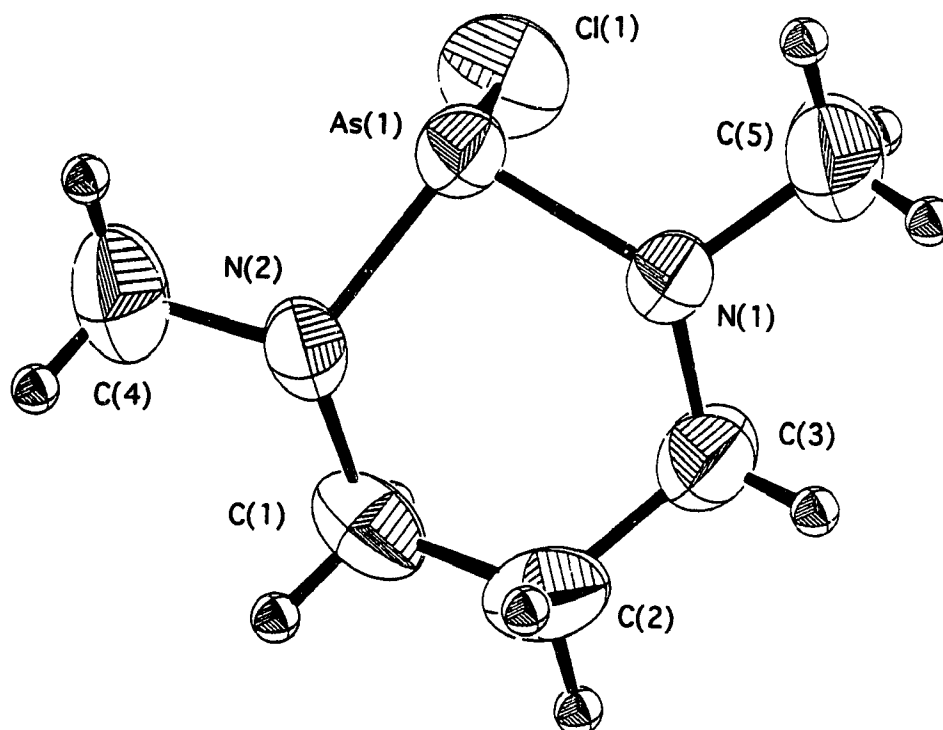


Figure 2.21: ORTEP view of the chloroarsenane **61a** (50% probability ellipsoids).

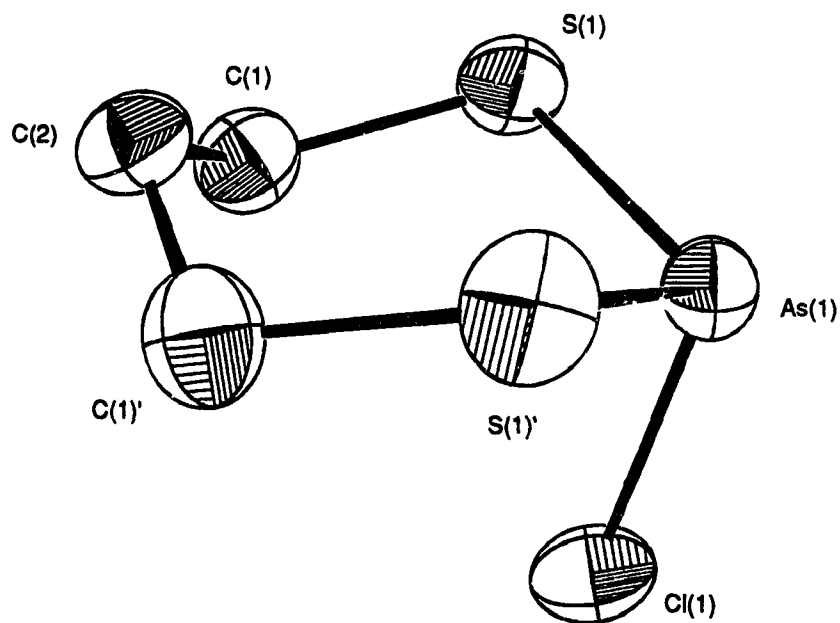


Figure 2.22: ORTEP view of the chloroarsenane **61b** (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity.

the average of the two As–N bond lengths in **38a** (1.77 Å and 1.83 Å). Although published values for As–N bonds are limited, single bonds are typically in the range of 1.82 to 1.88 Å.¹⁰⁶ The slight shortening of the observed As–N bonds may be indicative of a small amount of π -bonding between the arsenic and nitrogen atoms. Consistently, the sum of the bond angles around the nitrogen atoms is 348° [N(1)] and 347° [N(2)], approximately midway between those expected for an sp^2 (360°) and an sp^3 (328.5°) hybridized nitrogen atom. The As–Cl bond is significantly shorter than that seen in **38a**, due to the lack of intermolecular interactions, but is still longer than a normal As–Cl bond (2.161 Å).⁴¹ The ν_3 As–Cl stretching frequency is observed (as a shoulder) at the lower wavenumber of approximately 290 cm⁻¹ (*c.f.* arsenic trichloride, 370 cm⁻¹), consistent with a relatively long bond.

The crystal structure of **61b** exhibits traits similar to those of **61a**. There is a crystallographic mirror plane running through the Cl(1), As(1) and C(2) atoms of the molecule. All bonds are consistent with normal single bonds (As–S, 2.20 to 2.27 Å;¹⁰⁹ C–S, 1.82 Å;⁴¹ C–C, 1.54 Å⁴¹). In the arsolidine analogue **38b**, the two As–S bonds are significantly different (2.19 and 2.23 Å) due to the dimer contacts, and the length of the bonds in **61b**, lacking these contacts, is exactly the average of the two values (2.21 Å). The lack of shortening observed in the As–S bonds, as opposed to the definite shortening observed in the As–N bonds of **61a**, is a result of the lesser ability of sulfur, as compared to nitrogen, to form an effective π -bond with arsenic. As for the chloroarsolidines **38** and the other chloroarsenane **61a**, the As–Cl bond in **61b**, at 2.223 Å, is longer than a normal As–Cl bond (2.161 Å).⁴¹ The IR spectrum of **61b** exhibits the ν_3 As–Cl stretching frequency at approximately 330 cm⁻¹, consistent with the observed length of the bond.

A study of the ¹H NMR characteristics of **61b** in C₆D₆ has previously been reported and the species was characterized as a complex AA'BB'CD spin system.¹⁵¹ In benzene-*d*₆ the compound exhibits multiplets in the spectrum at 2.98, 2.23, 1.56, and 1.24

ppm with an integration ratio of 2:2:1:1. These signals are assigned to the axial and equatorial protons on the CH₂S carbons, and the axial and equatorial protons of the unique methylene, respectively. Coupling constants indicate that the chair conformation is preferred in solution with the chlorine atom axial, consistent with other similar compounds,¹⁵² and is usually associated with the *anomeric effect*.¹⁵³ Inversion at the arsenic centre is slow at room temperature. In dichloromethane-*d*₂ the chemical shifts are significantly different and the two upfield multiplets overlap. The multiplet signals are observed at 3.46, 3.04, and 2.24 ppm and exhibit an integration ratio of 1:1:1. These signals are assigned to the axial and equatorial protons on the CH₂S carbons, and both protons on the unique methylene carbon, respectively. No appreciable change in the ¹H NMR spectrum is observed on cooling the sample to –80 °C. The carbon atoms exhibit signals in the ¹³C spectrum at 26.8 and 26.1 ppm for the CH₂S and unique methylene carbons, respectively.

The diazachloroarsenane **61a** exhibits a ¹H NMR spectrum somewhat similar to **61b** in dichloromethane-*d*₂. An AA'BB'CD system is observed with an additional peak resulting due to the six methyl protons. The differences in chemical shifts for the axial and equatorial protons on the methylene carbons adjacent to the heteroatoms are not as different from each other in the case of **61a** as they are in **61b** and this results in the multiplets for these two types of protons overlapping, producing a single multiplet centred at 2.88 ppm. Likewise, the two multiplets for the different protons of the unique methylene group overlap, resulting in a single multiplet centred at 1.94 ppm. Between these two multiplets, at 2.63 ppm, is a singlet resulting from the methyl groups. The integration ratio of these signals is 4:6:2, respectively. Performing the ¹H NMR experiment after cooling the sample to –80 °C produces little change in the spectrum of this compound with the exception of a slight broadening of all peaks. The ¹³C NMR spectrum of **61a** exhibits three signals: 48.4 ppm for the two CH₂N carbons, 40.3 ppm for the two methyl carbons, and 27.8 ppm for

the unique methylene carbon.

2.3.2 Solution ^1H and ^{13}C NMR Spectroscopy

The room temperature solution ^1H and ^{13}C NMR spectra for reaction mixtures of 1:1 or 2:1 reactions of chloroarsenanes **61a** or **61b** with GaCl_3 are consistent with the formation of cationic arsyliene products. Distinct downfield shifts relative to the neutral chloroarsenanes are observed, ranging from 0.21 to 0.71 ppm for the aza derivatives **63a** and **65a**, and 0.03 to 0.14 ppm for the thia derivatives **63b** and **65b** (Table 2.18). In all cases the chemical shifts of the complex **65** lie between that of the dimer **63** and the chloroarsenane **61**.

The aza derivatives **63a** and **65a** each exhibit three sets of peaks, with a 4:6:2 integration ratio, assignable to the protons on the methylene carbons adjacent to the

Table 2.18: Solution ^1H and ^{13}C NMR chemical shifts (δ , ppm, CD_2Cl_2) of the chloroarsenanes **61** and proposed arsylienes **63** and **65** (referenced to TMS and calibrated to the internal solvent signal).

Compound	Assignment	^1H (mult. int)	^{13}C
61a	CH_2N	2.88 (m, 4H)	48.4
	CH_3	2.63 (s, 6H)	40.3
	CH_2	1.94 (m, 2H)	27.8
63a (GaCl_4) ₂	CH_2N	3.49 (m, 4H)	51.6
	CH_3	3.34 (s, 6H)	42.6
	CH_2	2.29 (m, 2H)	26.2
65a GaCl_4	CH_2N	3.23 (m, 4H)	50.3
	CH_3	3.04 (s, 6H)	41.7
	CH_2	2.15 (m, 2H)	27.0
61b	$\text{CH}_2\text{S}_{(\text{a})}$	3.46 (m, 2H)	26.8
	$\text{CH}_2\text{S}_{(\text{e})}$	3.04 (m, 2H)	
	CH_2	2.24 (m, 2H)	26.1
63b (GaCl_4) ₂	CH_2S	3.43 (t, 4H)	29.3
	CH_2	2.38 (quintet, 2H)	26.9
65b GaCl_4	CH_2S	3.38 (t, 4H)	28.7
	CH_2	2.34 (quintet, 2H)	27.0

nitrogen atoms, the methyl protons, and the protons on the unique methylene group, respectively. The signals appear as a multiplet, a singlet, and a multiplet, respectively, and are very similar in appearance to those observed in the spectrum of the chloroarsenane **61a**. This implies that the spin system has not changed from AA'BB'CD. Such a spin system is unexpected since formation of

the free arsyldene species **62a** should result in an A_4X_2 system, assuming rapid interchange between the two chair conformers, and the dimeric dication **63a** is expected to exhibit an ABMNXY spin system.

The sulfur derivatives **63b** and **65b** each exhibit two sets of peaks, with a 4:2 integration ratio, which are assignable to the protons on the methylene carbons adjacent to the sulfur atoms, and the protons on the unique methylene group, respectively. These signals appear as a broadened triplet and a quintet, respectively, indicative of an A_4X_2 spin system, which is in marked contrast to the $AA'BB'CD$ spin system observed in the neutral chloroarsolidines **61**, as well as the results observed for the aza derivatives. Removal of the chlorine atom decreases the energy barrier to inversion at arsenic, thereby allowing ready interconversion between the two chair conformers. This equilibrates all four protons on the carbon atoms adjacent to sulfur atoms, and the two protons on the unique methylene carbon. The observed broadening of the triplet peak is evidence for retention of a small barrier to interconversion. The increased fluxionality encountered upon warming the sample to +30 °C results in better definition of the triplet.

Variable temperature ^1H NMR studies of solutions of **63a** and **65a** display markedly different results. Dication **63a** exhibits broadening of all peaks as the temperature is reduced (Figure 2.23). The upfield multiplet loses all definition, becoming a single broad signal, by -60 °C. The downfield multiplet loses its definition by -80 °C, the same temperature at which the upfield multiplet exhibits coalescence and splits into two separate signals. By -90 °C, the lowest temperature possible in dichloromethane solution, the downfield multiplet exhibits further broadening and shoulders are visible on the side of the peak. An ABMNXY spin system would result if the dimeric structure proposed for **63a** was to be locked into place. The observed spectrum could be such a spin system assuming that there is still some fluxionality present which produces the broadening of the resulting three multiplets. The VT ^1H NMR spectra of complex **65a** exhibit less

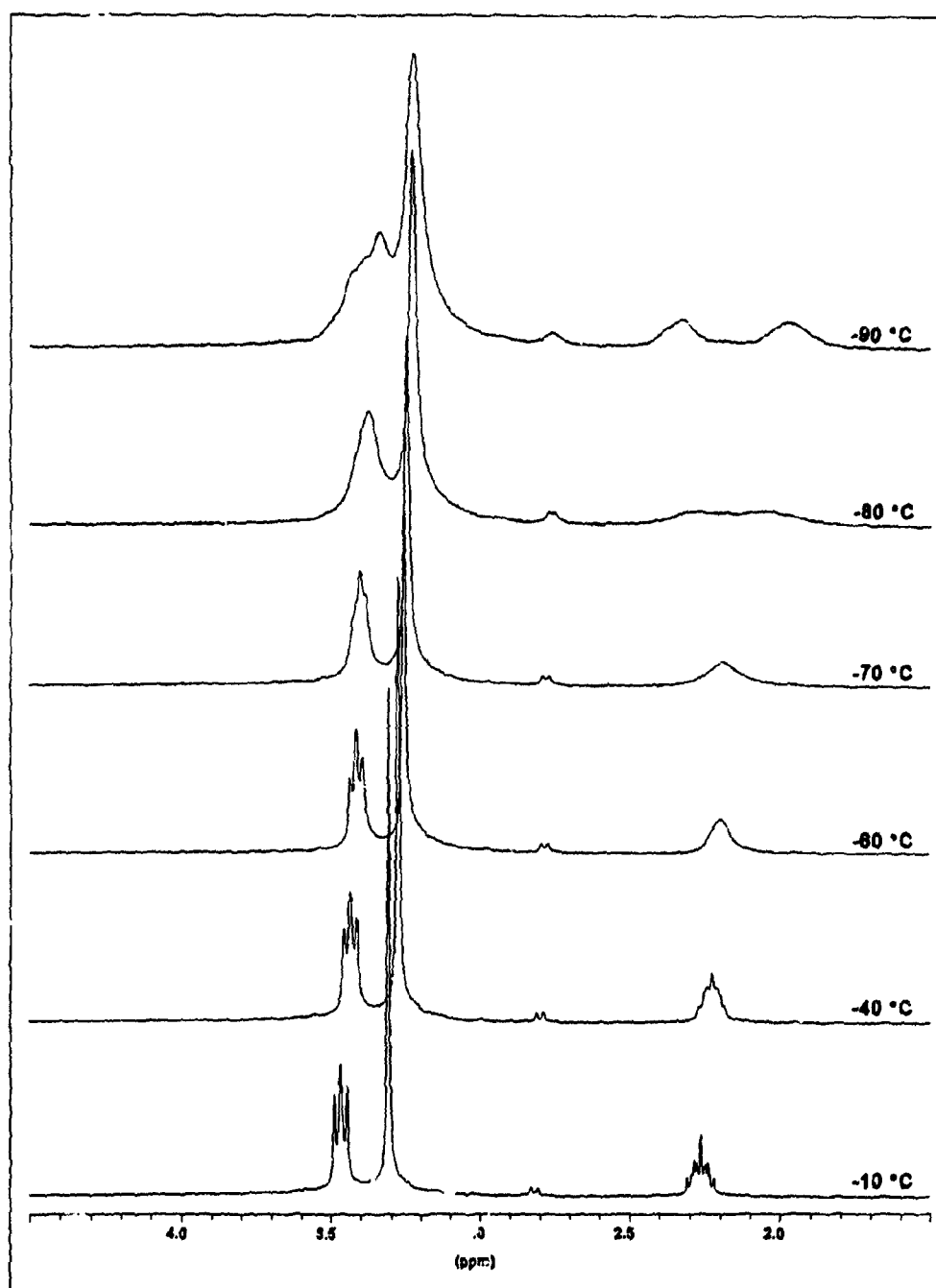


Figure 2.23: Variable temperature ^1H NMR spectra at 250 MHz of a reaction mixture containing the dicatic 63a in CD_2Cl_2 .

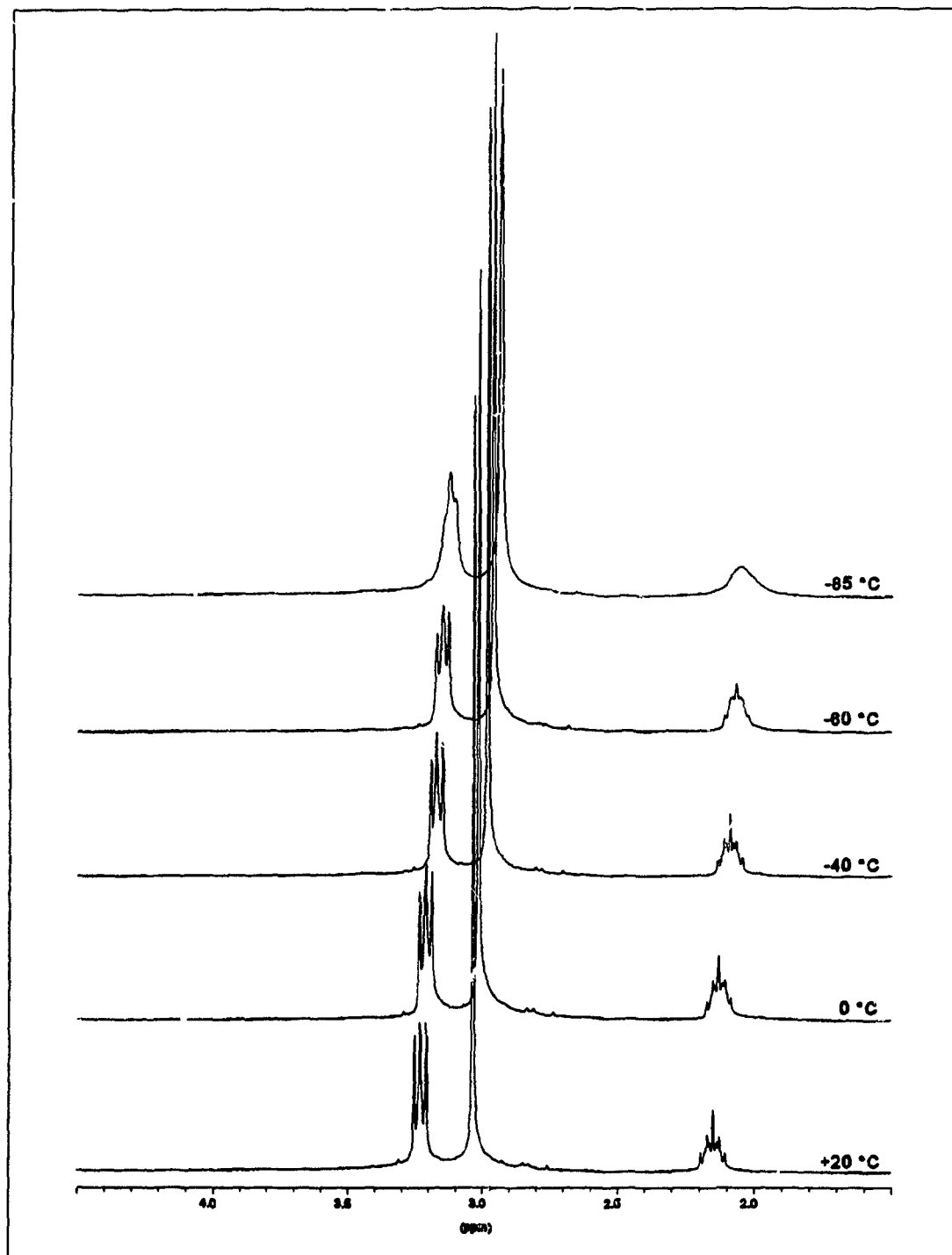


Figure 2.24: Variable temperature ^1H NMR spectra at 250 MHz of a reaction mixture containing the monocation **65a** in CD_2Cl_2 .

information (Figure 2.24). At $-85\text{ }^{\circ}\text{C}$ the upfield multiplet has lost definition, becoming a single broad peak and the downfield multiplet is broadened, but not yet featureless. All peaks in this spectrum exhibit considerably less broadening than do those in the spectrum of **63a** at the same temperatures. Apparently this species possesses a greater degree of fluxionality than does **63a**, although why this should be the case is unclear.

In the VT ^1H NMR the dithia derivatives **62b** and **65b** exhibit traits considerably different from those observed for the diaza derivatives **63a** and **65a**. By $0\text{ }^{\circ}\text{C}$, the reaction mixture presumably containing **63b**, exhibits a broadened downfield peak while the upfield peak has lost virtually all definition (Figure 2.25). By $-20\text{ }^{\circ}\text{C}$ the downfield peak has split into two. By $-40\text{ }^{\circ}\text{C}$ and below, each of the three peaks begins to exhibit second order characteristics. No further change is observed in the spectrum down to $-90\text{ }^{\circ}\text{C}$. Such a spectrum is consistent with the freezing out of the fluxional motion of **63b** with the concomitant formation of an ABMNXY spin system. This is good evidence for the existence of **63b** as a dimer, rather than as discrete arsyldene units **62b**, which would produce an A_4X_2 system. The downfield signal in the spectrum of **65b** loses its triplet features and becomes a single broad peak by $+10\text{ }^{\circ}\text{C}$ (Figure 2.26). The upfield signal remains a well defined quintet. By $-30\text{ }^{\circ}\text{C}$ the upfield signal has also lost all definition and the downfield peak exhibits a shoulder. By $-50\text{ }^{\circ}\text{C}$ this shoulder has become a separate peak at 3.6 ppm which exhibits some fine structure, while the upfield peak has undergone coalescence, producing a multiplet at around 2.45 ppm. More splitting occurs as the temperature continues to be reduced and by $-80\text{ }^{\circ}\text{C}$ the upfield signal has changed into a complex broad multiplet and the downfield signal has split into three sets of signals with one, one, and two protons, respectively. Such a spectrum could be consistent with the structure of the complex **65b**, assuming rapid rotation about the As-S interring connection, however the presence of a small quantity of an impurity, initially observed at 3.15 ppm, clouds the issue and makes the spectrum more difficult to analyze.

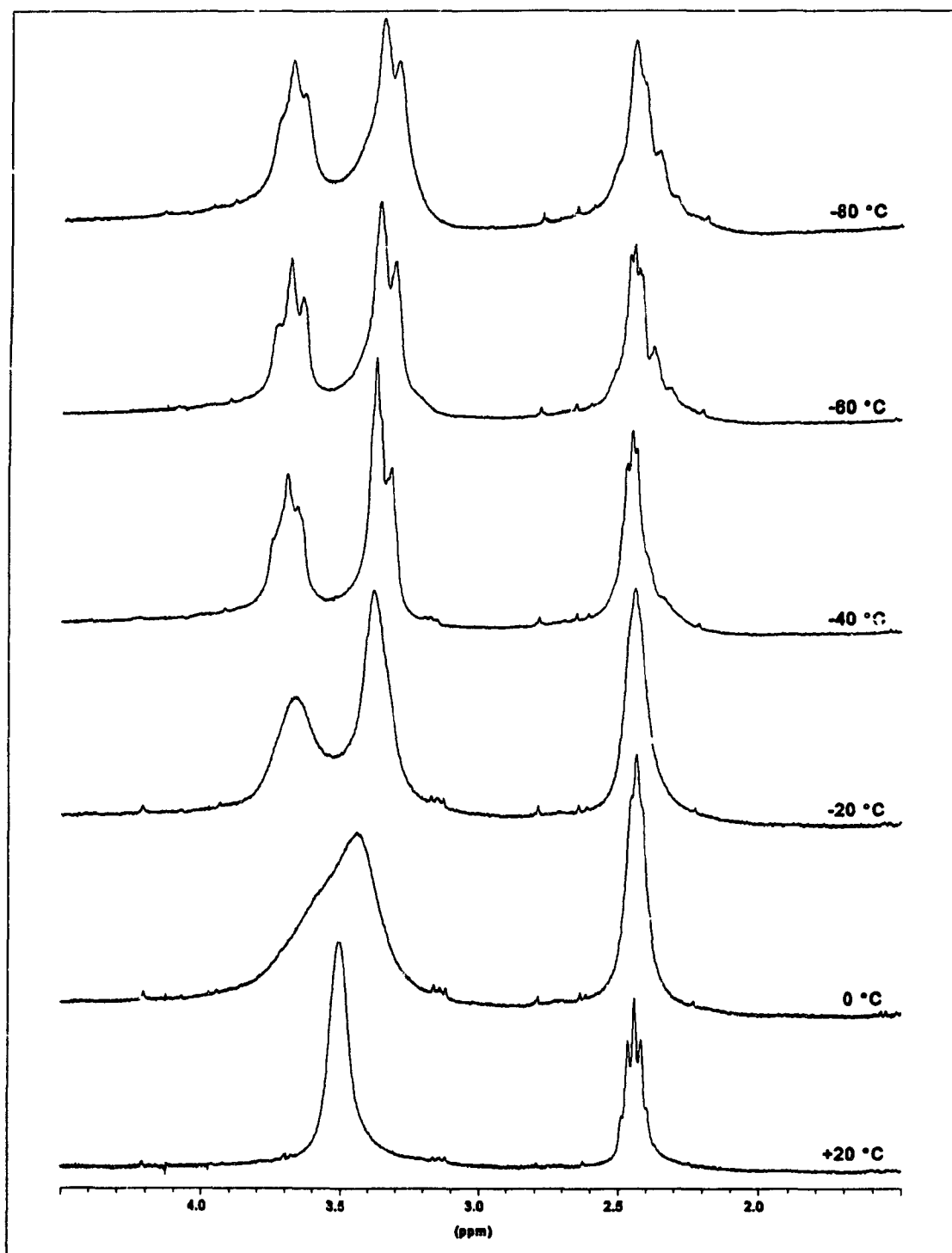


Figure 2.25: Variable temperature ^1H NMR spectra at 250 MHz of a reaction mixture containing the dication **63h** in CD_2Cl_2 .

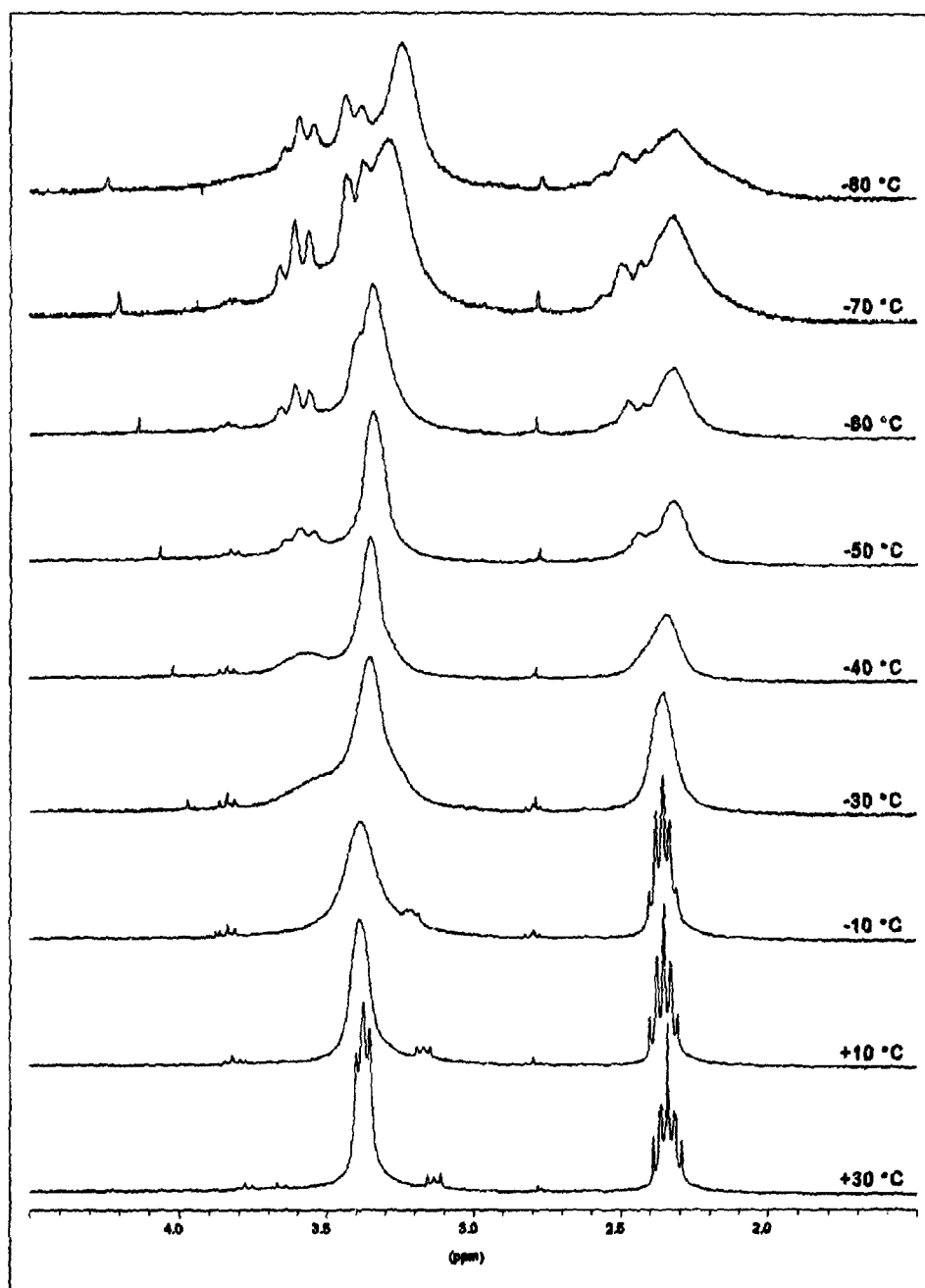
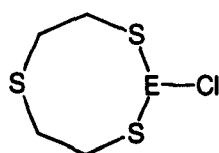


Figure 2.26: Variable temperature ^1H NMR spectra at 250 MHz of a reaction mixture containing the monocation **65h** in CD_2Cl_2 .

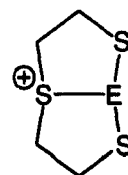
Although the solid state structure is unknown, the VT NMR data can be interpreted in the context of the arsolidinium species. The assignments made for compounds **63** and **65** are based on parallels with the analogous arsolidinium species **40** and **41**. It seems reasonable to assume that similar types of fluctuonality are occurring in the arsenanium compounds as occur in the arsolidinium derivatives (see Section **2.2.3.1**), however the evidence for dimers and complexes (**63** and **65**) or independent arsyliene systems (**62**) is not completely conclusive. Since there is no incipient dimerization present in the solid state structures of the chloroarsenanes **61**, it is possible that there is not as great a penchant for dimer formation as there is in the arsolidinium case.

2.4 Bicyclic Intramolecular Base Stabilized Arsenium Cations

Intramolecular Lewis base stabilization has recently come into vogue as a technique for isolating inherently unstable or highly reactive centres.¹⁵⁴ This led to the realization that similar techniques might allow for the formation of new arsyliene systems. The family of 2-chloro-1,3,6-trithia-2-pnicocane **66** compounds, with the exception of the phosphocane **66a**, has been known for quite some time,¹⁵⁵ and by examining the solid state structures of the arsocane **66b** and stibocane **66c**,¹⁵⁶ it was apparent that a weak cross-ring interaction occurs between the pnicogen centre and the cross-ring sulfur atom. Such a species is well suited to halide ion abstraction due to the length and weakness of the As–Cl bond, and produces the bicyclic pnicogenium cation **58**. The cation, although possessing a formal charge on the sulfur atom, exhibits a long cross-ring interaction and

**66**

a: E = P
b: E = As
c: E = Sb
d: E = Bi

**58**

may be viewed as a pnicyclidene with an intramolecular close contact.

The slow addition of dichloromethane solutions containing one molar equivalent of GaCl₃ to dichloromethane solutions of **66b** or **66c** result in immediate reaction as evidenced by the formation of a light coloured precipitate. Reaction is not observed for the bismocane **66d**, possibly due to its extreme insolubility. These precipitates are characterizable as the tetrachlorogallate salts of the 1-thionia-4,6-dithia-5-pnicobicyclo[3.3.0]octanes **58b** and **58c**, which are examples of a Lewis base stabilized arsyliidene and stibyliidene, respectively. More information on the stibyliidene **58c** is presented in Section 3.0.

The chloropnicocanes **66b** and **66c** in dichloromethane solution exhibit ABCD spin systems in the ¹H NMR spectra. A comprehensive analysis of their spectra reveals¹⁵⁷ an equilibrium between a chair-chair and two enantiomers of a boat-chair conformation at room temperature in solution. This motion may be frozen out at lower temperatures. Eight peak multiplets of equal integration ratio are observed for each proton signal and are located at 3.45, 3.29, 3.20, and 2.84 ppm for **66b**, and at 3.52, 3.40, 3.25, and 2.84 ppm for **66c**. The ¹³C signals are observed at 41.5 and 35.1 ppm for **66b** and 42.0 and 32.1 ppm for **66c**. Four poorly defined signals are observed at 2.13, 1.56, 1.27, and 0.86 ppm for CD₂Cl₂ solutions of **66d**, however these are at high field when compared to the arsenic and antimony derivatives and could result from slightly soluble impurities.

The solid state crystal structure of the chloroarsocane **66b**^{156(a)} shows a distorted boat conformation in which the “bow” and “stern” of the boat are parallel planes connected by a long As–S interaction. The crystal system consists of two enantiomeric species which each exhibit slight differences in certain As–S and C–C bond lengths and As–S–C and S–C–C bond angles. Also apparent is the fact that each of the four carbon atoms present in the structure is in a different, but similar, environment. Consistent with this is the solid state ¹³C CP MAS NMR spectrum, performed for the present study, which shows four

separate signals at 46.3, 41.1, 37.3, and 35.7 ppm.

In contrast to the relatively simple arrangement encountered in the solid state structure of **66b**, the chlorostibocene **66c**^{156(b)} crystallizes in a rather complex space group ($P2_12_12_1$), with two conformationally similar but different molecules present. The two different molecules, combined with the three screw axes in the crystal structure and the presence of various intermolecular contacts, produces numerous environments about the various carbon atoms. The solid state ¹³C CP MAS NMR spectrum of this compound, performed for the present study, exhibits six different signals, located at 47.6, 43.8, 40.5, $\approx$ 35.5 (sh), 34.5, and 32.7 ppm.

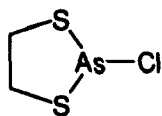
Although infrared spectral data has been previously reported for compounds **66b**

Table 2.19: As–Cl bond lengths (Å) and ν_3 stretching frequencies (cm⁻¹) for some chlorothiaarsines.

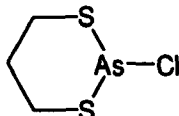
Compound	Bond Length	Frequency
38b	2.2525(8)	310
61b	2.223(2)	330
66b	2.356(3)	255

and **66c**,¹⁵⁵ use of caesium iodide optics in this study enabled observation of the As–Cl signal in **66b** at 255 cm⁻¹, however the Sb–Cl stretch in **66c** still lies beyond the effective range of the spectrometer (225 cm⁻¹). The observed As–Cl stretching frequency is

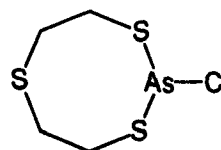
consistent with a long As–Cl bond. The importance of the transannular As---S interaction is apparent when comparing the frequency of the ν_3 stretch and the length of the As–Cl bond of **66b** with the related chlorothiaarsine species **38b** and **61b**, neither of which possesses the transannular interaction (Table 2.19). The presence of this cross-ring S→As electron donation radically weakens the As–Cl bond, resulting in a longer bond and a lower



38b



61b



66b

stretching frequency.

The ^1H NMR spectrum of the bicyclic cation **58b** reveals an ABCD spin system in dichloromethane- d_2 solution. All signals exhibit downfield shifts of between 0.66 and 0.99 ppm relative to the chloroarsocane **66b**, consistent with the formation of a cationic species, and the three upfield multiplets are now overlapping, resulting in two separate multiplets in the spectrum, centred at 4.11 and 3.83 ppm, with integration ratios of 1:3, respectively.

The crystal structure of **58b** is shown in Figure 2.19 in Section 2.2.4.2, and selected bond lengths and bond angles are shown in Tables 2.20 and 2.21 respectively. Two similar but different molecules of **58b** are present in the structure. Each molecule consists of two fused five membered rings and resembles a partially open book with an angle of approximately 100° (molecule 1) or 105° (molecule 2) between the front and back covers. Each of the rings consists of a planar four atom unit (planar to within a maximum of 6.4°) with the fifth atom displaced from planarity. In all cases, the displaced atom is the carbon bound to the dicoordinate sulfur and opposite the ring to the long As–S interaction [molecule 1, C(1) and C(4); molecule 2, C(5) and C(8)]. In molecule 1, one of the carbon atoms is displaced towards the interior of the book [C(1)] and the other is displaced

Table 2.20: Selected bond lengths (Å) for **58b**GaCl₄.

As(1)–S(1)	2.204(3)	S(3)–C(4)	1.76(1)
As(1)–S(2)	2.390(4)	S(4)–C(5)	1.82(2)
As(1)–S(3)	2.236(4)	S(5)–C(6)	1.79(1)
As(2)–S(4)	2.212(4)	S(5)–C(7)	1.79(1)
As(2)–S(5)	2.347(4)	S(6)–C(8)	1.76(2)
As(2)–S(6)	2.224(5)	C(1)–C(2)	1.49(2)
S(1)–C(1)	1.81(1)	C(3)–C(4)	1.51(2)
S(2)–C(2)	1.83(1)	C(5)–C(6)	1.53(2)
S(2)–C(3)	1.80(1)	C(7)–C(8)	1.54(2)

towards the exterior [C(4)], while in molecule 2, both carbon atoms are displaced towards the centre of the book. In molecule 1 all three of the As–S bonds are of significantly different lengths with the bond to the tricoordinate sulfur atom [As(1)–S(2), 2.390(4) Å] substantially longer than the other

Table 2.21: Selected bond angles (°) for **58b**GaCl₄.

S(1)–As(1)–S(2)	91.6(1)	S(4)–As(2)–S(5)	91.2(2)
S(1)–As(1)–S(3)	102.3(2)	S(4)–As(2)–S(6)	106.7(2)
S(2)–As(1)–S(3)	89.8(1)	S(5)–As(2)–S(6)	91.3(2)
As(1)–S(1)–C(1)	98.3(4)	As(2)–S(4)–C(5)	100.3(4)
As(1)–S(2)–C(2)	96.5(5)	As(2)–S(5)–C(6)	99.9(5)
As(1)–S(2)–C(3)	99.4(5)	As(2)–S(5)–C(7)	99.4(5)
As(1)–S(3)–C(4)	98.9(5)	As(2)–S(6)–C(8)	102.7(5)
C(2)–S(2)–C(3)	102.5(7)	C(6)–S(5)–C(7)	106.2(7)
S(1)–C(1)–C(2)	109(1)	S(4)–C(5)–C(6)	110(1)
S(2)–C(2)–C(1)	115(1)	S(5)–C(6)–C(5)	115.0(9)
S(2)–C(3)–C(4)	114(1)	S(5)–C(7)–C(8)	114(1)
S(3)–C(4)–C(3)	113(1)	S(6)–C(8)–C(7)	112(1)

two [As(1)–S(1), 2.204(3) Å; As(1)–S(3), 2.236(4) Å]. Molecule 2 exhibits more symmetry and the two shorter As–S bonds are crystallographically identical in length [As(2)–S(4), 2.212(4) Å; As(2)–S(6), 2.224(5) Å]. The bond to the tricoordinate sulfur atom is substantially longer [As(2)–S(5), 2.347(4) Å] than those to the dicoordinate sulfur atoms but is still slightly shorter than the corresponding bond in molecule 1. Both interactions are substantially shorter than that observed in the chloroarsocane **66b** [2.719(3) Å],^{156(a)} but are considerably longer than normal As–S single bonds (2.20 to 2.27 Å).¹⁰⁹ All other As–S bond lengths in **58b** lie within this range. These long interactions can be viewed as donation of a lone pair of electrons on the sulfur atom into the formally vacant 4*p*-orbital on the As centre.

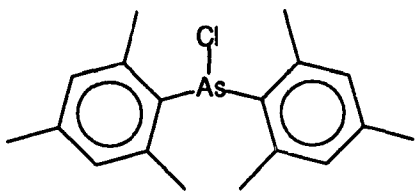
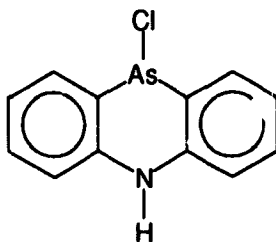
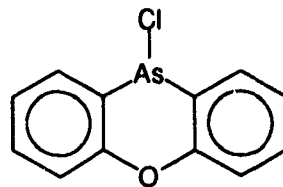
The arsenic atoms in molecules 1 and 2 each have close contacts to two chlorine atoms of the tetrachlorogallate anions. In all cases, these contacts are within the sum of the van der Waals radii for the atoms involved (As, 2.0 Å; Cl, 1.80 Å),⁸⁴ ranging in length from 3.413(7) to 3.670(5) Å [molecule 1, As(1)---Cl(3), 3.461(4) Å, As(1)---Cl(1), 3.505(4) Å; molecule 2, As(2)---Cl(8), 3.413(7) Å, As(2)---Cl(6), 3.670(5) Å]. These

contacts impose an octahedral geometry around each arsenic atom, with two chlorine atoms, three sulfur atoms, and a lone pair of electrons in the coordination sphere. Close contacts are also observed between chlorine atoms and all sulfur atoms, except for S(5), with the shortest of these contacts, Cl(1)---S(3), being 3.479(5) Å. The presence of these contacts provides additional stability for the cationic arsyldene system (see Section 2.2.2.1).

As a result of the slightly different structures of molecules 1 and 2 and the way the molecules pack in the crystal lattice, a variety of different environments for the carbon atoms are encountered. This is reflected in the solid state ^{13}C CP MAS NMR spectrum of **58h** which shows a complicated pattern with at least five separate carbon chemical shifts present (54.0, 52.9, 49.0, 43.5, and 41.0 ppm).

2.5 Other Arsenium Cations

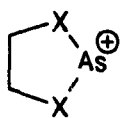
Preliminary investigations have begun into other types of arsyldene systems. The familiar halide ion abstraction technique utilizing GaCl_3 to remove chloride from each of the three chloroarsines dimesitylchloroarsine (Mes_2AsCl) **67**, 10-chloro-5,10-dihydrophenarsazine (adamsite) **68**, and 10-chloro-5,10-dihydrophenoxarsine (phenoxarsine chloride) **69** has been performed with varying results. These three species were chosen due to their ready availability and their potential to offer stabilization to an arsyldene centre through both steric protection and delocalization, with the former mode

**67****68****69**

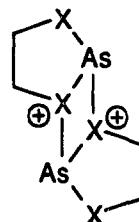
being dominant for **67** and the latter for **68** and **69**. Dimesitylchloroarsine is available commercially and adamsite¹⁵⁸ and phenoxarsine chloride¹⁵⁹ have both been known for some time and are easily synthesized.

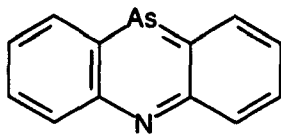
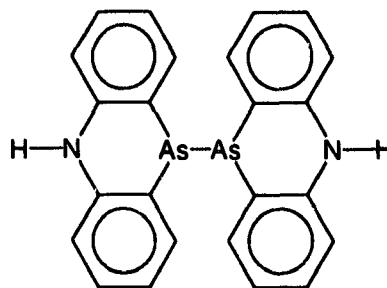
Quickly mixing dichloromethane solutions containing equimolar quantities of Mes_2AsCl and GaCl_3 results in an immediate reaction as evidenced by a colour change to deep red, presumably due to Mes_2As^+ , however the colour fades within seconds. Evidently the stabilizing effects of the mesityl groups are not sufficient to support or protect a naked arsyldiene centre. Further reaction may involve some type of dimerization or oligomerization, or, more likely, reaction with the solvent.¹³³ The stability of smaller arsyldiene species, such as **39**, comes about through formation of a weak dimer complex **40** involving mutual donor-acceptor interactions, as well as through π -donation from the electron rich atoms adjacent to the arsyldiene (see Section 2.2.2.3). Due to the steric demands of the mesityl groups, the likelihood of dimerization is lessened, yet still possible. However, the type of mutual donor-acceptor interactions observed in **40** are not possible due to the lack of a suitable donor species.

Addition of a dichloromethane solution containing a slight molar excess of GaCl_3 to a dichloromethane solution of adamsite results in an immediate reaction as evidenced by a dramatic colour change to intense purple. The ^1H NMR spectrum of the reaction mixture exhibits four multiplets, of equal integration, located at 8.84, 8.59, 8.29, and 7.79 ppm. The ^{13}C NMR spectrum shows signals at 158.7, 139.4, 135.9, 134.7, 125.0, and 123.3

**39**

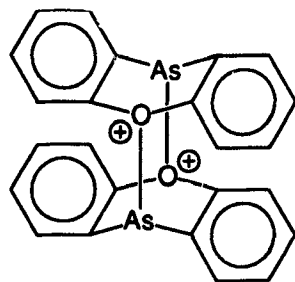
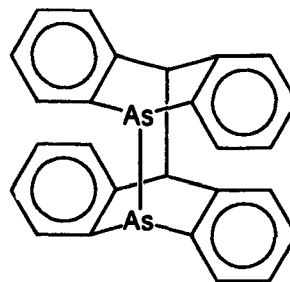
a: $\text{X} = \text{N}(\text{Me})$
b: $\text{X} = \text{S}$

**40**

**70****71**

ppm. These spectra are consistent with formation of the fully conjugated compound phenarsazine **70**, which is expected to exhibit more shielded signals by virtue of the increased delocalization present in a fully conjugated system. Phenarsazine was reported as long ago as 1921,¹⁶⁰ however a more recent study has shown that the compound identified as phenarsazine was the dimeric species 10,10'-bis(5,10-dihydrophenarsaziny) **71**.¹⁶¹ In the present case, phenarsazine could be formed through an initial step involving chloride ion abstraction to form an arsyldene system. The resulting arsyldene species is apparently a sufficiently strong acid to protonate the tetrachlorogallate anion to form HGaCl_4 , which presumably disproportionates to GaCl_3 and HCl . Previous attempts to carry out chloride ion abstraction on adamsite have utilized bases such as pyridine¹⁶² or 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU)¹⁶³ without success. Gallium trichloride is a very powerful chloride ion abstracting reagent and seems to perform as expected.

Attempts to isolate **70** from solution have produced only deep purple crystals which are shown by X-ray crystallography to consist of two molecules of **68** to one molecule of benzene. It is interesting to note that benzene is not used in the production or purification of **68**, nor is it used at any time during the reaction of **68** with GaCl_3 . The surprising presence of benzene in the crystal lattice indicates that the phenarsazine **70** decomposes during crystallization or isolation to produce a molecule of benzene, although the pathway of such decomposition is unknown. Exposing this purple material to the air results in an

**72****73**

immediate colour change to bright yellow, reminiscent of the adamsite starting material.

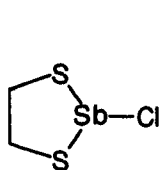
Phenoxarsine chloride **69** might be expected to behave in a fashion similar to that of adamsite when reacted with GaCl_3 , however this appears not to be the case. Slow addition of a dichloromethane solution of phenoxarsine chloride to a dichloromethane solution containing an equimolar quantity of GaCl_3 produces an immediate deep red colour. After reaction with GaCl_3 the NMR spectra become much more complex than those of **69**, with the ^1H spectrum exhibiting a very broad and very complex multiplet stretching from 7.82 to 6.96 ppm and the ^{13}C spectrum showing at least 15 different signals, between 136.4 to 117.3 ppm, within the range expected for aromatic carbon atoms (110 to 150 ppm).¹²¹

Whereas the cation of adamsite appears to satisfy the coordinative unsaturation at the arsenic centre by losing an acidic proton and forming a delocalized Hückel system, it seems likely that the cation of phenoxarsine chloride solves the same problem through some sort of dimerization or oligomerization. The analogue of the dimer **71** is a possible candidate for formation. Also possible is the head-to-tail dimeric compound **72** which is held together through mutual acid-base interactions, much as are the dimers **40**. Such a structure is reminiscent of the head-to-head dimerization observed for 9-arsaanthracene **73**.¹⁶⁴

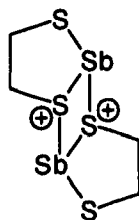
3.0 Stibylidenes

Preliminary investigations into species containing “naked” (without the benefit of steric or Hückel stabilizing factors) stibylidene centres support the observation that stibylidenes rely on coordination to provide them with their stability. Systems observed in this study possess significant amounts of inter- or intramolecular coordination in the form of electron rich atoms, which act as Lewis bases, donating electrons to the Lewis acidic stibylidene centres.

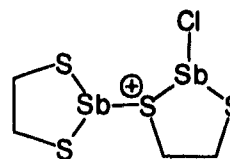
Three different types of stibylidenes have been examined, all of them analogues of arsylienes reported here. The first of these species is formed through the addition of a dichloromethane solution of 2-chloro-1,3-dithia-2-stibolidine **74** to a dichloromethane solution of GaCl₃ (equimolar quantities). The ¹H and ¹³C NMR spectra of the reaction mixture (*vide infra*) can be considered to be consistent with the formation of the dimeric dication **75**, directly analogous to the dimeric arsyliene species **40b**. Precipitation of a yellow powder from the solution upon removal of most of the solvent is irreversible, and a crystal structural determination of a single isolated crystal (*vide infra*) indicates that the monocationic complex **76**, directly comparable to the arsyliene **41b**, is produced. Such a



74



75



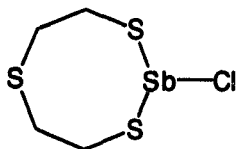
76

species can be viewed as a stibolidinium cation (stibylidene) complexed to a molecule of chlorostibolidine. The IR spectrum of the yellow powder is consistent with structure **76**, exhibiting a strong signal at 370 cm⁻¹, characteristic of GaCl₄⁻,⁹⁹ and a weaker signal at 268 cm⁻¹, assignable to the Sb-Cl stretch. The Sb-Cl stretch in the chlorostibolidine **74** is

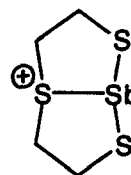
observed at 259 cm^{-1} .¹⁶⁵

A second stibylidene species may be formed in a fashion similar to the first, except that two equivalents of **74** are used and a solution of GaCl_3 is added to a solution or suspension of **74**. The ^1H and ^{13}C NMR spectra of the reaction mixture are consistent with the formation of **76**, the product expected by analogy with the corresponding arsyliidene reaction. Removal of the majority of the solvent *in vacuo* from the reaction mixture results in the irreversible precipitation of a green powder. IR data of the green powder is not consistent with the structure of **76**, the Sb–Cl signal being noticeably absent, but does resemble the spectrum of the arsyliidene dimer **40b**, and likely corresponds to the stibylidene dimer **75**. Solid state ^{13}C NMR spectroscopy of this species is also consistent with structure **75**, showing only two signals (*vide infra*).

The third stibylidene species is the intramolecularly base stabilized cation **58c**, analogous to the arsyliidene **58b**, which is made by addition of a dichloromethane solution of GaCl_3 to a suspension containing an equimolar quantity of the chlorostibocene **66c**. The chlorostibocene is taken up into solution during the course of addition and then a buff coloured precipitate is formed. Solubility of this species is very low and solution NMR data is difficult to obtain, however solid state CP MAS ^{13}C NMR shows a pattern which is very similar to that observed for the arsyliidene derivative **58b** GaCl_4 (*vide infra*). In addition, the carbon and hydrogen elemental analyses are consistent with the composition **58c** GaCl_4 and the IR spectrum is very similar to that of the corresponding arsyliidene.



66c



58c

3.1 Solid State Structural Features

Unfortunately it is difficult to crystallize the above stibylidene species due to their extremely low solubility. In one experiment Victoria Aylett¹⁶⁶ was able to obtain a single small crystal from the product of a 1:1 reaction of **74** and GaCl₃ that was characterized crystallographically as **76**GaCl₄.

Table 3.1: Selected bond lengths (Å) for compound 76 GaCl ₄ .		
Sb(2)–Cl(1)	2.453(4)	
Sb(1)–S(1)	2.380(4)	
Sb(1)–S(2)	2.423(4)	
Sb(1)–S(3)	2.659(4)	
Sb(2)–S(3)	2.535(4)	
Sb(2)–S(4)	2.396(4)	
S(1)–C(1)	1.81(2)	
S(2)–C(2)	1.83(2)	
S(3)–C(3)	1.83(1)	
S(4)–C(4)	1.81(2)	
C(1)–C(2)	1.38(2)	
C(3)–C(4)	1.53(2)	

Selected bond lengths and bond angles for **76**GaCl₄ (Figure 3.1) are given in Tables 3.1 and 3.2 respectively. Cation **76** is a bicyclic monocation made up of two five-membered rings with a single inter-ring Sb–S connection. The two rings adopt an eclipsed type structure with one ring over top of the other. Disorder in the structure is encountered at C(1) and C(2), and this is responsible for the large ellipses in the ORTEP structure as well as the anomalous bond lengths and angles about

these two atoms. The structure of **76** is remarkably similar to that of **41b**, which suffers from disorder at the same two atoms, both adopting a *Pna2*₁ space group.

The intra-ring Sb–S bond is a weak interaction (2.66 Å). Published data on Sb–S

Table 3.2: Selected bond angles (°) for compound 76 GaCl ₄ .			
Cl(1)–Sb(2)–S(3)	86.4(1)	Sb(1)–S(3)–Sb(2)	99.3(1)
Cl(1)–Sb(2)–S(4)	97.3(1)	Sb(1)–S(3)–C(3)	108.0(4)
S(1)–Sb(1)–S(2)	89.5(1)	Sb(2)–S(3)–C(3)	100.8(5)
S(1)–Sb(1)–S(3)	98.3(1)	Sb(2)–S(4)–C(4)	97.9(5)
S(2)–Sb(1)–S(3)	91.9(1)	S(1)–C(1)–C(2)	119(1)
S(3)–Sb(2)–S(4)	86.6(1)	S(2)–C(2)–C(1)	117(1)
Sb(1)–S(1)–C(1)	98.4(6)	S(3)–C(3)–C(4)	110.8(9)
Sb(1)–S(2)–C(2)	99.0(6)	S(4)–C(4)–C(3)	113(1)

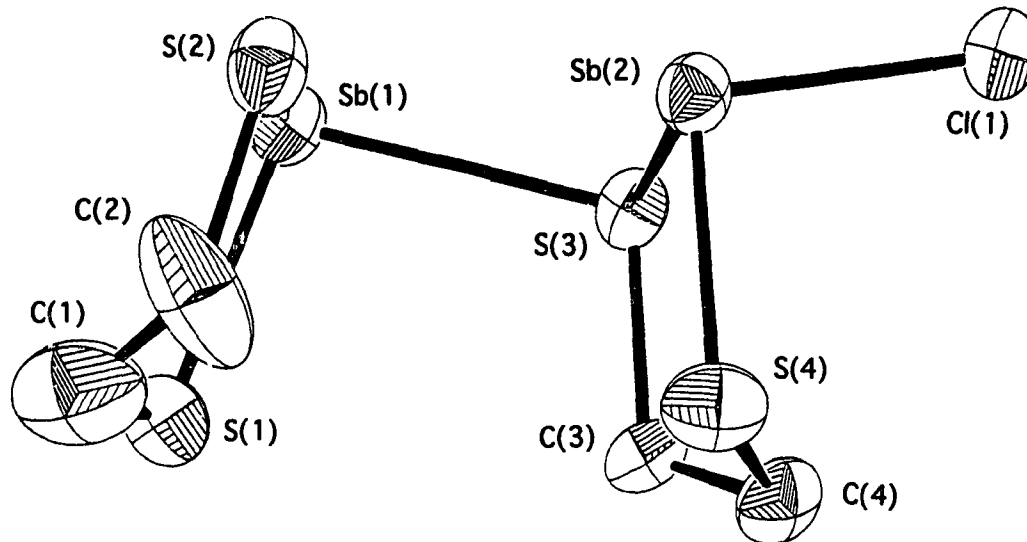


Figure 3.1: ORTEP view of the monocation **76** (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity.

bonds is limited, however single bonds tend to lie within the range 2.40 to 2.45 Å.^{156(b),167} Of the four intra-ring Sb–S bonds present in **76**, the three adjacent to dicoordinate sulfur centres lie at the lower end of this range (avg. 2.400 Å) and are comparable in length to the Sb–S single bonds observed in the chlorostibolidine **74** (avg. 2.405 Å).^{167(a)} Two of the three bonds [Sb(1)–S(1) and Sb(2)–S(4)] are crystallographically identical in length and the other [Sb(1)–S(2)] is slightly longer. The fourth intra-ring Sb–S bond [Sb(2)–S(3)], which is adjacent to the tricoordinate sulfur atom, is significantly longer.

Three interactions are observed between each antimony atom and chlorine atoms of the anions or another cation, giving them an octahedral coordination sphere. These interactions range in length from 3.160(4) Å [Sb(1)···Cl(1)'] to 3.669(5) Å [Sb(1)···Cl(3)'] and are well within the sum of the van der Waals radii for antimony and sulfur (Sb, 2.2 Å; Cl, 1.80 Å).⁸⁴ Contacts are not observed to any of the sulfur atoms. Such contacts provide stability to the low coordinate antimony centres through donation of electron density and have been previously encountered in stibylidene systems.⁷¹

Solid state ^{13}C CP MAS NMR studies have been performed on each of the three stibylidene species. The yellow powder isolated from the 1:1 reaction of **74** with GaCl_3 exhibits only a single broad and ill-defined signal centred at 46.6 ppm and provides little information. The green solid recovered from the 2:1 reaction of **74** with GaCl_3 shows two peaks, at 48.1 and 46.0 ppm, consistent with the structure of **75**, despite the fact that the solution NMR of the reaction mixture indicates that the product is **76**. The spectrum of the bicyclic stibylidene **58c** exhibits a complex spectrum with at least five carbon signals (50.2, 48.2, 45.9, 43.2, and 38.1 ppm) and is similar to that of the chlorostibocene precursor **66c** (see Section 2.4) but is shifted downfield by approximately 6 ppm, as expected for a cationic species. The complexity of the signals is likely the result of the presence of two or more different molecules of **58c** in the crystal structure, as encountered in **66c**.

3.2 Solution ^1H and ^{13}C NMR Features

Solution NMR data from reaction mixtures is consistent with the formation of the products analogous to those observed from the corresponding arsyliidene reactions (*i.e.* 1:1 reaction gives **75**; 2:1 reaction gives **76**), in contrast to the materials that are isolated from solution. The isolated products are extremely insoluble and it has not been possible to obtain NMR data on the redissolved material.

Table 3.3: Solution ^1H and ^{13}C NMR chemical shifts (δ , ppm, CD_2Cl_2) of the chlorostibolidine **74** and proposed stibylidenes **75** and **76** (referenced to TMS and calibrated to the internal solvent signal).

Compound	^1H	^{13}C
74	3.81	43.3
75 (1:1 reaction)	4.15	43.5
76 (2:1 reaction)	3.93	43.3

Dichloromethane- d_2 solutions of the species proposed as cations **75** and **76** exhibit only single lines in the ^1H NMR spectrum and show distinct downfield shifts of between 0.12 and 0.34 ppm when compared to the chlorostibolidine **74** (Table 3.3). The chemical shift of the monocationic species **76** lies

between those of the chlorostibolidine **74** and the dication **75**. The ^{13}C NMR data is less informative, exhibiting only slight chemical shift differences.

Variable temperature NMR data is very difficult to obtain on these species due to their low solubility, especially at reduced temperatures. Nevertheless, it is possible to observe peak broadening in the case of the 1:1 reaction, eventually resulting in coalescence at $-70\text{ }^{\circ}\text{C}$ and the emergence of two separate peaks, both of which are broad and ill-defined, below this temperature. Such behaviour is also observed, albeit very close to the freezing point of the solvent, in the arsyliene analogue of **75**.

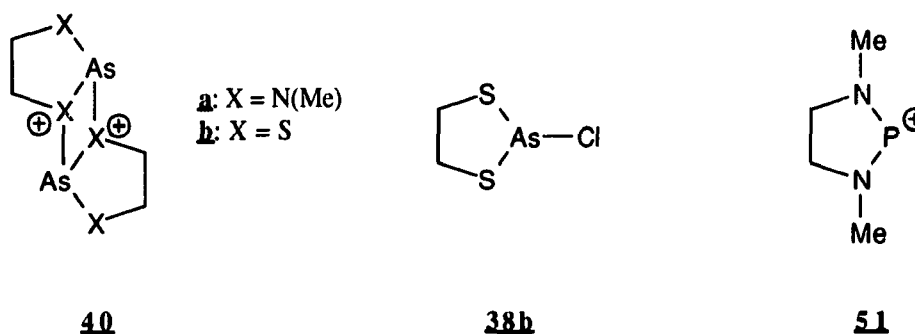
The ^1H NMR spectrum of the reaction mixture of the bicyclic stibylidene **58c** exhibits a number of very weak signals, with the strongest being an ill-defined group at 3.77 ppm. A saturated CD_2Cl_2 solution of redissolved **58c** shows four broad peaks (3.93, 3.79, 3.52, and 3.35 ppm; 1:1:1:1 integration ratio) which are downfield of the three multiplets observed for the ABCD spin system of the chlorinated precursor **66c** (3.46, 3.25, and 2.84 ppm), consistent with the formation of a cationic species.

4.0 Mass Spectrometry of Pnicogylidenes

Since little is known about the gas phase behaviour of pnicogylidenes, a mass spectrometric study of these species was bound to provide interesting results. The phospholidinium **51**GaCl₄ and the arsolidiniums **40**(GaCl₄)₂ were deemed suitable for this study because of their relative ease of handling. For comparison, the chlorinated precursor compounds **38b** and **52** were also examined. The results were interesting and often unexpected.

4.1 Gas Phase Study of Pnicolidines

In a study of the gas phase characteristics of the dimeric arsyldene species **40**, electron impact mass spectrometry (EI-MS) was performed on crystalline samples of the tetrachlorogallate salts of these compounds, as well as on the chlorinated precursor of **40b**, the dithiachloroarsolidine **38b**. The analogous monomeric phosphylidene species **51** was



also examined. The milder ionization technique of Fast Atom Bombardment (FAB) was not suitable for studying these compounds as the matrices necessarily employed for FAB, such as glycerol and thioglycerol, react rapidly with **40** and **51**.

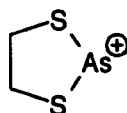
EI-MS involves harsh ionization conditions and this often results in fragmentation of the molecular species. Such fragmentation often provides information about the molecular structure as well as the relative strengths of the bonds present. Of interest is the nature of the weak dimeric linkages encountered in the solid state of **40**, as determined by

X-ray crystallographic studies (see Section [2.2.1.1](#)).

Previous studies involving pnicylidene species,¹⁶⁸ as well as other nonmetal cations,¹⁶⁹ with complex polyhalogenated anions (such as AlCl_4^- , AlBr_3Cl^- , and AsF_6^-) have revealed a tendency of these compounds to reabstract halides from the anions under EI-MS conditions. This may be a result of reaction of the cation and anion within the mass spectrometer source, or it may be due to hydrolysis occurring while loading the samples into the probe. The current study included efforts to ensure the viability of the sample and to limit hydrolysis as much as possible. To this end, all samples were prepared in a drybox atmosphere and then loaded into the sample probe which was enclosed in a glove bag and under a positive pressure of dry nitrogen. Spectra of the pnicylidene compounds [40](#) and [51](#) showed peaks for the radical cations of the chlorinated precursors, produced as a result of the reabstraction of a chlorine atom from the tetrachlorogallate anion, of from 25 to 50% of the relative intensity of the pnicylidene peak. This allows the tentative conclusion that the reabstraction encountered with these types of materials occurs primarily in the source of the mass spectrometer.

The EI-MS of the neutral chloroarsolidine [38b](#) (Figure 4.1) exhibits a base peak at 167 amu attributable to the monomeric arsyldene species [39b](#), the result of loss of chloride from [38b](#). The peak for the parent ion, at $m/z = 202$, possesses a relative intensity of 54%. This peak also exhibits an obvious chlorine isotope satellite at 204. The only other prominent peak occurs at 107 amu (50%) and is assigned to $\text{As}=\text{S}^+$.

The spectrum of [40b](#)(GaCl_4)₂ (Figure 4.2) shows similarities to the spectrum of [38b](#) (Table 4.1). Prominent peaks are again apparent for [38b](#), [39b](#), and $\text{As}=\text{S}^+$, however



[39b](#)

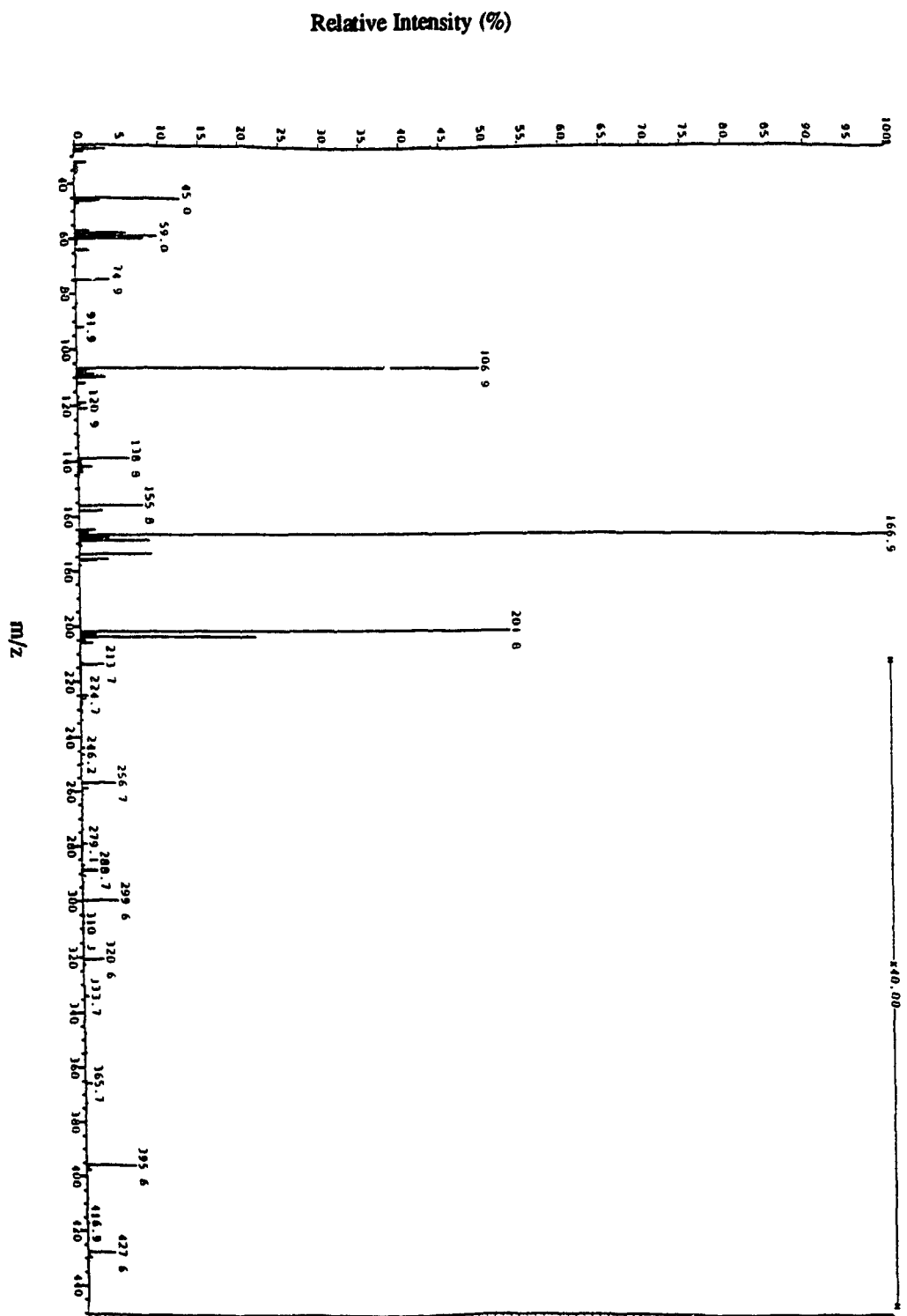


Figure 4.1: Low resolution 70eV EI-MS of 38b.

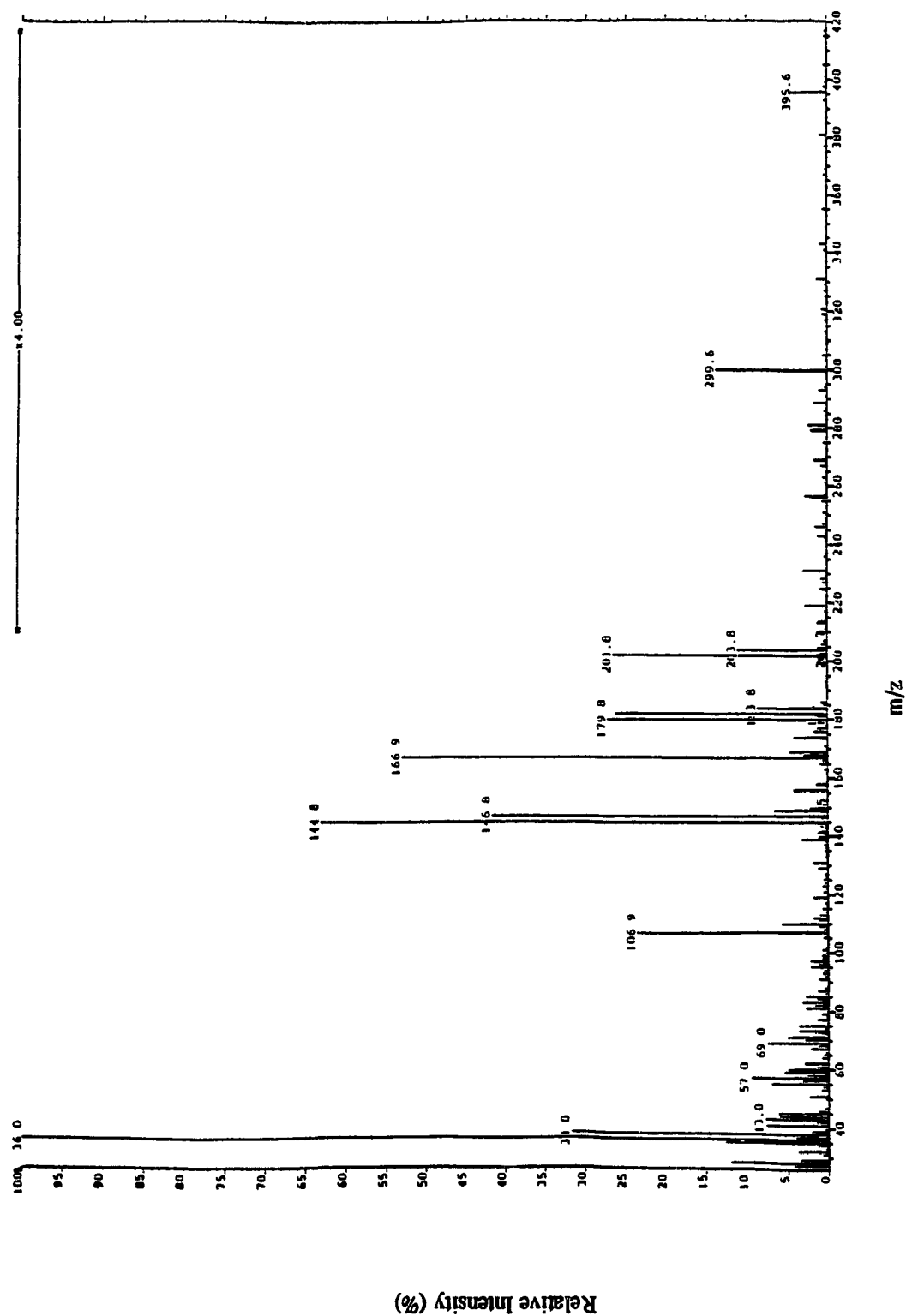


Figure 4.2: Low resolution 70eV EI-MS of $40b(GaCl_4)_2$.

Table 4.1: EI-MS peak summary for **40b**(GaCl₄)₂ and **38b**.

<i>m/z</i>	Relative Intensity (%) 40b	Relative Intensity (%) 38b	Assignment
300	14		39b + AsSC ₂ H ₂
202	27	54	38b
180	23		AsCl ₃ ⁺
167	53	100	39b
145	63		AsCl ₂ ⁺
107	23	50	As≡S ⁺
38	32		H ³⁷ Cl ⁺
36	100		H ³⁵ Cl ⁺

there are a number of more intense peaks present which are not observed in the spectrum of **38b**. The most notable amongst these is the base peak, occurring at $m/z = 36$, which is attributable to HCl⁺, and its chlorine isotope satellite at 38 amu. Also prominent in the spectrum are peaks attributable to AsCl₂⁺ and AsCl₃⁺. Both peaks are accompanied by the appropriate chlorine isotope satellite peaks. Since the only source of chlorine in these samples is the tetrachlorogallate anion, either significant fragmentation of this species must occur, or there is some sort of reaction between cation and anion. An additional signal occurs at $m/z = 300$, at a significantly higher mass than that of **38b**, and may be a result of either loss of H₂S from the dimer **40b**, or the addition of an AsSC₂H₂ fragment to the monomer **39b**. The presence of the species HCl and AsCl₃ is further evidence for rearrangement reactions occurring within the sample probe and not prior to introduction, since both species are unlikely hydrolysis products.

Interestingly, the spectrum of **40b**(GaCl₄)₂ shows no signal attributable to the dimeric species. Though not seen in the EI-MS, the electrospray mass spectrum (ESMS) of a dichloromethane solution of **40b**(GaCl₄)₂, a technique which uses a much milder ionization method than that of EI-MS, reveals a singly charged dimeric species, with a peak at 334 amu (see Section 2.2.3.2). Additionally, the presence of the dicationic dimer

Table 4.2: EI-MS peak summary for **40a**(GaCl₄)₂.

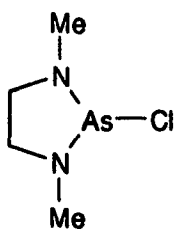
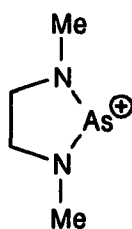
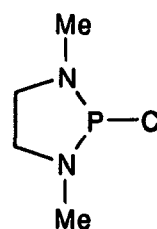
<i>m/z</i>	Relative Intensity (%)	Assignment
196	26	38a ⁺
161	52	39a
153	100	C ₂ H ₅ NAsCl ⁺
118	44	C ₂ H ₅ NAs ⁺
104	7	CH ₃ NAs ⁺
42	54	C ₂ H ₄ N ⁺

would result in a weak half integral isotope peak in the EI-MS at *m/z* = 167.5. The absence of these two peaks indicates that the energy required to generate the gas phase ions of these compounds, a requirement for EI-MS, is sufficient to break

the inter-monomer connections holding the dimers together and to produce monomeric arsyldene cations in the gas phase.

The EI-MS of **40a**(GaCl₄)₂ (Figure 4.3), similar to that of **40b**(GaCl₄)₂, shows no evidence of the dimer in the gas phase. The base peak of the spectrum is found at *m/z* = 153 (Table 4.2), and is attributed to the radical cation C₂H₅NAsCl⁺, which results from the loss of C₂H₅N from **38a**. The chlorine isotope peak at 155 amu is also apparent. Other prominent peaks in the spectrum include those attributed to **39a**, C₂H₄N⁺, C₂H₅NAs⁺, and the radical cation of **38a**. A weaker peak of interest occurs at 104 amu and is assigned to CH₃NAs⁺.

The phosphylidene salt **51**GaCl₄ is known to be a monomer in the solid state.¹³³ Consistently, there are no observed signals for a dimer in the EI-MS (Figure 4.4). Not surprisingly, the base peak of the spectrum occurs at *m/z* = 117 and is assigned to **51**

**38a****39a****51**

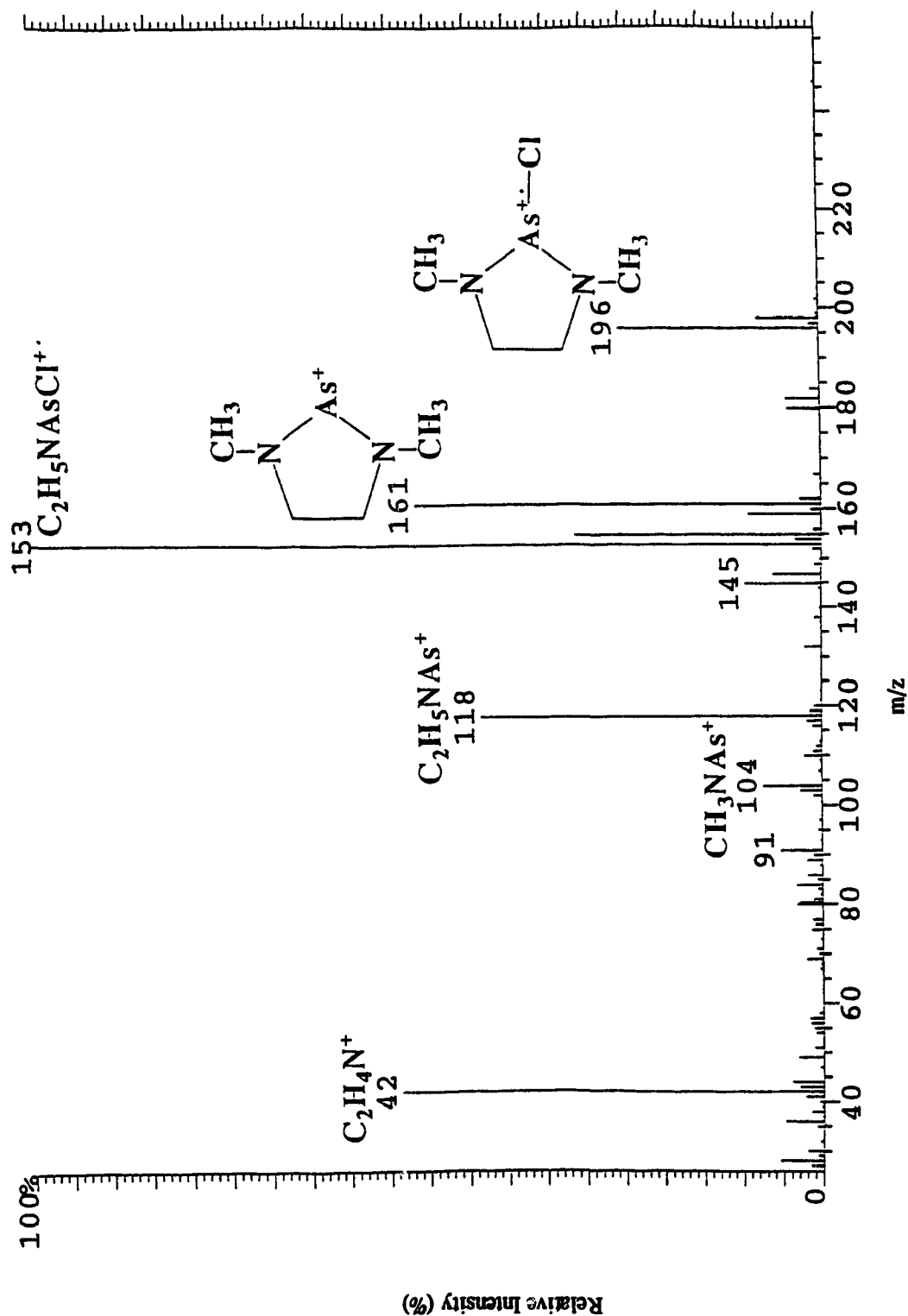


Figure 4.3: Low resolution 70eV EI-MS of 40a(GaCl₄)₂.

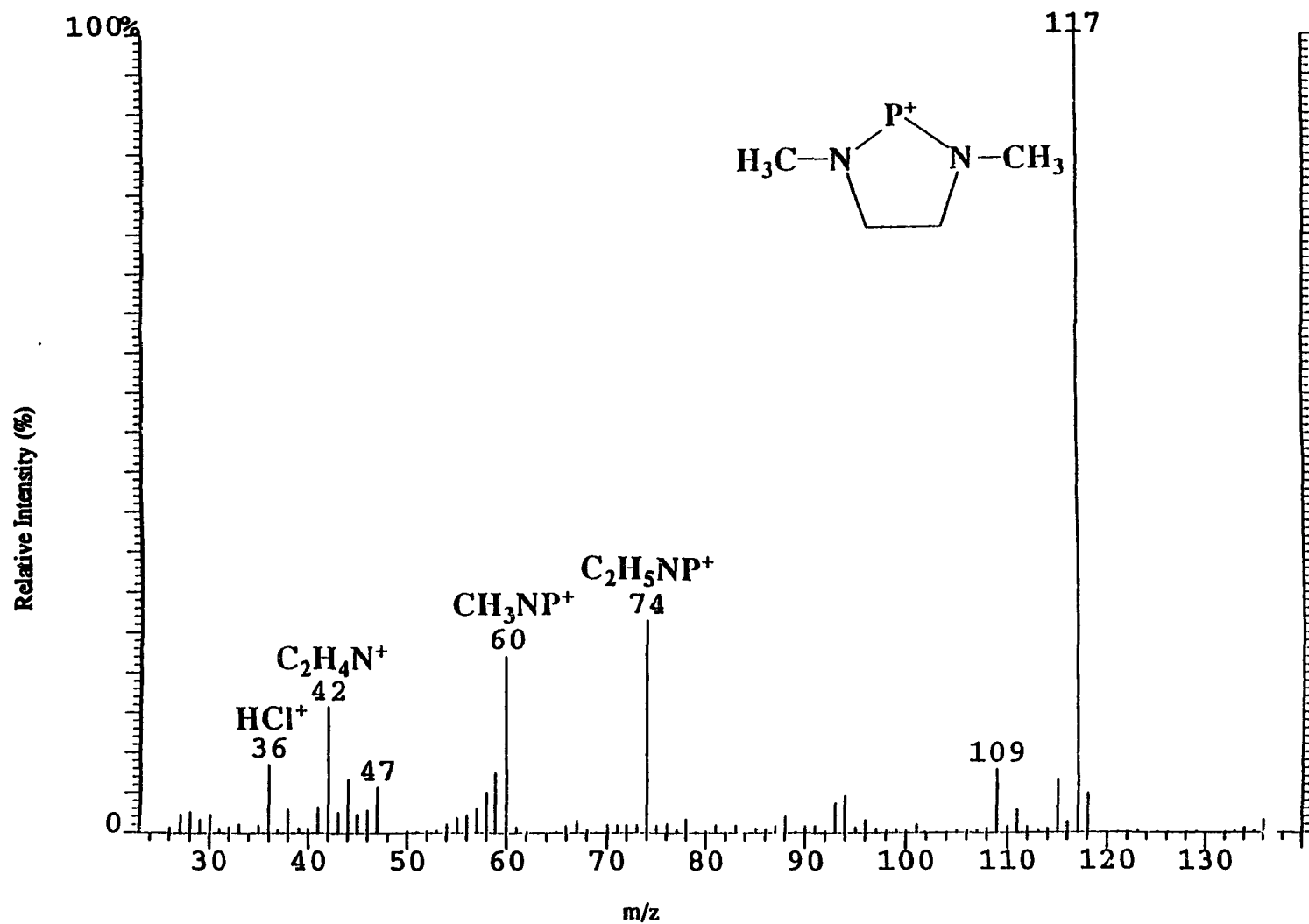


Figure 4.4: Low resolution 70eV EI-MS of $^{51}\text{GaCl}_4$.

Table 4.3: EI-MS peak summary for **51**GaCl₄.

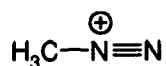
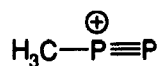
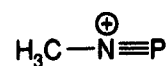
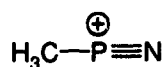
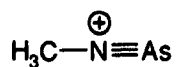
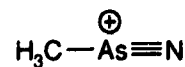
<i>m/z</i>	Relative Intensity (%)	Assignment
152	20	52
117	100	51
74	27	C ₂ H ₅ NP ⁺
60	25	CH ₃ NP ⁺
42	16	C ₂ H ₄ N ⁺
36	9	HCl ⁺

(Table 4.3). Other peaks of interest include those produced by C₂H₅NP⁺ and C₂H₄N⁺. A peak corresponding to the chlorinated precursor **52** is present (152 amu) as well as a weak signal for HCl⁺. Of interest is the peak at

m/z = 60, which has been assigned to CH₃NP⁺. All of these signals are directly comparable to those observed in the spectrum of the analogous arsyldiene species **40a** (Figure 4.3).

4.2 Identification of MeNP⁺ and MeNAs⁺ in the Gas Phase

Ab initio molecular orbital calculations on the phosphorus analogues of methyldiazonium ions¹⁷⁰ **77** and the protonated forms¹⁷¹ of N₂, P₂ and PN have recently been reported. Ion **78** was named diphosponium by analogy with **77**, while **79** and **80** were described as phosphoazonium (alternatively described as iminophosphenium)¹⁷² and azophosphonium ions, respectively. Theoretical studies¹⁷⁰ indicate that both **78** and **79** should be stable and may be detectable in the gas phase. Theoretical methyl cation affinities

**77****78****79****80****81****82**

(MCA, the reaction energy for $\text{CH}_3\text{XY}^+ \rightarrow \text{CH}_3^+ + \text{XY}$) indicate that CH_3NP^+ (**79**, MCA = 420 kJmol^{-1}) should exhibit substantially greater thermochemical stability than CH_3PN^+ (**80**, MCA = 176 kJmol^{-1}).¹⁷¹ The very small calculated energy barrier (2.5 kJmol^{-1}) between **79** and **80**, indicates that, if **80** is formed, it quickly isomerizes to **79**.

Alkyldiazonium ions such as **77**, are reactive species known to exist in superacid media¹⁷³ and in the gas-phase,¹⁷⁴ and have been described theoretically.¹⁷⁵ The mass spectrum of the methyldiazonium ion was first reported about 40 years ago,¹⁷⁶ but the other ions **78** to **82** are not yet known. The present studies on compounds **40a** and **51** have revealed the presence of both **81** and **79**, respectively, in the gas phase. The sterically imposing substituent 2,4,6-tri-*tert*-butylphenyl (super-mesityl or Mes*), has been employed in place of methyl to stabilize the only isolated derivative of **79**.^{13,145,172,177}

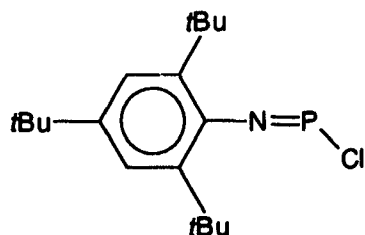
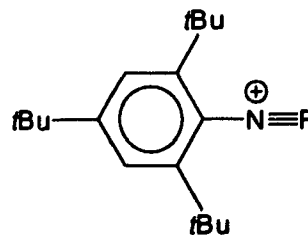
While examining the low coordinate pnictogen compounds **40** and **51** (*vide supra*) their potential as precursors for novel ionic species, such as **78** to **82**, was recognized.¹⁷⁸ Previous MS studies of these types of compounds have been rare since most are highly moisture sensitive and difficult to work with. The peaks exhibited by the electron impact mass spectra of **51** and **40a** (at $m/z = 60$ and 104 , respectively) were identified and tentatively assigned to the species $\text{CH}_3\text{N}^+\equiv\text{P}$, **79**, and $\text{CH}_3\text{N}^+\equiv\text{As}$, **81**. High resolution and tandem mass spectrometry were used in an attempt to identify these and closely related ions.

The low resolution 70 eV EI-MS of 1,3-dimethyl-1,3-diazaphospholidinium **51** tetrachlorogallate is shown in Figure 4.4. The three most intense fragment ions at $m/z = 74$, 60 , and 42 , are assigned to $\text{C}_2\text{H}_5\text{NP}^+$, CH_3NP^+ , and $\text{C}_2\text{H}_4\text{N}^+$ respectively. High resolution experiments unambiguously distinguish between CH_2 (14.015650074 amu) and N (14.003074008 amu), and indicate that $m/z = 74$ corresponds to $\text{C}_2\text{H}_5\text{NP}^+$ rather than $\text{CH}_3\text{N}_2\text{P}^+$, and $m/z = 42$ corresponds to $\text{C}_2\text{H}_4\text{N}^+$ rather than CH_2N_2^+ . From this one can conclude that either **79**, or **80**, or both are formed in the gas phase and are stable on the

timescale of the experiment (tens of microseconds). While the empirical formula has been established, the actual atomic connectivity of the ion is in question. However, based on the structure of **51**, the species CH_3NP^+ is most likely to possess $\text{H}_3\text{C}-\text{N}-\text{P}$ connectivity rather than $\text{H}_3\text{C}-\text{P}-\text{N}$. The lack of intense signals in the spectrum which can be attributed to fragments containing P bound to an alkyl group provides additional circumstantial evidence. As the EI-MS of the chlorophospholidine **52** is very similar to that of **51**, one can conclude that the fragmentation responsible for the formation of $\text{CH}_3\text{N}^+\equiv\text{P}$ most likely occurs through initial formation of the cation **51**.

The low resolution 70 eV EI-MS of bis(1,3-dimethyl-1,3-diazarsolidinium **40a** tetrachlorogallate) is shown in Figure 4.3 and shows no evidence of a dimer in spite of being known to possess a dimeric structure in the solid state. Accurate mass determinations indicate that the peak at $m/z = 161$ corresponds to the monomer unit and fragments at 118 and 104 amu correspond to $\text{C}_2\text{H}_5\text{NAs}^+$ and CH_3NAs^+ , respectively (Table 4.2). The latter is likely to be the arsenoazonium ion **81** based on the known solid state structure of **40a** and the absence of fragments of the type AsR^+ , although the isomeric structure **82**, formed by rearrangement, cannot be ruled out. The peak at $m/z = 42$ is again confirmed, through high resolution experiments, as $\text{C}_2\text{H}_4\text{N}^+$.

For comparison, the EI-MS of 2,4,6-tri-*tert*-butylphenyliminophosphine chloride **83** was obtained and is shown in Figure 4.5. The peak at $m/z = 290$ corresponds to $\text{Mes}^*\text{N}^+\equiv\text{P}$ **84**, a derivative of **79**. Also of interest is the peak at 259 amu which is due to

**83****84**

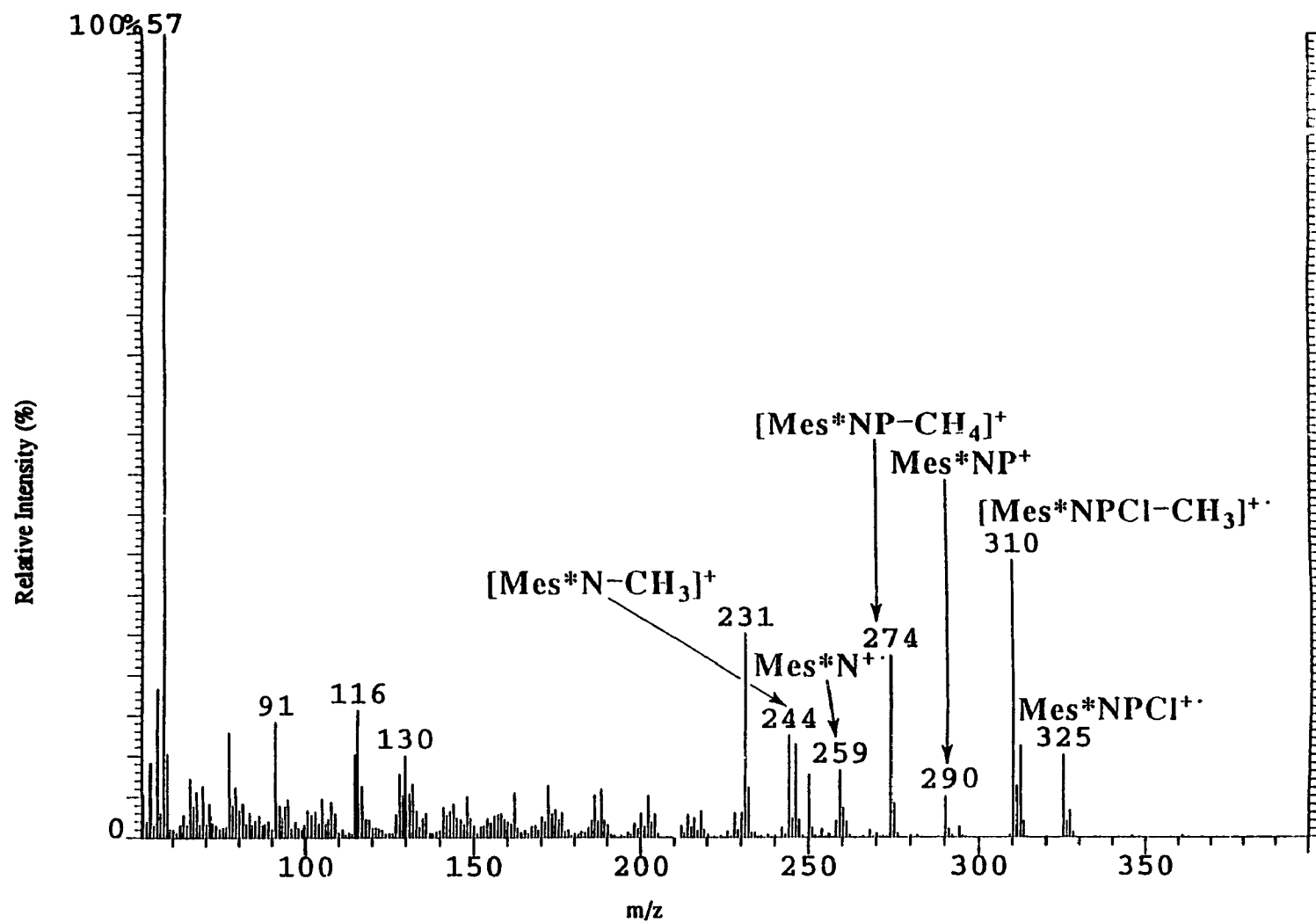


Figure 4.5: Low resolution 70eV EI-MS of **83**.

Mes*N⁺. A very weak signal, <1% relative intensity, is seen for the species Mes*P⁺ (276 amu). This indicates that rearrangements involving the breaking of R–N and the formation of R–P bonds are uncommon. This is further evidence to support the conclusion that the $m/z = 60$ and $m/z = 104$ species observed in the spectra of **51** and **40a**, respectively, are in fact **79** and **81**, the CH₃N⁺=E derivatives, and not **80** and **82**, the CH₃E⁺=N derivatives. Surprisingly, salts of 2,4,6-tri-*tert*-butylphenyliminophosphonium **84**¹⁴⁵ did not show the molecular ion Mes*N⁺=P in the EI-MS.

The chloropnicolidines **38a** and **52**, and the pnicyglidenes **40a** and **51** seem to be particularly adept at forming the CH₃N⁺=E species **81** and **79**, respectively. Since these species have remained unknown until now, it appears that more than simply having the proper connectivities in the precursors is required for their formation. To explore this hypothesis tris(dimethylamino)phosphine [(Me₂N)₃P], a compound containing a tricoordinate phosphorus centre, was examined. (Me₂N)₃P contains the proper connectivities to form **79** (CH₃–N–P), however the EI-MS showed no signal at $m/z = 60$. This suggests that the CH₃–N–P arrangement within a molecule is not the only prerequisite for observing CH₃N⁺=P in the mass spectrum.

Further supporting evidence for the proposed connectivities of **79** and **81** is obtained by examining their high energy fragment ion spectra (Figure 4.6). The major fragment ions are virtually identical for the respective pnicygens [phosphorus in Figure 4.6(a) and arsenic in Figure 4.6(b)], although the spectra do differ in some minor respects. The minimum scan calibrated mass for Figure 4.6(a) was lower, making it possible to scan down to about $m/z = 25$ and hence observe the fragment ion CH₂N⁺. This fragment is only likely from a structure of type **79**, and not type **80**. Structure **79** is further supported by the absence of any fragments of the type CH_xP⁺ ($x = 1,2,3$), which would be indicative of **80**.

Both single and double hydrogen shifts are evident in the fragment ion spectra of

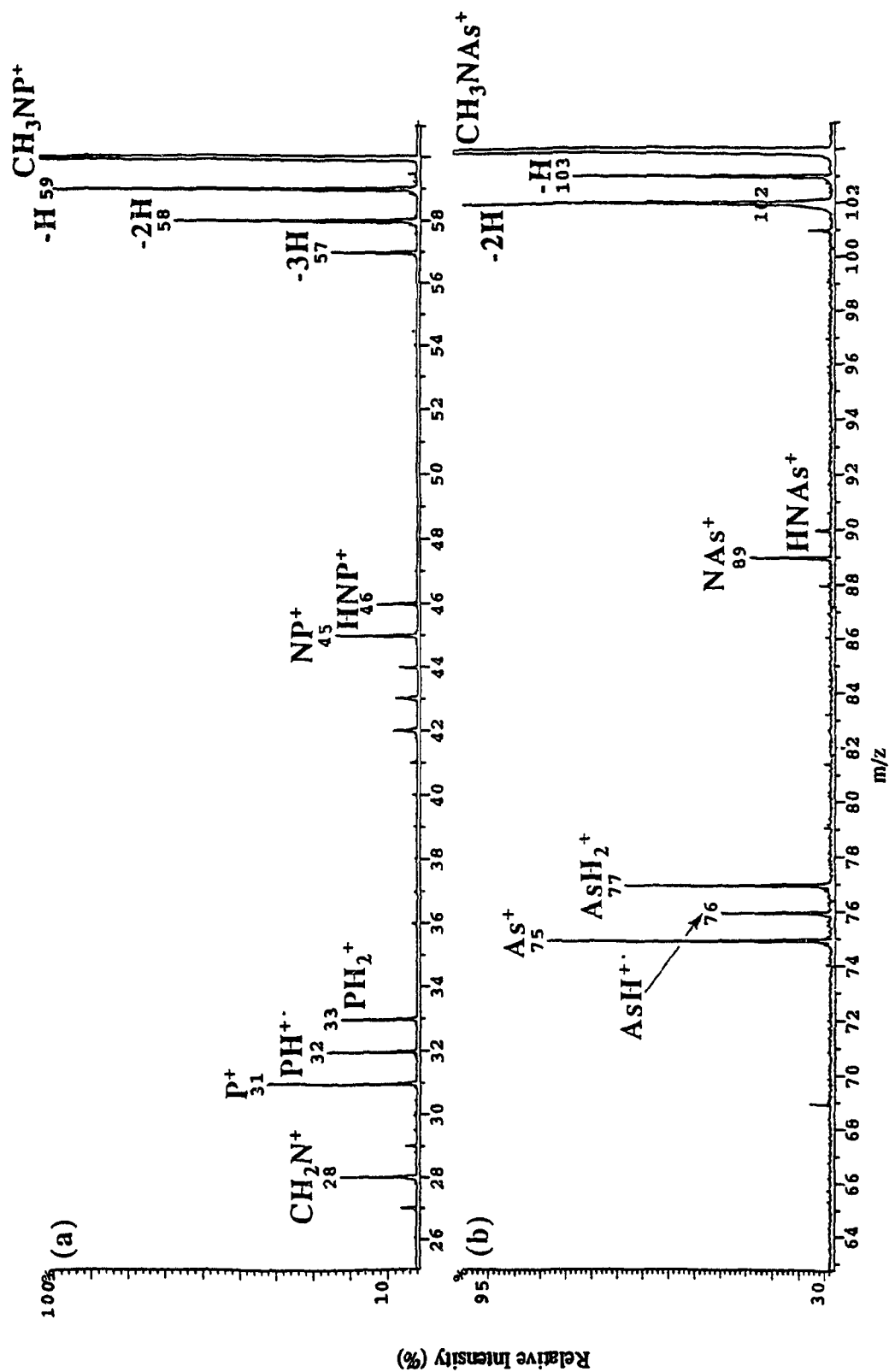


Figure 4.6: High energy fragment ion spectrum (linked scan at constant B/E , He collision gas, 8 keV collision energy) of (a) CH_3NP^+ from 51GaCl_4 , and (b) CH_3NAS^+ from $40\text{a}(\text{GaCl}_4)_2$.

CH_3NP^+ and CH_3NAs^+ , resulting in the formation of the ions EH^+ , EH_2^+ , and HNE^+ ($\text{E} = \text{P}$ or As). These hydrogen migration reactions are well-known in EI and tandem mass spectrometric studies.¹⁷⁹ The low energy fragment ion spectra recorded using the hybrid tandem mass spectrometer provide a further illustration of this rearrangement (Figure 4.7). In this experiment the precursor ions CH_3NP^+ [Figure 4.7(a)] and CH_3NAs^+ [Figure 4.7(b)] are selected using the double focusing mass spectrometer. Doing so eliminates the likelihood of artefact ions occurring in the resulting spectra. Due to the experimental conditions, the ions travel slowly through the collision cell of the mass spectrometer, residing for times approaching a millisecond, as compared to standard high energy scans where residence times are in the low microsecond range. This increased residence period allows time for rearrangements to occur and so it is not surprising that AsH_2^+ is the only As-containing fragment present [Figure 4.7(b)]. One should note, however, that the experiments did not allow distinction of other possible isomeric precursor ions such as $\text{H}_2\text{C}=\text{N}^+=\text{EH}$ or $\text{HC}\equiv\text{N}^+-\text{EH}_2$ ($\text{E} = \text{P}$ or As). The observation of both CH_2N^+ and PH_2^+ (or AsH_2^+) in the high and low energy spectra indicates that either both structures are formed in the ion source or that hydrogen migration has occurred.

Three small peaks present in the high energy fragment ion spectrum of CH_3NP^+ at $m/z = 42, 43$, and 44 [Figure 4.6(a)] have no equivalents in the spectrum of CH_3NAs^+ [Figure 4.6(b)]. These peaks are believed to be artefacts which have arisen due to either poor precursor ion resolution or fragmentation of unrelated ions occurring within one of the fields of the mass spectrometer.¹⁸⁰ In the former case the artefact peaks would be due to intense fragments of precursor ions with masses similar to that of CH_3NP^+ . For example, there is an unidentified ion with a mass of 60.0217 amu, which compares closely with the mass of CH_3NP^+ at 60.0004 amu. It should be noted that since the elemental formula is known to be CH_3NP^+ from the accurate mass measurements, a fragment ion of mass 42 is not a possibility. Because of this, the suggestion that $m/z = 42-44$ are artefacts in the

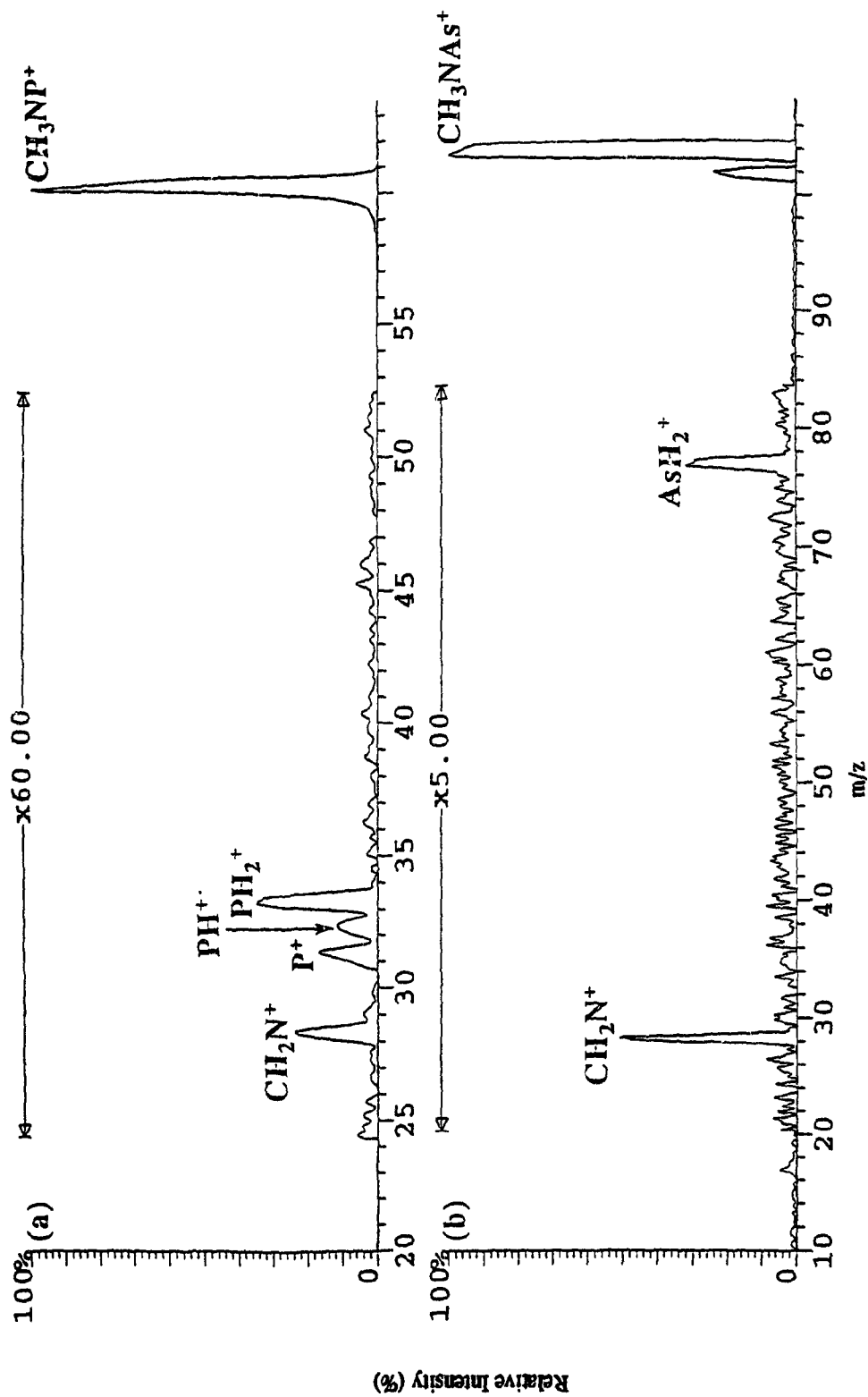
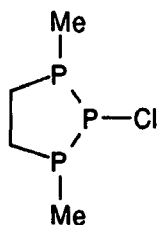
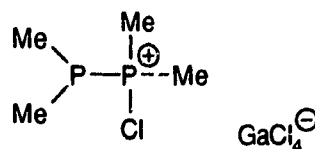


Figure 4.7: Low energy fragment ion spectrum (quadrupole scan, He collision gas, 50eV collision energy) of (a) CH_3NP^+ from 51GaCl_4 , and (b) CH_3NAS^+ from $40\text{g}(\text{GaCl}_4)_2$.

spectrum of CH_3NP^+ is plausible. The low energy fragment ion spectrum of CH_3NP^+ [Figure 4.7(a)] supports this conclusion since there are no fragment ions observed in this range.

These results have provided the first evidence for the existence of the methylphosphoazonium **79** and methylarsenoazonium **81** ions in the gas phase. No evidence was obtained for the isomeric azophosphonium **80** or azoarsenonium **82** ions, consistent with theoretical results.¹⁷¹ It is possible that the success in observing phosphoazonium and arsenoazonium ions is a result of the choice of unusual precursors having 2-coordinate P or As centres, since no evidence of the phosphoazonium species was encountered when using the tricoordinate phosphorous containing species $(\text{Me}_2\text{N})_3\text{P}$. Although the chloropnicolidine species **38a** and **52** initially contain tricoordinate pnictogen centres, the principal fragmentation in the source of the mass spectrometer involves loss of Cl^+ and the concomitant production of dicoordinate arsyldiene and phosphylidene ions. It is possible that the further use of low coordinate precursor molecules, such as **85** and **49**,¹⁸¹ will lead to the discovery of other novel ionic species, such as the diphosphonium ion $\text{CH}_3\text{P}^+\equiv\text{P}$ **78**.

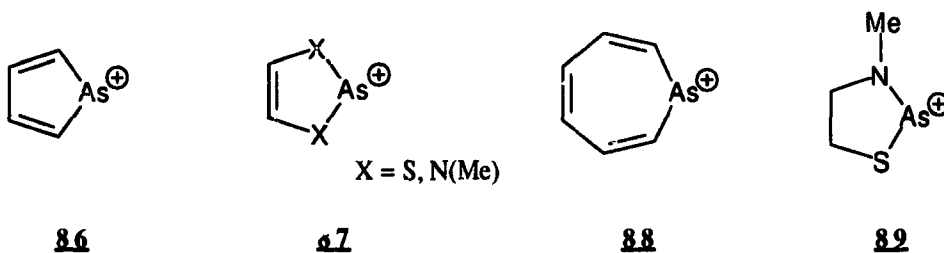
**85****49**

5.0 Future Work

There is much that is still unknown about arsylienes and pnicylienes in general. Future work in this area should focus on both the synthesis of new arsylienes and higher pnicylienes, as well as further investigations into their chemical properties.

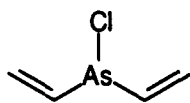
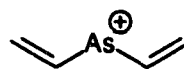
5.1 New Arsylienes

Many arsines are prone to thermal degradation to give elemental arsenic. However, cyclic derivatives seem to exhibit a stability that the acyclic species lack, and this should allow for further investigation and synthetic exploitation. Cations of the types **86** and **87** would provide information on the potential for generalization and diversification of non-hindered arsyliene centres. Preparation of the permethylated precursor chloroarsine for **86**¹⁸² has been reported. Hückel derivatives, such as **88**, offer obvious means of stabilization and may produce favourable results. Also of interest are mixed species containing two different heteroatoms, such as **89**. Will dimerization be evident as it is when both heteroatoms are the same, and if so, will the dimerization occur through the



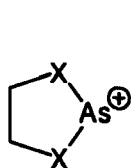
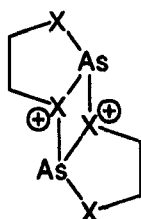
sulfur or the nitrogen centres? Work on the arsenanium systems (see Section **2.3**) and on the more sterically hindered arsolidinium systems (see Section **2.2**) has given some indication of the steric and electronic requirements necessary to stabilize such arsyliene centres.

Aside from the above cyclic species, there has been an acyclic compound reported that may allow for production of the first example of an acyclic arsyliene species.

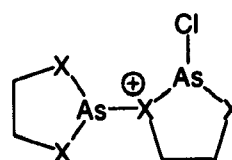
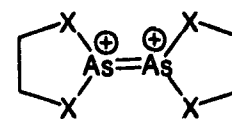
**20****21**

Diethenylchloroarsine¹⁸³ **20** is a secondary vinyl arsine that should be amenable to chloride ion abstraction by the usual reagent (GaCl_3), producing the acyclic arsyldene **21**, which represents a conjugated five atom framework.

The structures adopted by **39**, to give the dimers **40**, are in contrast to the ethene type dimer **45** which would be exhibited by a carbene, but might be rationalized in terms of the weak $\text{As}=\text{As}$ π -bond, which is likely further weakened by the close proximity of the positive charges at the arsenic centres. In this context, the novel weakly associative arrangements which are encountered in these arsyldenes offer insight into the structural and electronic features of the non-metal elements and highlight their differences with carbon. It is expected that similar associative interactions will be present in related systems, but that the small energy barriers evident between different structures will provide different possible structural arrangements. Examination of interactions between different arsyldene systems, such as a combination of **39a** and **39b** for example, might provide alternative associative arrangements. It is possible that variations in the effective electronegativities at the different arsenic centres will introduce an electrostatic component capable of disturbing the delicate inter-ring connections and imposing a 2-centre, 4-electron

**39****40**

a: $\text{X} = \text{N}(\text{Me})$
b: $\text{X} = \text{S}$

**41****45**

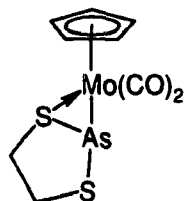
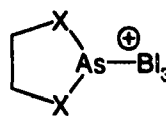
As=As double-bond, such as in **45**. Further reactions between arsyldiene and phosphylidene systems may shed some light on the factors principally responsible for the observed association in the solid state and the stability of the monomeric ylidene unit in general.

5.2 Chemistry of Arsyldiene Centres

Preliminary investigations have been made in the areas of Lewis acidity and basicity, as well as cycloaddition chemistry, however it is apparent that these studies have merely scratched the surface. In particular, the reactions of the dications **40a** and **40b** with various alkynes seem promising. It would also be of interest to further scrutinize the Diels-Alder type reactions observed between these same two species and butadiene, and to further explore the generality of these types of reactions.

Most of the present acid-base studies have explored the acidic behaviour of the arsyldienes, with little attention focusing on their basic character. Examining the donating abilities of arsyldienes **39a** and **39b** towards transition metal centres would be an interesting exercise and would provide invaluable information about the donor characteristics of these species. In one case, involving the molybdenum containing compound **22**, the arsyldiene **39b** (formed *in situ*) has already been observed to behave as a ligand and acts as a four electron donor.¹³⁹ It may also prove possible to form a complex between these arsyldienes and a sufficiently strong Lewis acid, such as BI₃, resulting in compounds such as **23**.

Very preliminary investigations into the Staudinger reactivity of arsyldienes have not produced viable reactions. Nevertheless, it is possible that arsyldienes, when subjected to the right conditions, will undergo Staudinger type reactions. Future investigations should include a variety of Staudinger reagents, such as elemental sulfur, selenium, and tellurium. Also included would be a variety of organic azides RN₃, with R groups ranging

**22**

a: X = N(Me)
b: X = S

23

in size from small, such as methyl, to very large, such as super-mesityl (2,4,6-tri-*tert*-butylphenyl), and with electronic configurations ranging from strongly σ -donating, such as tertiarybutyl, to strongly σ -withdrawing, such as trifluoromethyl. Also to be included are oxygen atom donors such as N_2O and PhIO . The range of reactants with which Staudinger reactions occur will provide valuable information on the electronic properties of arsylienes.

The novel face to face step-like interaction which is observed for the dicationic species **40** is reminiscent of electronically significant stacking polymers.¹⁸⁴ With this in mind, it may be possible to exploit this dimeric interaction and to develop a polymeric array by assembling polycyclic dimeric cations that possess two or more sites of potential interactions between rings. If combined with stacking anions, such as tetracyanoquinodimethanide (TCNQ^-) it may be possible to form polymeric arrays of both cations and anions.

Mixed metal semiconductors such as gallium arsenide (GaAs) are important electronic materials and have properties that are vastly superior to silicon. However, the commercial production of analytically pure gallium arsenide involves the use of expensive, difficult, and inefficient procedures.¹⁸⁵ Of potential interest is the elemental composition of the new arsylienes, which are often prepared as the tetrachlorogallate salts (GaCl_4^-). It is possible that these species may have some significance as precursors in a much sought after simplified synthesis of gallium arsenide. Such a synthesis could offer a low temperature

technique for the generation of GaAs under much more benign conditions.

6.0 Experimental

Due to the extreme reactivity of the arsylienes and other pnicylidenes, air and moisture must be rigorously excluded from all experiments. All starting materials, solvents, and products were stored and manipulated under either vacuum or an atmosphere of dry inert gas, usually nitrogen, and all reagents were introduced into, and reactions performed within, sealed vessels. Solid starting materials were prepared for use by exposure to dynamic vacuum (10^{-3} Torr) for a minimum period of 30 minutes. Liquid starting materials were degassed using the standard freeze-pump-thaw technique.

6.1 Safety

Caution - The historical toxicity of arsenic is well known and low coordinate arsenic compounds are carcinogenic. As such, all chemicals in this study should be treated with respect. Proper handling techniques and the use of fume hoods is highly recommended. All waste solutions and solids should be stored until they can be disposed of properly, in accordance with applicable municipal, provincial, and federal laws.

6.2 The Handling of Air Sensitive Reagents

Special apparatus and techniques are required for performing reactions of pnicylidenes. The heart of this apparatus is based on the revolutionary vacuum H-tube reactor described by Wayda and Dye in 1985.¹⁸⁶ The reactor, referred to as a *bridge*,¹⁸⁷ is a vacuum tight vessel which has two or more separate compartments.⁹⁸ The entire bridge is connected directly to the vacuum line by means of a standard ground glass joint which is associated with the main stopcock. The practicality and versatility of this system is conferred through the use of demountable and interchangeable reaction chambers or compartments. The reactors are constructed from borosilicate glass components which are connected through the use of nylon or teflon bushings seated in threaded glass connectors.

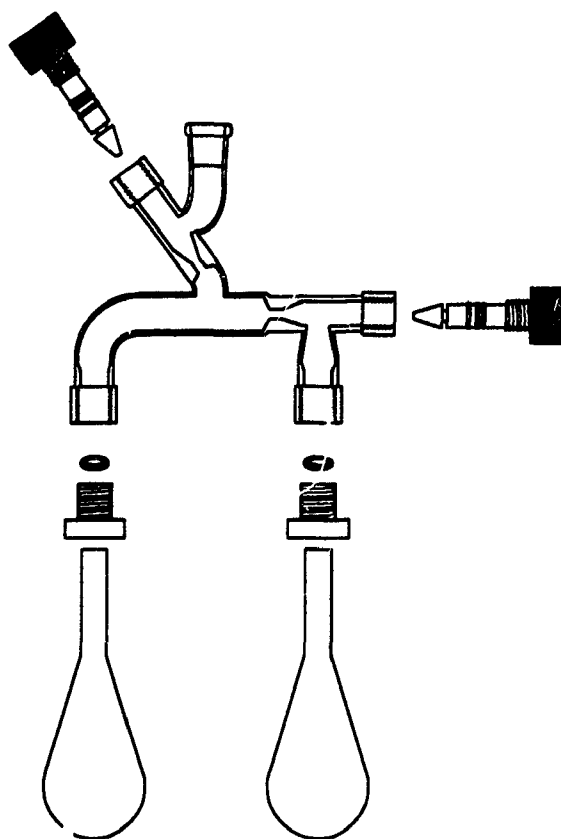


Figure 6.1: A diagrammatic representation (to scale) of the parts of a typical dual compartment bridge.

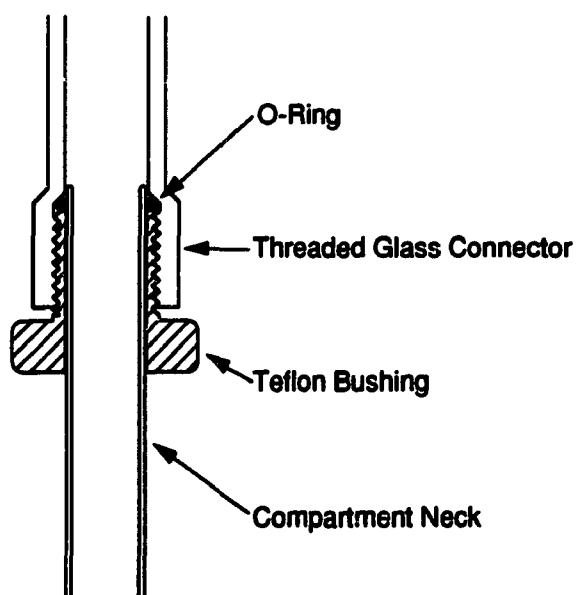


Figure 6.2: Cutaway view of a typical O-ring seal on a glass compartment neck.

A vacuum tight seal is formed by a FETFE, Viton, or other appropriate material O-ring between the bushing and a glass flange of the connector. Teflon stopcocks are used to isolate the compartments. A diagrammatic representation of a dual compartment bridge is shown in Figure 6.1, and an expanded view of the O-ring seal is illustrated in Figure 6.2. These seals typically maintain a vacuum as high as 10^{-3} torr for a period of two weeks or more, and can withstand pressures of up to at least two atmospheres, such as are encountered in warming dichloromethane solutions in hot water ($\approx 60^{\circ}\text{C}$). As with any vessel under vacuum there are certain cautionary procedures which should be followed in case of implosion, such as careful shielding of the apparatus.

The practical range of sizes for the demountable reaction compartments is 5 to 500 mL, and the bushings are available commercially in sizes of from 7.5 to 76.5 mm inside diameter. The interchangeable compartments may be reaction chambers or *bulbs*, as illustrated in Figure 6.1, or they may be NMR tubes, UV/VIS, solution IR, or electrochemical cells. Additional types of attachments may also be constructed for more specialized needs. A typical reactor for a one millimolar scale reaction is constructed from 22 mm diameter glass tubing fitted with 0-5 mm aperture stopcocks and 15 mm threaded glass connectors (o.d. of the thread is 26 mm). An assembled triple compartment vessel (most commonly used when reaction mixture NMR is required) measures approximately 28 x 10 x 30 cm (28 x 10 x 46 cm with NMR tube fitted) and weighs approximately 500 g. Such a vessel may be constructed by a master glassblower in approximately 12 hours.

To prepare the apparatus for use, the empty reactor is placed under dynamic vacuum and flame dried with a bunsen burner for approximately 10 minutes, then allowed to slowly cool to room temperature. It is possible to heat the glass sections of these vessels close to the melting point of borosilicate without obvious detriment to the teflon or FETFE components, however nylon bushings or stopcock heads may ignite if heated directly.

The evacuated reactor and solid reagents are taken into a drybox where the reagents

are weighed and introduced into separate demounted compartments. The reactor is then reassembled, removed from the drybox, and re-evacuated. Introduction of liquid starting materials into a bridge occurs within a standard polyethylene glove bag which has been flushed three times with dry nitrogen. Volatile reagents and solvents are vacuum distilled into the appropriate compartment of the reactor while the other compartments are isolated by the stopcocks. Combining of reagents can be performed in a variety of fashions including slow (dropwise) addition, the rate of which is controlled by the separating stopcocks. Reaction mixtures may be readily warmed or cooled. Additionally, the reactor has no orientational restrictions and it does not need to be clamped into position.

A bridge may be constructed with a sintered glass frit separating reaction compartments, or a small adaptor containing a frit may be attached between one of the threaded glass ports and a compartment. This allows filtration of solid materials from solution, although it is usually sufficient to use simple decantation to separate a solution from a solid. The separated solid may be washed by repeated "cold spot" back distillation of solvent using a liquid nitrogen cooled cotton ball

Precipitation of materials may be enhanced by concentration techniques which involve slow removal of solvent from the solution by cooling one of the other compartments of the reactor, either with liquid nitrogen for fast concentration (minutes) or with cold water for slow concentration (hours or days). Use of these techniques has resulted in crystal growth where other approaches have been unsuccessful. The resulting solids are then washed by repeated "cold spot" back distillations, as above.

Isolation of reaction products is completed by removal of the solvent from the reactor *in vacuo*, and then recovering the materials in a drybox. Alternatively, since the stopcocks between compartments allow for the *in situ* preparation and purification of a reagent, compartments may be exchanged in order to introduce other reagents without compromising the quality of the reactor environment and without necessarily requiring a

manipulation in the drybox. Such an approach is commonly employed in order to obtain solution NMR samples of a reaction mixture when using a dual compartment bridge. After decanting an appropriately sized aliquot of the reaction mixture into an attached NMR tube, the solvent of the NMR sample may be exchanged for a suitable deuterated solvent and the frozen sample flame sealed. Samples are prepared for IR spectroscopy (as nujol mulls) and X-ray crystallography (in pyrex capillary tubes) within the dry nitrogen atmosphere of the drybox. Products are stored under nitrogen in flame sealed glass tubes.

The apparatus described above is robust, extremely versatile, and easy to clean and use, but perhaps its most important feature is the ready interchangeability of the components and the possibility of expanding the number and type of compartments almost indefinitely. The form and function of this system has undergone continual evolution (and should continue to do so) through its use in this laboratory over a six year period, especially with the contributions of Drs. Bruce Royan, Rupert Spence, and Mel Schriver.

6.3 General Procedures

Arsenic trichloride and triethylamine (both BDH) were distilled under N₂ before use. Aluminium trichloride, gallium trichloride, antimony trichloride, bismuth trichloride, and 1-azidoadamantane (all Aldrich) were sublimed under vacuum before use. Dimethyl acetylenedicarboxylate, 2,3-dimethyl-1,3-butadiene, and 2-butyne (all Aldrich) were distilled under vacuum before use. N,N'-Dimethylethylenediamine, 1,2-ethanedithiol, sodium tetrafluoroborate, silver cyanide, silver carbonate, silver hexafluoroarsenate, silver tosylate, silver triflate, silver tetrafluoroborate, silver heptafluorobutyrate, N,N'-diisopropylethylenediamine, N,N'-dibenzylethylenediamine, 2-methylaminoethanol, triphenylphosphine oxide, diiron nonacarbonyl, diphenylacetylene, 1,3-propanedithiol, N,N'-dimethyl-1,3-propanediamine, 2-mercaptoethyl sulfide, phenyl ether (all Aldrich), ethyl acetate, silver sulfate, ethylene glycol (all Baker), silver trifluoroacetate,

diphenylamine (both Eastman), sodium tetraphenylboron, silver acetate (both BDH), silver hexafluorophosphate, tris(diethylamino)phosphine (both Strem), silver nitrate (Fisher), silver cyanate (Kodak), silver perchlorate (Alfa), hexafluorobut-2-yne (PCR), 20% phenyl azide in hexane (Pfaltz & Bauer), and dimesitylchloroarsine (Quantum Design) were used as received. 2-Chlorobenzo-1,3,2-thiazarsole,⁶⁸ lithium tetracyanoquinodimethanide,¹⁸⁸ 2-chloro-1,3-dimethyl-1,3-diaza-2-phospholidine,¹⁸⁹ 1,3-dimethyl-1,3-diaza-2-phosphenium tetrachlorogallate,¹³³ adamsite,¹⁵⁸ and phenoxarsine chloride¹⁵⁹ were prepared using the literature procedures. 2,4,6-Tri-*tert*-butylphenyliminophosphine chloride¹⁷² and 2,4,6-tri-*tert*-butylphenyliminophosphenium tetrachlorogallate and heptachlorodigallate¹⁴⁵ for mass spectrometric studies were prepared by Jason Clyburne using the literature procedures. Dichloromethane was dried over P₂O₅ and CaH₂. Toluene, benzene and THF were dried over Na/benzophenone. Acetone was dried over anhydrous CaSO₄. Triethylamine was dried over CaH₂. All solvents were stored in evacuated bulbs. Deuterated solvents were dried over P₂O₅ or CaH₂. All solids were manipulated in Vacuum/Atmospheres or MBraun dryboxes containing an atmosphere of 99.998% prepurified nitrogen constantly circulated through drying trains to maintain its oxygen and water free state. Glass equipment was flame dried before use. Reactions were performed in evacuated (10⁻³ Torr) dual or triple compartment vessels (see Section 6.2), unless otherwise indicated. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany. IR spectra were recorded as neat liquids or Nujol mulls on CsI plates using a Perkin-Elmer 283B spectrophotometer or a Nicolet 510P FT-IR spectrometer. Solution NMR spectra were recorded on either a Nicolet NT-360, Bruker AC250, or Bruker AMX400 spectrometer in 5 or 10 mm evacuated flame sealed pyrex tubes. Chemical shifts are reported in ppm relative to TMS (¹H and ¹³C), 85% H₃PO₄ (³¹P), or CFCl₃ (¹⁹F) and are calibrated to the internal solvent signal (¹H and ¹³C). Variable temperature NMR

studies involved equilibrium times of ten minutes at each temperature. Reaction mixture NMR samples were prepared by decanting an aliquot of the reaction mixture into an NMR tube, removing the solvent *in vacuo*, and distilling in an appropriate amount of deuterated solvent. Solid state ^{13}C CP MAS NMR spectra were recorded on a Bruker AMX400 spectrometer in 3 mm zirconium oxide spinners at spinning rates of from 8000 to 9000 Hz. All electron impact mass spectra were recorded on a VG Analytical ZAB-EQ mass spectrometer of BEQQ geometry. Samples were introduced into the mass spectrometer by means of a standard water-cooled solids probe. Electrospray mass spectra were obtained on a SCIEX API-III mass spectrometer in the ionspray mode of operation with ultra-pure nitrogen as the nebulizer gas. All solution samples were dissolved in dry distilled dichloromethane and introduced into the electrospray source by means of a syringe driver attached to a silica capillary. Crystals suitable for crystallography were obtained as described below for each compound and mounted in pyrex capillaries in a drybox. X-ray crystallographic data were collected on Rigaku AFC5R or Enraf-Nonius CAD-4 diffractometers with graphite-monochromated Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$ or $\lambda = 0.70926 \text{ \AA}$, respectively). Structures were solved by Dr. Bozena Borecka, Dr. T. Stanley Cameron, Dr. John F. Richardson, or Pradip K. Bakshi, with the exception of **40a**(GaCl $_4$) $_2$ which was solved by the author. Full details on the data collection and structure solution procedures used are available from the references as indicated in the appropriate discussion section for each compound.

6.4 Specific Procedures

[C $_6$ H $_4$ SN(H)As] **28** [AlCl $_4$]: A solution of 2-chlorobenzo-1,3,2-thiazarsole (0.332 g, 1.42 mmol) in CH $_2$ Cl $_2$ (30 mL) was added dropwise to a stirred suspension of AlCl $_3$ (0.193 g, 1.45 mmol) in CH $_2$ Cl $_2$ (30 mL) over a period of 25 minutes. A deep yellow solution initially formed and later produced a bright yellow microcrystalline precipitate.

The solution was decanted and the solid was washed twice by cold spot back distillation. The precipitate was characterized as benzo-1,3,2-thiazarsolium tetrachloroaluminate (0.391 g, 1.07 mmol, 75.4%), mp. 135-137 °C. Recrystallization from a dilute CH₂Cl₂ solution by slow removal of solvent produced small pale yellow crystals suitable for crystallography.

IR: 3230m, 1555m, 1545m, 1245m, 1220m, 760vs, 720s, 710s, 540m, 530s, 505vs, 475vs, 450s, 290m cm⁻¹.

NMR (CD₂Cl₂): ¹H, 8.40-7.60 ppm (ABCD), 8.4 ppm (NH); ¹³C, 130, 128, 127, 119 ppm (quaternary carbons not observed).

X-ray: monoclinic, space group *P*2₁/*c*, *a* = 6.4259(5) Å, *b* = 23.654(3) Å, *c* = 8.5859(7) Å, β = 98.203(6) °, *V* = 1291.7(2) Å³, *Z* = 4, *D*_{calcd} = 1.887 g cm⁻³, μ = 36.5 cm⁻¹, *R*_w = 0.054.

N(Me)CH₂CH₂N(Me)AsCl **38a**.¹⁰¹ A solution of AsCl₃ (20.59 g, 113.6 mmol) in diethyl ether (50 mL) was slowly added dropwise to a stirred solution of N,N'-dimethylethylenediamine (20.00 g, 226.9 mmol) in diethyl ether (200 mL) in a three-necked flask over a period of one hour under a continuous stream of dry nitrogen gas. Immediate reaction produced copious white precipitate, and the mixture was stirred for 90 minutes. The solution was decanted from the solid, which was filtered and washed with fresh solvent. The washings were added to the solution. The solvent was removed *in vacuo*, by rotary evaporation, and the resulting liquid was distilled under vacuum to produce a colourless, thermally unstable liquid, characterized as 2-chloro-1,3-dimethyl-*cyclo*-1,3-diaza-2-arsapentane (50%, not optimized) bp. 45 °C (3mm), mp. ≈19 °C. Crystals of crystallographic quality were grown by cooling (3 °C) a sealed evacuated tube of the product for a period of several months. Large crystals of **38a** formed on the walls of the tube by sublimation.

IR (neat liquid): 3018w, 2965vs, 2800w, 2729w, 2694w, 2452w, 1493w, 1465s, 1442s, 1423m, 1365w, 1335w, 1253m, 1199s, 1133vs, 1029s, 1005m, 921s, 847m, 806w, 583s, 569s, 410m, 341m, 279s, 247s cm^{-1} .

NMR (CD_2Cl_2): ^1H , 3.29 ppm (CH_2), 2.82 ppm (CH_3); ^{13}C , 56.9 ppm (CH_2), 36.0 ppm (CH_3).

X-ray: ~~monoclinic~~, space group $P2_1/n$, $a = 6.959(7)$ Å, $b = 9.23(2)$ Å, $c = 12.14(2)$ Å, $95.4(1)^\circ$, $V = 777(4)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.681$ g cm^{-3} , $\mu = 46.24$ cm^{-1} , $R_w = 0.0587$.

[N(Me)CH₂CH₂N(Me)As]₂ 40a [GaCl₄]₂: A solution of N(Me)CH₂CH₂N(Me)AsCl (1.31 g, 6.65 mmol) in CH_2Cl_2 (11 mL) was added to a stirred solution of GaCl₃ (1.17 g, 6.65 mmol) in CH_2Cl_2 (11 mL) over a period of 30 minutes. The bright yellow reaction mixture was stirred for 20 minutes, during which time the color gradually darkened to a light orange. Slow removal of solvent (>75%) *in vacuo* promoted precipitation/crystallization of a buff-colored solid, which was isolated from the solution by decantation. The solid was then recrystallised from fresh warm (65 °C) CH_2Cl_2 (22 mL) by slow cooling to room temperature and very slow removal of solvent *in vacuo*. The resulting crystals were washed three times by back distillation and the pale orange solid (crystallographic quality) was characterized as *bis*(1,3-dimethyl-1,3-diaza-2-arsolidinium tetrachlorogallate) (2.01 g, 2.70 mmol, 81.2%), mp. 104-105 °C.

Elemental anal. Calcd: C, 12.90; H, 2.71; N, 7.52%.

Found: C, 13.02; H, 2.77; N, 7.58%.

IR: 1330w, 1265s, 1223s, 1208w, 1173s, 1130s, 1113s, 1080s, 1041vs, 1013s, 988s, 891vs, 819s, 605w, 576m, 521vs, 448s, 418m, 395vs, 379vs, 363vs, 330w, 292m, 266w cm^{-1} .

NMR (CD₂Cl₂): ¹H, 3.83 ppm (CH₂), 3.20 ppm (CH₃); ¹³C, 57.8 ppm (CH₂), 37.6 ppm (CH₃).

X-ray: see below.

[N(Me)CH₂CH₂N(Me)As]₂ **40a** [AlCl₄]₂:¹⁰⁷ A crystalline sample (31% yield) of this compound was obtained in a manner similar to that described above for the GaCl₄ salt. However, the material gave a broad melting point and poor chemical analysis, and was difficult to obtain in a pure form.

X-Ray Crystallographic Determination of [N(Me)CH₂CH₂N(Me)As]₂ **40a**

[GaCl₄]₂: Crystals of [N(Me)CH₂CH₂N(Me)As]₂ [GaCl₄]₂ suitable for crystallography

Table 6.1: Crystallographic data for [N(Me)CH ₂ CH ₂ N(Me)As] ₂ 40a [GaCl ₄] ₂ .	
Formula	C ₈ H ₁₀ Ga ₂ As ₂ Cl ₈ N ₄
fw	745.18
cell	monoclinic
Space group	P2 ₁ /n
a (Å)	9.324(1)
b (Å)	13.719(2)
c (Å)	9.692(2)
β (°)	101.62(2)
V (Å ³)	1214.35(21)
Z	4
D _{calcd} (gcm ⁻³)	2.038
μ (cm ⁻¹)	58.04
R	0.0329
R _w	0.0349
GoF	1.117
T (K)	291

were obtained as described in the above text, and were selected and mounted in pyrex capillaries in the drybox. Crystal data and data collection parameters are presented in Table 6.1. Data were collected using an ω/2θ scan (width 1.0 + 0.35 tanθ). The space group was determined from systematic absences. Structures were solved by direct methods and refined by full matrix least squares for 1284 reflections. The hydrogen atoms were placed geometrically. The final fractional atomic positional parameters for the atoms are presented in Table 6.2 and a representation of the structure is given in Figure 2.6.

Table 6.2: Fractional atomic positional parameters and equivalent isotropic temperature factors for [N(Me)CH₂CH₂N(Me)As]₂ **40a** [GaCl₄]₂ with e.s.d.s in parentheses.

Atom	x/a	y/b	z/c	U _{eq}
As(1)	0.1047(6)	0.0855(4)	0.9870(6)	0.0343
Ga(1)	-0.0617(1)	0.3853(1)	0.2050(1)	0.0429
Cl(1)	0.1065(2)	0.3039(1)	1.1291(2)	0.0626
Cl(2)	0.0189(3)	0.5280(1)	1.2731(3)	0.0843
Cl(3)	-0.2574(2)	0.3922(2)	1.0431(2)	0.0700
Cl(4)	-0.1050(2)	0.3036(2)	1.3841(2)	0.0683
N(1)	0.0152(6)	0.1211(3)	0.8179(5)	0.0399
N(2)	0.0747(5)	-0.0488(3)	0.9220(5)	0.0329
C(1)	0.0004(7)	0.2238(5)	0.7677(7)	0.0497
C(2)	-0.0603(7)	0.0440(4)	0.7272(6)	0.0432
C(3)	0.0293(7)	-0.0465(5)	0.7650(6)	0.0461
C(4)	0.2044(7)	-0.1151(5)	0.9676(7)	0.0483

NMR Spectroscopic Identification of [N(Me)CH₂CH₂N(Me)As-

N(Me)As(Cl)N(Me)CH₂CH₂] **41a** [GaCl₄]: A solution of

N(Me)CH₂CH₂N(Me)AsCl (0.41 g, 2.1 mmol) in CH₂Cl₂ (7 mL) was added to a stirred solution of [N(Me)CH₂CH₂N(Me)As]₂ [GaCl₄]₂ (0.775 g, 1.04 mmol) in CH₂Cl₂ (20 mL) over a period of 15 minutes. No change was observed and the solution was stirred for two days, after which a small quantity of an orange precipitate was observed. An aliquot of the reaction mixture was decanted into an NMR tube where the solvent was exchanged for an equivalent volume of CD₂Cl₂. The ¹³C and VT ¹H NMR experiments revealed the presence of [N(Me)CH₂CH₂N(Me)As–N(Me)As(Cl)N(Me)CH₂CH₂] [GaCl₄] (*vide supra*), however only [N(Me)CH₂CH₂N(Me)As]₂ [GaCl₄]₂ could be isolated by recrystallization or solvent removal.

NMR (reaction mixture - CD₂Cl₂): ¹H, 3.58 ppm (CH₂), 3.03 ppm (CH₃); ¹³C, 57.6 ppm (CH₂), 37.1 ppm (CH₃).

Transformation of [N(Me)CH₂CH₂N(Me)As–N(Me)As(Cl)N(Me)CH₂CH₂] 41a [GaCl₄] into [N(Me)CH₂CH₂N(Me)As]₂ 40a [GaCl₄]₂: A solution of [N(Me)CH₂CH₂N(Me)As–N(Me)As(Cl)N(Me)CH₂CH₂] [GaCl₄] (1.5 mmol, 45 mL CH₂Cl₂) was prepared *in situ* as above. GaCl₃ (0.270 g, 1.53 mmol) in CH₂Cl₂ (15 mL) was slowly added over a period of 25 minutes and the mixture was stirred overnight, forming a large quantity of buff precipitate. The solution was carefully decanted and an aliquot of the reaction mixture was placed into a 5 mm NMR tube where the solvent was exchanged for an equivalent volume of CD₂Cl₂. [N(Me)CH₂CH₂N(Me)As]₂ [GaCl₄]₂ was identified in solution.

NMR (reaction mixture - CD₂Cl₂): ¹H, 3.84 ppm (CH₂), 3.21 ppm (CH₃).

NMR Studies of Mixtures of [N(Me)CH₂CH₂N(Me)As]₂ 40a [GaCl₄]₂ and N(Me)CH₂CH₂N(Me)AsCl 38a: Five equivalents of [N(Me)CH₂CH₂N(Me)As]₂ [GaCl₄]₂ and one equivalent of N(Me)CH₂CH₂N(Me)AsCl were combined in CD₂Cl₂, and the ¹H NMR spectrum showed only two peaks, at 3.78 and 3.16 ppm, with an integration ratio of 3:2. Twenty equivalents of N(Me)CH₂CH₂N(Me)AsCl and one equivalent of [N(Me)CH₂CH₂N(Me)As]₂ [GaCl₄]₂ showed a similar spectrum, but with chemical shifts of 3.34 and 2.86 ppm.

SCH₂CH₂SAsCl 38b:¹⁹⁰ A slightly milky solution of ethanedithiol (14.48 g, 153.7 mmol) in CCl₄ (70 mL) was slowly added dropwise to a stirred solution of AsCl₃ (27.90 g, 153.9 mmol) in CCl₄ (55 mL) over a period of one hour. The liberation of HCl gas (vented) was almost instantaneous and accompanied by self-cooling of the reaction mixture. The solution was sealed and stirred overnight, then cooled over dry ice, producing copious white crystals of crystallographic quality. The cold supernatant was decanted and the crystals were dried *in vacuo* and characterized as 2-chloro-*cyclo*-1,3-

dithia-2-arsapentane (27.00 g, 133.3 mmol, 86.72%) mp. 38.5-39.0 °C.

IR (yellow colouration on the plates): 1405s, 1280s(sh), 1275s, 1230s, 1145m, 1105m, 990m, 930s, 830vs, 660m, 645s, 445vs, 385vs, 355vs, 320vs(sh), 310vs, 280s(sh) cm^{-1} .

NMR (CD_2Cl_2): ^1H , 5.25 ppm; ^{13}C , 44.6 ppm.

[SCH₂CH₂SAs]₂ 40b [GaCl₄]₂: A solution of SCH₂CH₂SAsCl (0.981 g, 4.84 mmol) in CH₂Cl₂ (30 mL) was added to a stirred solution of GaCl₃ (0.856 g, 4.86 mmol) in CH₂Cl₂ (30 mL) over a period of 20 minutes. Immediate reaction gave a bright yellow solution. The reaction mixture was stirred overnight. Slow removal of the solvent (>75%) *in vacuo*, left a bright yellow oil which crystallized when agitated. The remaining solution was decanted from the solid, which was recrystallized from fresh warm CH₂Cl₂ (60 °C, 10 mL) by slow cooling to room temperature. The pale yellow crystalline solid, suitable for crystallography, was characterized as *bis*(1,3-dithia-2-arsolidinium tetrachlorogallate) (1.56 g, 2.06 mmol, 85.0%), mp. 94.0-95.5 °C.

Elemental anal. Calcd: C, 6.34; H, 1.06; S, 16.94%.

Found: C, 6.33; H, 1.16; S, 16.97%.

IR: 1400m, 1280m, 1230m, 1150m, 1110m, 990w, 925m, 830s, 735w, 650m, 620m, 450m, 390vs, 380vs, 360vs, 345s, 320s cm^{-1} .

NMR (CD_2Cl_2): ^1H , 4.06 ppm; ^{13}C , 45.8 ppm.

X-ray: monoclinic, space group $P2_1/c$, $a = 6.454(2)$ Å, $b = 14.360(3)$ Å, $c = 11.536(2)$ Å, $\beta = 104.62(2)^\circ$, $V = 1034.5$ Å³, $Z = 2$, $D_{\text{calcd}} = 2.43$ g cm^{-3} , $\mu = 71.9$ cm^{-1} , $R_w = 0.037$.

[SCH₂CH₂SAs]₂ 40b [Ga₂Cl₇]₂: A solution of SCH₂CH₂SAsCl (0.513 g, 2.53 mmol) in CH₂Cl₂ (15 mL) was added to a stirred solution of GaCl₃ (0.900 g, 5.11 mmol)

in CH_2Cl_2 (15 mL) over a period of 23 minutes. Immediate reaction gave a bright yellow solution. The reaction mixture was stirred for 15 minutes and slow removal of the solvent *in vacuo* left bright yellow crystals which were washed by repeated back distillation of solvent. The yellow crystalline solid, suitable for crystallography, was characterized as *bis*(1,3-dithia-2-arsolidinium heptachlorodigallate) (1.097 g, 0.989 mmol, 78.2%), mp. 83.0-84.5 °C.

Elemental anal. Calcd: C, 4.33; H, 0.73%.

Found: C, 4.25; H, 1.38%.

IR: 1413m, 1277w, 1242w, 1228w, 1152w, 921m, 815m, 772w, 650w, 622m, 452w, 420vs(sh), 407vs, 380vs, 369vs, 353s, 308vs, 267m, 248m, 228w cm^{-1} .

NMR (CDCl_3): ^1H , 3.79 ppm; ^{13}C , 45.1 ppm.

X-ray: monoclinic, space group $P2_1/c$, $a = 13.545(1) \text{ \AA}$, $b = 11.458(4) \text{ \AA}$, $c = 11.209(1) \text{ \AA}$, $\beta = 119.46(2)^\circ$, $V = 1515.77(2) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 2.432 \text{ g cm}^{-3}$, $\mu = 208.1 \text{ cm}^{-1}$, $R_w = 0.0593$.

$[\text{SCH}_2\text{CH}_2\text{SAs}]_2 [\text{Ga}_2\text{Cl}_7]_2$ has also been obtained from adding $[\text{SCH}_2\text{CH}_2\text{SAs}]_2 [\text{GaCl}_4]_2$ (0.440 g, 0.581 mmol) in CH_2Cl_2 (12 mL) to GaCl_3 (0.205 g, 1.16 mmol) in CH_2Cl_2 (4 mL) over a period of 21 minutes, giving a yield of 0.396 g, 0.357 mmol, 61.4%, mp. 82.0-83.0 °C.

$[\text{SCH}_2\text{CH}_2\text{SAs-SAs}(\text{Cl})\text{SCH}_2\text{CH}_2]$ 41b $[\text{GaCl}_4]$: A solution of GaCl_3 (0.740 g, 4.20 mmol) in CH_2Cl_2 (20 mL) was added to a stirred solution of $\text{SCH}_2\text{CH}_2\text{SAsCl}$ (1.703 g, 8.407 mmol) in CH_2Cl_2 (40 mL) over a period of 25 minutes. The initially pale yellow reaction mixture darkened during the addition. The mixture was stirred at room temperature overnight, during which time a pale yellow, microcrystalline precipitate formed. The solution volume was halved *in vacuo* and the remainder of the solution was

carefully decanted from the solid, which was washed by repeated back distillation and dried under vacuum. Recrystallization from fresh warm CH_2Cl_2 (60 °C, 10 mL) by slow cooling to room temperature gave crystals of crystallographic quality. The solid was characterized as 2-chloro-*cyclo*-1,3-dithia-2-arsapentane-1,3-dithia-2-arsolidinium tetrachlorogallate (2.13 g, 3.67 mmol, 87.3%), mp. 116-117 °C.

Elemental anal. Calcd: C, 8.27; H, 1.39; S, 22.07%.

Found: C, 8.36; H, 1.44; S, 21.79%.

IR: 1415w(sh), 1410m, 1290m, 1270w, 1235s, 1150m, 1145m, 1105m, 1000m, 980w, 935m, 925s, 825vs, 660m, 650m 635s, 450vs, 405vs(sh), 395vs(sh), 385vs, 375vs, 365vs, 350vs, 340vs, 320vs, 300m, 280m(sh), 270s, 260m(sh) cm^{-1} .

NMR (CD_2Cl_2): ^1H , 3.90 ppm; ^{13}C , 45.0 ppm.

X-ray: orthorhombic, space group $Pna2_1$, $a = 14.830(4)$ Å, $b = 13.610(3)$ Å, $c = 8.581(2)$ Å, $V = 1731.9$ Å³, $Z = 4$, $D_{\text{calcd}} = 2.23$ g cm^{-3} , $\mu = 65.9$ cm^{-1} , $R_w = 0.028$.

$[\text{SCH}_2\text{CH}_2\text{SAs-SAs}(\text{Cl})\text{SCH}_2\text{CH}_2]$ $[\text{GaCl}_4]$ has also been obtained from the reactions:

- (a) $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ $[\text{GaCl}_4]_2$ (0.30 g, 0.39 mmol) and $\text{SCH}_2\text{CH}_2\text{SAsCl}$ (0.16 g, 0.79 mmol) in CH_2Cl_2 (20 mL), giving a yield of 0.39 g, 0.67 mmol, 85%, mp. 113.5-114.5 °C.
- (b) $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ $[\text{GaCl}_4]_2$ (0.05 g, 0.06 mmol) and Ph_3PO (0.02 g, 0.06 mmol) in CH_2Cl_2 (10 mL) gave a ^{31}P NMR signal at 49 ppm, distinctive for $\text{Ph}_3\text{PO-GaCl}_3$,¹⁴³ and a tiny amount of the impure isolated solid gave a melting point of 110-113.5 °C.

Reactions of $\text{SCH}_2\text{CH}_2\text{SAsCl}$ **38h** with a Series of Chloride Ion

Abstracting Reagents: These reactions are summarized in Table 6.3. All reactions were

Table 6.3: Summary of reaction conditions for reactions of various chloride ion abstracting reagents with SCH₂CH₂SAsCl **38b**.

Number	Compound	Amount [g (mmol)]	Solvent (mL)	38b [g (mmol)]	Solvent (mL)	Time (mins)
1	Ethyl Acetate	0.19 (2.2)	10	0.436 (2.15)	20	20
2	NaBF ₄	0.198 (1.80)	13	0.365 (1.80)	38	25
3	AgPF ₆	0.100 (0.396)	11	0.102 (0.504)	22	15
4	AgCN	0.111 (0.829)	8	0.167 (0.824)	8	10
5	Ag ₂ CO ₃	0.126 (0.457)	12	0.185 (0.913)	12	5
6	Ag ₂ SO ₄	0.182 (0.584)	12	0.236 (1.17)	23	10
7	NaBPh ₄	0.155 (0.453)	11	0.092 (0.45)	21	15
8	AgAsF ₆	0.124 (0.418)	12	0.085 (0.42)	12	15
9	Ag Tosylate	0.203 (0.727)	14	0.147 (0.726)	55	30
10	Ag Triflate	0.147 (0.572)	6	0.115 (0.568)	19	10
11	AgNO ₃	0.154 (0.907)	9	0.183 (0.903)	26	20
12	AgCNO	0.146 (0.974)	23	0.197 (0.973)	11	10
13	AgClO ₄	0.178 (0.859)	23	0.174 (0.859)	8	5
14	LiTCNQ	0.215 (1.02)	35	0.207 (1.02)	12	1
15	AgBF ₄	0.134 (0.688)	9	0.139 (0.686)	18	10
16	AgCF ₃ COO	0.153 (0.693)	9	0.140 (0.691)	18	15
17	AgCF ₃ CF ₂ CF ₂ COO	0.181 (0.564)	8	0.114 (0.563)	24	10
18	AgCH ₃ COO	0.133 (0.797)	18	0.161 (0.795)	9	5

performed in toluene solution with the exception of 1, 8 (THF), 13 (dichloromethane), and 14 (acetone). A given amount (column 3) of a compound (column 2) was dissolved or suspended in a given amount of solvent (column 4). To this solution or rapidly stirred suspension was added a solution containing a given amount of SCH₂CH₂SAsCl **38b** (column 5) dissolved in a given amount of solvent (column 6) over a period of several minutes (column 7). No visible change was apparent for reactions 1-6. Reactions 7-14 produced copious precipitate either immediately or upon stirring overnight. Reactions 15-18 apparently resulted in immediate formation of the dication [SCH₂CH₂SAs]₂ (**40b**), as evidenced by formation of the distinctive bright yellow colour, followed by its rapid

decomposition (fading of the solution to colourless). Copious quantities of a colourless precipitate were also produced from reactions 15-18. It was not possible to isolate solids from any of the reaction mixtures.

$N(iPr)CH_2CH_2N(iPr)AsCl$ 38c: A solution of N,N' -diisopropylethylenediamine (4.82 g, 33.4 mmol) and triethylamine (≈ 10 mL) in diethyl ether (50 mL) was slowly added dropwise to a stirred solution of $AsCl_3$ (6.04 g, 33.3 mmol) in diethyl ether (100 mL) in a three-necked flask under a continuous stream of dry nitrogen gas over a period of 40 minutes. Immediate reaction produced copious white precipitate, and the mixture was stirred overnight. The solution was filtered under nitrogen and the solid was washed with fresh solvent. The washings were added to the solution. The solvent was removed *in vacuo*, by rotary evaporation, and the resulting liquid was distilled under vacuum to produce a pale yellow, thermally unstable liquid, characterized as 2-chloro-1,3-diisopropyl-*cyclo*-1,3-diaza-2-arsapentane (4.22 g, 16.7 mmol, 50.2%) bp. 78-84 °C (3mm).

IR (neat liquid): 1470s, 1460s, 1385s, 1365s, 1355s, 1345s, 1320s, 1250s, 1215s(sh), 1180vs(br), 1145s, 1130s(sh), 1120s, 1105s, 1080s, 1060s, 1020s, 1005s, 965s, 935s, 920m, 875m, 860m, 835s, 630m, 605s, 600s(sh), 595s(sh), 590s(sh), 565m, 490w, 470m, 425m, 400m, 350m, 310m(sh), 270s(sh), 260vs, 250vs cm^{-1} .

NMR (CD_2Cl_2): 1H , 3.30 ppm (CH_2 , s, 4H), 3.30 ppm (CH, sept, 2H), 1.24 ppm (CH_3 , d, 12H); ^{13}C , 51.5 ppm (CH_2), 50.7 ppm (CH), 36.0 ppm (CH_3).

Reaction of $N(iPr)CH_2CH_2N(iPr)AsCl$ 38a with $GaCl_3$: A solution of $N(iPr)CH_2CH_2N(iPr)AsCl$ (2.58 g, 10.2 mmol) in CH_2Cl_2 (21 mL) was added to a stirred solution of $GaCl_3$ (1.795 g, 10.2 mmol) in CH_2Cl_2 (21 mL) over a period of 30 minutes, giving a bright yellow reaction mixture, consistent with that observed for the formation of

other dimeric arsyldenes. The product was not further characterized.

N(Bz)CH₂CH₂N(Bz)AsCl 38d: A solution of N,N'-dibenzylethylenediamine (25.96 g, 108.0 mmol) in diethyl ether (175 mL) was slowly added dropwise to a stirred solution of AsCl₃ (19.59 g, 108.1 mmol) and triethylamine (≈34 mL) in diethyl ether (200 mL) in a three-necked flask over a period of 105 minutes. Immediate reaction produced copious white precipitate, and the mixture was stirred for 90 minutes. The solution was filtered under nitrogen and the solid was washed with fresh solvent. The washings were added to the solution. The solvent was removed *in vacuo*, by rotary evaporation, and the resulting liquid was distilled under vacuum to produce a viscous bright yellow liquid, characterized as 2-chloro-1,3-dibenzyl-*cyclo*-1,3-diaza-2-arsapentane (22.62 g, 65.63 mmol, 60.8%) bp. 166-170 °C (3mm).

IR (neat liquid): 3080m(sh), 3060s, 3030s, 1955w, 1880w, 1870w, 1810w, 1605m, 1585m, 1490s, 1450vs, 1440s(sh), 1385s, 1355vs, 1320s(br), 1265s, 1205s, 1155s, 1110vs(br), 1070vs, 1050vs, 1030s, 1000m, 985m, 955m(br), 930s, 915s, 855s, 845s, 815m, 805m, 750vs, 735vs(sh), 690vs, 665s, 610m, 575m, 550s, 480m, 455s, 425m, 330m, 320m, 265vs, 255vs, 240vs cm⁻¹.

NMR (CD₂Cl₂): ¹H, 6.85 ppm (C₆H₅, m, 10H), 3.71 ppm (CH₂(benzyl), s, 4'H), 2.82 ppm (CH₂(ring), s, 4H); ¹³C, 138.6, 128.7, 128.5, 127.6 ppm (phenyl), 54.1 ppm (CH₂(benzyl)), 53.9 ppm (CH₂(ring)).

NMR Spectroscopic Identification of [N(Bz)CH₂CH₂N(Bz)As]₂ 40d

[GaCl₄]₂: A solution of (Bz)₂NCH₂CH₂N(Bz)AsCl (0.35 g, 1.02 mmol) in CH₂Cl₂ (32 mL) was added to a stirred solution of GaCl₃ (0.180 g, 1.02 mmol) in CH₂Cl₂ (32 mL) over a period of 15 minutes. The bright yellow reaction mixture was stirred for 30 minutes, and an aliquot of the reaction mixture was decanted into an NMR tube where the

CH_2Cl_2 was exchanged for an equal volume of CD_2Cl_2 . Removal of the remainder of the solvent from the reaction mixture produced only an intractable yellow-brown oil. NMR of the reaction mixture is consistent with the formation of *bis*(1,3-dibenzyl-1,3-diaza-2-arsolidinium tetrachlorogallate).

NMR (reaction mixture - CD_2Cl_2): ^1H , 7.43 ppm (C_6H_5 , m, 10H), 4.55 ppm ($\text{CH}_2(\text{benzyl})$, s, 4H), 4.04 ppm ($\text{CH}_2(\text{ring})$, s, 4H).

$\text{OCH}_2\text{CH}_2\text{OAsCl}$ 38e:¹¹⁰ A solution of AsCl_3 (29.28 g, 161.5 mmol) in diethyl ether (75 mL) was slowly added dropwise over a period of 40 minutes to a cooled (0 °C) suspension of ethylene glycol (10.05 g, 161.9 mmol) in triethylamine ($\approx$ 50 mL) and diethyl ether (175 mL) in a three-necked flask. Immediate reaction produced copious white precipitate, and after the addition was complete the solution was slowly warmed to room temperature. The solution was vacuum filtered and the solid was washed with fresh solvent. The washings were added to the solution. The solvent was removed *in vacuo*, by rotary evaporation, and the resulting liquid was distilled under vacuum to produce an oily yellow liquid, characterized as 2-chloro-*cyclo*-1,3-dioxa-2-arsapentane (yield not measured) bp. 45-85 °C (3mm).

IR (neat liquid): 2940s, 2880s, 1455m, 1225m, 1210m, 1065m, 1020vs, 905vs, 845s, 830s, 620vs, 535s, 435m, 330m, 320m, 290m, 280m, 255m, 235m cm^{-1} .

NMR (CD_2Cl_2): ^1H (AA'BB'), 4.20 ppm (CH_2 , m, 2H), 4.04 ppm (CH_2 , m, 2H); ^{13}C , 68.0 ppm.

Reaction of $\text{OCH}_2\text{CH}_2\text{OAsCl}$ 38e with GaCl_3 : A solution of $\text{OCH}_2\text{CH}_2\text{OAsCl}$ (3.78 g, 22.2 mmol) in CH_2Cl_2 (33 mL) was added to a stirred solution of GaCl_3 (3.911 g, 22.2 mmol) in CH_2Cl_2 (17 mL) over a period of 20 minutes. A small amount of a white precipitate was initially formed and later redissolved, and the solution grew slightly warm

as the addition was performed. On completion of addition, the majority of the solvent (>85%) was removed from the pale orange solution, leaving 7.164 g of a light brown solid. A portion of this material was recrystallized from benzene and produced a nearly colourless, microcrystalline product which is currently unidentified. mp. 84.0-85.0 °C.

Elemental anal. Calcd: C, 6.93; H, 1.16% (for $[\text{OCH}_2\text{CH}_2\text{OAs}]_2 \mathbf{40e}$ $[\text{GaCl}_4]_2$).

Found: C, 8.89; H, 1.58%.

IR: 1240m, 1220m, 1110m, 1020vs, 975m, 890s, 860s, 785s, 675m, 650s(sh), 630s, 610s, 530m(sh), 520s(sh), 505s, 430s(sh), 415s, 395s, 345m cm^{-1} .

NMR (CD_2Cl_2): ^1H , 4.49 ppm (m), 4.33 ppm (m); ^{13}C , 69.2 ppm.

$\text{OCH}_2\text{CH}_2\text{N}(\text{Me})\text{AsCl}$ **38f**:¹⁰⁴ Under a continuous flow of dry nitrogen, a solution of 2-methylaminoethanol (12.62 g, 168.0 mmol) in diethyl ether (75 mL) was slowly added dropwise over a period of 40 minutes to a cooled (0 °C) solution of AsCl_3 (30.47 g, 168.1 mmol) in triethylamine ($\approx$ 23 mL) and diethyl ether (175 mL) in a three-necked flask.

Immediate reaction produced copious white precipitate, and on completion of addition the solution was warmed slowly to room temperature. The solution was filtered under nitrogen and the solid was washed with fresh solvent. The washings were added to the solution. A small amount of precipitate was separated from the solution by decantation. The solvent was removed *in vacuo* and the resulting liquid was distilled under vacuum to produce an oily yellow liquid, characterized as 2-chloro-1-methyl-cyclo-1-oxa-3-aza-2-arsapentane (yield not measured) bp. 37-45 °C (3mm).

IR (neat liquid): 1333w, 1247m, 1205s, 1176m, 1150w, 1116s, 1100s, 1020s, 990s, 901s(br), 845m, 737w, 660vs, 579s, 552s, 424s, 339vs(vbr), 273vs, 245s cm^{-1} .

NMR (CD_2Cl_2): ^1H , 4.34 ppm (CH_2O , t, 2H), 3.24 ppm (CH_2N , t, 2H), 2.84 ppm (CH_3 , s, 3H); ^{13}C , 71.9 ppm (CH_2O), 55.6 ppm (CH_2N), 34.1 ppm (CH_3).

Reaction of $\text{OCH}_2\text{CH}_2\text{N}(\text{Me})\text{AsCl}$ 38f with GaCl_3 : A solution of $\text{OCH}_2\text{CH}_2\text{N}(\text{Me})\text{AsCl}$ (0.12 g, 0.65 mmol) in CH_2Cl_2 (24 mL) was added to a stirred solution of GaCl_3 (0.115 g, 0.653 mmol) in CH_2Cl_2 (24 mL) over a period of 20 minutes, resulting in a pale yellow solution. An aliquot of the reaction mixture was decanted into an NMR tube where the solvent was exchanged for CD_2Cl_2 . ^1H NMR spectra of the reaction mixture exhibit a very complex system with at least 11 second order multiplets and broad peaks. Removal of the solvent *in vacuo* from the reaction mixture resulted in an dark intractable oil.

Reaction of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ 40a $[\text{GaCl}_4]_2$ with Ph_3PO : A solution of Ph_3PO (0.196 g, 0.705 mmol) in CH_2Cl_2 (18 mL) was added to a stirred solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2 [\text{GaCl}_4]_2$ (0.525 g, 0.705 mmol) in CH_2Cl_2 (37 mL) over a period of 7 minutes. The solution was allowed to stir for two days, after which the ^{31}P NMR spectrum of the reaction mixture exhibited a single peak at 47.5 ppm, indicative of $\text{Ph}_3\text{PO} \rightarrow \text{GaCl}_3$.

Reaction of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ 40b $[\text{GaCl}_4]_2$ with Ph_3PO : A solution of Ph_3PO (0.127 g, 0.457 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2 [\text{GaCl}_4]_2$ (0.335 g, 0.443 mmol) in CH_2Cl_2 (9 mL) over a period of 8 minutes. The solution was allowed to stir overnight, after which the ^{31}P NMR spectrum of the reaction mixture exhibited a single peak at 47.5 ppm, indicative of $\text{Ph}_3\text{PO} \rightarrow \text{GaCl}_3$. Removal of the solvent *in vacuo* produced 0.377 g of material which was identified as a mixture of $\text{Ph}_3\text{PO} \rightarrow \text{GaCl}_3$ and $[\text{SCH}_2\text{CH}_2\text{SAs}-\text{SAs}(\text{Cl})\text{SCH}_2\text{CH}_2]$ 41b $[\text{GaCl}_4]$ by IR.

Reaction of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ 40a $[\text{GaCl}_4]_2$ with $\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{PCl}$ 52: A solution of $\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{PCl}$ (0.12 g, 0.79

mmol) in CH_2Cl_2 (13 mL) was slowly added to a stirred solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2 [\text{GaCl}_4]_2$ (0.285 g, 0.382 mmol) in CH_2Cl_2 (27 mL) over a period of 15 minutes. After stirring overnight an oily orange material separated from solution. An aliquot of the reaction mixture was decanted into an NMR tube where the solvent was exchanged for CD_2Cl_2 . ^1H NMR indicated a complex mixture of products, however after 10 days the spectrum had changed and the single product in solution was identified as 1,4,6,9-tetramethyl-1,4,6,9-tetraaza-5 λ^5 -phosphoniaspiro[4.4]nonane **53** tetrachlorogallate. Stirring of the solution for ten days resulted in a brown precipitate and colourless solution. Removal of the solvent *in vacuo* produced colourless amorphous material and more brown precipitate.

An alternative technique for the formation of **53** GaCl_4 involved rapid addition of a solution of $\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{PCl}$ (0.16 g, 1.0 mmol) in CH_2Cl_2 (13 mL) to a stirred solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2 [\text{GaCl}_4]_2$ (0.285 g, 0.382 mmol) in CH_2Cl_2 (26 mL). The mixture was refluxed under static vacuum for 2.5 hours, after which the solution was allowed to slowly cool to room temperature and stirred for two days. During this period the colour of the solution faded to pale yellow and a large quantity of brown precipitate was apparent. Solution NMR data is identical to that obtained after 10 days of stirring for the above technique.

NMR (reaction mixture - CD_2Cl_2): ^1H , 3.39 ppm (CH_2 , d, 8H, $^3J_{\text{H-P}} = 9.6$ Hz), 2.67 ppm (CH_3 , d, 12H, $^3J_{\text{H-P}} = 10.8$ Hz); ^{13}C , 46.6 ppm (CH_2 , d, $^2J_{\text{C-P}} = 14.8$ Hz), 31.0 ppm (CH_3 , $^2J_{\text{C-P}} = 5.2$ Hz); ^{31}P , 43.1 ppm.

Reaction of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ **40a $[\text{GaCl}_4]_2$ with $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{P}]$ **51** $[\text{GaCl}_4]$:** A solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{P}]$ $[\text{GaCl}_4]$ (0.52 mmol in 28 mL of CH_2Cl_2) was formed *in situ* by slowly adding a solution

of $\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{PCl}$ (0.08 g, 0.52 mmol) in CH_2Cl_2 (14 mL) to a stirred solution of GaCl_3 (0.093 g, 0.53 mmol) in CH_2Cl_2 (14 mL) over a period of 10 minutes. This solution was then slowly added to a solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2 [\text{GaCl}_4]_2$ (0.195 g, 0.262 mmol) in CH_2Cl_2 (21 mL) over a period of 20 minutes. The solution was stirred overnight and an aliquot of the reaction mixture was decanted into an NMR tube where the solvent was exchanged for CD_2Cl_2 . NMR data revealed that no reaction had occurred.

Reaction of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ 40a $[\text{GaCl}_4]_2$ with Ph_3P : A solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2 [\text{GaCl}_4]_2$ (0.104 g, 0.140 mmol) in CH_2Cl_2 (17 mL) was slowly added to a stirred solution of Ph_3P (0.073 g, 0.28 mmol) in CH_2Cl_2 (17 mL) over a period of 15 minutes. The solution was allowed to stir for 30 minutes and an aliquot of the reaction mixture was decanted into an NMR tube where the solvent was exchanged for CD_2Cl_2 . Slow removal of the solvent *in vacuo* from the remainder of the solution resulted in a bright yellow oil which produced a small number of colourless crystals after sitting for 10 days at room temperature. The crystals were characterized by X-ray crystallography as $\text{Ph}_3\text{P} \rightarrow \text{GaCl}_3$ 56.

NMR (reaction mixture - CD_2Cl_2): ^1H , 7.57 ppm (m, 20H), 3.35 ppm (s, 4H), 2.88 ppm (s, 6H); ^{13}C , 134.3 ppm, 134.1 ppm, 132.8 ppm, 130.1 ppm, 130.0 ppm, 57.3 ppm, 36.3 ppm; ^{31}P , 66.4 ppm (1P), 47.5 ppm (9P), 28.0 ppm (13P), -5.6 ppm (br, 32P).

Reaction of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ 40a $[\text{GaCl}_4]_2$ with Ph_3As : A solution of Ph_3As (0.170 g, 0.555 mmol) in CH_2Cl_2 (16 mL) was slowly added to a stirred solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2 [\text{GaCl}_4]_2$ (0.208 g, 0.279 mmol) in CH_2Cl_2 (31 mL) over a period of 10 minutes. The solution was allowed to stir for 30 minutes and an

aliquot of the reaction mixture was decanted into an NMR tube where the solvent was exchanged for CD_2Cl_2 . Both ^1H and ^{13}C NMR indicated that no reaction had occurred.

Reaction of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ 40b $[\text{GaCl}_4]_2$ with Benzene: $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ $[\text{GaCl}_4]_2$ (0.096 g, 0.127 mmol) was dissolved in benzene (9.02 g), forming a pale yellow solution. Slow removal of the solvent *in vacuo* resulted in a dark intractable oil which produced a small number of crystals after sitting overnight. These crystals were identified by melting point and X-ray crystallographic cell parameters as $[\text{SCH}_2\text{CH}_2\text{SAs-SAs}(\text{Cl})\text{SCH}_2\text{CH}_2]_2$ 41b $[\text{GaCl}_4]$. mp. 112.5-115.0 °C.

Reaction of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ 40b $[\text{GaCl}_4]_2$ with $\text{Fe}_2(\text{CO})_9$: A solution of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ $[\text{GaCl}_4]_2$ (0.229 g, 0.307 mmol) in CH_2Cl_2 (15 mL) was slowly added to a stirred solution/suspension of $\text{Fe}_2(\text{CO})_9$ (0.112 g, 0.308 mmol) in CH_2Cl_2 (31 mL) over a period of 20 minutes. The solution was protected from light and stirred for 36 hours, after which the colour had changed to bright green and a quantity of a flocculent bright green precipitate was present. An aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged for CD_2Cl_2 . ^1H data showed the presence of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ $[\text{GaCl}_4]_2$ only. After one month of stirring, no further change was observed. The green material is likely a reaction product between $\text{Fe}_2(\text{CO})_9$ and CH_2Cl_2 .¹⁹¹

Reaction of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ 40a $[\text{GaCl}_4]_2$ with $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{CH}_2$: A solution of 2,3-dimethyl-1,3-butadiene (0.11 g, 1.3 mmol) in CH_2Cl_2 (4 mL) was slowly added to a stirred solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ $[\text{GaCl}_4]_2$ (0.315 g, 0.423 mmol) in CH_2Cl_2 (21 mL) over a period of 8 minutes. The pale yellow solution was allowed to stir for 30 minutes. Slow

removal of the solvent *in vacuo* produced a quantity of colourless crystals which were characterized as 1-azonia-1,3,4,7-tetramethyl-7-aza-6-arsabicyclo[4.3.0]non-3-ene **57** tetrachlorogallate (0.211 g, 0.464 mmol, 54.8%), mp. 142.0-144.5 °C. Crystals of crystallographic quality were obtained by dissolving the product in a minimum of warm (60 °C) CH₂Cl₂ and cooling the solution to -18 °C.

Elemental anal. Calcd: C, 26.41; H, 4.43%.

Found: C, 26.02; H, 4.49%.

IR: 1657w, 1413m, 1325w, 1300w, 1270m, 1241m, 1171m, 1116m, 1073m, 1058w, 1009m, 984m, 967s, 940w, 924w, 885w, 867m, 798w, 784m, 737w, 655w, 597w, 581m, 569m, 525w, 453w, 423w, 383vs, 366s, 349m, 313w, 228w cm⁻¹.

NMR (CD₂Cl₂): ¹H, 3.90 ppm (d of d of d, 1H), 3.85 ppm (d, 1H), 3.69 ppm (d of d, 1H), 3.55 ppm (d, 1H), 3.49 ppm (d of d, 1H), 3.22 ppm (s, 3H), 3.15 ppm (t of d, 1H), 3.10 ppm (d, 1H), 2.97 ppm (s, 3H), 2.67 ppm (d, 1H), 1.95 ppm (m, 6H); ¹³C, 130.4 ppm, 128.8 ppm, 62.8 ppm, 62.2 ppm, 59.1 ppm, 52.2 ppm, 41.8 ppm, 37.6 ppm, 20.7 ppm, 20.3 ppm.

X-ray: orthorhombic, space group *Pca*2₁, *a* = 18.471(2) Å, *b* = 7.000(2) Å, *c* = 13.738(1) Å, *V* = 1776.2(8) Å³, *Z* = 4, *D*_{calcd} = 1.70 g cm⁻³, *μ* = 39.84 cm⁻¹, *R*_w = 0.0437.

Reaction of [SCH₂CH₂SAs]₂ **40b** [GaCl₄]₂ with

H₂C=C(CH₃)C(CH₃)=CH₂: A solution of 2,3-dimethyl-1,3-butadiene (0.14 g, 1.7 mmol) in CH₂Cl₂ (6 mL) was slowly added to a stirred solution of [SCH₂CH₂SAs]₂ [GaCl₄]₂ (0.346 g, 0.457 mmol) in CH₂Cl₂ (30 mL) over a period of 8 minutes. During the course of addition the colour of the solution darkened to a light orange. The solution was allowed to stir for 30 minutes and then an aliquot of the reaction mixture was decanted into an NMR tube where the CH₂Cl₂ was exchanged for CD₂Cl₂. The ¹H and ¹³C NMR

spectra revealed a number of products in the reaction mixture. Slow removal of the majority (>85%) of the solvent *in vacuo* resulted in the formation of a brown powder and small quantity of a pale yellow crystalline material, which was identified by X-ray crystallography as 1-thionia-4,6-dithia-5-arsabicyclo[3.3.0]octane **58b** tetrachlorogallate (*vide infra*) (0.068 g, 0.157 mmol, 17.2%), mp. 221-231 °C. Removal of the solvent from the bulk of the solution left a dark red oil which produced another crop of crystals upon sitting at room temperature for one week (0.045 g, 0.103 mmol, 11.2%), mp. 173-200 °C. The brown material was not identified. This compound has also been prepared quantitatively by an alternate reaction (*vide infra*).

Reaction of [N(Me)CH₂CH₂N(Me)As]₂ **40a [GaCl₄]₂ with MeC≡CMe:** A solution of [N(Me)CH₂CH₂N(Me)As]₂ [GaCl₄]₂ (0.758 g, 1.02 mmol) in CH₂Cl₂ (39 mL) was slowly added to a stirred solution of 2-butyne (0.15 g, 2.8 mmol) in CH₂Cl₂ (13 mL) over a period of 25 minutes. The solution was allowed to stir for 48 hours, after which the colour had darkened and a quantity of an oily orange precipitate was present. The yellow supernatant was decanted off of the precipitate and an aliquot of the reaction mixture was decanted into an NMR tube where the CH₂Cl₂ was exchanged for CDCl₃. Removal of the solvent *in vacuo* from the supernatant resulted in an intractable orange oil. The ¹H NMR spectrum of the reaction mixture showed peaks at 3.39 ppm (s, 2H) and 2.91 ppm (s, 3H).

Reaction of [N(Me)CH₂CH₂N(Me)As]₂ **40a [GaCl₄]₂ with PhC≡CPh:** A solution of [N(Me)CH₂CH₂N(Me)As]₂ [GaCl₄]₂ (0.218 g, 0.293 mmol) in CH₂Cl₂ (13 mL) was slowly added to a stirred solution of diphenylacetylene (0.104 g, 0.584 mmol) in CH₂Cl₂ (13 mL) over a period of 10 minutes. The solution was allowed to stir overnight, after which the yellow colour had darkened. An aliquot of the reaction mixture was

decanted into an NMR tube where the CH_2Cl_2 was exchanged for CDCl_3 . The ^1H NMR spectrum of the reaction mixture showed only starting materials and much of the **40a** GaCl_4 was recoverable from the mixture (0.127 g, 0.170 mmol, 58.3%).

Reaction of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ **40a $[\text{GaCl}_4]_2$ with DMAD:** A solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2 [\text{GaCl}_4]_2$ (0.272 g, 0.365 mmol) in CH_2Cl_2 (15 mL) was slowly added to a stirred solution of $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ (0.29 g, 2.0 mmol) in CH_2Cl_2 (15 mL) over a period of 10 minutes. The solution was allowed to stir for 5 days, after which the yellow colour had darkened. An aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged for CDCl_3 . The ^1H NMR spectrum of the reaction mixture showed a complex mixture of products. Removal of the solvent *in vacuo* resulted in an intractable orange oil.

Reaction of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ **40a $[\text{GaCl}_4]_2$ with $\text{F}_3\text{CC}\equiv\text{CCF}_3$:** A solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2 [\text{GaCl}_4]_2$ (0.205 g, 0.275 mmol) in CH_2Cl_2 (19 mL) was slowly added to a stirred solution of hexafluorobut-2-yne (0.81 g, 5.0 mmol) dissolved in CH_2Cl_2 (19 mL) over a period of 20 minutes. The solution was stirred for 30 minutes, resulting in a small quantity of a light coloured precipitate. An aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged for CD_2Cl_2 . The ^1H and ^{13}C NMR spectra of the reaction mixture exhibited peaks consistent with unreacted **40a** $[\text{GaCl}_4]_2$. ^{19}F NMR revealed that no fluorine was present in the reaction mixture, the unreacted volatile $\text{F}_3\text{CC}\equiv\text{CCF}_3$ having been removed along with the CH_2Cl_2 during preparation of the NMR sample.

Reaction of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ **40b $[\text{GaCl}_4]_2$ with $\text{MeC}\equiv\text{CMe}$:** A solution of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2 [\text{GaCl}_4]_2$ (0.701 g, 0.926 mmol) in CH_2Cl_2 (51 mL) was slowly added

to a stirred solution of 2-butyne (0.10 g, 1.8 mmol) in CH_2Cl_2 (13 mL) over a period of 20 minutes. Addition resulted in the solution darkening in colour to orange. The solution was allowed to stir for 4 hours, after which there was a large quantity of brown precipitate. The orange supernatant was decanted off of the precipitate and an aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged for CD_2Cl_2 . The ^1H NMR spectrum revealed a complicated mixture with a multitude of products present. Continued stirring over the course of a week continued to produce brown precipitate. Slow removal of the solvent *in vacuo* resulted a brown sludge interspersed with small crystals. These crystals were identified crystallographically as $[\text{SCH}_2\text{CH}_2\text{SAs}-\text{SAs}(\text{Cl})\text{SCH}_2\text{CH}_2]$ **41h** $[\text{GaCl}_4]$ (0.070 g, 0.12 mmol).

X-ray: Orthorhombic, space group $Pna2_1$, $a = 14.833(5) \text{ \AA}$, $b = 13.620(3) \text{ \AA}$, $c = 8.584(4) \text{ \AA}$, $V = 1734(1) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 2.213 \text{ g cm}^{-3}$, $\mu = 65.40 \text{ cm}^{-1}$, $R_w = 0.0340$.

Reaction of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ **40h $[\text{GaCl}_4]_2$ with $\text{PhC}\equiv\text{CPh}$:** A solution of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2 [\text{GaCl}_4]_2$ (0.244 g, 0.322 mmol) in CH_2Cl_2 (21 mL) was slowly added to a stirred solution of diphenylacetylene (0.115 g, 0.645 mmol) in CH_2Cl_2 (21 mL) over a period of 15 minutes. The solution was allowed to stir for 9 days, after which a slight colour change was observed. An aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged CD_2Cl_2 . The ^1H NMR spectrum revealed a complicated reaction mixture with a multitude of products. Slow removal of the solvent *in vacuo* produced an intractable orange oil.

Reaction of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ **40h $[\text{GaCl}_4]_2$ with DMAD:** A solution of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2 [\text{GaCl}_4]_2$ (0.212 g, 0.280 mmol) in CH_2Cl_2 (22 mL) was slowly added to a stirred solution of dimethyl acetylenedicarboxylate ($\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$) (0.08 g, 0.56

mmol) in CH_2Cl_2 (7 mL) over a period of 15 minutes. The solution was allowed to stir for 5 days, after which an aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged for CD_2Cl_2 . The ^1H NMR spectrum of the reaction mixture showed a complex mixture of products. Removal of the solvent *in vacuo* resulted in a yellow-brown oil which crystallized upon standing overnight. Attempts to wash the crystals resulted in their dissolution and attempts to regrow them were unsuccessful.

Reaction of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ 40b $[\text{GaCl}_4]_2$ with $\text{F}_3\text{CC}\equiv\text{CCF}_3$: A solution of $[\text{SCH}_2\text{CH}_2\text{SAs}]_2$ $[\text{GaCl}_4]_2$ (0.101 g, 0.133 mmol) in CH_2Cl_2 (15 mL) was slowly added to a stirred solution of hexafluorobut-2-yne (0.60 g, 3.7 mmol) dissolved in CH_2Cl_2 (15 mL) over a period of 10 minutes. The solution was stirred for 30 minutes and an aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged for CD_2Cl_2 . The ^1H and ^{13}C NMR spectra of the reaction mixture showed the presence of only 40b $[\text{GaCl}_4]_2$. ^{19}F NMR revealed that no fluorine was present in the reaction mixture, the unreacted volatile $\text{F}_3\text{CC}\equiv\text{CCF}_3$ having been removed along with the CH_2Cl_2 during preparation of the NMR sample.

Reaction of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ 40a $[\text{GaCl}_4]_2$ with PhN_3 : 0.18 g of a 20% hexane solution of phenyl azide (0.036 g, 0.30 mmol) was slowly added to a stirred solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ $[\text{GaCl}_4]_2$ (0.115 g, 0.154 mmol) in CH_2Cl_2 (45 mL) over a period of 12 minutes. The solution was stirred for 40 minutes and an aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged for CD_2Cl_2 . The ^1H NMR spectrum was consistent with that of unreacted starting materials. Removal of the solvent *in vacuo* resulted in the recovery of a small amount of unreacted 40a $[\text{GaCl}_4]_2$ (0.010 g, 0.013 mmol) as shown by IR.

Reaction of $[N(Me)CH_2CH_2N(Me)As]_2$ 40a $[GaCl_4]_2$ with AdN_3 : A solution of $[N(Me)CH_2CH_2N(Me)As]_2 [GaCl_4]_2$ (0.221 g, 0.297 mmol) in CH_2Cl_2 (20 mL) was slowly added to a stirred solution of 1-azidoadamantane (0.105 g, 0.592 mmol) in CH_2Cl_2 (20 mL) over a period of 15 minutes. The solution was stirred overnight and an aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged for CD_2Cl_2 . The 1H NMR spectrum was consistent with that of the unreacted starting materials. Removal of the solvent *in vacuo* resulted in the recovery of a quantity of unreacted 40a $[GaCl_4]_2$ (0.106 g, 0.142 mmol) as shown by IR.

$N(Me)CH_2CH_2CH_2N(Me)AsCl$ 61a: Under a continuous stream of dry nitrogen gas a solution of N,N'-dimethyl-1,3-propanediamine (4.96 g, 48.5 mmol) and triethylamine (≈ 25 mL) in diethyl ether (20 mL) was slowly added dropwise to a stirred solution of $AsCl_3$ (8.80 g, 48.5 mmol) in diethyl ether (125 mL) in a three-necked flask over a period of 45 minutes. Immediate reaction produced copious white precipitate, and the mixture was stirred overnight. The mixture was filtered under nitrogen and the solid was washed with two approximately 25 mL portions of fresh diethyl ether. The washings were added to the filtrate. The solution was then transferred into a bridge in the glove bag and the majority of the solvent was removed *in vacuo*. Cooling the solution to $-18^\circ C$ overnight resulted in the formation of colourless crystals which were recrystallized from fresh diethyl ether (crystallographic quality) and characterized as 2-chloro-1,3-dimethyl-*cyclo*-1,3-diaza-2-arsahexane (5.806 g, 27.56 mmol, 56.9%), mp. $47.0-48.5^\circ C$.

IR: 2744m, 2718m, 2702m, 2687w, 1276vs, 1227vs, 1207m, 1146vs, 1133vs, 1125vs(sh), 1091s, 1050vs, 1037vs, 941vs, 925s, 891s, 837vs, 570vs, 540m, 414m, 361vs, 342m, 320w, 285s(sh), 280s(sh), 263vs, 239vs, 233vs cm^{-1} .

NMR (CD_2Cl_2): 1H , 2.88 ppm (CH_2N , m, 4H), 2.63 ppm (CH_3 , s, 6H), 1.94 ppm (CH_2 , m, 2H); ^{13}C , 48.4 ppm (CH_2N), 40.3 ppm (CH_3), 27.8 ppm (CH_2).

X-ray: monoclinic, space group $P2_1/n$, $a = 7.206(1)$ Å, $b = 9.650(1)$ Å, $c = 13.021(2)$ Å, $\beta = 99.61(2)^\circ$, $V = 892.8(2)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.566$ g cm⁻³, $\mu = 40.27$ cm⁻¹, $R_w = 0.0289$.

[N(Me)CH₂CH₂CH₂N(Me)As]₂ 63a [GaCl₄]₂: A solution of N(Me)CH₂CH₂CH₂N(Me)AsCl (0.435 g, 2.07 mmol) in CH₂Cl₂ (31 mL) was added to a stirred solution of GaCl₃ (0.365 g, 2.07 mmol) in CH₂Cl₂ (15 mL) over a period of 15 minutes. Addition resulted in an immediate colour change to reddish-purple, through greyish-yellow, and finally bright yellow. An aliquot of the reaction mixture was decanted into an NMR tube where the CH₂Cl₂ was exchanged for CD₂Cl₂. NMR spectra of the reaction mixture revealed a single product. Removal of the solvent *in vacuo* resulted in an orange-brown solid which could not be recrystallized. This material was characterized by NMR and IR as *bis*(1,3-dimethyl-1,3-diaza-2-arsenanium tetrachlorogallate) (0.589 g, 0.762 mmol, 87.6%), mp. 52.0-54.5 °C.

IR: 1347w, 1284vs, 1242vs, 1205s, 1184w, 1152vs, 1118vs, 1102m, 1084s, 1049vs, 1040vs, 955vs, 913w, 879s, 862m, 806w, 752w, 601s, 588s, 551w, 493w, 408s, 387vs(sh), 378vs, 362vs, 339vs, 301w, 266w, 255w, 232s cm⁻¹.

NMR (CD₂Cl₂): ¹H, 3.49 ppm (CH₂N, m, 4H), 3.34 ppm (CH₃, s, 6H), 2.29 ppm (CH₂, m, 2H); ¹³C, 51.6 ppm (CH₂N), 42.6 ppm (CH₃), 26.2 ppm (CH₂).

NMR Spectroscopic Identification of [N(Me)CH₂CH₂CH₂N(Me)As-

N(Me)As(Cl)N(Me)CH₂CH₂CH₂] 65a [GaCl₄]: A solution of N(Me)CH₂CH₂CH₂N(Me)AsCl (0.603 g, 2.86 mmol) in CH₂Cl₂ (37 mL) was added to a stirred solution of GaCl₃ (0.252 g, 1.43 mmol) in CH₂Cl₂ (19 mL) over a period of 21 minutes. Addition resulted in a pale yellow solution which was stirred for 1 hour and an aliquot of the reaction mixture was decanted into an NMR tube where the CH₂Cl₂ was

exchanged for CD_2Cl_2 . NMR spectra of the reaction mixture revealed a single product with chemical shifts consistent with those expected for $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}-\text{N}(\text{Me})\text{As}(\text{Cl})\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{CH}_2] [\text{GaCl}_4]$. Removal of the solvent from the bulk of the solution produced only an intractable dark orange oil.

NMR (reaction mixture - CD_2Cl_2): ^1H , 3.23 ppm (CH_2N , m, 4H), 3.04 ppm (CH_3 , s, 6H), 2.15 ppm (CH_2 , m, 2H); ^{13}C , 50.3 ppm (CH_2N), 41.7 ppm (CH_3), 27.0 ppm (CH_2).

Reaction of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2$ **63a $[\text{GaCl}_4]_2$ with $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{CH}_2$:** A solution of $[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{As}]_2 [\text{GaCl}_4]_2$ (0.855 g, 1.11 mmol) in CH_2Cl_2 (99 mL) was formed *in situ* as described above. To this was slowly added a solution of 2,3-dimethyl-1,3-butadiene (0.24 g, 2.9 mmol) in CH_2Cl_2 (6 mL) over a period of 4 minutes. The mixture was allowed to stir for 20 minutes, after which the solvent was slowly removed *in vacuo*, giving a viscous yellow oil which solidified upon sitting overnight. This material was characterized as 1-azonia-1,3,4,7-tetramethyl-7-aza-6-arsabicyclo[4.4.0]dec-3-ene **64** tetrachlorogallate (0.849 g, 1.81 mmol, 81.5%), mp. 83.5-87.5 °C.

IR: 1343w, 1313m, 1301m, 1286w, 1267m, 1234m, 1204s, 1200s, 1184m, 1156vs, 1135s, 1123m, 1097w, 1074m, 1051m, 1042s, 1029m, 1003s, 982vs, 946s, 913s, 884s, 847vs, 806w, 788w, 770vs, 738w, 657m, 611m, 583s, 548w, 503s, 405m(sh), 381vs(br), 365vs, 343s, 330m, 317m, 288w, 257w cm^{-1} .

NMR (CD_2Cl_2): ^1H (COSY), 3.71 ppm (m, 3H), 3.71 ppm (m, 3H), 3.69 ppm (m, 3H), 3.39 ppm (d, 1H), 3.36 ppm (d, 1H), 3.14 ppm (s, 3H), 3.05 ppm (s, 3H), 3.01 ppm (m, 2H), 3.01 ppm (m, 2H), 2.47 ppm (d, 1H), 2.39 ppm (m, 1H), 1.90 ppm (s, 3H), 1.74 ppm (s, 3H), 1.74 ppm (m, 1H); ^{13}C , 124.6 ppm, 122.8 ppm,

65.0 ppm, 57.4 ppm, 48.9 ppm, 45.6 ppm, 43.9 ppm, 33.1 ppm, 22.2 ppm, 19.5 ppm, 19.0 ppm.

SCH₂CH₂CH₂SAsCl 61b:¹⁵¹ A quantity of propanedithiol (5.50 g, 50.8 mmol) was slowly added dropwise to a stirred solution of AsCl₃ (9.11 g, 50.3 mmol) in CCl₄ (25 mL) over a period of 15 minutes. The liberation of HCl gas was instantaneous and accompanied by self-cooling of the reaction mixture. The solution was stirred overnight, then half of the solvent was removed *in vacuo* by rotary evaporation. The solution was cooled over dry ice, producing copious white crystals (crystallographic quality). The cold supernatant was decanted and the crystals were dried *in vacuo* and characterized as 2-chloro-*cyclo*-1,3-dithia-2-arsahexane (yield ≈85%) mp. 47-48 °C.

IR: 1419m, 1342w, 1297m, 1272m, 1251m, 1244m, 1199w, 1181m, 1146w, 1115w, 1057w(sh), 1051w, 1001m, 952w, 901m, 857m, 840m(sh), 823m(sh), 803s, 755m(sh), 676w, 653w, 623m, 491m, 480m, 457w, 373s, 342vs, 332vs, 297m(sh) cm⁻¹.

NMR (CD₂Cl₂): ¹H, 3.46 ppm (CH₂S_(axial), m, 2H), 3.04 ppm (CH₂S_(equatorial), m, 2H), 2.24 ppm (CH₂, m, 2H); ¹³C, 26.8 ppm (CH₂S), 26.1 ppm (CH₂).

X-ray:¹⁹² orthorhombic, space group *Pnma*, *a* = 10.144(2) Å, *b* = 9.850(2) Å, *c* = 7.157(1) Å, *V* = 715.0 Å³, *Z* = 4, *D*_{calcd} = 2.01 g cm⁻³, *μ* = 55.7 cm⁻¹, *R*_w = 0.029.

NMR Spectroscopic Identification of [SCH₂CH₂CH₂SAs]₂ 63b [GaCl₄]₂: A solution of SCH₂CH₂CH₂SAsCl (0.131 g, 0.605 mmol) in CH₂Cl₂ (15 mL) was added to a stirred solution of GaCl₃ (0.106 g, 0.602 mmol) in CH₂Cl₂ (15 mL) over a period of 13 minutes. The solution was stirred for 30 minutes and an aliquot of the reaction mixture was decanted into an NMR tube where the CH₂Cl₂ was exchanged for CD₂Cl₂. The NMR

spectra of the reaction mixture revealed a single product consistent with *bis*(1,3-dithia-2-arsenanium tetrachlorogallate). Removal of the bulk of the solvent *in vacuo* resulted in an intractable yellow-brown oil.

NMR (reaction mixture - CD_2Cl_2): ^1H , 3.43 ppm (CH_2S , t, 4H), 2.38 ppm (CH_2 , quintet, 2H); ^{13}C , 29.3 ppm (CH_2S), 26.9 ppm (CH_2).

NMR Spectroscopic Identification of $[\text{SCH}_2\text{CH}_2\text{CH}_2\text{SAs-}$

$\text{SAs}(\text{Cl})\text{SCH}_2\text{CH}_2\text{CH}_2]$ **65a** $[\text{GaCl}_4]$: A solution of $\text{SCH}_2\text{CH}_2\text{CH}_2\text{SAsCl}$ (0.502 g, 2.32 mmol) in CH_2Cl_2 (38 mL) was added to a stirred solution of GaCl_3 (0.203 g, 1.15 mmol) in CH_2Cl_2 (19 mL) over a period of 15 minutes. The pale yellow solution was stirred overnight and an aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged for CD_2Cl_2 . The NMR spectra of the reaction mixture revealed a single product with chemical shifts consistent with those expected for $[\text{SCH}_2\text{CH}_2\text{CH}_2\text{SAs-SAs}(\text{Cl})\text{SCH}_2\text{CH}_2\text{CH}_2]$ $[\text{GaCl}_4]$. Removal of the solvent from the bulk of the solution produced an intractable bright yellow oil.

NMR (reaction mixture - CD_2Cl_2): ^1H , 3.38 ppm (CH_2S , t, 4H), 2.34 ppm (CH_2 , quintet, 2H); ^{13}C , 28.7 ppm (CH_2S), 27.0 ppm (CH_2).

$\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SAsCl}$ **66b**:¹⁵⁵ A solution of 2-mercaptoethyl sulfide (16.09 g, 104.3 mmol) in benzene (40 mL) was added rapidly to a stirred solution of AsCl_3 (18.87 g, 104.1 mmol) in benzene (200 mL) in a three necked flask. Addition resulted in the immediate liberation of HCl gas and the formation of a small quantity of white precipitate. The solution was refluxed for 17 hours, resulting in dissolution of the precipitate, after which no further evidence of HCl generation was observed. The solution was allowed to slowly cool to room temperature, resulting in the formation of large colourless crystals. These were recovered by vacuum filtration and washed with three 40 mL portions of benzene. The crystalline product was characterized as 2-chloro-1,3,6-trithia-2-arsocane

(21.90 g, 83.38 mmol, 80.1%), mp. 120.5-121.5 °C.

IR: 1286m, 1255m, 1238w, 1161w, 1155m, 1130w, 1111w, 1001w, 927s, 902s, 840s, 825vs, 687w, 660m, 633w, 549w, 441w, 424s, 378s, 360vs, 324w, 281s, 261vs(sh), 251vs, 232s cm^{-1} .

NMR (CD_2Cl_2): ^1H , (ABCD) 3.45 ppm (m, 2H), 3.29 ppm (m, 2H), 3.20 ppm (m, 2H), 2.84 ppm (m, 2H); ^{13}C , 41.5 ppm, 35.1 ppm (CH_2); ^{13}C CP MAS, 46.3 ppm, 41.1 ppm, 37.3 ppm, 35.7 ppm.

[SCH₂CH₂SAsSCH₂CH₂] 58b [GaCl₄]: A solution of GaCl₃ (0.266 g, 1.51 mmol) in CH_2Cl_2 (4 mL) was added to a stirred solution of SCH₂CH₂SCH₂CH₂SAsCl (0.397 g, 1.51 mmol) in CH_2Cl_2 (36 mL) over a period of 55 minutes to give an immediate white precipitate. The majority (>85%) of the solvent was removed *in vacuo* and the remainder of the solution was decanted from the precipitate, which was washed by repeated back distillations of solvent and dried *in vacuo*. The precipitate was characterized as 1-thionia-4,6-dithia-5-arsabicyclo[3.3.0]octane tetrachlorogallate (0.518 g, 1.18 mmol, 78.1%), mp. chars 200 °C, melts 216-218 °C.

Elemental anal. Calcd: C, 10.95; H, 1.84%.

Found: C, 11.27; H, 1.95%.

IR: 1416m, 1282w, 1252m, 1149w, 1137w, 941w, 932w, 907m, 831m, 811m, 668w, 652w, 597w, 441w, 429w, 377vs, 370vs cm^{-1} .

NMR (CD_2Cl_2): ^1H , 4.10 ppm (m, 4H), 3.85 ppm (m, 4H); ^{13}C , 49.8 ppm, 43.2 ppm; ^{13}C CP MAS, 54.0 ppm, 52.9 ppm, 49.0 ppm, 43.5 ppm, 41.0 ppm.

X-ray: monoclinic, space group $P2_1/n$, $a = 14.669(2)$ Å, $b = 12.647(5)$ Å, $c = 15.112(2)$ Å, $\beta = 100.20(2)^\circ$, $V = 2759(2)$ Å³, $Z = 8$, $D_{\text{calcd}} = 2.112$ g cm^{-3} , $\mu = 55.44$ cm^{-1} , $R_w = 0.0583$.

SCH₂CH₂SSbCl ~~66c~~:¹⁵⁵ A solution of 2-mercaptoethyl sulfide (11.06 g, 71.67 mmol) in benzene (20 mL) was added rapidly to a stirred solution of SbCl₃ (16.32 g, 71.54 mmol) in benzene (100 mL) in a three necked flask. Addition resulted in the immediate formation of a white precipitate. The solution was refluxed for 20 hours, during which the precipitate dissolved and later reprecipitated. The solution was allowed to slowly cool to room temperature. The solid was recovered by vacuum filtration, washed with two 25 mL portions of benzene, and allowed to air dry. The product was characterized as 2-chloro-1,3,6-trithia-2-stibocane (20.31 g, 65.62 mmol, 91.72%), mp. 142-144 °C.

IR: 1292m, 1280m, 1262w, 1245w, 1166w, 1158w, 1009w, 924m, 899s, 837s, 827s, 812w, 771w, 681w, 659w, 654w(sh), 438w, 418m, 346s, 328vs, 308m, 247vs, 228w cm⁻¹.

NMR (CD₂Cl₂): ¹H, (ABCD) 3.52 ppm (m, 2H), 3.40 ppm (m, 2H), 3.25 ppm (m, 2H), 2.84 ppm (m, 2H); ¹³C, 42.0 ppm, 32.1 ppm (CH₂); ¹³C CP MAS, 47.6 ppm, 43.8 ppm, 40.5 ppm, ≈35.5 (sh) ppm, 34.5 ppm, 32.7 ppm.

[SCH₂CH₂SSbSCH₂CH₂] ~~58c~~ **[GaCl₄]**: A solution of GaCl₃ (0.163 g, 0.926 mmol) in CH₂Cl₂ (14 mL) was added to a stirred solution of SCH₂CH₂SSbSCH₂CH₂SSbCl (0.289 g, 0.934 mmol) in CH₂Cl₂ (28 mL) over a period of 35 minutes, immediately producing an off-white precipitate. The majority (>85%) of the solvent was removed *in vacuo* and the remainder of the solution was decanted from the precipitate, which was washed by repeated back distillations of solvent and dried *in vacuo*. The precipitate was characterized as 1-thionia-4,6-dithia-5-stibabicyclo[3.3.0]octane tetrachlorogallate (0.285 g, 0.587 mmol, 63.4%), mp. 104.5-106.5 °C.

Elemental anal. Calcd: C, 9.89; H, 1.66%.

Found: C, 10.04; H, 1.75%.

IR: 1286m, 1258w, 1241w, 1158w, 934w, 901m, 833m, 827m, 806w, 654w, 611w,

429w, 385vs, 376vs, 366vs, 350s, 320m(sh), 313m, 305m(sh) cm^{-1} .

NMR (CD_2Cl_2): ^1H , 3.93 ppm (br, 2H), 3.79 ppm (br, 2H), 3.52 ppm (br, 2H), 3.35 ppm (br, 2H); ^{13}C CP MAS, 50.2 ppm, 48.2 ppm, 45.9 ppm, 43.2 ppm, 38.1 ppm.

$\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SBiCl}$ 66d:¹⁵⁵ A solution of 2-mercaptoethyl sulfide (8.27 g, 53.6 mmol) in benzene (20 mL) was added rapidly to a rapidly stirred suspension of BiCl_3 (16.87 g, 53.5 mmol) in benzene (100 mL) in a three necked flask, resulting in an immediate colour change to yellow. The solution was stirred at room temperature for 28 hours and the solid yellow material was recovered by vacuum filtration, washed with three 30 mL portions of benzene, and allowed to air dry. The product was characterized as 2-chloro-1,3,6-trithia-2-bismocane (18.01 g, 45.40 mmol, 84.9%), mp. d 93 °C.

IR: 668w, 375w, 351w, 328w, 303w, 290w, 279w, 266w, 255w, 243w cm^{-1} .

NMR: ^{13}C CP MAS, 43.0 ppm, 37.0 ppm.

Reaction of $\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SBiCl}$ 66d with GaCl_3 : A solution of GaCl_3 (0.151 g, 0.858 mmol) in CH_2Cl_2 (12 mL) was added to a rapidly stirred suspension of $\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SBiCl}$ (0.338 g, 0.852 mmol) in CH_2Cl_2 (36 mL) over a period of 15 minutes. The mixture was stirred for 11 days resulting in a very slight darkening of the colour. The majority (>85%) of the solvent was removed *in vacuo* and the remainder of the solution was decanted off of the solid, which had coalesced into lumps. The solid was washed by repeated back distillations of solvent, dried *in vacuo*, and characterized by IR as unreacted $\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SBiCl}$.

Reaction of Dimesitylchloroarsine 67 with GaCl_3 : A suspension of Mes_2AsCl (0.501 g, 1.44 mmol) in CH_2Cl_2 (22 mL) was quickly added to a rapidly stirred solution

of GaCl_3 (0.256 g, 1.45 mmol) in CH_2Cl_2 (22 mL), instantly giving a deep red solution which became colourless within one minute. The reaction was not further characterized.

$\text{C}_6\text{H}_4\text{As}(\text{Cl})\text{N}(\text{H})\text{C}_6\text{H}_4 \cdot x\text{CCl}_4$ 68 (Adamsite):¹⁵⁸ Diphenylamine (8.01 g, 47.3 mmol) and AsCl_3 (9.42 g, 52.2 mmol) were combined in a round bottom flask, resulting in a dark green solution. The solution was set to reflux, resulting in the liberation of HCl gas. Reflux was continued for 5 hours, after which the solution was allowed to slowly cool to room temperature, producing a solid mass of pale green crystals in virtually quantitative yield. This was washed with hexane and recovered by vacuum filtration. The resulting sticky greenish-yellow powder was air dried on the suction. Approximately 25% of this material was recrystallized from about 200 mL of boiling CCl_4 . Upon cooling this produced a mass of greenish-yellow crystals which were filtered off and air dried, transforming them to a bright yellow powder, which was characterized as $\text{C}_6\text{H}_4\text{As}(\text{Cl})\text{N}(\text{H})\text{C}_6\text{H}_4 \cdot x\text{CCl}_4$, mp. 188 °C.

IR: 3340m, 1605m, 1575m, 1515w, 1505w, 1235m, 1160w, 1135w, 1065w, 1020w, 895w, 845w, 750s, 740s, 595m(br), 440m, 380w, 370w, 290w, 285w, 270m, 255m, 245m, 240m cm^{-1} .

NMR (CD_2Cl_2): ^1H , 7.88 ppm (m, 2H), 7.47 ppm (m, 3H), 7.10 ppm (m, 4H); ^{13}C , 140.2 ppm (quaternary), 135.7 ppm, 133.0 ppm, 121.3 ppm, 120.9 ppm (quaternary), 116.7 ppm.

Reaction of Adamsite 68 with GaCl_3 : A solution of GaCl_3 (0.049 g, 0.278 mmol) in CH_2Cl_2 (7 mL) was added to a rapidly stirred solution of $\text{C}_6\text{H}_4\text{As}(\text{Cl})\text{N}(\text{H})\text{C}_6\text{H}_4 \cdot x\text{CCl}_4$ (0.076 g, <0.274 mmol) in CH_2Cl_2 (7 mL) over a period of 15 minutes, immediately resulting in a deep purple solution. The solution was stirred overnight and then an aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged

for CD_2Cl_2 . Both the ^1H and ^{13}C NMR spectra of the reaction mixture differ considerably from that of adamsite and have been tentatively assigned to phenarsazine **70**. The solvent was removed *in vacuo* from the bulk of the solution, leaving dark purple crystals. These crystals were exposed to dynamic vacuum overnight to remove all traces of excess GaCl_3 were then identified as adamsite by IR. X-ray crystallography indicated that the adamsite had crystallized as $\text{C}_6\text{H}_4\text{As}(\text{Cl})\text{N}(\text{H})\text{C}_6\text{H}_4 \cdot 1/2\text{C}_6\text{H}_6$ (0.059g, 0.17 mmol), mp. 155-159 °C. When exposed to the air the purple material immediately reverts to the bright yellow colour of the starting material.

NMR (reaction mixture - CD_2Cl_2): ^1H , 8.84 ppm (d, 2H), 8.59 ppm (br, 2H), 8.29 ppm (m, 2H), 7.79 ppm (br, 2H); ^{13}C , 158.7 ppm (quaternary), 139.4 ppm, 135.9 ppm (quaternary), 134.7 ppm, 125.0 ppm, 123.3 ppm.

X-ray: orthorhombic, space group *Pbca*, $a = 26.969(11)$ Å, $b = 16.252(9)$ Å, $c = 13.035(11)$ Å, $V = 5712(10)$ Å³, $Z = 8$, $D_{\text{calcd}} = 1.472$ g cm⁻³, $\mu = 25.42$ cm⁻¹, $R_w = 0.0483$.

$\text{C}_6\text{H}_4\text{As}(\text{Cl})\text{OC}_6\text{H}_4$ **69**:¹⁵⁹ Phenyl ether (9.60 g, 56.4 mmol) and AsCl_3 (10.22 g, 56.4 mmol) were combined in a round bottom flask. A catalytic amount of AlCl_3 was added and the mixture was set to reflux for 150 minutes, resulting in a deep red solution. The solution was allowed to slowly cool to room temperature and to sit undisturbed for a period of 3 weeks, resulting in a small quantity (≈ 3 g) of colourless crystals. These were washed with hexane and recovered by vacuum filtration. This material was characterized as phenoxarsine chloride, mp. 120.0-121.5 °C.

IR: 1591m, 1578vs, 1315s, 1305s, 1264vs, 1222vs, 1200s, 1161m, 1155m, 1125vs, 1113s, 1071m, 1063s, 1027w, 989w, 984w, 947m, 883s, 870s, 863m, 802s, 765vs, 716m, 596w, 449s, 390s, 381s, 337vs, 309w, 288s, 255w, 222m cm⁻¹.

NMR (CD_2Cl_2): ^1H , 7.85 ppm (m, 2H), 7.59 ppm (m, 2H), 7.43 ppm (m, 2H), 7.29

ppm (m, 2H); ^{13}C , 135.2 ppm, 133.8 ppm, 124.2 ppm, 119.0 ppm, quaternary carbons not observed.

Reaction of Phenoxarsine Chloride 69 with GaCl_3 : A solution of phenoxarsine chloride (0.180 g, 0.646 mmol) in CH_2Cl_2 (11 mL) was added to a rapidly stirred solution of GaCl_3 (0.133 g, 0.642 mmol) in CH_2Cl_2 (11 mL) over a period of 10 minutes. An immediate colour change to deep purplish-red was observed. The colour lightened as the addition was continued, finally becoming deep orange-red. The solution was stirred overnight and an aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged for CD_2Cl_2 . The solvent was removed *in vacuo* from the bulk of the solution, leaving behind an intractable dark red oil.

NMR (reaction mixture - CD_2Cl_2): ^1H , 7.82-6.96 ppm (m); ^{13}C , 136.4 ppm, 135.6 ppm, 135.5 ppm, 135.1 ppm, 133.8 ppm, 132.3 ppm, 131.5 ppm, 127.2 ppm, 125.5 ppm, 125.4 ppm, 125.0 ppm, 121.3 ppm, 120.4 ppm, 120.1 ppm, 119.4 ppm, 117.3 ppm.

$\text{SCH}_2\text{CH}_2\text{SSbCl}$ 74:¹⁹³ In a round bottom flask SbCl_3 (8.07 g, 35.4 mmol) was dissolved in approximately 20 mL of concentrated HCl. To this was added all at once a portion of 1,2-ethanedithiol (3.30 g, 35.0 mmol), resulting in a two phase reaction mixture. The mixture was heated for 20 minutes in a hot water bath and then cooled slowly to room temperature. The solution was allowed to sit for 24 hours, after which agitation of the flask resulted in formation of off-white crystals. These were collected by vacuum filtration and recrystallized from hot benzene and dried *in vacuo*. These crystals were characterized as 2-chloro-*cyclo*-1,3-dithia-2-stibapentane (5.20 g, 20.9 mmol, 59.7%) mp. 123-124 °C.

IR: 925m, 835m, 653m, 638m, 440s, 361vs, 324vs, 303m, 279s, 266s, 255s, 249m,

231s cm⁻¹.

NMR (CD₂Cl₂): ¹H, 3.81 ppm; ¹³C, 43.3 ppm.

Reaction of SCH₂CH₂SSbCl 74 with 1 Equivalent of GaCl₃: A solution of SCH₂CH₂SSbCl (0.295 g, 1.18 mmol) in CH₂Cl₂ (42 mL) (heating was required to effect dissolution) was added to a stirred solution of GaCl₃ (0.209 g, 1.19 mmol) in CH₂Cl₂ (21 mL) over a period of 27 minutes. Addition was accompanied by a colour change to dark yellow-brown. After addition was complete, an aliquot of the reaction mixture was decanted into an NMR tube where the CH₂Cl₂ was exchanged for CD₂Cl₂. Slow removal of solvent (>75%) *in vacuo* promoted precipitation of a bright yellow solid, which was isolated from the solution by decantation. This material was washed by repeated back distillation of solvent and dried *in vacuo* (0.126 g), mp. 108-110 °C. The solid material would not redissolve in CH₂Cl₂. A single crystal which was isolated from the reaction mixture was crystallographically characterized as 2-chloro-*cyclo*-1,3-dithia-2-stibopentane-1,3-dithia-2-stibolidinium 76 tetrachlorogallate.

IR: 1289m, 1278w, 1237w, 1154w, 1113w, 925w, 916w, 832m, 825m, 651w, 630w, 440w, 414s, 387vs, 365vs, 356vs, 345s(sh), 326m, 305w, 287m(sh), 278m(sh), 268m, 238w cm⁻¹.

NMR (reaction mixture - CD₂Cl₂): ¹H, 4.15 ppm; ¹³C, 43.5 ppm; ¹³C CP MAS, 46.6 ppm (br).

X-ray: orthorhombic, space group *Pna*2₁, *a* = 15.848(6) Å, *b* = 13.763(4) Å, *c* = 8.190(4) Å, *V* = 1783(2) Å³, *Z* = 4, *D*_{calcd} = 2.514 g cm⁻³, *μ* = 57.11 cm⁻¹, *R*_w = 0.0207.

Reaction of SCH₂CH₂SSbCl 74 with 2 Equivalents of GaCl₃: A solution of GaCl₃ (0.216 g, 1.23 mmol) in CH₂Cl₂ (16 mL) was added to a rapidly stirred suspension of SCH₂CH₂SSbCl (0.614 g, 2.46 mmol) in CH₂Cl₂ (49 mL) over a period of 35

minutes. During the course of addition the $\text{SCH}_2\text{CH}_2\text{SSbCl}$ was taken up into solution. The solution was allowed to stir for 3 hours and an aliquot of the reaction mixture was decanted into an NMR tube where the CH_2Cl_2 was exchanged for CD_2Cl_2 . Slow removal of solvent (>75%) *in vacuo* promoted precipitation of a dark green solid, which was isolated from the solution by decantation. This material was washed by repeated back distillation of solvent, lightening the colour to pale green, and dried *in vacuo* (0.465 g), mp. 97.5-99.0 °C. The solid material would not redissolve in CH_2Cl_2 .

IR: 1282s, 1238s, 1114s, 923m, 651w, 628m, 439m, 385vs, 378vs, 370vs, 360vs, 345m(sh) 306m cm^{-1} .

NMR (reaction mixture - CD_2Cl_2): ^1H , 3.93 ppm; ^{13}C , 43.3 ppm; ^{13}C CP MAS, 48.1 ppm, 46.0 ppm.

7.0 References and Notes

1. See, for example, (a) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic: New York, 1971. (b) Hine, J. *Divalent Carbon*; Ronald: New York, 1964. (c) Gilchrist, T.L.; Rees, C.W. *Carbenes, Nitrenes and Arynes*; Thomas Nelson and Sons: London, 1969.
2. Igau, A.; Baceirido, A.; Trinquier, G.; Bertrand, G. *Angew. Chem. Int. Ed. Engl.* **1989**, 28, 621.
3. Gillette, G.R.; Baceirido, A.; Bertrand, G. *Angew. Chem. Int. Ed. Engl.* **1990**, 29, 1429.
4. Arduengo, A.J., III; Harlow, R.L.; Kline, M.J. *J. Am. Chem. Soc.* **1991**, 113, 361.
5. See, for example, Quast, H.; Hünig, S. *Angew. Chem. Int. Ed. Engl.* **1964**, 3, 800.
6. See, for example, (a) Meller, A.; Gräbe, C.-P. *Chem. Ber.* **1985**, 118, 2020. (b) Satgé, J. *J. Organomet. Chem.* **1990**, 400, 121.
7. See, for example, (a) Grützmacher, H.; Pritzkow, H.; Edelmann, F.T. *Organometallics* **1991**, 10, 23, and references therein. (b) Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, 113, 7785.
8. First reported in Pearson, T.G.; Purcell, R.H.; Saigh, G.S. *J. Chem. Soc.* **1938**, 409.
9. See, for example, Lachmann, B.; Steinmaus, H.; Wanzlick, H.-W. *Tetrahedron* **1971**, 27, 4085.
10. Arduengo, A.J., III; Rasika Dias, H.V.; Harlow, R.L.; Kline, M. *J. Am. Chem. Soc.* **1992**, 114, 5530.
11. Olah, G.A. *J. Am. Chem. Soc.* **1972**, 94, 808.
12. Cowley, A.H.; Kemp, R.A. *Chem. Rev.* **1985**, 85, 367.
13. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O.J., Eds.; Thieme: New York, 1990.
14. Dimroth, K.; Hoffmann, P. *Angew. Chem. Int. Ed. Engl.* **1964**, 3, 384.
15. Lambert, J.B.; Schulz, W.J., Jr. *J. Am. Chem. Soc.* **1983**, 105, 1671.
16. See, for example, Olah, G.A. *Halonium Ions*; John Wiley & Sons: New York, 1975.
17. (a) Baxter, S.G.; Collins, R.L.; Cowley, A.H.; Sena, S.F. *J. Am. Chem. Soc.* **1981**, 103, 714. (b) Baxter, S.G.; Collins, R.L.; Cowley, A.H.; Sena, S.F.

Inorg. Chem. **1983**, *22*, 3475.

18. Cowley, A.H.; Mehrotra, S.K. *J. Am. Chem. Soc.* **1983**, *105*, 2074.
19. Burford, N.; Royan, B.W.; Linden, A.; Cameron, T.S. *J. Chem. Soc., Chem. Commun.* **1988**, 842.
20. Thomas, M.G.; Schultz, C.W.; Parry, R.W. *Inorg. Chem.* **1977**, *16*, 994.
21. Alton, E.R.; Montemayor, R.G.; Parry, R.W. *Inorg. Chem.* **1974**, *13*, 2267.
22. Cowley, A.H.; Lattman, M.; Wilburn, J.C. *Inorg. Chem.* **1981**, *20*, 2916.
23. Nöth, H.; Ullmann, R. *Chem. Ber.* **1976**, *109*, 1942.
24. Fleming, S.; Lupton, M.K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534.
25. Maryanoff, B.E.; Hutchins, R.O. *J. Org. Chem.* **1972**, *37*, 3475.
26. Kopp, R.W.; Bond, A.C.; Parry, R.W. *Inorg. Chem.* **1976**, *15*, 3042.
27. Schultz, C.W.; Parry, R.W. *Inorg. Chem.* **1976**, *15*, 3046.
28. Abel, E.W.; Armitage, D.A.; Willey, G.R. *J. Chem. Soc.* **1965**, 57.
29. Mazières, M.R.; Sanchez, M.; Bellan, J.; Wolf, R. *Phosphorus Sulfur Relat. Elem.* **1986**, *26*, 97.
30. Mazières, M.R.; Roques, C.; Sanchez, M.; Majoral, J.P.; Wolf, R. *Tetrahedron* **1987**, *43*, 2109.
31. Friedrich, P.; Huttner, G.; Lubner, J.; Schmidpeter, A. *Chem. Ber.* **1978**, *111*, 1558.
32. Lubner, J.; Schmidpeter, A. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 111.
33. Gudat, D.; Nieger, G.; Niecke, E. *J. Chem. Soc., Dalton Trans.* **1989**, 693.
34. Baxter, S.G.; Cowley, A.H.; Mehrotra, S.K. *J. Am. Chem. Soc.* **1981**, *103*, 5572.
35. Gudat, D.; Niecke, E.; Krebs, B.; Dartmann, M. *Chimia* **1985**, *39*, 277.
36. Data for this table, with the exception of **6**, has been taken from Reference 13, p 132, and references therein. The structure of **6** was first reported by David, G.; Niecke, E.; Nieger, M. *Tetrahedron Lett.* **1992**, *33*, 2335. Structural data reported is from Clyburne, J.A.C., Dalhousie University, unpublished results.
37. Cowley, A.H.; Cushner, M.C.; Szobota, J.S. *J. Am. Chem. Soc.* **1978**, *100*, 7784.

38. Cowley, A.H.; Cushner, M.C.; Lattman, M.; McKee, L.; Szobota, J.S.; Wilburn, J.C. *Pure Appl. Chem.* **1980**, *52*, 789.
39. Rømming, C.; Songstad, J. *Acta. Chem. Scand.* **1978**, *A32*, 689.
40. Wells, A.F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1984.
41. See, for example, Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, 1983.
42. (a) Cowley, A.H.; Norman, N.C. In *Phosphorus 31, NMR Spectroscopy in Stereochemical Analysis. Organic Compounds and Metal Complexes*; Verkade, J.G.; Quin, L., Eds.; VCH: Weinheim, 1987; Chapter 17. (b) Tebby, J.C. *Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; CRC Press: 1992.
43. See, for example, Wilkie, C.A.; Parry, R.W. *Inorg. Chem.* **1980**, *19*, 1499.
44. Data taken from Reference 12 and references therein.
45. Haraguchi, H.; Fujiwara, S. *J. Phys. Chem.* **1969**, *73*, 3467.
46. Akitt, J.W. In *Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987; pp 259-292.
47. Trinquier, G.; Marre, M.-R. *J. Phys. Chem.* **1983**, *87*, 1903.
48. Cowley, A.H.; Cushner, M.C.; Riley, P.E. *J. Am. Chem. Soc.* **1980**, *102*, 624.
49. Sanchez, M.; Mazières, M.R.; Lamandé, L.; Wolf, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O.J., Eds.; Thieme: New York, 1990; pp 129-148.
50. Farfán, N.; Contreras, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 771.
51. Pullmann, P.; Hensen, K.; Bats, J.W. *Z. Naturforsch.* **1982**, *37b*, 1312.
52. Reed, R.; Réau, R.; Dahan, F.; Bertrand, G. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 399.
53. Montemayor, R.G.; Sauer, D.T.; Fleming, S.; Bennett, D.W.; Thomas, M.G.; Parry, R.W. *J. Am. Chem. Soc.* **1978**, *100*, 2231.
54. See, for example, Corbridge, D.E.C. *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology*, 4th ed.; Studies in Inorganic Chemistry 10; Elsevier: New York, 1990; Chapter 8.
55. (a) Cowley, A.H.; Kemp, R.A.; Lasch, J.G.; Norman, N.C.; Stewart, C.A.; Whittlesey, B.R.; Wright, T.C. *Inorg. Chem.* **1986**, *25*, 740. (b) Cowley, A.H.; Stewart, C.A.; Whittlesey, B.R.; Wright, T.C. *Tetrahedron Lett.* **1984**, *25*, 815.

56. (a) Fongers, K.S.; Hogeveen, H.; Kingma, R.F. *Tetrahedron Lett.* **1983**, 24, 643. (b) Lochschmidt, S.; Mathey, F.; Schmidpeter, A. *Tetrahedron Lett.* **1986**, 27, 2635.
57. (a) Conlin, R.T.; Gaspar, P.P. *J. Am. Chem. Soc.* **1976**, 98, 3715. (b) Seyferth, D.; Annarelli, D.C.; Vick, S.C. *J. Am. Chem. Soc.* **1976**, 98, 6382.
58. Stone, F.G.A. *Angew. Chem. Int. Ed. Engl.* **1984**, 23, 89.
59. Gololobov, Y.G.; Zhmurova, I.N.; Kasukhin, L.F. *Tetrahedron* **1981**, 37, 437.
60. (a) Marre, M.R.; Sanchez, M.; Wolf, R. *Phosphorus Sulfur Relat. Elem.* **1982**, 13, 327. (b) Sanchez, M.; Marre, M.R.; Brazier, J.F.; Wolf, R. *Phosphorus Sulfur Relat. Elem.* **1983**, 14, 331.
61. Mazières, M.-R.; Kim, T.C.; Wolf, R.; Sanchez, M.; Jaud, J. *Zeitsch. für Kristall.* **1988**, 184, 147.
62. Burford, N.; Spence, R.E.v.H.; Richardson, J.F. *J. Chem. Soc., Dalton Trans.* **1991**, 1615.
63. Burford, N., Dalhousie University, personal communication, 1994.
64. Marre, M.-R.; Sanchez, M.; Wolf, R. *J. Chem. Soc., Chem. Commun.* **1984**, 566.
65. Märkl, G.; Lieb, F. *Tetrahedron Lett.* **1967**, 36, 3489.
66. Gamon, N.; Reichardt, C.; Allmann, R.; Waśkowska, A. *Chem. Ber.* **1981**, 114, 3289.
67. Jutzi, P.; Wippermann, T.; Krüger, C.; Kraus, H.-J. *Angew. Chem. Int. Ed. Engl.* **1983**, 22, 250.
68. Burford, N.; Royan, B.W.; White, P.S. *J. Am. Chem. Soc.* **1989**, 111, 3746.
69. Burford, N.; Parks, T.M.; Royan, B.W.; Richardson, J.F.; White, P.S. *Can. J. Chem.* **1992**, 70, 703.
70. Burford, N.; Royan, B.W.; Linden, A.; Cameron, T.S. *Inorg. Chem.* **1989**, 28, 144.
71. Veith, M.; Bertsch, B.; Huch, V. *Z. Anorg. Allg. Chem.* **1988**, 559, 73.
72. Burford, N.; Royan, B.W. *J. Chem. Soc., Chem. Commun.* **1989**, 19.
73. Payraastre, C.; Madaule, Y.; Wolf, J.-G. *Tetrahedron Lett.* **1992**, 33, 1273.
74. Payraastre, C.; Madaule, Y.; Wolf, J.G.; Kim, T.C.; Mazières, M.-R.; Wolf, R.; Sanchez, M. *Heteroatom Chem.* **1992**, 3, 157.

75. For a similar effect encountered in the Group 15 heterobenzenes see Ashe, A.J., III *Top. Curr. Chem.* **1982**, 105, 125.
76. Dräger, M. *Chem. Ber.* **1974**, 107, 2601, and references therein.
77. Pappalardo, G.C.; Chakravorty, R.; Irgolic, K.J.; Myers, E.A. *Acta Crystallogr.* **1983**, C39, 1618.
78. Veith, M.; Bertsch, B. *Z. Anorg. Allg. Chem.* **1988**, 557, 7.
79. Herberhold, M.; Schamel, K.; Herrmann, G.; Gieren, A.; Ruiz-Pérez, C.; Hübner, T. *Z. Anorg. Allg. Chem.* **1988**, 562, 49.
80. Chivers, T.; Dhathathreyan, K.S.; Lensink, C.; Richardson, J.F. *Inorg. Chem.* **1988**, 27, 1570.
81. Burford, N.; Dipchand, A.I.; Royan, B.W.; White, P.S. *Inorg. Chem.* **1990**, 29, 4938.
82. Burford, N.; Royan, B.W. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, 41, 37.
83. Burford, N.; Dipchand, A.I.; Royan, B.W.; White, P.S. *Acta Crystallogr.* **1989**, C45, 1485.
84. *CRC Handbook of Chemistry and Physics*, 67th ed.; CRC: Boca Raton, Florida, 1986, p D-188.
85. (a) Cardinal, G.; Gillespie, R.J.; Sawyer, J.F.; Verkis, J.E. *J. Chem. Soc., Dalton Trans.* **1982**, 765. (b) McMullan, R.K.; Prince, D.J.; Corbett, J.D. *Inorg. Chem.* **1971**, 10, 1749.
86. Bader, R.F.W.; Gillespie, R.J.; MacDougall, P.J. From Atoms to Polymers. In *Molecular Structure and Energetics*; Liebman, J.F.; Greenberg, A., Eds.; VCH: New York, 1989; Vol.11, p 1.
87. Cameron, T.S.; Linden, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, 41, 75.
88. See, for example, (a) Schmidbauer, H.; Probst, T.; Huber, B.; Steigelmann, O.; Müller, G. *Organometallics* **1989**, 8, 1567. (b) Turner, R.W.; Amma, E.L. *J. Am. Chem. Soc.* **1966**, 88, 1877. (c) Fan, B.; Shen, Q.; Lin, Y. *J. Organomet. Chem.* **1989**, 376, 61. (d) Cesari, M.; Pedritti, U.; Zazetta, A.; Lugli, G.; Marconi, N. *Inorg. Chim. Acta* **1971**, 5, 439.
89. Barbier, P.; Mairesse, G.; Wignacourt, J.-P. *Cryst. Struct. Comm.* **1976**, 5, 633.
90. Dixon, K.R. In *Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987; Chapter 13.

91. Wehrli, F.W. *Annu. Rep. NMR Spectrosc.* **1979**, 9, 126, and references therein.
92. Olah, G.A.; Grant, J.L. *J. Org. Chem.* **1977**, 42, 2237.
93. Matsumoto, T.; Yamamoto, H.; Inoue, S. *J. Am. Chem. Soc.* **1984**, 106, 4829.
94. Morris, J.L.; Rees, C.W. *J. Chem. Soc., Perkin Trans. I* **1987**, 217.
95. Payraastre, C.; Wolf, J.G.; Kim, T.C.; Sanchez, M. *Bull. Soc. Chim. Fr.* **1992**, 129, 157.
96. (a) Bartlett, R.A.; Dias, H.V.R.; Hope, H.; Murray, B.D.; Olmstead, M.M.; Power, P.P. *J. Am. Chem. Soc.* **1986**, 108, 6921. (b) Critchlow, S.C.; Corbett, J.D. *Inorg. Chem.* **1984**, 23, 770.
97. (a) Ashe, A.J., III; Kampf, J.W.; Al-Taweel, S.M. *Organometallics* **1992**, 11, 1491. (b) Ashe, A.J., III; Diephouse, T.R.; Kampf, J.W.; Al-Taweel, S.M. *Organometallics* **1991**, 10, 2068. (c) Ashe, A.J., III *J. Am. Chem. Soc.* **1971**, 93, 6690.
98. Burford, N.; Müller, J.; Parks, T.M. *J. Chem. Educ.*, in press.
99. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Interscience: Toronto, 1986.
100. Burford, N.; Royan, B.W.; Whalen, J.M.; Richardson, J.F.; Rogers, R.D. *J. Chem. Soc., Chem. Commun.* **1990**, 1273.
101. Scherer, O.J.; Schmidt, M. *Angew. Chem. Int. Ed. Engl.* **1964**, 3, 702.
102. Rueggeberg, W.H.C.; Ginsburg, A.; Cook, W.A. *J. Am. Chem. Soc.* **1946**, 68, 1860.
103. Kamai, G.; Khisamova, Z.L. *J. Gen. Chem. USSR* **1954**, 23, 1387.
104. Aksnes, D.W.; Amer, F.A.; Bergesen, K. *Acta Chem. Scand.* **1976**, A30, 109.
105. Burford, N.; Parks, T.M.; Bakshi, P.K.; Cameron, T.S. *Angew. Chem. Int. Ed. Engl.*, **1994**, 33, 1267.
106. See, for example, (a) Weiss, J.; Eisenhuth, W. *Z. Anorg. Allg. Chem.* **1967**, 350, 9. (b) Gieren, A.; Betz, H.; Hübner, T.; Lamm, V.; Herberhold, M.; Guldner, K. *Z. Anorg. Allg. Chem.* **1984**, 513, 160. (c) Reference 78. (d) Bohra, R.; Roesky, H.W.; Noltemeyer, M.; Sheldrick, G.M. *Acta Cryst.* **1984**, C40, 1150. (e) Grützmacher, H.; Pritzkow, H. *Chem. Ber.* **1989**, 122, 1417.
107. Royan, B.W. Ph.D. Thesis, Dalhousie University, July 1990.
108. Burford, N.; Parks, T.M.; Royan, B.W.; Borecka, B.; Cameron, T.S.; Richardson, J.F.; Gabe, E.J.; Hynes, R. *J. Am. Chem. Soc.* **1992**, 114, 8147.

109. Christian, B.H.; Gillespie, R.J.; Sawyer, J.F. *Inorg. Chem.* **1981**, *20*, 3410.
110. Aksnes, D.W.; Vikane, O. *Acta Chem. Scand.* **1973**, *27*, 1337.
111. See, for example, a) Dixon, D.A.; Arduengo, A.J., III; Fukunaga, T. *J. Am. Chem. Soc.* **1986**, *108*, 2461. b) Arduengo, A.J., III; Dixon, D.A.; Roe, D.C. *J. Am. Chem. Soc.* **1986**, *108*, 6821. c) Dixon, D.A.; Arduengo, A.J., III. *J. Am. Chem. Soc.* **1987**, *109*, 338. d) Arduengo, A.J., III; Dixon, D.A.; Roe, D.C.; Kline, M. *J. Am. Chem. Soc.* **1988**, *110*, 4437.
112. Song, S.K.; Watkins, C.L.; Krannich, L.K. *Magn. Reson. Chem.* **1987**, *25*, 484.
113. See, for example, (a) Klapötke, T.; Passmore, J. *Acc. Chem. Res.* **1989**, *22*, 234 and references therein. (b) Reference 81. (c) Reference 85.
114. Burford, N.; Losier, P.; Bakshi, P.K.; Cameron, T.S. *J. Chem. Soc., Dalton Trans.* **1993**, 201.
115. Burford, N.; Mason, S.; Spence, R.E.v.H.; Whalen, J.M.; Richardson, J.F.; Rogers, R.D. *Organometallics* **1992**, *11*, 2241.
116. Fisher, R.A.; Nielsen, R.B.; Davis, W.M.; Buchwald, S.L. *J. Am. Chem. Soc.* **1991**, *113*, 165.
117. Atwood, J.L.; Bott, S.G.; Jones, C.; Raston, C.L. *Inorg. Chem.* **1991**, *30*, 4868.
118. Bates, P.A.; Huisthouse, M.B.; Davies, A.G.; Slater, S.D. *J. Organomet. Chem.* **1989**, *363*, 45.
119. Arduengo, A.J., III; Bock, H.; Chen, H.; Denk, M.; Dixon, D.A.; Green, J.C.; Herrmann, W.A.; Jones, N.L.; Wagner, M.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 6641.
120. It has also been suggested that the observed splittings are a result of inadequate shimming at the various temperatures, a hypothesis supported by the similar magnitudes of splitting of all peaks, including that of the solvent. The samples were reshimmied at each temperature, however it is possible that the lock was lost at some point during data acquisition.
121. Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; John Wiley & Sons: Toronto, 1988.
122. See, for example, (a) Moriarty, R.M. *J. Org. Chem.* **1963**, *28*, 1296. (b) Jackman, L.M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: Oxford, 1969; pp 246-248.
123. duMont, W.W.; Kroth, H.-J.; Schumann, H. *Chem. Ber.* **1976**, *109*, 3017.

124. Shagvaleev, F.S.; Zykova, T.V.; Tarasova, R.I.; Sitdikova, T.S.; Moskva, V.V. *Zh. Obshch. Khim. Engl. Trans.* **1990**, *60*, 1775.
125. Burford, N.; Losier, P.; Sereda, S.V.; Cameron, T.S.; Wu, G. *J. Am. Chem. Soc.*, **1994**, *116*, 6474.
126. See, for example, Smith, R.D.; Loo, J.A.; Edmonds, C.G.; Barinaga, C.J.; Udseth, H.R. *Anal. Chem.* **1990**, *62*, 882.
127. See, for example, (a) Fenn, J.B.; Mann, M.; Meng, C.K.; Wong, S.F.; Whitehouse, C.M. *Science (Washington, D.C.)* **1989**, *246*, 64. (b) Ganem, B.; Li, Y.-T.; Hsieh, Y.-L.; Henion, J.D.; Kaboord, B.F.; Frey, M.W.; Benkovic, S.J. *J. Am. Chem. Soc.* **1994**, *116*, 1352.
128. (a) Wilson, S.R.; Wu, Y. *J. Am. Chem. Soc.* **1993**, *115*, 10334. (b) Wilson, S.R.; Wu, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 784.
129. Canty, A.J.; Colton, R.; Thomas, I.M. *J. Organomet. Chem.* **1993**, *455*, 283.
130. Wilson, S.R.; Wu, Y. *Organometallics* **1993**, *12*, 1478.
131. Caudle, M.T.; Stevens, R.D.; Crumbliss, A.L. *Inorg. Chem.* **1994**, *33*, 843.
132. Colton, R.; James, B.D.; Potter, I.D.; Traeger, J.C. *Inorg. Chem.* **1993**, *32*, 2626.
133. Burford, N.; Losier, P.; Macdonald, C.; Kyrimis, V.; Bakshi, P.K.; Cameron, T.S. *Inorg. Chem.* **1994**, *33*, 1434.
134. Curtis, J.M.; Blay, P.; Burford, N.; Parks, T.M.; Mason, S. *41st American Society for Mass Spectrometry Conf., ThP 213*, San Francisco, **1993**.
135. See, for example, (a) Arduengo, A.J., III; Rasika Dias, H.V.; Calabrese, J.C.; Davidson, F. *J. Am. Chem. Soc.* **1992**, *114*, 9724. (b) Arduengo, A.J., III; Rasika Dias, H.V.; Davidson, F.; Harlow, R.L. *J. Organomet. Chem.* **1993**, *462*, 13. (c) Arduengo, A.J., III; Tamm, M.; Calabrese, J.C. *J. Am. Chem. Soc.* **1994**, *116*, 3625. (d) Arduengo, A.J., III; Gamper, S.F.; Calabrese, J.C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391.
136. Schmidpeter, A.; Lochschmidt, S. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 253.
137. Hutchins, L.D.; Duesler, E.N.; Paine, R.T. *Organometallics* **1982**, *1*, 1254.
138. David, G.; Niecke, E.; Nieger, M.; Radseck, J. *J. Am. Chem. Soc.* **1994**, *116*, 2191.
139. Abel, E.W.; Allen, S.R.; Bates, P.A.; Hursthouse, M.B.; Khandelwal, B. *J. Chem. Soc., Chem. Commun.* **1987**, 983.
140. Abel, E.W.; Allen, S.R.; Khandelwal, B. *J. Chem. Soc. Dalton Trans.* **1989**, 885.

141. Mazieres, M.-R.; Kim, T.C.; Wolf, R.; Sanchez, M.; Jaud, J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *55*, 147.
142. An alternate pathway involves hydrolysis of the reaction mixture, but due to the reproducibility of the experiment, the rigorousness of the reaction conditions with respect to exclusion of air and moisture, and the quantitative nature of the reaction (by ^{31}P NMR), this alternate mechanism is highly unlikely.
143. Burford, N.; Royan, B.W.; Spence, R.E.v.H.; Cameron, T.S.; Linden, A.; Rogers, R.D. *J. Chem. Soc., Dalton Trans.* **1990**, 1521.
144. Clyburne, J.A.C., Dalhousie University, unpublished results.
145. Burford, N.; Clyburne, J.A.C.; Bakshi, P.K.; Cameron, T.S. *J. Am. Chem. Soc.* **1993**, *115*, 8829.
146. See, for example, (a) Roesky, H.W.; Witt, M.; Clegg, W.; Isenberg, W.; Noltemeyer, M.; Sheldrick, G.M. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 943. (b) Hitchcock, P.B.; Lappert, M.F.; Rai, A.K.; Williams, H.D. *J. Chem. Soc., Chem. Commun.* **1986**, 1633. (c) Krannich, L.K.; Thewalt, U.; Cook, W.J.; Jain, S.R.; Sisler, H.H. *Inorg. Chem.* **1973**, *12*, 2304. (d) Bailey, K.; Gosney, I.; Gould, R.O.; Lloyd, D.; Taylor, P. *J. Chem. Res.* **1988**, 386, 2950.
147. (a) SooHoo, C.K.; Baxter, S.G. *J. Am. Chem. Soc.* **1983**, *105*, 7443. (b) Cowley, A.H.; Kemp, R.A.; Lasch, J.G.; Norman, N.C.; Stewart, C.A. *J. Am. Chem. Soc.* **1983**, *105*, 7444.
148. Igau, A.; Baceiredo, A.; Grützmacher, H.; Pritzkow, H.; Bertrand, G. *J. Am. Chem. Soc.* **1989**, *111*, 6853.
149. Grützmacher, H.; Pritzkow, H. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 709.
150. Kasukhin, L.F.; Ponomarchuk, M.P.; Kim, T.V.; Kukhar, V.P. *Dokl. Akad. Nauk SSSR* **1986**, *290*, 1375.
151. Aksnes, D.W.; Vikane, O. *Acta Chem. Scand.* **1972**, *26*, 4170.
152. Eccleston, G.; Wyn-Jones, E.; Orville-Thomas, W.J. *J. Chem. Soc. B* **1971**, 1551.
153. Eliel, E.L. *Acc. Chem. Res.* **1970**, *3*, 1.
154. (a) Cowley, A.H.; Gabbai, F.P.; Atwood, D.A.; Carrano, C.J.; Mokry, L.M.; Bond, M.R. *J. Am. Chem. Soc.* **1994**, *116*, 1559. (b) Olazábal, C.A.; Gabbai, F.P.; Cowley, A.H.; Carrano, C.J.; Mokry, L.M.; Bond, M.R. *Organometallics* **1994**, *13*, 421. (c) Mocker, M.; Robl, C.; Schnöckel, H. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 862.
155. Engler, R. *Z. Anorg. Allg. Chem.* **1974**, *406*, 74.

156. (a) As: Reference 76. (b) Sb: Dräger, M.; Engler, R. *Z. Anorg. Allg. Chem.* **1974**, 405, 183.
157. Dräger, M. *Z. Anorg. Allg. Chem.* **1981**, 482, 7.
158. Burton, H.; Gibson, C.S. *J. Chem. Soc.* **1926**, 450.
159. Lewis, W.L.; Lowry, C.D.; Bergeim, F.H. *J. Am. Chem. Soc.* **1921**, 43, 891.
160. Wieland, H.; Rheinheimer, W. *Liebigs Ann. Chem.* **1921**, 423, 1.
161. Vermeer, H.; Lourens, R.; Bickelhaupt, F. *Tetrahedron* **1975**, 31, 2529.
162. Jay, M.; Martin, G.E. *J. Heterocycl. Chem.* **1982**, 19, 241.
163. Oediger, H.; Möller, F. *Angew. Chem. Int. Ed. Engl.* **1967**, 6, 76.
164. (a) Jutzi, P.; Deuchert, K. *Angew. Chem. Int. Ed. Engl.* **1969**, 8, 991. (b) Vermeer, H.; Bickelhaupt, F. *Angew. Chem. Int. Ed. Engl.* **1969**, 8, 992.
165. Gates, P.N.; Powell, P.; Steele, D. *J. Mol. Struct.* **1971**, 8, 477.
166. Aylett, V., Dalhousie University, personal communication, 1993.
167. See, for example, (a) Bush, M.A.; Lindley, P.F.; Woodward, P. *J. Chem. Soc. A* **1967**, 221. (b) Dräger, M. *Z. Anorg. Allg. Chem.* **1976**, 424, 183. (c) Hoffmann, H.M.; Dräger, M. *J. Organomet. Chem.* **1985**, 295, 33. (d) Hoffmann, H.M.; Dräger, M. *J. Organomet. Chem.* **1987**, 329, 51.
168. Phosphylidene: (a) Reference 70. (b) Reference 72. Arsyliidene and Stibylidene: Reference 107.
169. MacLean, G.K.; Passmore, J.; Rao, M.N.S.; Schriver, M.J.; White, P.S. *J. Chem. Soc. Dalton Trans.* **1985**, 1405.
170. Glaser, R.; Horan, C.J.; Haney, P.E. *J. Phys. Chem.* **1993**, 97, 1835.
171. Glaser, R.; Horan, C.J.; Choy, G.S.-C.; Harris, B.L. *J. Phys. Chem.* **1992**, 96, 3689.
172. Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 1715.
173. McGarrity, J.F.; Cox, D. *J. Am. Chem. Soc.* **1983**, 105, 3961.
174. (a) McMahon, T.B.; Heinis, T.; Nicol, G.; Hovey, J.K.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, 110, 7591. (b) Foster, M.S.; Beauchamp, J.L. *J. Am. Chem. Soc.* **1972**, 94, 2425. (c) Lebedev, A.T. *Mass Spectrom. Rev.* **1991**, 10, 91.
175. (a) Glaser, R. *J. Phys. Chem.* **1989**, 93, 7993. (b) Glaser, R. *J. Am. Chem.*

- Soc.* **1983**, *113*, 1109. (c) Glaser, R.; Choy, G.S.-C.; Hall, M.K. *J. Org. Chem.* **1992**, *57*, 215.
176. Langer, A.; Hipple, J.A.; Stevenson, D.D. *J. Chem. Phys.* **1954**, *22*, 1836.
 177. Niecke, E.; Nieger, M.; Reichert, F.; Schoelker, W.W. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1713.
 178. Curtis, J.M.; Burford, N.; Parks, T.M. *Org. Mass Spectrom.*, in press.
 179. See, for example, (a) Bursey, J.T.; Bursey, M.M.; Kingston, D.G. *Chem. Rev.* **1973**, *73*, 191. (b) Marcasiu, D.; Miller, G.; Hsu, C.S. *Org. Mass Spectrom.* **1990**, *25*, 409 and references therein.
 180. Boyd, R.K. *Spectrosc. Int. J.* **1982**, *1*, 169.
 181. Burford, N.; Losier, P. Dalhousie University, unpublished results.
 182. Sendlinger, S.C.; Haggerty, B.W.; Rheingold, A.L.; Theopold, K.H. *Chem. Ber.* **1991**, *124*, 2453.
 183. Guillemin, J.-C.; Lassalle, L. *Organometallics* **1994**, *13*, 1525.
 184. See, for example, (a) Inokuchi, H. *Angew. Chem. Int. Ed. Engl.* **1983**, *27*, 1747. (b) Williams, J.M.; Wang, H.H.; Emge, T.J.; Geiser, U.; Beno, M.A.; Leung, P.C.W.; Carlson, K.D.; Thorn, R.J.; Schultz, A.J.; Whangbo, M.-H. *Prog. Inorg. Chem.* **1987**, *35*, 51. (c) Wudl, F. *Acc. Chem. Res.* **1984**, *17*, 227. (d) Torrance, J.B. *Acc. Chem. Res.* **1979**, *12*, 79. (e) Perlstein, J.H. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 519.
 185. See, for example, Birenbaum, R. *Canadian Research* **1985**, Dec., 14.
 186. Wayda, A.L.; Dye, J.L. *J. Chem. Educ.* **1985**, *52*, 356.
 187. The bridge has been previously described in a preliminary manner. See, (a) Reference 107. (b) Spence, R.E.v.H. Ph.D. Thesis, Dalhousie University, February 1991.
 188. Melby, L.R.; Harder, R.J.; Hertler, W.R.; Mahler, W.; Benson, R.E.; Mochel, W.E. *J. Am. Chem. Soc.* **1962**, *84*, 3374.
 189. Ramirez, F.; Patwardhan, A.V.; Kugler, H.J.; Smith, C.P. *J. Am. Chem. Soc.* **1967**, *89*, 6280.
 190. A modification of the procedure mentioned in Reference 102.
 191. *Inorganic Syntheses*; Holtzclaw, H.F., Jr., Ed.; McGraw-Hill: Toronto, 1966; Vol. 8, pp 178-181.
 192. Crystals of this compound were first synthesized and prepared for crystallography by Dr. B.W. Royan in 1990.

193. Clark, R.E.D. *J. Chem. Soc.* **1932**, 1826.