Coordination Chemistry of Phosphenium Centers

by

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For Kathy Ann

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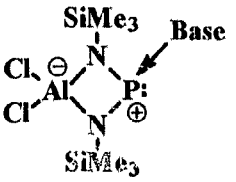
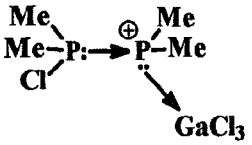
Abstract

Low coordinate and unsaturated non-metal centers offer attractive sites for oxidative addition and coordination chemistry. The phosphenium cations (analogues of carbenes) $[\overline{N(Me)CH_2CH_2N(Me)P}]^+$ and $[(^iPr_2N)_2P]^+$ are stable in CH_2Cl_2 solutions due to the coordinative interactions of the counterion $[GaCl_4]^-$ with the phosphorus center which is referred to as *"anionic protection"*. However, in the presence of the weakly coordinating anion $[BPh_4]^-$, the reactivity of the phosphenium cations is enhanced and oxidative addition of a CH_2Cl_2 molecule or phenyl transfer to the phosphorus center is observed. The neutral phosphenium derivative $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ undergoes a one-atom oxidative addition with elemental chalcogens to give a dimer with a P_2E_2 ring (E = S and Se) in a bis(spiro)tricyclo framework.



Amine, ether and phosphine bases react with the zwitterion to give the first examples of coordination complexes involving a neutral phosphorus center. Phosphenium species typically possess at least one electron-rich substituent (e.g. NR_2, SR) which is responsible for stabilizing the electron deficient phosphorus site through π-donation. Attempts to synthesize a series of dialkylphosphenium cations $[R_2P]^+$ via halide abstraction from R_2PCl (R = Me, Et, Ph, ^{i}Pr, ^{t}Bu) with $GaCl_3$ lead to phosphinophosphonium cations $[R_2PPR_2Cl]^+$ or covalent adducts $R_2PCl{\cdot}GaCl_3$. Moreover, the methyl derivative $[Me_2PPMe_2Cl]^+$ complexes to an equivalent of $GaCl_3$ to give the first example of *"base induced"* coordination.



List of Abbreviations Used

Å	angstrom	m	multiplet
Ad	adamantyl	(m)	medium
avg.	average	MAS	magic angle spinning
br	broad	Me	methyl
^{t}Bu	*tert*-butyl	Mes*	2,4,6-tri-*tert*-butylphenyl
cm^{-1}	reciprocal centimeter	MHz	megahertz
CP	cross polarization	mL	milliliter
d	doublet	mmol	millimole
d.p.	decomposition point	MO	molecular orbital
°	degrees	m.p.	melting point
°C	degrees Celsius	N/A	not available
Et	ethyl	NMR	nuclear magnetic resonance
Fc	ferrocene	Ph	phenyl
FT	Fourier transform	ppm	part per million
g	gram	^{i}Pr	isopropyl
HOMO	highest occupied molecular orbital	s	strong
hrs	hours	sh	shoulder
Hz	hertz	t	triplet
IR	infrared	THF	tetrahydrofuran
kHz	kilohertz	TPP	tetraphenylporphyrinate
LUMO	lowest unoccupied molecular orbital	w	weak

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Chapter 1 Introduction

Conventional coordination chemistry most often refers to complexes involving a metal or metal ion center surrounded by ligands and indeed there are numerous examples of such coordination compounds.[1] Nevertheless, $[I_3]^-$, $[SF_5]^-$ and $[PBr_4]^-$ represent σ-complexes of halide anions to non-metal species[2] but the number of coordination compounds containing a non-metal center is limited.

Phosphenium cations **1a** represent ideal "building blocks" for the formation of non-metal complexes due to their electron deficient center and electrophilic nature (*vide infra*). These unsaturated six valent electron species contain a dicoordinate phosphorus center and a formal positive charge making them isoelectronic with carbenes **1b**.[3] Calculations performed on the models $[H_2P]^+$,[4,5] $[H(F)P]^+$,[4] $[H_2N(H)P]^+$ [6] and $[(H_2N)_2P]^+$ [7] indicate a singlet ground state in accordance with a lone pair of electrons in a trigonal planar arrangement with the two bonding pairs around the phosphorus atom.

Phosphenium cation

1a

Carbene

1b

The first isolated phosphenium ions were reported in 1972 by Fleming, Jekot and Lupton[8] as well as Maryanoff and Hutchins.[9] Since then, nearly 70 derivatives have been identified, mostly by spectroscopic methods although a few isolated phosphenium cations have been crystallographically characterized. In 1985, Cowley

and Kemp[10] extensively reviewed the synthesis, structure, bonding and reactivity of phosphenium cations which Sanchez and co-workers updated shortly thereafter (literature survey until 1988) in a book dedicated to low coordinate phosphorus environments.[11]

1.1 Syntheses of Phosphenium Cations

As shown in Figure 1, most phosphenium species were obtained through heterolytic P-halogen bond cleavage from a halophosphine with Lewis acids (e.g. $AlCl_3$, PF_5) or metathesis reagents, $AgSO_3CF_3$ or $Me_3SiSO_3CF_3$, although in some derivatives the halide anion was extruded following the formation of the cyclic precursors.[12] Electrophilic attack of the $^{\delta+}P{=}E^{\delta-}$ bond in iminophosphines[13] or phosphaalkenes[14] (R-P=E-R', E = N, CR) via protonation with triflic acid (HSO_3CF_3) was used to form the corresponding phosphenium cations while Lewis acids $AlCl_3$ and $GaCl_3$ were complexed to iminophosphines to generate zwitterionic species containing phosphenium centers.[15,16,17] Metathesis reactions of the pre-formed chlorophosphenium cation $[Cl\text{-}P\text{-}R]^+$ with trimethylsilylated species Me_3SiX (X = NR_2, CN, N_3, $N{=}PR_3$,[18] $N{=}CR_2$,[19] $P{=}CR_2$[20]) give phosphenium derivatives but most double bonded substituents further react to afford heterocyclic cations. A novel approach to phosphenium cation formation involved the monocoordinate phosphoazonium species $[Mes^*\text{-}NP]^+$ (Mes* = 2,4,6-tri-*tert*-butylphenyl) which can add to multiple bonds in alkynes[21] or iminophosphines and alkyl azides[22] to yield cyclic phosphenium species. Alternatively, hydridic bases such as Mes^*NH_2, Mes*OH and Mes*SH can add in a 1,2 fashion to

the phosphoazonium cation to give the corresponding dicoordinate phosphenium cations.[23] Table 1 catalogues all known phosphenium species (only species reported since Cowley's review[10] are referenced).

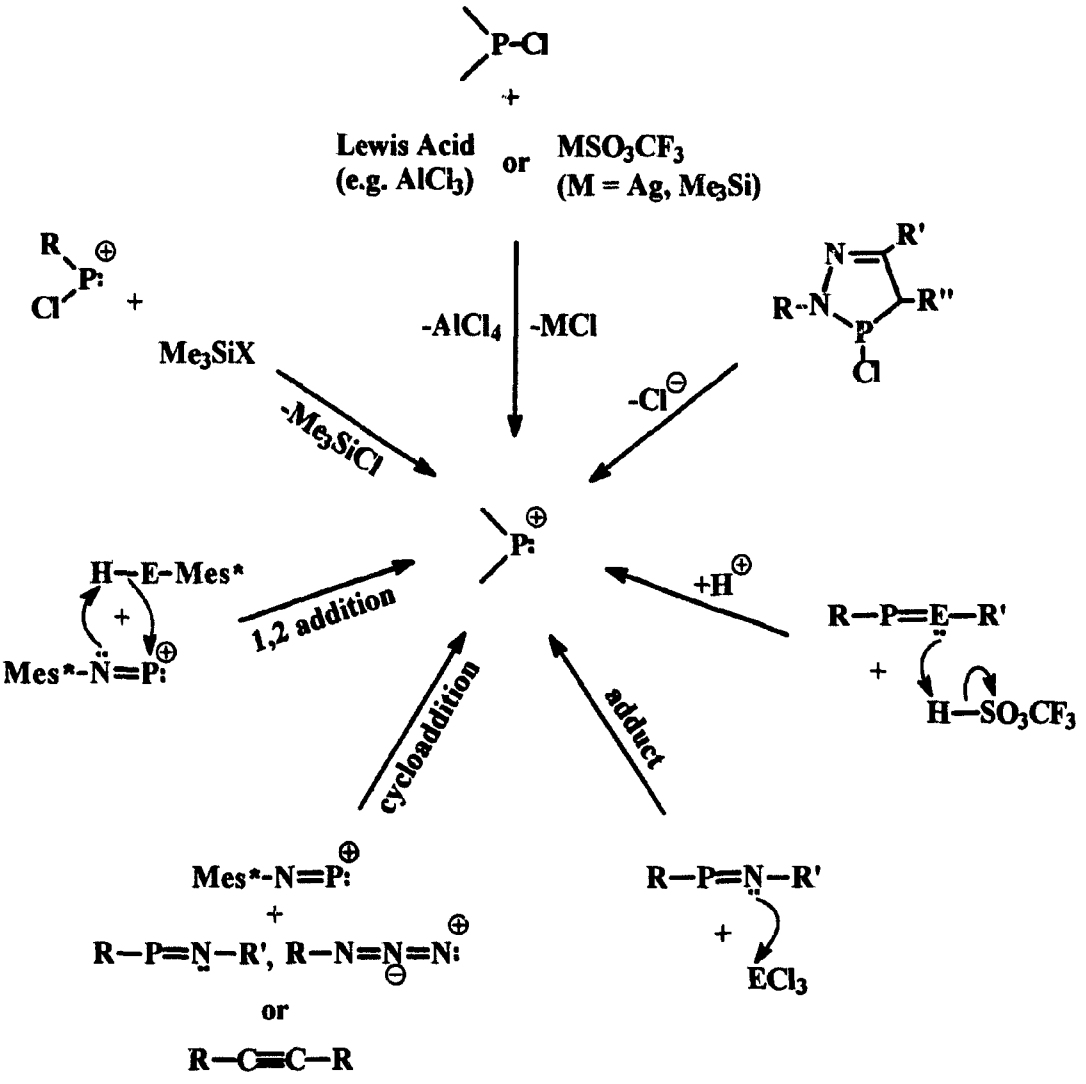
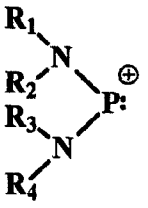
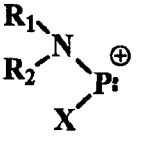


Figure 1. Synthetic routes to phosphenium species.

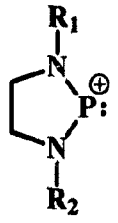
Table 1. Reported phosphenium species.



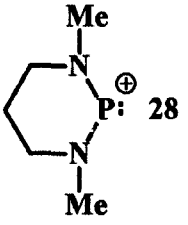
R_1	R_2	R_3	R_4	#
Me	Me	Me	Me	2
Et	Et	Et	Et	3
^{i}Pr	^{i}Pr	^{i}Pr	^{i}Pr	4
Me_3Si	Me_3Si	Me_3Si	Me_3Si	5
Me	Me	^{i}Pr	^{i}Pr	6
Me	Me	Me_3Si	Me_3Si	7
Me	Me	^{t}Bu	Me_3Si	8
Me	Me	H	Mes*	9[17]
H	Mes*	^{i}Pr	^{i}Pr	10[23]
H	Mes*	H	Mes*	11[23]



R_1	R_2	X	#
Me	Me	Cl	12
^{i}Pr	^{i}Pr	Cl	13
Me	Me	Fc	14
Me	Me	^{t}Bu	15
Me	Me	C_5Me_5	16
H	^{t}Bu	C_5Me_5	17[13]
^{i}Pr	^{i}Pr	$Ph_3P{=}N$	18[11]
^{i}Pr	^{i}Pr	$(Me_2N)_3P{=}N$	19[11]
Me	Me	$(Me_2N)_3P{=}N$	20[18]
Et	Et	$Cl_2C{=}C(Me)O$	21[14]
^{i}Pr	^{i}Pr	CN	22[14]
Me	Me	CN	23[14]
Mes*	H	OMes*	24[23]
Mes*	H	SMes*	25[23]



R_1	R_2	#
Me	Me	26
Ph	Ph	27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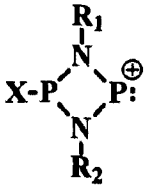
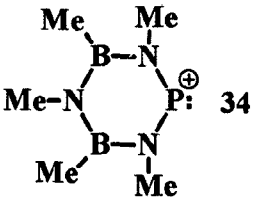


R_1	R_2	X	#
tBu	tBu	Cl	29
tBu	tBu	Me_2N	30
tBu	tBu	Me	31
tBu	Mes*	iPr	32[22]
tBu	Mes*	Me_3Si	33[22]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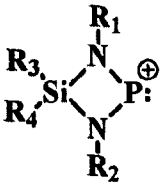
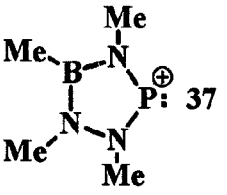


R_1	R_2	R_3	R_4	#
Me_3Si	Me_3Si	Cl	Cl	35
tBu	tBu	Me	Me	36[11]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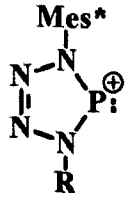
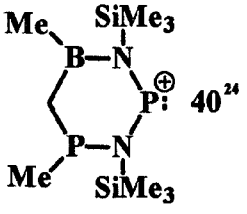


R	#
tBu	38[22]
CEt_3	39[22]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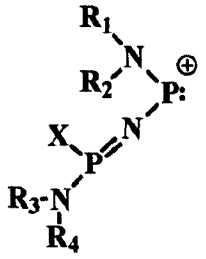
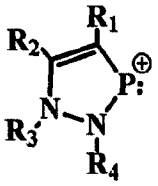
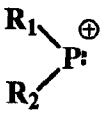


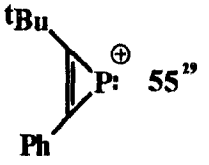
R_1	R_2	R_3	R_4	X	#
iPr	iPr	iPr	iPr	Cl	41
Me	Me	Me	Me	Cl	42
iPr	iPr	iPr	iPr	N_3	43

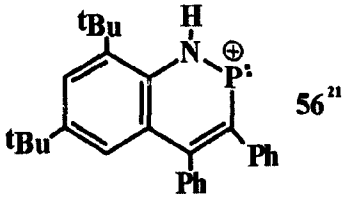


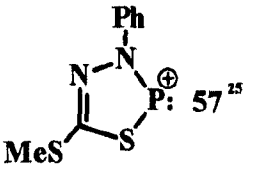
R_1	R_2	R_3	R_4	#
H	Me	H	Me	44
CH_2-CH_2-CH_2		H	Me	45
Me	Me	H	Me	46
H	Me	Me	H	47
CH_2-CH_2-CH_2		Me	H	48
H	Me	Me	Me	49
SMe	Me	H	Me	50
SPh	Me	H	Me	51

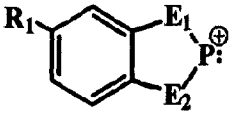


R_1	R_2	#
Fc	Fc	52
C_5Me_5	tBu	53
C_5Me_5	$(Me_3Si)_2CH$	54

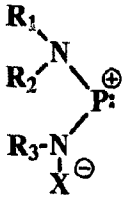




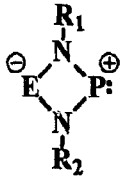




R_1	E_1	E_2	#
H	S	S	58[33]
Me	S	S	59[32]
H	NH	S	60[31]
H	NMe	NMe	61[30]



R_1	R_2	R_3	X	#
Me_3Si	Me_3Si	Me_3Si	$AlCl_3$	62
Me	Me	Mes*	$AlCl_3$	63
Me	Me	Mes*	$GaCl_3$	64[17]
^iPr	^iPr	Mes*	$AlCl_3$	65[17]
^iPr	^iPr	Mes*	$GaCl_3$	66[17]
H	Mes*	Mes*	$AlCl_3$	67[17]
Me_3Si	Me_3Si	Me_3Si	$GaCl_3$	68[16]



R_1	R_2	E	#
Me_3Si	Me_3Si	$AlCl_2$	69
Mes*	Mes*	$AlMe_2$	70[11]
Me_3Si	Me_3Si	$GaCl_2$	71[16]
Me_3Si	^tBu	$GaCl_2$	72[16]

1.2 Characterization of Phosphenium Cations

The crystal structures of fourteen phosphenium salts have been reported and the remaining derivatives have been spectroscopically characterized. Indeed, ^{31}P NMR spectroscopy is the primary tool in the characterization and investigation of phosphenium compounds. ^{31}P NMR chemical shifts characteristic of dicoordinate phosphenium centers cover a wide range (100-500 ppm), however the majority are typically deshielded (>250 ppm) and resonate at higher frequency than the halogen precursors ($\Delta\delta^{31}P$ = ~100 ppm). Complementing ^{1}H and ^{13}C NMR data in addition to other NMR active nuclei (e.g. ^{15}N, ^{29}Si,[26] and ^{27}Al [27]) provide further support for structural elucidation. Recently, mass spectrometry has been employed to identify phosphenium cations[28] but other conventional techniques such as melting point, elemental analysis and infrared spectroscopy are used to comprehensively charaterize the isolated salts.

1.3 Bonding and Stability of Phosphenium Cations

With the exception of $[Fc_2P]^+$ {Fc = $(C_5H_5)_2Fe$}(**52**), $[(C_5Me_5)P(^tBu)]^+$ (**53**) and $[C(Ph)C(^tBu)P]^+$ [29] (**55**), all identified phosphenium species contain at least one electron-rich functional group (possessing a lone pair, e.g. NR_2, SR) adjacent to the phosphorus center. This observation suggests that phosphenium cation stability requires effective π-donation from the neighbouring atom to the formally vacant 3p orbital on phosphorus. Solid state P-E (E = N,[30] S[31,32,33]) bond lengths corroborate this interpretation with values lying between typical single and double bond lengths.

Furthermore, a molecular orbital model for $[(H_2N)_2P]^+$ (Figure 2)[7] shows a three-center π-bonding MO of b_1 symmetry. The σ-lone pair on phosphorus is represented by the a_1 symmetric MO lying just below the non-bonding HOMO which is an out-of-phase combination of 2p nitrogen atomic orbitals with a_2 symmetry. The LUMO is of b_1 symmetry and is the π-antibonding combination of out-of-plane 2p atomic orbitals on the nitrogen centers and the 3p atomic orbital of phosphorus which provides a greater contribution. The stability of $[C(Ph)C(^tBu)P]^+$ (**55**) as well as the heteronaphthalenic (**56, 58-61**) and cyclic diazaphospholium species (**44-51**) is rationalised in terms of a Hückel number (2, 10 and 6 respectively) of π-electrons and effective $p\pi$-delocalization of molecular charge. Similarly, the existence of $[Fc_2P]^+$ [10] (**52**) and $[(C_5Me_5)P(^tBu)]^+$ [34] (**53**) is attributed to delocalization of the positive charge.

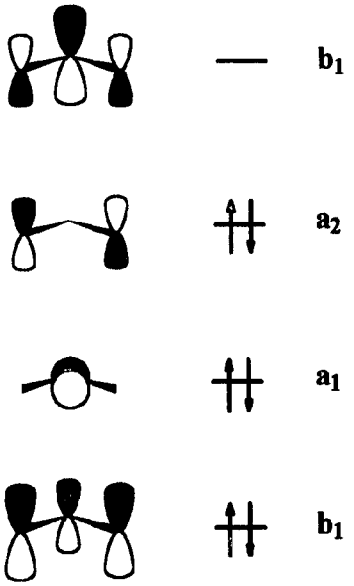


Figure 2. Molecular orbital diagram for $[(H_2N)_2P]^+$.

1.4 Reactivity of Phosphenium Cations

Coordinative unsaturation and a formal positive charge render phosphenium cations attractive sites for nucleophilic addition and coordination chemistry. From the MO diagram in Figure 2, nucleophilic attack is expected to occur at the acidic phosphorus center (LUMO) while basic behaviour is anticipated for the lone pair on phosphorus. The amphoteric nature of phosphenium cations is demonstrated by reactions summarized in Figure 3. Although typical acid-base adducts with amines[35,36] and phosphines[36,37,13,21] have been spectroscopically characterized, only one recent example has been confirmed by X-ray crystallography.[38] Some intramolecular base stabilized species have been reported.[39,40] Phosphenium cations are well known for their ability to insert into single and multiple bonds. Oxidative addition of inter-[41] and intramolecular[42] C-H bonds as well as cyclic C-C bonds[43] yields four-coordinate phosphonium cations. Similarly, addition to alkynes gives the three-membered phosphirenium cyclic cation.[44] For heteroatomic double bonded species X=N (X = N, C, P), only iminophosphines R-N=P-R have shown direct 1,2-addition of the phosphenium cation.[13,45] Organic azides R-N_3 undergo a Staudinger type interaction[46] with release of molecular N_2 and formation of the postulated tricoordinate iminophosphonium cation which rapidly interacts with the counterion.[47,48] Two equivalents of imines R_2C=N-R or isocyanide C=N-R yield five-[49] and four-[19,50] membered heterocycles, respectively. Phosphenium cations can also behave as dienophiles towards a series of dienes[51,52,53,54] and their heteroatom analogues[55,56,57] resulting in cycloaddition products of varying ring size.

To my knowledge, only three examples[58,13,16] portray the basic/nucleophilic behaviour of phosphenium species via displacement of a ligand from a transition metal complex by coordinatien of the phosphorus lone pair to the metal center. Alternatively, similar complexes described as phosphenium units coordinated to metal centers have been prepared by abstraction of a substituent (e.g. halide,[58,59] alkoxide,[60,61] hydride[60]) on a tricovalent phosphorus ligand already coordinated to the metal moiety.

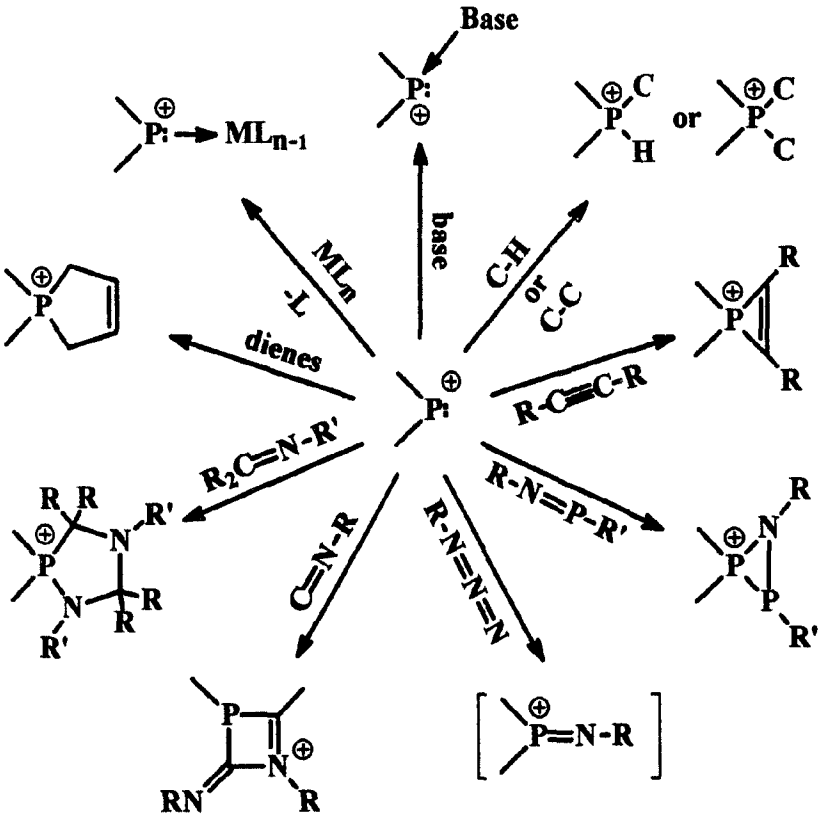


Figure 3. Reactions of phosphenium cations.

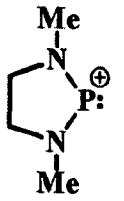
1.5 The Thesis

This work commences with a revival of phosphenium chemistry; in chapter 2 the solid state features of the original phosphenium cation $[\overline{N(Me)CH_2CH_2N(Me)P}]^+$ **(26)** are reported for the first time, revealing discrete monomeric units in contrast to the arsenic analogue which dimerises in the solid state. In chapter 3, the coordinative interactions of the counterion $[GaCl_4]^-$ with the phosphenium cations $[\overline{N(Me)CH_2CH_2N(Me)P}]^+$ **(26)** and $[(^iPr_2N)_2P]^+$ **(4)** are shown to mediate the reactivity of these unsaturated species and in particular, their stability in the commonly used CH_2Cl_2 solvent. In an attempt to eliminate the influence of anions on phosphenium centers, the chemistry of the neutral phosphenium species $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ **(69)** was investigated. Reactions of the zwitterion **69** with chalcogens and coordination complexes of **69** with amines, ethers and phosphines are discussed in chapter 4. Chapter 5 deals with a series of dialkylphosphenium cations and their preferred constitutional isomers in the absence of a π-delocalization of electron density.

Note: The nomenclature employed in this manuscript is not exclusively IUPAC but rather reflects the terminology found in the literature.

Chapter 2 Structural Characterization of the Monomeric $[\overline{N(Me)CH_2CH_2N(Me)P}][GaCl_4]$

Although the phosphenium cation $[\overline{N(Me)CH_2CH_2N(Me)P}]^+$ (**26**) was the first of its kind reported by Fleming and co-workers in 1972 as its $[BF_4]^-$ and $[PCl_6]^-$ salts (*vide supra*),[8] the only existing crystallographic data for **26** was the corresponding molecular fragment bound as a ligand to $CpMo(CO)_2^-$ (**73**).[62] X-ray structural confirmation of a phosphenium salt was first reported in 1978 for the species $[(^tPr_2N)_2P][AlCl_4]$ (**4**$[AlCl_4]$).[30]



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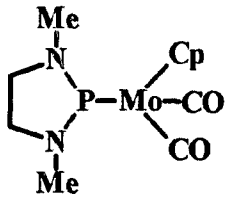

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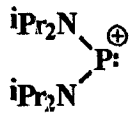


4

In this work, phosphenium cations **26** and **4** were synthesized as their $[GaCl_4]^-$ salts and comprehensively characterized, including the first X-ray analysis of **26** (Figure 4). Heterolytic P-Cl bond cleavage from chloroprecursors $\overline{N(Me)CH_2CH_2N(Me)PCl}$ (**74**) and $(^tPr_2N)_2PCl$ (**75**) by the Lewis acid $GaCl_3$ afforded isolable solids. The ionic nature of **26**$[GaCl_4]$ and **4**$[GaCl_4]$ is evident from the typically deshielded ^{31}P NMR resonances[11,10] (**26**, 269 ppm; **4**, 313 ppm), with respect to **74** (169 ppm) and **75** (141 ppm). Characteristic absorption bands of the $[GaCl_4]^-$ anion in the IR spectra (υ = 382 and 375 cm^{-1} for Ga-Cl in **26** and **4** respectively)[63]

and the observation of discrete ions in the crystal structures of **26**[$GaCl_4$] and **4**[$GaCl_4$] provide further support for the ionic formulation. The structural features of the $[(^iPr_2N)_2P]^+$ cation in **4**[$GaCl_4$] are consistent with those previously reported for the isostructural tetrachloroaluminate salt.[30] The P-N bond lengths of **26** [1.56(2) and 1.58(2)Å] and the corresponding sum of angles around the nitrogens [360(3) and 358(3)°] are identical to those found in **4**. The N-P-N angle imposed by the cyclic framework of **26** [99.0(11)°] is accordingly smaller than in **4** [117.0(7)°] and it can be seen that the phosphorus atom in **26** is less shielded than in **4** due to the steric hindrance provided by the isopropyl groups in **4** (see Figure 7).

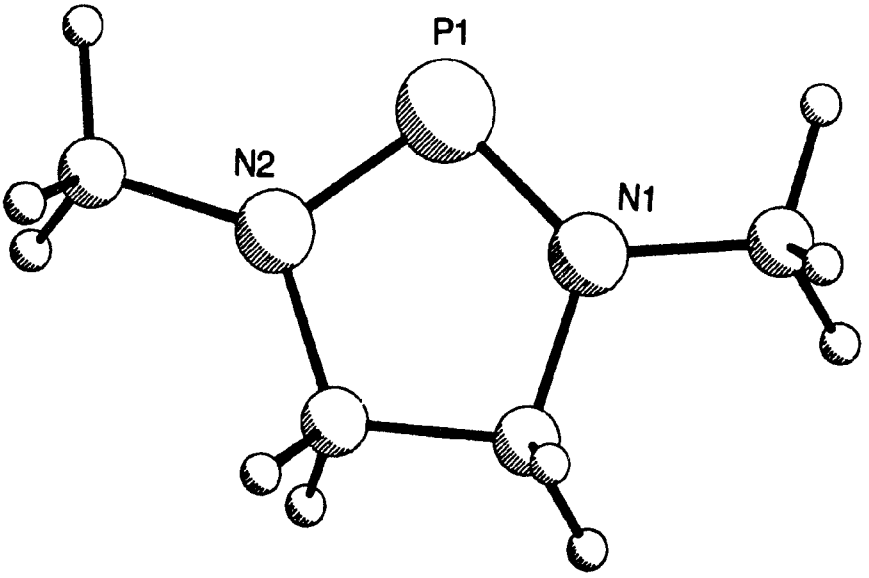
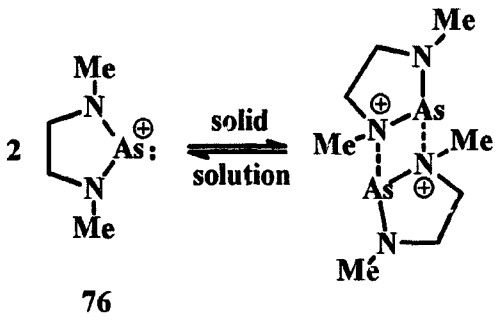


Figure 4. PLUTO view of compound 26. Selected parameters (Å and °): P1-N1 = 1.56(2), P1-N2 = 1.58(2), N1-P1-N2 = 99.0(11).

The most important realization for the solid state structure of **26**[$GaCl_4$] is the monomeric existence for the cation **26**, in contrast to the arsenic analogue **76** which exists as distinct units in solution but adopts a dimeric structure in the solid state (Figure 5).[64] The different structural features are attributed to an effective nitrogen-phosphorus π-interaction in **26** which is preferred over the inter-ring σ-bonding present in the arsenic dimer **76**.



76

Figure 5. Dimerization of 76.

Chapter 3 The Reactivity of Phosphenium Cations: The Role of the Anion[65]

Attempts to isolate interesting cationic species such as the elusive silylenium cation $[R_3Si]^+$ [66,67] or the coordinatively unsaturated $[Fe(TPP)]^+$ (TPP = tetraphenylporphyrinate)[68,69] have been hindered by the interaction between the low coordinate site and the counterion. Consequently, there has been tremendous effort focussed[70] on developing anions which have weak or less coordinative abilities than classical "non-coordinating" anions such as $[ClO_4]^-$, $[CF_3SO_3]^-$, $[FSO_3]^-$, $[BF_4]^-$, $[PF_6]^-$, $[AsF_6]^-$, $[SbF_6]^-$ and $[BiF_6]^-$.[71] The criteria for a "least coordinating" or "weakly coordinating" anion are: (1) relative chemical inertness, (2) minimal numbers of electron dense sites (lone pairs) and/or effective delocalization of electron density, (3) low ionic charge, and (4) steric bulkiness. Reed and co-workers are pursuing this goal with carboranes and their halogenated derivatives.[69,72,73] Tetraarylborates (e.g. $[BPh_4]^-$) and their fluorinated derivatives (e.g. $[B(C_6F_5)_4]^-$, $[B(3,5\text{-}C_6H_3(CF_3)_2)_4]^-$)[74,75,76] as well as polyoxometallates (e.g. $[XM_{12}O_{40}]^{n-}$, X = Si, P; M = W, Mo; n = 3, 4)[77] have had moderate success and a series of bulky anions containing metal (M = Pd, Ti, Nb, Ta, Sb, Bi) and non-metal (M = B, As) centers with the highly electronegative $OTeF_5$ group as substituents, $[M(OTeF_5)_n]^{x-}$ (n = 4, 6; x = 1, 2), have shown promise as weakly basic anions.[71,78] The presence of tetraarylborate and carborane anions has allowed for the observation of novel metal cation environments, facilitated polymerization processes[79] and more recently has played a key role in the controversial search for a free silylenium cation $[R_3Si]^+$.[80,81] In other instances, the basicity of the anion is sufficiently weak that the cationic species interacts with the arene

solvent.[73,81,82]

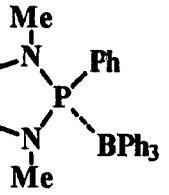
As outlined in the introduction, many derivatives of phosphenium cations have been identified (see Table 1), however the anion in almost every case has been a tetrachloroaluminate anion with a few examples of triflate salts. Since it is evident that anions play an important role in the chemistry of unsaturated cationic species, their effect on phosphenium cations warranted further investigation.

3.1 Preparation and Characterization of $[(^iPr_2N)_2P][BPh_4]$ and the Covalent $\overline{N(Me)CH_2CH_2N(Me)P(Ph)}\cdot BPh_3$

Reaction of $\overline{N(Me)CH_2CH_2N(Me)PCl}$ (**74**) or $(^iPr_2N)_2PCl$ (**75**) with $NaBPh_4$ afforded a single product in each case as indicated by NMR studies of the reaction mixtures ($\delta^{31}P$ = 80 and 284 ppm respectively). The formation of the phosphenium cation $[(^iPr_2N)_2P]^+$ (**4**) is shown by the deshielded ^{31}P NMR resonance ($\delta^{31}P$ = 308 ppm) and a single signal in the ^{11}B NMR at -7.0 ppm for $[BPh_4]^-$. However, crystals of $[(^iPr_2N)_2P][BPh_4]$ decay in the X-ray beam. It is interesting to note that the ^{31}P chemical shift of the phosphenium center is essentially identical in the two salts **4**$[GaCl_4]$ ($\delta^{31}P$ = 313 ppm) and **4**$[BPh_4]$, while the isopropyl hydrogen nuclei of the tetraphenylborate salt (3.92, 1.27 ppm) are significantly shielded with respect to those of the gallate salt (4.20, 1.52 ppm).

The reaction of **74** with $NaBPh_4$ produces the covalent phosphineborane **77** which has been crystallographically characterized (Figure 6). A relatively shielded ^{31}P NMR signal at 82 ppm is observed for 77 and is in contrast to an ionic isomer

26[BPh_4] ($\delta^{31}P$ expected at ~270 ppm). The structure can be viewed as the result of insertion of the phosphorus center of **26** into a B-C bond or phenyl exchange and subsequent adduct formation between the phosphine and the borane. Such phenyl group transfers from [BPh_4]$^-$ are well established for metal centers.[83]



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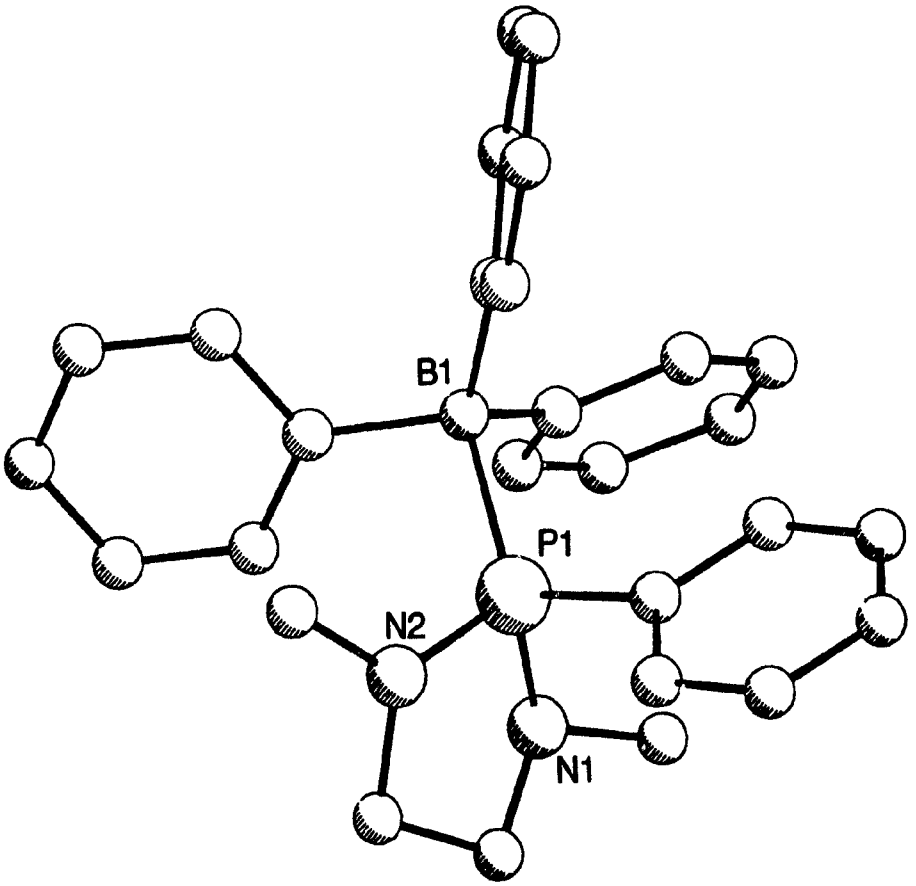
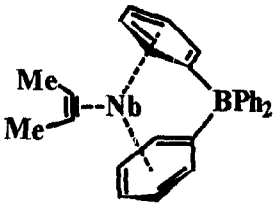


Figure 6. PLUTO view of compound 77. Selected parameters (Å and °): P1-B1 = 2.051(3), P1-N1 = 1.616(5), P1-N2 = 1.622(5), N1-P1-N2 = 113.3(3).

Although considered a weakly coordinating anion, $[BPh_4]^-$ does have the potential to complex to cationic sites through the phenyl groups as demonstrated for a series of metal salts (e.g. **78** and **79**).[84] Such an arrangement can be envisaged for **4**$[BPh_4]$ in which the electrophilic phosphenium site is either sandwiched between two of the phenyl substituents (η^{12}) of the tetraphenylborate anion **80**, or is involved in η^6 coordination to one of the phenyl substituents **81**. The potential for cationic phosphorus sites to engage in such π-arene complexation has been demonstrated.[85] As compound **77** represents a covalent alternative of **26**$[BPh_4]$, the conclusion is that the ionic nature of **4**$[BPh_4]$ relies on the steric shield provided by the isopropyl substituents which prevent interaction between the B-C bond of the anion and the phosphenium site of the cation. As depicted in Figure 7, such a shield is not present in **26** (phosphorus atom in black) allowing for rearrangement of the salt to the covalent alternative phosphineborane **77**.



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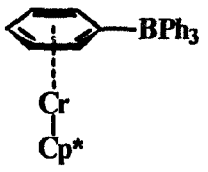

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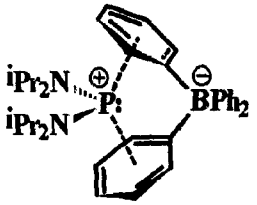

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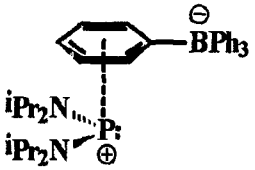
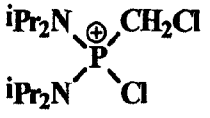


81

3.2 Stability of $[(^{i}Pr_2N)_2P][BPh_4]$ in Halogenated Solvents

^{31}P NMR studies on solutions of **4**$[BPh_4]$ in CH_2Cl_2, $CHCl_3$ and $CH_2Cl_2/CHCl_3$ show reaction within hours at room temperature. Many products are formed, but a single signal at -7.0 ppm in the ^{11}B NMR spectra indicates that the tetraphenylborate anion is unchanged. In one instance the phosphonium salt $[(^{i}Pr_2N)_2P(CH_2Cl)Cl][BPh_4]$ (**82**$[BPh_4]$) was isolated from a 50:50 solution of CH_2Cl_2 and $CHCl_3$, and $[^{i}Pr_2NH_2][BPh_4]$ has been isolated on a number of occasions (both compounds characterized by X-ray crystallography). These observations imply that cation **4** in the presence of $[BPh_4]^-$ reacts with the solvent; a behaviour consistent with $[Me_3Si][(3,5\text{-}C_6H_3(CF_3)_2)_4B]$ which has been shown to react with halogenated hydrocarbon solvents.[76]



82

In the present case, cation **82** can be viewed as the result of an oxidative addition of CH_2Cl_2 to the phosphenium center of **4**. Cation **4** reacts faster with $CHCl_3$ than with CH_2Cl_2 and this is attributed to $[CHCl_2]^+$ being a more stable carbocation than $[CH_2Cl]^+$. The corresponding solvent reaction(s) for **26**$[BPh_4]$ are not observed possibly due to the preferential and faster rearrangement to the covalent phosphineborane **77**. In contrast, the tetrachlorogallate (and presumably aluminate)

salts of cations **26** and **4** have essentially indefinite lifetimes in CH_2Cl_2 at room temperature (^{31}P NMR spectra are unchanged in excess of one year).

3.3 Anionic Protection[86]

The stability of $[Me_3Si][ClO_4]$ in a solution of CH_2Cl_2[66] is in sharp contrast to the fluorinated borate salt and stems from the covalent association of its ions as depicted in the solid state.[67] Complexation of the anion $[CF_3SO_3]^-$ to a phosphenium cation has been observed in NMR spectra.[87] The inert nature (relative to **26** and **4**[BPh_4]) of the tetrachlorogallate (and presumably aluminate) salts of both **26** and **4** in chlorinated solvents must be similarly attributed to the relationship between cation and anion in solution. Solid state structural features of the salts involving polyhalogenated anions confirm the intimacy of the cation-anion relationship. Figure 7 illustrates the packing of anions around the cation in the structures of **26**[$GaCl_4$] (a) and **4**[$GaCl_4$] (b). In spite of the different space groups, the different size and shape of the cations and the different degrees of steric shielding present on the cations, the structures consist of cationic units surrounded by a total of three anions; above, below and in the N-P-N plane. The closest inter-ion distances occur between the chlorine atoms and the phosphorus center, although the distances {**4**[$GaCl_4$]: P---Cl(1) 3.976(6)Å, P---Cl(3) 3.867(6)Å, P---Cl(4) 4.020(6)Å; **26**[$GaCl_4$]: P---Cl(1) 3.548(1)Å, P---Cl2 3.982(2)Å, P---Cl3 4.03(2)Å, P---Cl4 4.04(2)Å} are in excess of the sum of the van der Waals radii (P--Cl, 3.7Å).[88] Cation-anion distances slightly less than the sum of the van der Waals radii are common for non-metal salts[89] and other phosphenium salts.[31,32,90,91] Although

such interactions are considered as donations from the anion to the cation,[92] they generally have little or no effect on the structural features within the cation or the anion.[93]

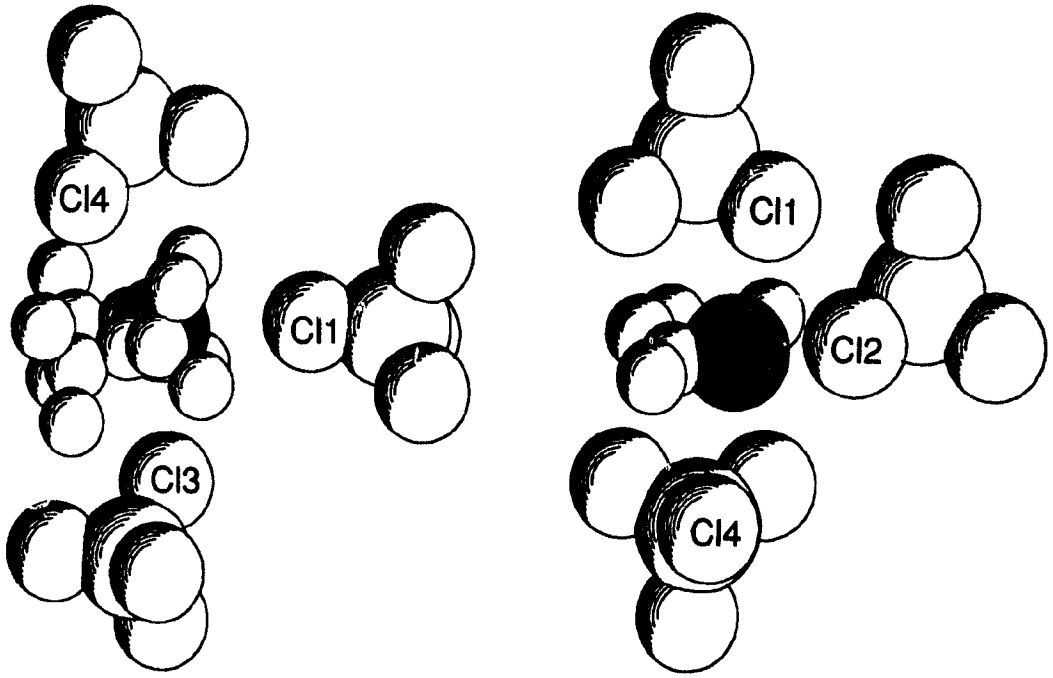


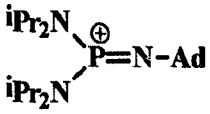
Figure 7. Crystallographic views of (a) 4[$GaCl_4$] and (b) 26[$GaCl_4$] showing the array of anions around each cation. Phosphorus atoms are in black. P-Cl distances (Å): P···Cl1 = 3.976(6), P···Cl3 = 3.867(6), P···Cl4 = 4.020(6); (b) P···Cl1 = 3.548(1), P···Cl2 = 3.982(2), P···Cl3 = 4.03(2), P···Cl4 = 4.04(2).

Nevertheless, the results of this study show mediation in solution of the Lewis acidity (and possibly electrophilicity and general reactivity) of the phosphenium cations **26** and **4** in the presence of electron-rich polyhalogenated anions. The localized non-bonding electron pairs available on these anions offer sites for effective electrostatic interaction with the cation and allow for ion pairing or clustering which inhibits the reactivity or *'protects'* the phosphenium center. The tetraphenylborate anion is expected to form weaker interactions rendering the Lewis acidity of cation **4** sufficiently high to engage the solvent molecules that are small enough to penetrate the steric shield of the cation. However, both the cation and the anion are sufficiently bulky to prevent an electrophilic attack of the phosphenium center on the B-phenyl bond as seen for cation **26**.

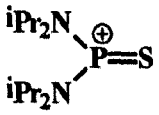
3.4 Reactions of $[(^{i}Pr_2N)_2P][A]$ (A = $GaCl_4$ or BPh_4) with Elemental Sulfur and Organic Azides: Attempts at the Formation of a Tricoordinate Phosphonium Cation

Reactions of phosphenium cations typically lead to tetracoordinate phosphonium products (see Figure 3). Tricoordinate phosphonium environments **83** analogous to alkenes have been observed for only five methylene derivatives (**83a**), however, none were prepared via phosphenium cations.[94] In an attempt to synthesize imino- and thioxo- tricoordinate phosphonium cations (**83b** and **83c** respectively), the aminophosphenium cation **4** was added stoichiometrically to a solution of adamantyl azide (as **4**[$GaCl_4$]) and to a suspension of elemental sulfur (as **4**[$AlCl_4$]) respectively.

83a

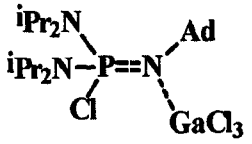


83b

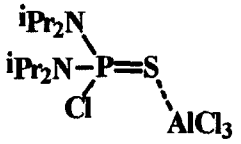


83c

In both cases, signals in the ^{31}P NMR spectra of the reaction mixtures correspond to the complexes of the heterophosphoryl chlorides **84** ($\delta^{31}P$ = 38 ppm) and **85** ($\delta^{31}P$ = 62 ppm). Such complexes have been previously obtained through the reaction of $(^{i}Pr_2N)_2P(Cl)NPh$ and $(^{i}Pr_2N)_2P(Cl)S$ with the Lewis acid $AlCl_3$ and represent covalent alternatives to the elusive tricoordinate phosphonium cations.[48,95]



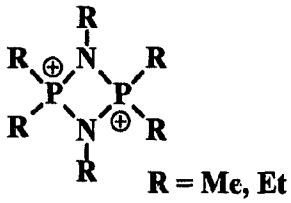
84



85

Their formation from the phosphenium cation **4** is rationalized in terms of a reabstraction of a chloride ion from the tetrachloroanion upon generation of **83** to give the covalent phosphoryl chloride which in turn coordinates to the free Lewis acid. The increased reactivity of $[(^{i}Pr_2N)_2P]^+$ in **4**$[BPh_4]$ relative to **4**$[GaCl_4]$ prompted further efforts to synthesize the elusive tricoordinate phosphonium cations. ^{31}P NMR spectra of reactions involving **4**$[BPh_4]$ and S_8 in CH_2Cl_2 show the slow appearance of a multitude of phosphorus containing species, but the ^{11}B NMR spectra of these

complex mixtures confirm the passivity of the $[BPh_4]^-$ anion ($\delta^{11}B$ = -6.8 ppm). The thiophosphoryl chloride $(^iPr_2N)_2P(Cl)S$ ($\delta^{31}P$ = 69 ppm) is a dominant product formed presumably by chloride ion abstraction from the solvent[95] however a second major species ($\delta^{31}P$ = 86 ppm) remains unidentified ($[(^iPr_2N)_2P(Cl)SCH_2Cl]^+$ and the dimer $[(^iPr_2N)_2PS]^{2+}$, $\delta^{31}P$ = 60 and 18 ppm respectively, are not observed).[95] Unfortunately, isolation yielded a solid void of phosphorus nuclei. Similarly, the reaction of **4**$[BPh_4]$ with adamantyl azide gave a series of phosphorus compounds (by ^{31}P NMR) and $[BPh_4]^-$ is unaffected. Although three dominant products are observed ($\delta^{31}P$ = 36, 33 and 5 ppm), they have yet to be identified. As in the reaction with sulfur, $(^iPr_2N)_2P(Cl)NAd$ is a plausible product. In fact, addition of $(^iPr_2N)_2P(Cl)NPh$ to $NaBPh_4$ showed no reaction ($\delta^{31}P$ = -8 ppm) indicating a preference for the iminophosphoryl chloride. Even if dimerization of the tricoordinate thioxophosphonium cation is not observed, such a process is possible for the imino derivative since analogous diphosphonium heterocyclic phosphetidines $[(R_2N)_2PNR]_2^{2+}$ (**86**, R = Me and Et, $\delta^{31}P$ = ~30 ppm in CH_3CN) have been reported.[96]



86

3.5 Conclusions Regarding the Degree of "Phosphenium Character"

Albeit the coordinative nature of the anion mediates the reactivity of phosphenium centers in **26** and **4**, the well documented cycloaddition reaction (Figure 8) of phosphenium cations with 1,3-dienes occurs readily for both $[BPh_4]^-$ and $[GaCl_4]^-$ salts of **4** to give phospholenium cations **87** (^{31}P NMR studies).[51]

4 **87**

Figure 8. Cycloaddition of the phosphenium cation 4 to dienes.

Evidently the influence of the anion in this cycloaddition reaction, and possibly other known reactions of phosphenium cations, is insignificant. Nevertheless, enhancing the "phosphenium character" (more precisely the acidity and electrophilicity) by diminishing the strength of the interaction between the cation and the anion(s) may allow slow or forbidden reactions to take place. It has been stated[70,97] that in the condensed phase (solution and solid state) such unsaturated species will always interact with solvent and/or counterions and therefore the concept of a free phosphenium cation is conceivable only in the gas phase.

Chapter 4 Chemistry of a Neutral Phosphenium Derivative

1,3,2,4-Diazaphosphoniaaluminatacyclobutane[15,98] **69** represents an important and novel example of a system containing a phosphenium center. Although neutral, its zwitterionic form is demonstrated by the ^{31}P NMR shift of 380 ppm which is characteristic of phosphenium centers. Despite the novelty of this compound, little has been reported on its reaction chemistry (Figure 9).

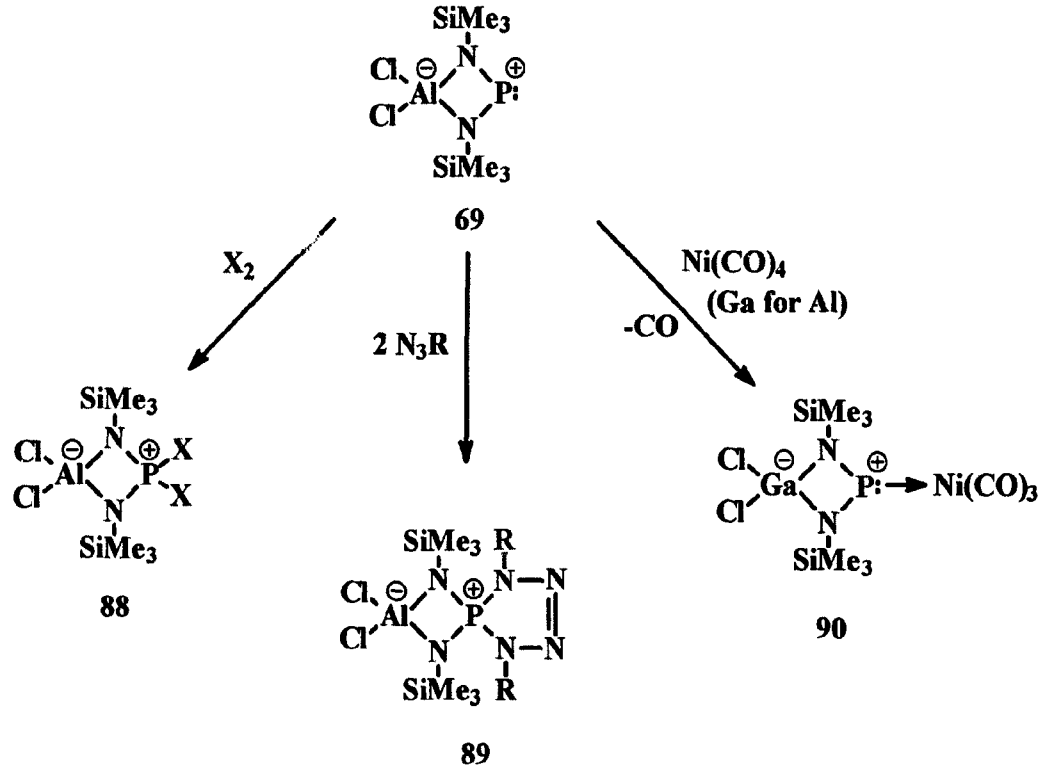


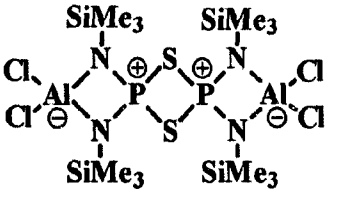
Figure 9. Chemistry of $\overline{N(SiMe_3)AlCl_2(SiMe_3)NP}$.

For example, the addition of halogens Cl_2, Br_2, I_2 and EtI to **69** gives the corresponding tetracoordinate phosphonium cations[99] **88** while the gallium (replacing

aluminium) derivative (**71**) displaces a CO ligand from $Ni(CO)_4$ **90**.[16] Reaction of **69** with two equivalents of organic azides N_3R gives the heterospirocycle **89**.[15,99] In this chapter, the reactions of **69** with chalcogens are discussed and the first coordination complexes of this neutral phosphenium derivative behaving as an acid are reported.

4.1 Reaction of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)}P$ with Elemental Sulfur [100]

Reaction of **69** in toluene with S_8 occurs within minutes to give the new *bis*(spiro)tricyclodialuminatetrazadithiadiphosphetane **91** which precipitates rapidly as a fine white powder. Compound **91** is the major product in solution (> 90% observed by ^{31}P NMR spectroscopy -18 ppm), independent of stoichiometry, although the reaction time is decreased when compound **69** is in excess (a precipitate is observed immediately in a 2:1 mixture but slowly appears after ~10 min in a 1:1 reaction stoichiometry). Solid state ^{31}P NMR spectra of the bulk precipitate confirm **91** as the single phosphorus containing component ($\delta^{31}P$ = -17 ppm).



91

Recrystallization of the precipitate provided crystals suitable for X-ray analysis and confirmation of the bis(spiro)tricyclic structure in **91** (Figure 10).

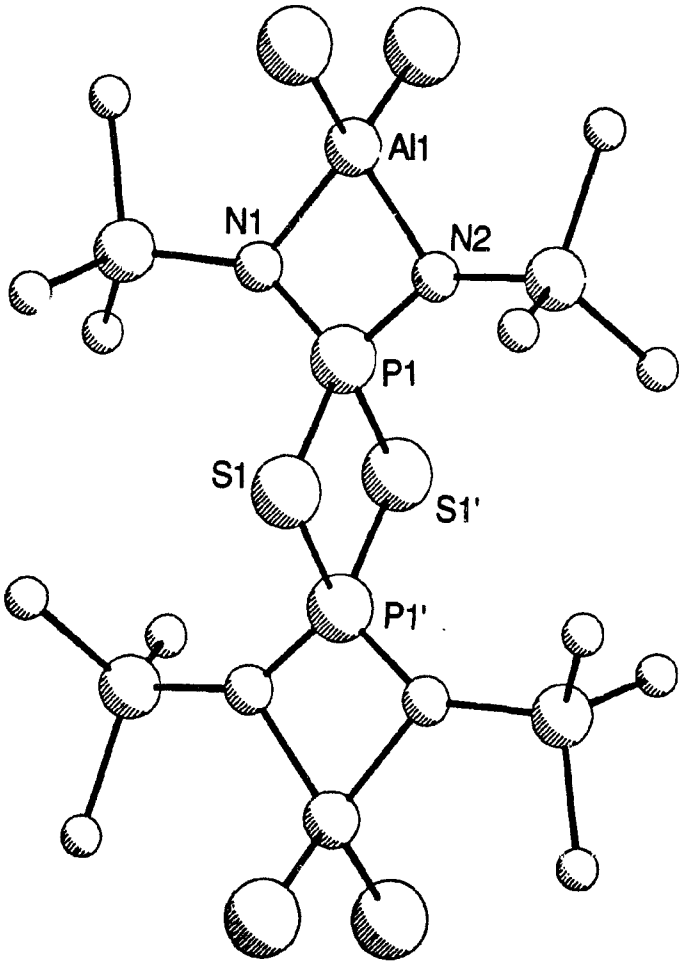
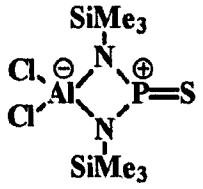


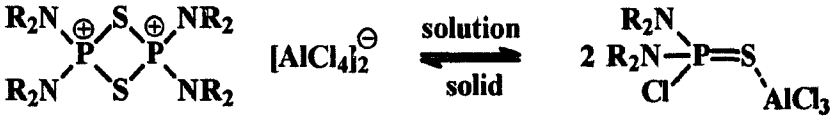
Figure 10. PLUTO view of compound 91. Selected parameters (Å and °): P1-S1 = 2.120(2), P1-S1' = 2.119(2), P1-N1 = 1.593(3), P1-N2 = 1.598(3), S1-P1-S1' = 92.39(6), P1-S1-P1' = 87.61(6), N1-P1-N2 = 99.5(2).

The centrosymmetric tricyclic framework has a dithiadiphosphonium bridge as a central feature which is orthogonal to the terminal rings. The geometry of the P_2S_2 ring is typical of dithiadiphosphetane[101,102,103] or dithiadiphosphonium **92**[95] systems with single P-S bonds [2.120(2)and 2.119(2)Å c.f. $(PhS)_3P$, 2.122(8)Å].[104] The terminal heterocycles are structurally similar to **69**.[98] Spirocyclic geometries are common for phosphorus, however, the bis(spiro) structure is novel.

Formation of **91** represents a simple one atom (Staudinger-type)[46] oxidative addition to the phosphenium center of **69**. However, the dimer **91** can be considered a structural alternative to the monomeric tricoordinate thioxophosphonium **93** and is a neutral zwitterionic analogue of the ionic dithiadiphosphonium cations **92** which only exist in the solid state as a bis(tetrachloroaluminate) salt and dissociates in solution to the covalent phosphoryl chloride-$AlCl_3$ complex **94** (Figure 11).



93



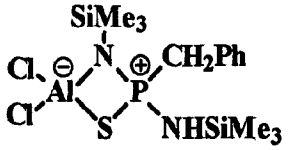
R = Me, Et

92 **94**

Figure 11. Covalent alternatives in solution for dithiadiphosphonium cations.

Solid state ^{31}P NMR data indicate that compound **91** maintains the same structure in solution and solid state. Unlike the dithiadiphosphonium cations **92** there are no obvious structural alternatives for **91** other than a monomeric system containing the elusive tricoordinate thioxophosphonium center. The observation of **91** is consistent with the recognized thermodynamic instability of tricoordinate thioxo-[95] and iminophosphonium species.[39,48]

Solution ^{31}P NMR spectra of the reaction mixtures in toluene after 2 weeks reveal a new species **95** ($\delta^{31}P$ =55 ppm) which is formed at the expense of **91** (note: **91** is still the major product in the form of a precipitate).[105] Spectroscopic and crystallographic characterization of the isolated solid identify the new compound **95** (Figure 12) as an example of a "genuine heterocycle" (a ring system containing only one atom of each element in the heterocyclic framework).[93]



95

The heterocyclic [PNAlS] structural parameters of **95** are comparable to those of reported derivatives.[106] Although the mechanism of the reaction has not been determined, an intermediate thioxophosphonium **93** zwitterion is anticipated in the formation of **91** and the involvement of **93** in the formation of **95** is plausible. The P-N bonds in **93** (as well as **69**) can be envisaged as having partial π character (Figure 13), enabling the addition of the C-H bond of toluene to one of the P-N sites and

resulting in cleavage of the adjacent Al-N bond. Rotation about the other P-N bond positions the sulfur atom for linkage to the aluminium center to give **95**. Although the production of **95** follows that of **91**, toluene solutions of **91** in pure form are indefinitely stable, attesting to the preference for dimerization of **93**.

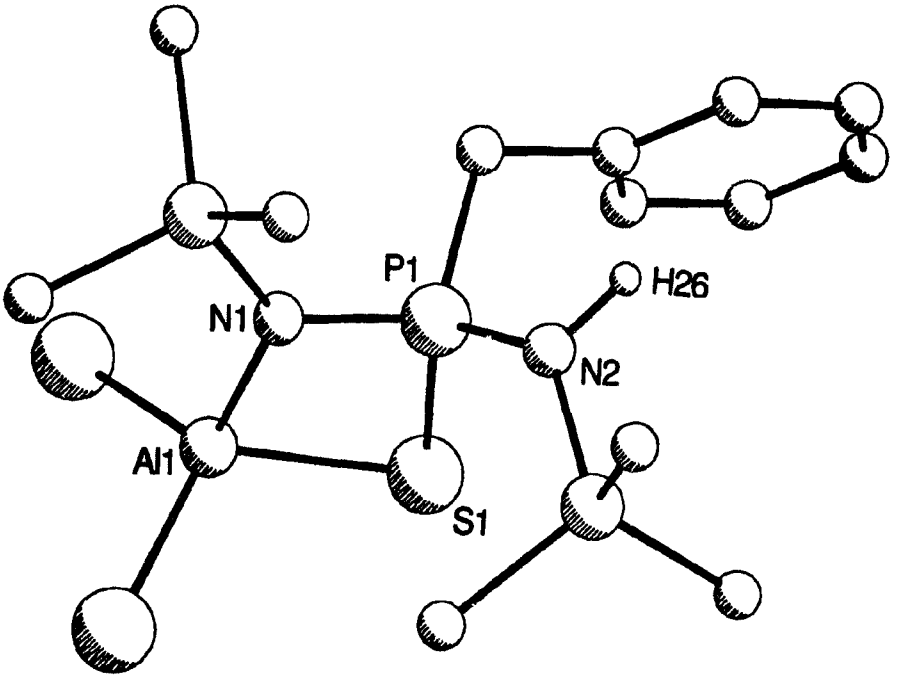


Figure 12. PLUTO view of compound 95. Selected parameters (Å and °): P1-N1 = 1.636(8), N1-Al1 = 1.855(8), Al1-S1 = 2.272(5), P1-S1 = 2.045(4), N1-P1-S1 = 99.9(3), Al1-N1-P1 = 98.4(4), N1-Al1-S1 = 85.9(3), Al1-S1-P1 = 75.4(2).

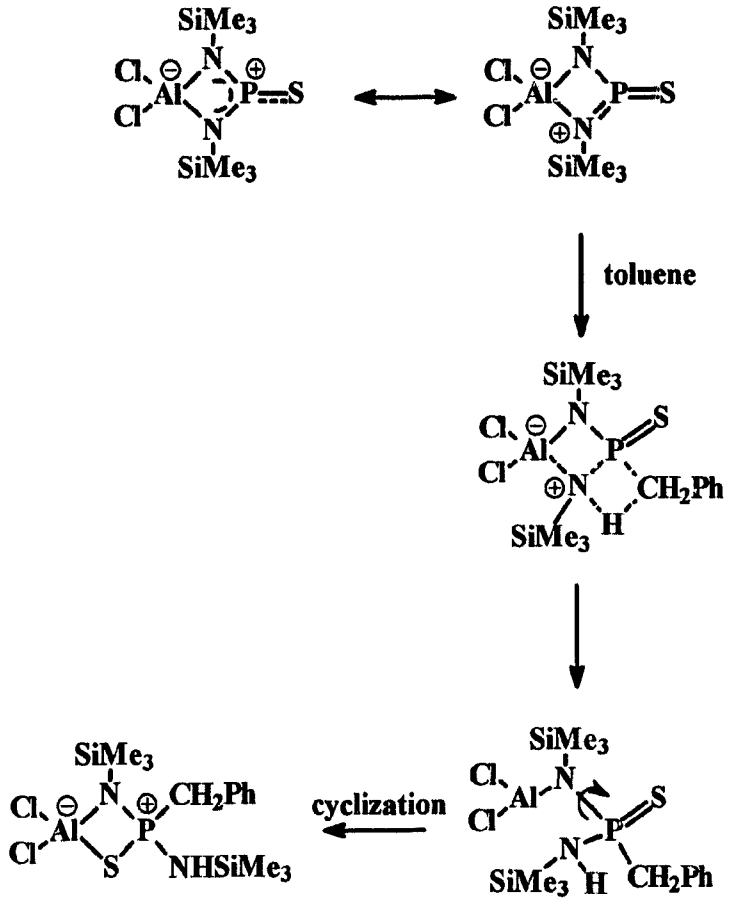
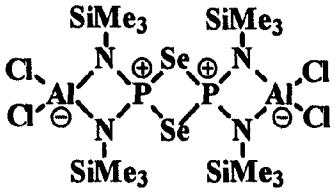


Figure 13. Proposed mechanism for formation of 95.

4.2 Reaction of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ with Elemental Selenium and Tellurium

Reaction of **69** with elemental Se in toluene occurs slowly (over a week independent of stoichiometry, in contrast to S_8) to give a bright yellow-green precipitate but no reaction is observed with Te. This trend in reactivity reflects the lower oxidative potential of heavier chalcogens. The impure solid (traces of Se present) is poorly soluble in common solvents (^{31}P NMR shows a weak signal at -63 ppm in CH_2Cl_2) but the solid state ^{31}P NMR spectra indicate the presence of only one phosphorus containing species in the powder ($\delta^{31}P$ = -57 ppm) which is assigned the structure **96**.



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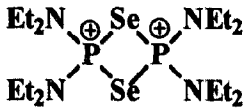


97

Characterization of compound **96** is presently incomplete and recrystallization of the precipitate is expected to yield suitable crystals for structural determination of **96**. Nevertheless, **96** can be assigned to the selenium derivative of the heterospirocycle **91** by spectroscopic comparisons with other P_2E_2 (E = S or Se) ring-containing species. The selenium derivative of the dimeric dithiadiphosphonium **92** ($\delta^{31}P$ = 21 ppm), the dication **97**, has been isolated ($\delta^{31}P$ = -8 ppm in CH_2Cl_2) and structurally characterized as its bis(tetrachloroaluminate) salt.[48] The ^{31}P NMR solution chemical shifts of **92** and **97** are both observed at lower field from the neutral analogues **91** and **96** ($\delta^{31}P$ = -18, -63 ppm and $\Delta\delta^{31}P$ = 39, 55 ppm respectively).

This trend in chemical shifts and the formation of dichalcogenodiphosphonium cations for both sulfur (**92**) and selenium (**97**) support the assignment of **96** as the selenium derivative of **91**.

4.3 Intermolecular Coordination Interactions in the Solid State Structure of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$

The formal electron deficiency and coordinative unsaturation at the phosphorus center in **69** labels it as an obvious site for coordination chemistry. While **69** cannot benefit from the cation-anion interaction in solution, the solid state structure[98] reveals a number of intermolecular phosphorus-chlorine contacts (Figure 14, P-Cl1 = 3.73Å, P-Cl2 = 3.89Å) that are comparable if not shorter than the cation-anion interactions in the phosphenium salts **26**[$GaCl_4$] and **4**[$GaCl_4$] (see Figure 7). A weak electrostatic intermolecular association of **69** in solution is demonstrated by its inertness in CH_2Cl_2. However, **69** reacts slowly with $CHCl_3$ (first signs of unidentified products, including $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}(Cl)CHCl_2$, are observed by ^{31}P NMR after one day). Reaction with $CHCl_3$ but not CH_2Cl_2 is attributed to the relative stability of the proposed intermediate carbocation $[CHCl_2]^+$ with respect to $[CH_2Cl]^+$ (see section **3.2**).

4.4 Coordination of Amines to $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$

Reactions of **69** with the amines quinuclidine (1:1), 1,4-diazabicyclo[2.2.2] octane [DABCO] (2:1) and N,N,N',N'-tetramethylethylenediamine [TMEDA] (2:1) are instantaneous at room temperature and each gives a single product ($\delta^{31}P$ = 205, 282

and 285 ppm in CD_2Cl_2 respectively). Isolated materials have been comprehensively characterized as adducts **98**, **99** and **100** respectively and X-ray crystal structures reveal that all amine nitrogen centers are bound to phosphorus (Figures 15, 16 and 17).

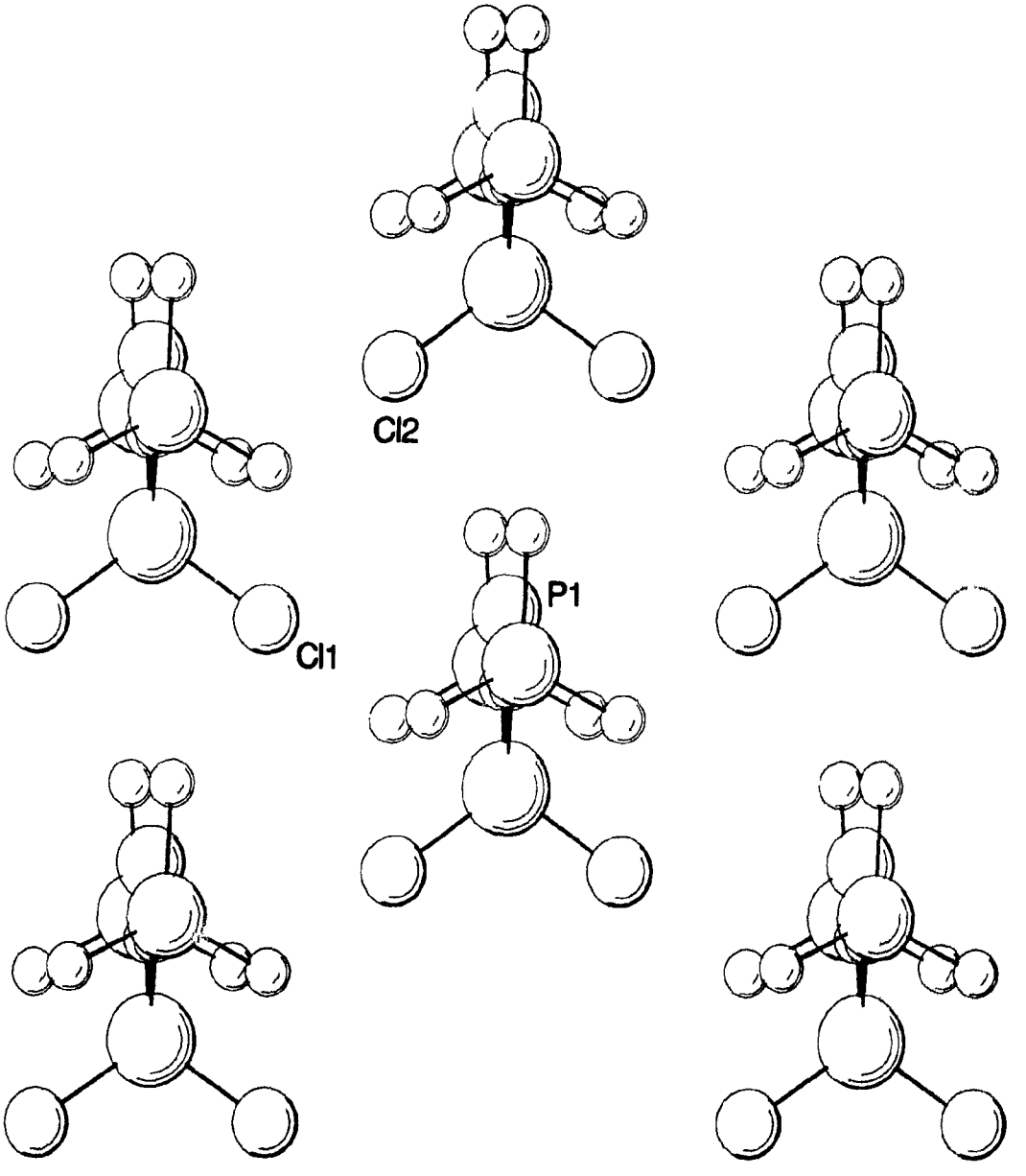
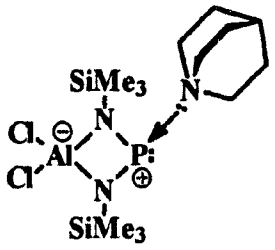


Figure 14. Crystallographic view of compound 69. P-Cl distances (Å): P1···Cl1 = 3.73, P1···Cl2 = 3.89.



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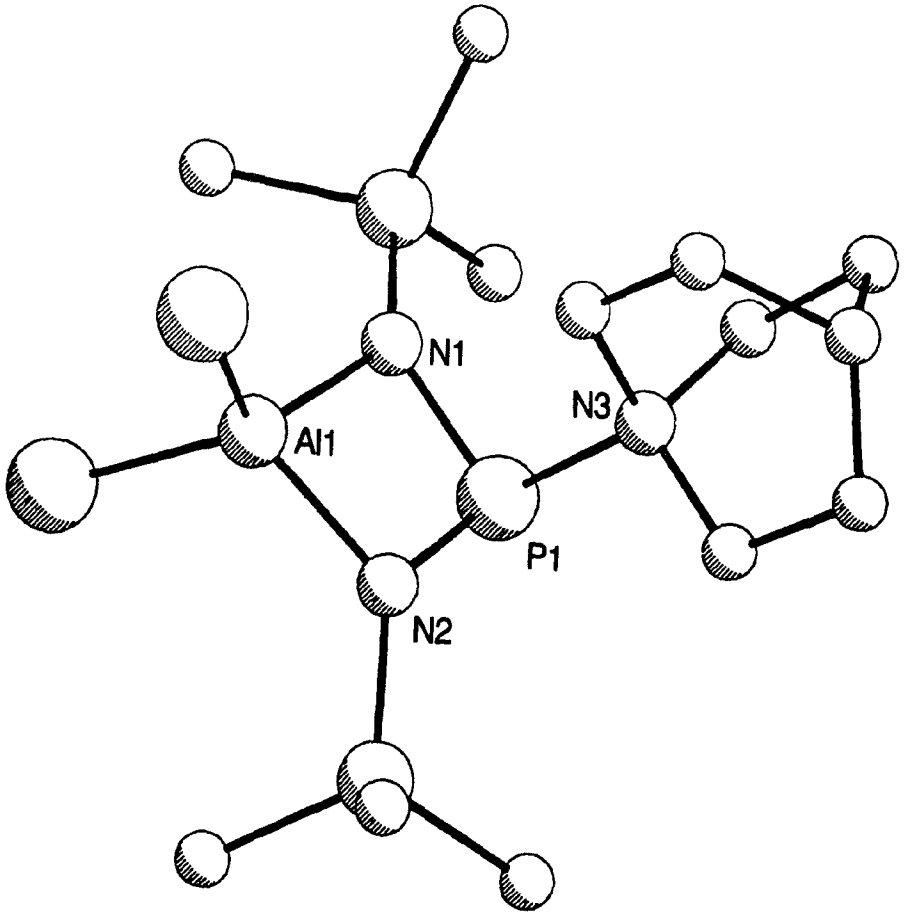
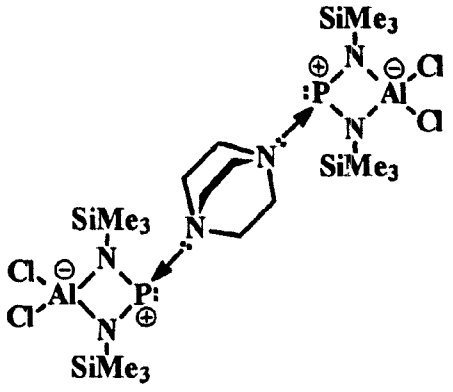


Figure 15. PLUTO view of compound 98. Selected parameters (Å and °): P1-N3 = 2.038(9), P1-N1 = 1.686(9), P1-N2 = 1.660(9), N1-Al1 = 1.85(1), N2-Al1 = 1.860(9), N1-P1-N2 = 93.9(5).



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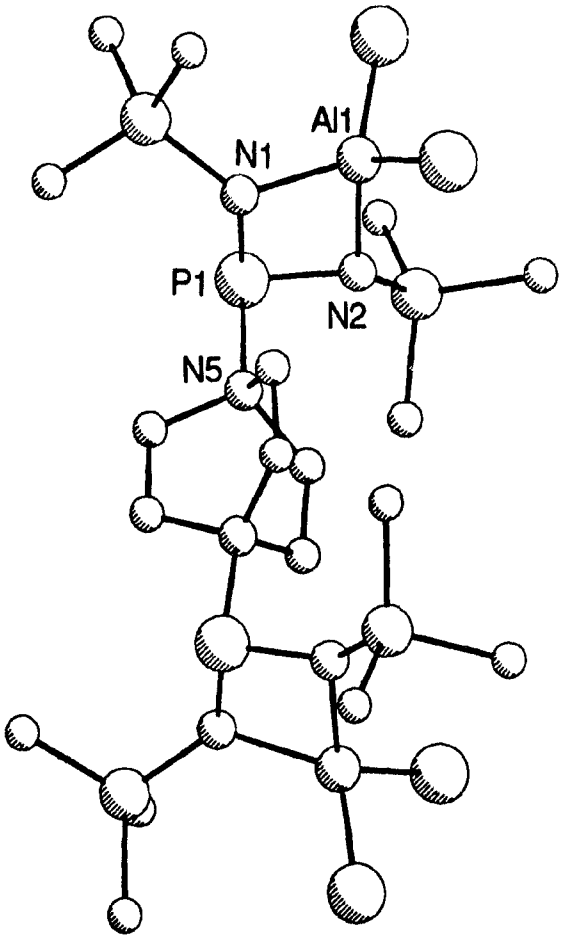
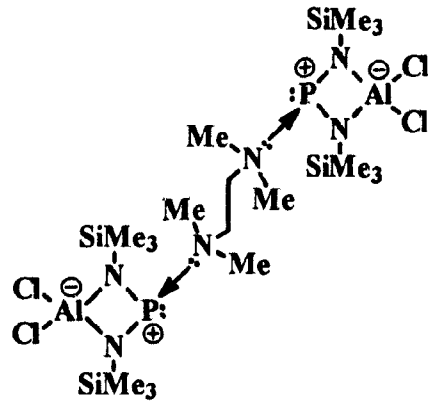


Figure 16. PLUTO view of compound 99. Selected parameters (Å and °): P1-N5 = 2.07(4), P1-N1 = 1.68(5), P1-N2 = 1.71(6), N1-Al1 = 1.86(5), N2-Al1 = 1.87(6), N1-P1-N2 = 92(3).



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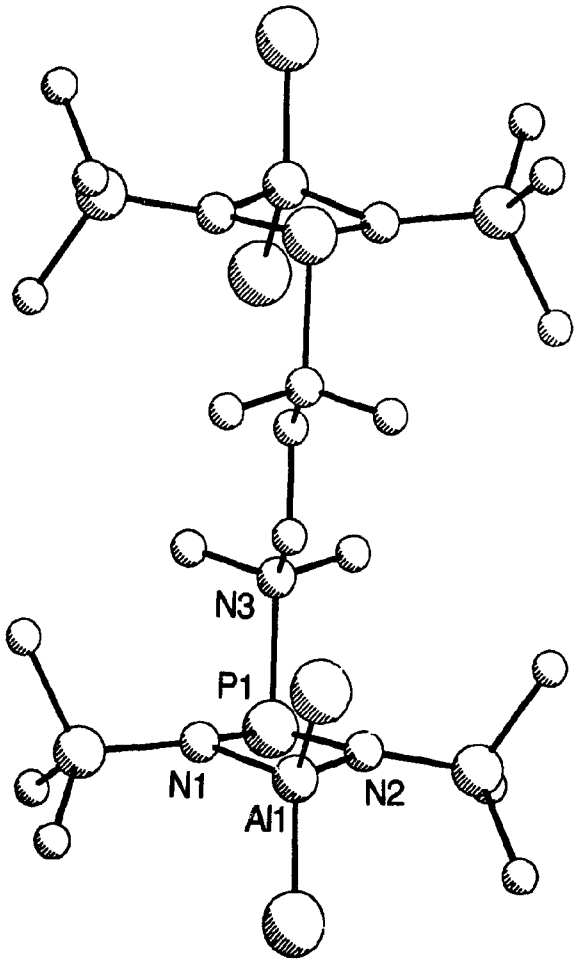
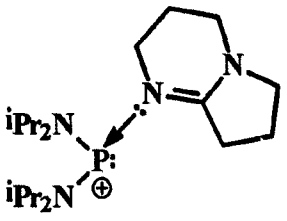


Figure 17. PLUTO view of compound 100. Selected parameters (Å and °): P1-N3 = 2.110(6), P1-N1 = 1.658(5), P1-N2 = 1.661(5), N1-Al1 = 1.863(6), N2-Al1 = 1.866(5), N1-P1-N2 = 94.3(3).



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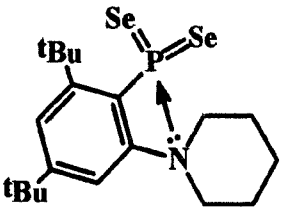

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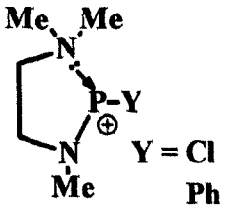


103

As may be expected, in each case the N-P linkage to the ligand (**98** 2.2038(9)Å; **99** 2.07(4)-2.14(4)Å; **100** 2.110(6)Å) is longer than those within the four-membered ring (avg. 1.666(11)Å).[107] In fact, the adduct bonds are substantially longer than the "single" bond in $[O_3PNH_3]^-$ (1.77Å)[108]as well as known N→P coordinative bonds found in the intermolecular **101** (1.796(3)Å)[38] or intramolecular **102** (2.039(5)Å)[109] and **103** (1.84Å {Y = Cl, anion = $[Cl]^-$} and 1.88Å {Y = Ph, anion = $[BPh_4]^-$})[40] complexes involving phosphorus centers. Although all N→P bonds currently discussed are well within the sum of the van der Waals radii (3.4 Å for N-P),[88] the coordinative linkages of **98**, **99** and **100** are, to my knowledge, the longest N-P bonds yet reported. The endocyclic P-N bonds are slightly lengthened [avg. 1.666(11)Å] with respect to the free **69** [1.614(6)Å] which is an adjustment not observed for the novel spirocyclic species **91** [avg. 1.595(2)Å] obtained from reaction of **69** with sulfur (section **4.1**). In addition, the Al-N distances [avg. 1.860(6)Å] and NAlN angles [avg. 81.9(5)°] of the complexes are slightly altered from **69** [1.890(6)Å and 79.9(3)° respectively]. The donor nitrogen centre can interact with the formally vacant 3p orbital on phosphorus forming an average angle of 107.3(13)° with the

planar [PNAlN] ring. The distorted triangular pyramidal geometry around phosphorus is identical in **98**, **99** and presumably **100**[110] with exocyclic N-P←N angles [avg. 99.8(6)°] less than ideal (109.5°) and an endocyclic N-P-N angle [avg. 94.1(2)°] reduced from **69** [97.4(4)°]. These parameters are representative of the limited hybridization observed for third row elements (c.f. PF_3, 97.8°; PH_3, 93.4°).[111]

Solid state ^{31}P NMR data for each complex are consistent with the number of discrete molecules observed in the asymmetric unit; a single signal is observed for **98** ($\delta^{31}P$ = 203 ppm) and **99** ($\delta^{31}P$ = 234 ppm), while four unique phosphorus centers are evident in the spectrum of **100** ($\delta^{31}P$ = 246, 243, 239, 235 ppm). The solution ^{31}P NMR shift of **98** is identical to the solid state isotropic shift but signals observed in solution spectra for the adducts **99** and **100** are broad and shifted downfield ($\Delta\delta^{31}P$ = ~40-50 ppm) relative to the corresponding solid state isotropic chemical shifts. These observations are a result of weakening or possible dissociation of one of the N-P dative bonds in solution due to the weaker basicity of DABCO (pKa_1 = 8.82; pKa_2 = 2.97 for $[DABCOH]^+$ and $[DABCOH_2]^{2+}$ respectively) and presumably TMEDA with respect to quinuclidine (pKa = 11.0 for $[quinuclidineH]^+$).[112]

^1H and ^{13}C NMR solution spectra of the isolated materials are consistent with the stoichiometric ratios of amines to the acid **69**. It is interesting to note that in each case, the ^1H NMR spectra show a downfield shift relative to the free base while a slight shielding of the carbon nuclei in the complexed bases is observed in the ^{13}C NMR spectra (Table 2). Furthermore, solution ^{31}P NMR spectra of the isolated materials show that the adducts are stable in solution for hours but they do begin to

form multiple products within a day.

Table 2. ^{1}H and ^{13}C NMR chemical shifts of amine complexes of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$.

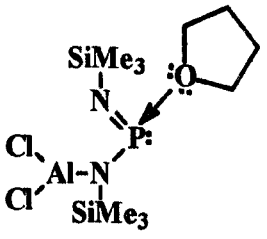
Compound	^{1}H NMR	^{13}C NMR
quinuclidine	2.76, 1.65, 1.48	48.2, 27.2, 24.0
98	2.90, 2.03, 1.81	45.7, 25.1, 21.5
DABCO	2.67	47.7
99	2.91	45.5
TMEDA	2.22, 2.07	58.0, 45.9
100	2.76, 2.44	N/A, 44.2

Preliminary ^{31}P NMR investigations of toluene solutions containing **69** with varying molar ratios of amines indicate that the isolated complexes of **98**, **99** and **100** are kinetic products. Reactions of **69** and quinuclidine in 2:1 and 1:2 molar ratios initially form the adduct **98** ($\delta^{31}P$ = 206 ppm), however both reactions progress to an unidentified major species ($\delta^{31}P$ = 198 ppm). This secondary reaction occurs faster when **69** is in excess (198 ppm > 90% after 2 days) while an excess of quinuclidine favours **98** (198 ppm < 10% after 2 days). Similarly, stoichiometric reactions of 1:1 and 1:2 for **69** and DABCO immediately give a single species ($\delta^{31}P$ = 214 ppm)

which is assigned to the 1:1 adduct **69**←DABCO. Within two days, the signal at 199 ppm is observed in the ^{31}P NMR spectra of both reactions and is more prominent with an equimolar amount of **69**. As for the reactions of **69** with TMEDA, an excess of the amine leads to the formation of the 2:1 complex **100** as the major species ($\delta^{31}P$ = 226 ppm cf. solid state $\delta^{31}P$ of 234 ppm; > 70%) but a 5:1 excess of **69** quickly yields a dominant species at 184 ppm in the ^{31}P NMR spectrum.

4.5 Coordination Complexes of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ with Oxygen Donor Ligands

Reactions of **69** with oxygenated bases tetrahydrofuran (THF) or 1,4-dioxane (also serving as the solvent) proceed over a period of 15-20 hrs to form the adducts **104** and **105** ($\delta^{31}P$ = 180 and 184 ppm respectively). Removal of the solvent yields a crude white powder in each case. Isolation of crystals is complicated by the reaction of **104** and **105** to multiple products in solution and the crystals obtained have been unsuitable for X-ray analysis.



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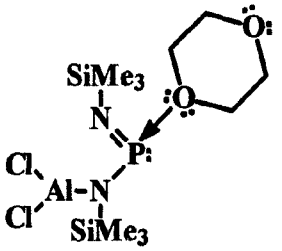


105

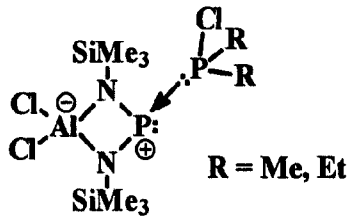
Solid state ^{31}P NMR spectra of the crude solids reveal more than one phosphorus center for **104** ($\delta^{31}P$ = 195, 192 ppm) and **105** ($\delta^{31}P$ = 169, 167, 165 ppm). The solid state chemical shielding anisotropy of the ^{31}P nucleus (span of the chemical shift tensor, $\Omega = \delta_{11}-\delta_{33}$) is sensitive to the bonding environment around phosphorus.[113] As shown in Table 3, compounds **104** and **105** have similar ^{31}P chemical shift parameters which are comparable to values for the amine complexes **98**, **99** and **100** but are markedly different from the chemical shielding anisotropy of the free acid **69**. The ^{1}H and ^{13}C solution NMR spectra of **105** account for one equivalent of 1,4-dioxane complexed to the phosphorus site of **69** and the ring-opened structure is based on the observation of two types of trimethylsilyl groups. The structure of **104** is similarly based on its ^{1}H and ^{13}C solution NMR spectra.

Table 3. ^{31}P NMR chemical shift parameters for complexes of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$.

Compound	δ_{11}	δ_{22}	δ_{33}	Ω
98	446.5	98.4	63.6	382.9
99	395.8	342.1	-0.9	396.7
100	523.0	109.4	68.6	454.4
104	391.7	133.8	51.0	340.7
105	353.6	156.8	-4.5	358.1
69	N/A	N/A	N/A	~800

4.6 Coordination Complexes of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ with Chlorophosphines

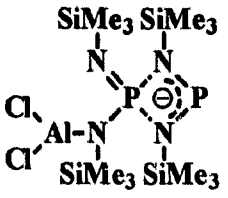
^{31}P NMR solution studies indicate the formation of the diphosphorus compounds **106** from complexation of the phosphines Me_2PCl and Et_2PCl to compound **69**. Coordination at the phosphorus site in **106** is implied by the presence of two distinct doublets in the ^{31}P NMR spectra with characteristic one bond P-P coupling (R = Me: 69, -21 ppm; $^1J_{PP}$ = 345 Hz, R = Et: 68, 6 ppm; $^1J_{PP}$ = 362 Hz). A single attempt at isolation of **106** yielded oils in both cases. No interaction of **69** with $^iPr_2PCl$ or Ph_3P is observed possibly as a result of steric hindrance.



106

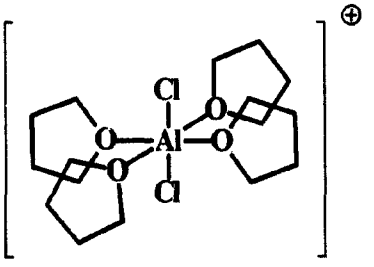
4.7 Evidence for Formation of a Chelate Complex of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$

Compounds **98**, **99**, **100**, **104** and **105** are kinetic products which further react in solution to give several species (many peaks in ^{31}P NMR spectra). Two doublets with P-P two bond coupling ($^2J_{PP}$ = 53 Hz) are observed in the spectra which are related to **98**, **99** and **100** ($\delta^{31}P$ = 150, 35 ppm) and are prominent in the ^{31}P NMR spectrum of **104** ($\delta^{31}P$ = 137, 69 ppm, >90%).



107

Reactions of **69** with acetonitrile or triethylamine give the similar doublets upon addition ($\delta^{31}P$ = 150, 40 ppm; $^{2}J_{pp}$ = 49 Hz) as the major products which are assigned to the diphosphorus anionic complex **107** based on preliminary data. X-ray analysis of a few crystals obtained in one experiment from a mixture of **69** in THF reveals the octahedral complex **108**[$AlCl_4$] with the $[AlCl_2]^+$ moiety surrounded by four THF ligands in the equatorial plane.[114]

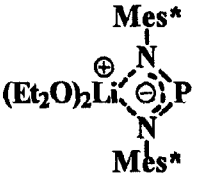


108

Although an oil is obtained from the triethylamine mixture, in one experiment a solid was isolated from the reaction of **69** with acetonitrile. The ^{31}P NMR spectrum of the redissolved solid shows two doublets ($\delta^{31}P$ = 150, 35 ppm; $^{2}J_{pp}$ = 53 Hz) while the ^{1}H and ^{13}C NMR spectra account for the three different methyl groups in **107**

coupled to phosphorus (δ^1H: 0.24 ppm, d, $^4J_{PH}$ = 1.8 Hz, 9H; 0.26 ppm, m, 18H; 0.31 ppm, d, $^4J_{PH}$ = 1.1 Hz, 9H; δ^{13}C: 0.4 ppm, apparent t, $^3J_{PC}$ = 3 Hz; 2.5 ppm, d, $^3J_{PC}$ = 5 Hz; 3.1 ppm, d, $^3J_{PC}$ = 10 Hz). Formation of **107** requires the presence of the 1,3-diaza-2-phosphaallyl anion **109**, whose derivative **110** is a known isolated species that chelates to the counterion Li^+ when the substituents at nitrogen are the bulky 2,4,6-^{t}Bu$_3$C$_6$H$_2$ aryl ligand (Mes*).[115] Generation of **109** can be envisaged via the abstraction of the $[AlCl_2]^+$ fragment from the ring-opened complexes of **69** followed by chelation to another equivalent of the zwitterion **69** to give the complex **107**. Compound **107** is stable in solution for at least two days (only species observed by ^{31}P NMR) but it proceeds to unidentified products (NMR investigation conducted after one year).

109



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Chapter 5 Dialkyl Phosphenium Cations

The chemistry of phosphines in the presence of typical Lewis acids $AlCl_3$ or $GaCl_3$ is very much dependent on the nature of the substituents at phosphorus In general, reactions with tertiary organo[116] or halophosphines[117] lead to typical acid-base complexes but as described in the introduction and throughout this work, disubstituted chlorophosphines represent important precursors for the synthesis of phosphenium cations. All isolated examples of phosphenium cations possess electron-rich ligands (e.g. NR_2, SR) which help stabilize the unsaturated species through a significant degree of π-donation from a neighbouring nitrogen or sulfur atom(s) to the phosphorus center. In an attempt to study genuine divalent phosphenium units, reactions of a series of dialkylchlorophosphines and one diarylchlorophosphine[118] (R_2PCl, R = Me, Et, Ph, ^{i}Pr and ^{t}Bu) with $GaCl_3$ have been examined.

5.1 Reactions of Chlorodimethylphosphine with $GaCl_3$[119]

NMR studies of the rapid reaction between Me_2PCl and $GaCl_3$ in CH_2Cl_2 show essentially quantitative formation of asymmetric P-P bonded products, the nature of which depends upon the stoichiometry. The ionic material 2-chloro-1,1,2,2-tetramethyl-1-phosphino-2-phosphonium-gallium trichloride tetrachlorogallate **111**[$GaCl_4$] was isolated from the equimolar reaction mixture, and the crystal structure, although disordered, conclusively reveals cation **111** (Figure 19) containing adjacent tetracoordinate phosphorus centers. The structure represents a Me_2PCl moiety (P2) coordinated to a phosphenium moiety Me_2P^+ (P1), which is in turn coordinated to a

$GaCl_3$ molecule. The P-P bond length [2.138(7)Å and 2.156(10)Å] is consistent with a diphosphonium structure (2.189Å)[120] and the P-Ga distance [2.450(6)Å and 2.474(6)Å] is identical to other P-Ga adduct bonds [2.455(4)Å].[116]

111 112

Figure 18. Dissociation of $[Me_2P(GaCl_3)PMe_2Cl]^+$ to $[Me_2PPMe_2Cl]^+$.

The solid-state ^{31}P CP-MAS NMR spectrum of **111**$[GaCl_4]$ exhibits a significantly smaller P-P coupling ($^1J_{PP}$ = 154 Hz) and ^{31}P chemical shift differential ($\delta^{31}P_{isotropic}$ = 84 ppm, -16 ppm) than the solution NMR spectrum of an equimolar reaction mixture ($\delta^{31}P$ = 96, -28 ppm, $^1J_{PP}$ = 311 Hz) and resembles that of a solution containing an excess of $GaCl_3$ ($\delta^{31}P$ = 89, -16 ppm, $^1J_{PP}$ = 219 Hz). A reaction mixture containing a 2-fold excess of Me_2PCl ($\delta^{31}P$ = 99, -33 ppm, $^1J_{PP}$ = 340 Hz) shows no evidence of free phosphine and is similar to solution spectra of **111**$[GaCl_4]$ ($\delta^{31}P$ = 98, -31 ppm, $^1J_{PP}$ = 332 Hz) or an equimolar reaction mixture. Moreover, solid obtained from this 2 Me_2PCl:$GaCl_3$ solution has a substantially higher melting point than **111**$[GaCl_4]$ and exhibits solid-state ^{31}P isotropic chemical shifts and a coupling constant ($\delta^{31}P_{isotropic}$ = 99, -36 ppm, $^1J_{PP}$ = 331 Hz) consistent with those observed in the 2:1 or 1:1 solution mixtures. Analysis of these spectroscopic observations support an uncomplexed phosphinophosphonium cation **112**$[GaCl_4]$ as the

species formed stoichiometrically in a 2:1 mixture and present in solutions of **111**[$GaCl_4$] or equimolar mixtures through a facile dissociation of **111** (Figure 18). An excess of $GaCl_3$ shifts the equilibrium in favour of **111**. Furthermore, the low-frequency signal (assigned to the $[Me_2P]^+$ moiety) in the solid-state ^{31}P NMR spectrum of **112**[$GaCl_4$] (-36 ppm) is a sharp doublet, while the corresponding signal (-16 ppm) for **111**[$GaCl_4$] is broadened by interaction with the quadrupolar gallium nucleus.

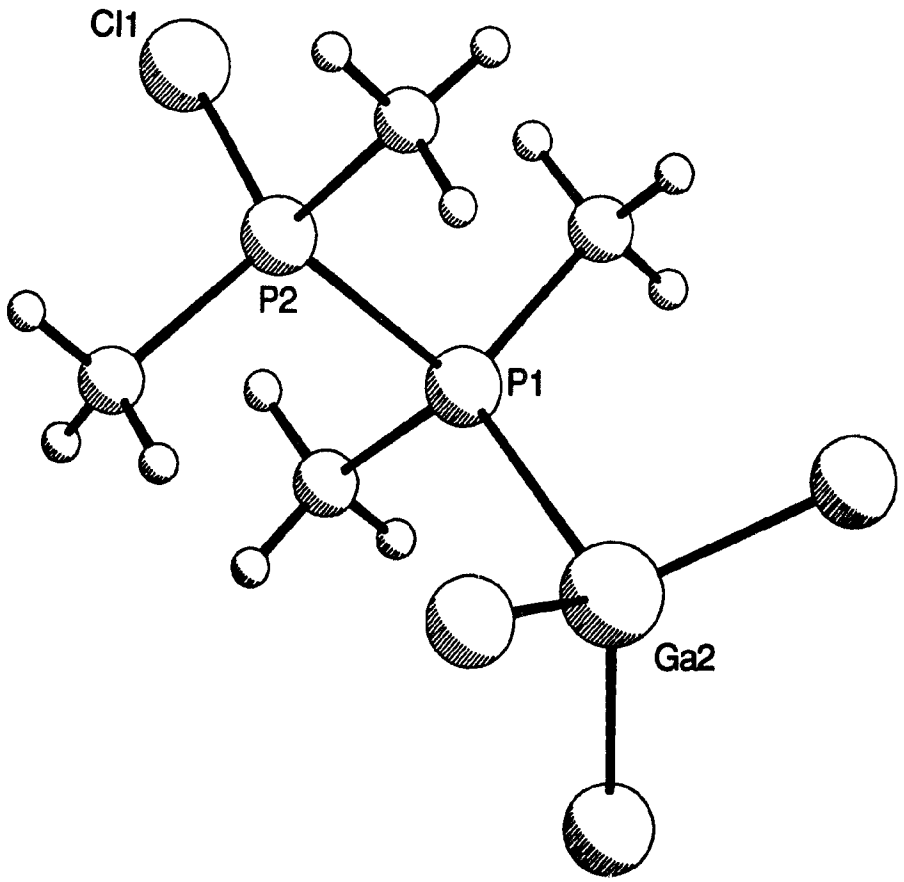
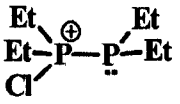


Figure 19. PLUTO view of compound 111. Selected parameters (Å): P1-P2 = 2.138(7), P1-Ga2 = 2.450(6).

5.2 Reaction of Chlorodiethylphosphine with $GaCl_3$

^{31}P solution NMR studies of the reactions of Et_2PCl with $GaCl_3$ in CH_2Cl_2 show formation of the previously reported[118] phosphinophosphonium complex **113** ($\delta^{31}P$ = 101, 0 ppm, $^1J_{pp}$ = 240 Hz for 1:1 mixture) regardless of stoichiometry which yields an oil upon removal of solvent. The uncomplexed phosphinophosphonium cation **113** is the only species present in solution; no free phosphine is seen in the $2Et_2PCl$:$GaCl_3$ mixture ($\delta^{31}P$ = 101, -4 ppm, $^1J_{pp}$ = 263 Hz), and unlike the methyl derivative, complexation of **113** to $GaCl_3$ is not observed at the phosphino site ($\delta^{31}P$ = 100, 0 ppm, $^1J_{pp}$ = 240 Hz) in the presence of excess $GaCl_3$.

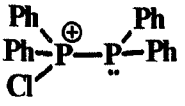


113

5.3 Reaction of Chlorodiphenylphosphine with $GaCl_3$

^{31}P NMR spectra of reactions with an equimolar and a two-fold excess of Ph_2PCl to $GaCl_3$ also indicate the formation of the phosphinophosphonium cation **114**[118] ($\delta^{31}P$ = 73, 1 ppm, $^1J_{pp}$ = 393 Hz) as well as a phosphine-gallium trichloride adduct **115** ($\delta^{31}P$ = 41 ppm) in smaller quantities. In the presence of excess $GaCl_3$, exclusive formation of **115** is observed. ^1H and ^{13}C NMR spectra of compound **115** support a structure with a four coordinate phosphorus centre. The ipso carbon chemical shift is situated upfield ($\Delta\delta^{13}C$ = 23.9 ppm) with respect to the free phosphine ($\delta^{13}C$ = 138.5 ppm)[121] and the coupling of phosphorus to carbon is large

($^1J_{PC}$ = 91 Hz). This trend is consistent with changing the geometry at phosphorus from three to four coordinate.[122] Isolation was not attempted.



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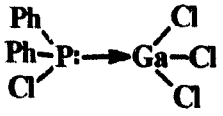
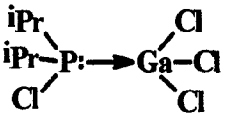


115

5.4 Reaction of Chlorodiisopropylphosphine with $GaCl_3$

The ^{31}P NMR spectrum of a CH_2Cl_2 solution containing a 1:1 stoichiometry of $^iPr_2PCl$ and $GaCl_3$ reveals two major phosphorus containing products; a dominant species observed as a broad signal at $\delta^{31}P$ = 91 ppm is assigned to the phosphine adduct **116** and a sharp singlet of half relative concentration at $\delta^{31}P$ = 86 ppm is assigned to the phosphonium cation **117**. An excess of $GaCl_3$ promotes formation of **117** but an excess of the phosphine favours **116** with the presence of the phosphinophosphonium complex **118** ($\delta^{31}P$ = 115, 14 ppm, $^1J_{PP}$ = 401 Hz, <5%) in trace amounts.



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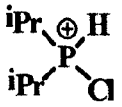

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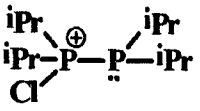


118

Crystals of **116** were isolated from a 1:1 reaction mixture and characterized by X-ray analysis as the acid-base adduct $^iPr_2PCl$-$GaCl_3$ (Figure 20). The ^{31}P NMR spectrum of redissolved solid confirms that **116** is the dominant species in solution at

$\delta^{31}P$ = 91 ppm. The ^{1}H and ^{13}C NMR spectra of **116** show restricted rotation of the isopropyl groups upon coordination to the acid. Two types of methyl groups are observed (Me_A: ^{1}H, 1.41 ppm, d of d, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{PH}$ = 5.0 Hz, ^{13}C, 16.3 ppm, d, $^{2}J_{PC}$ = 3 Hz; Me_B: ^{1}H, 1.48 ppm, d of d, $^{3}J_{HH}$= 7.1 Hz, $^{3}J_{PH}$ = 8.3 Hz, ^{13}C, 17.2 ppm, d, $^{2}J_{PC}$ = 3 Hz) and the methines are equivalent (^{1}H, 2.77 ppm, d of q of q, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HH}$ = 7.1 Hz, $^{2}J_{PH}$ = 2.6 Hz; ^{13}C, 28.7 ppm, d, $^{1}J_{PC}$ = 11 Hz).

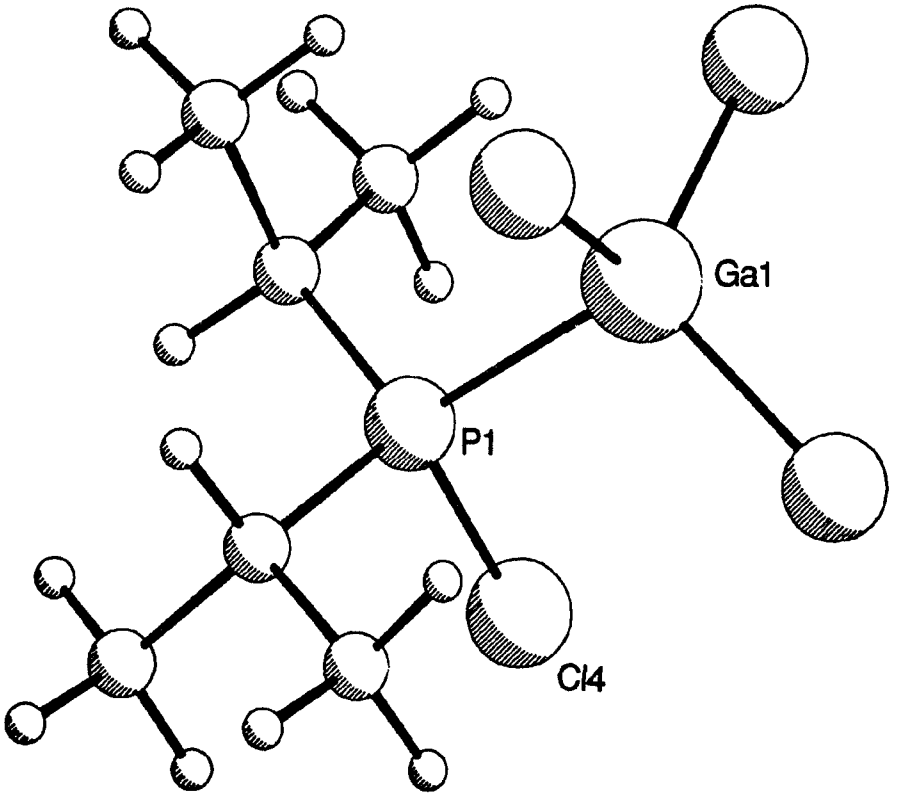
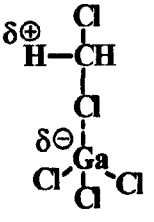


Figure 20. PLUTO view of compound 116. Selected parameters (Å): P1-Ga1 = 2.40(1).

The structure of compound **117** is based on NMR spectroscopic data from the reaction of $^{i}Pr_2PCl$ with excess $GaCl_3$. Once the signals in the ^{1}H and ^{13}C NMR

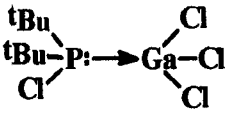
spectra for the isopropyl groups of adduct **116** are assigned (Me_A: δ^1H = 1.43 ppm, d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 3.4 Hz; $\delta^{13}C$ = 16.4 ppm, d, $^2J_{PC}$ = 3 Hz; Me_B: δ^1H = 1.51 ppm, d of d, $^3J_{HH}$ and $^3J_{PH}$ cannot be determined due to overlap of peaks; $\delta^{13}C$ = 17.2 ppm, d, $^2J_{PC}$ = 2 Hz; CH_{AB}: δ^1H = 2.85 ppm, d of q of q, $^3J_{HH}$ = 7.1 Hz, $^2J_{PH}$ = 2.1 Hz; $\delta^{13}C$ = 29.1 ppm, d, $^1J_{PC}$ = 11 Hz) the remaining peaks support the structure of **117**. The P-H proton in **117** is observed at δ^1H = 7.25 ppm (d of t, $^1J_{PH}$ = 516.4 Hz, $^3J_{HH}$ = 4.7 Hz) with a one bond P-H coupling typical for phosphonium cations.[123] As is the case for **116**, there is restricted rotation of the isopropyl groups in **117** (Me_C: δ^1H = 1.51 ppm, d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ cannot be determined due to overlap of peaks; $\delta^{13}C$ = 15.5 ppm, d, $^2J_{PC}$ = 4 Hz; Me_D: δ^1H = 1.61 ppm, d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 11.0 Hz; $\delta^{13}C$ = 16.9 ppm, d, $^2J_{PC}$ = 2 Hz; CH_{CD}: δ^1H = 3.06 ppm, d of d of q of q, $^3J_{HH}$ = 7.0 Hz, $^2J_{PH}$ = 1.5 Hz, $^3J_{PH}$ = 4.3 Hz; $\delta^{13}C$ = 26.6 ppm, $^1J_{PC}$ = 34 Hz). The Brönsted acidity of CH_2Cl_2 could be enhanced by the interaction of an electron-rich chlorine with $GaCl_3$ as shown in **119**. Therefore, formation of **117** is envisaged as a proton abstraction from the solvent complex **119** by the base $^iPr_2PCl$. The resulting carbanion $[CHCl_2]^-$,[124] which likely complexes with the $GaCl_3$, is observed in the ^1H and ^{13}C NMR spectra (δ^1H = 2.84 ppm; $\delta^{13}C$ = 33.6 ppm).



119

5.5 Reaction of Chlorodi-*tert*-butylphosphine with $GaCl_3$

Reactions of $^tBu_2PCl$ with $GaCl_3$ in CH_2Cl_2 (or CD_2Cl_2) lead to the *tert*-butyl derivatives of **116** and **117**. A broad major peak at $\delta^{31}P$ = 101 ppm (cf. 108 ppm for $^tBu_2PCl{\rightarrow}AlCl_3$[125]) is assigned to the adduct **120** (^1H NMR: Me = 1.59 ppm, d, $^3J_{PH}$ = 18.6 Hz; ^{13}C NMR: Me = 27.8 ppm, d, $^2J_{PC}$ = 4 Hz; Me_3C = 42.0 ppm, d, $^1J_{PC}$ = 1 Hz) and the phosphonium cation **121** is represented by a minor singlet at $\delta^{31}P$ = 96 ppm which with time (over 1 year) becomes the predominant species in an equimolar solution (^1H NMR: P-H = 6.92 ppm, d, $^1J_{PH}$ = 500.3 Hz; Me = 1.62 ppm, d, $^3J_{PH}$ = 21.36 Hz; ^{13}C NMR: Me =26.5 ppm, d, $^2J_{PC}$ = 3 Hz; Me_3C = 39.5 ppm, d, $^1J_{PC}$ = 22 Hz). Free $^tBu_2PCl$ ($\delta^{31}P$ = 148 ppm, lit. 146 ppm[126]) and an unidentified species (^{31}P = 158 ppm) are also present in the 1:1 reaction mixture but in smaller quantities. An excess of either reagent $GaCl_3$ or $^tBu_2PCl$ has no observable effect on rates of reactions although with an excess of phosphine, free $^tBu_2PCl$ is seen in the ^{31}P spectrum. Unfortunately, the counterion of **121**, the carbanion $[CHCl_2]^-$ or its complex to $GaCl_3$ (**119**) was not apparent in the NMR spectra.



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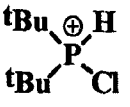

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5.6 First Structural Confirmation of a Phosphinophosphonium Cation and a Phosphine·$GaCl_3$ Adduct

Alkyl[118] and aminophosphinophosphonium[37,36] cations have been previously identified by solution NMR spectroscopy, infrared spectroscopy and conductivity measurements but **111**[$GaCl_4$] provides the first structural confirmation of the P-P coordinative bond in phosphinophosphonium cations. Similarly, the adduct $^tBu_2PCl{\rightarrow}AlCl_3$ was postulated from a signal at 108 ppm in a ^{31}P NMR spectrum[125] but complex **116** is the first structural report of a chlorophosphine-group (III) metal trichloride adduct. A closer look at the ^{31}P NMR spectra of all equimolar R_2PCl:$GaCl_3$ mixtures reveals the presence of a signal consistently downfield ($\Delta\delta^{31}P = \approx 40$ ppm) from the free chlorophosphine which is assigned to the acid-base adduct (Table 4). Thus, formation of the adduct is possible in all cases, however, it is predominant with the larger substituents.

Table 4. ^{31}P NMR chemical shifts of free and complexed chlorophosphines.

Compound	$\delta^{31}P$ of R_2PCl (ppm)	$\delta^{31}P$ of adduct (ppm)	$\Delta\delta^{31}P$ (ppm)
Me_2PCl	93	57	36
Et_2PCl	119	79	40
Ph_2PCl	80	41	39
$^iPr_2PCl$	135	91	44
$^tBu_2PCl$	146	101	45

5.7 Alternative Structures to Dialkylphosphenium Cations

Reaction of aminophosphinophosphonium cations with excess Lewis acid $AlCl_3$ results in quantitative formation of the corresponding aminophosphenium cations (Figure 21) due to the stabilization afforded by π-donation to phosphorus. In the absence of such stabilization for $[Me_2P]^+$, complexation of excess $GaCl_3$ to the phosphino site of chlorotetramethylphosphinophosphonium cation **111** yielding **112**$[GaCl_4]$ is thermodynamically favoured with respect to two equivalents of $[Me_2P][GaCl_4]$.

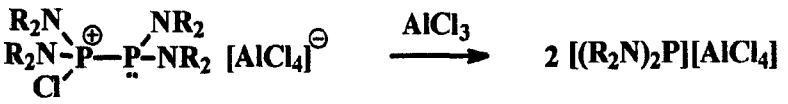


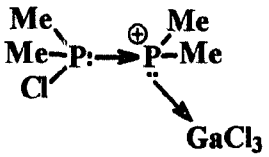
Figure 21. Preference for the formation of two aminophosphenium cations.

The ethyl substituents of **113** provide sufficient stability to the phosphino site and thus no complexation to $GaCl_3$ is observed but in the presence of excess acid, the phenyl derivative **114** leads to the formation of an acid-base adduct **115**. The stability of alkylated phosphinophosphonium cations with respect to acid-base adduct formation is dependent on the nature of the alkyl substituent. Rapid formation of the methyl, ethyl and phenyl phosphinophosphonium derivatives **111**, **113** and **114** in equimolar mixtures is attributed to small substituents while the larger isopropyl and *tert*-butyl groups yield the acid-base complexes **116** and **120**. However, the observation of the chlorotetraisopropylphosphinophosphonium cation **118** in the ^{31}P NMR spectra

suggests that the formation of an acid-base adduct over a phosphinophosphonium cation relies more on the electronic effects of the substituent (σ-donor ability: Ph<Me<Et<^{i}Pr<^{t}Bu) rather than its size (Me<Et<Ph<^{i}Pr<^{t}Bu). Nevertheless, both the phosphinophosphonium cations and the acid-base adducts represent alternative structural arrangements for the dialkylphosphenium cations.

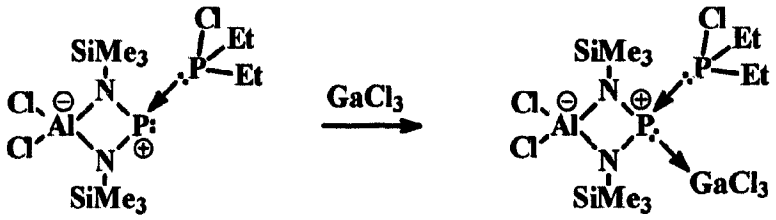
5.8 Amphoteric Nature of Phosphenium Cations

The salt of chlorotetramethylphosphinophosphonium-gallium trichloride complex **111** portrays an example of "in series" coordination via "base induction"; that is, a phosphine base (Me_2PCl) coordinates to a Lewis acidic phosphenium cation $[Me_2P]^+$ inducing a coordination to $GaCl_3$ **122**.



122

A similar "base induction" **123** is envisaged when the neutral phosphine-phosphenium complex **106** (described in section **4.6**) is exposed to $GaCl_3$ (Figure 22). Preliminary ^{31}P NMR solution investigations show a significant reduction in P-P coupling ($^{1}J_{PP}$ = 69 Hz) and ^{31}P chemical shift differential for the two characteristic doublets ($\delta^{31}P$ = 30, 8 ppm) with respect to **106** ($\delta^{31}P$ = 68, 6 ppm, $^{1}J_{PP}$ = 362 Hz). Such a trend is observed upon complexation of **111** with $GaCl_3$ to give **112**.



106 123

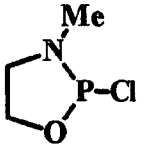
Figure 22. "Base induction" of a phosphine-phosphenium complex with $GaCl_3$.

Chapter 6 Future Work

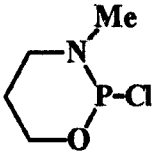
This work demonstrates some intrinsic (substituents) and extrinsic (counterion) effects on phosphenium centers which have lead to novel examples of non-metal coordination complexes. Future work should continue with this fundamental investigation but in addition, the potential for *macromolecular* chemistry involving phosphenium species as "molecular *LEGO* building blocks" is clear.

6.1 Novel Oxophosphenium Species

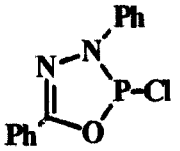
In general, the stability of phosphenium species requires at least one amino group adjacent to the phosphorus center (*vide supra*) and thus there are a few examples of phosphenium cations possessing other heteroatoms bound to the phosphorus center such as carbon, sulfur or chlorine (see Table 1). $[(Et_2N)(Cl_2CCMeO)P]^+$ **(21)**[14] and $[(Mes^*NH)(Mes^*O)P]^+$ **(24)**[23] are the only two examples of phosphenium cations with an oxygen-containing substituent but data on these two compounds are limited. Halide abstraction from the cyclic precursors **124-127**[127,128,129,39] should give a series of oxophosphenium cations with the derivatives from **126** and **127** possessing a Hückel number of electrons.



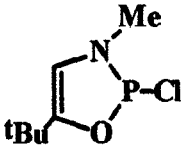
124



125



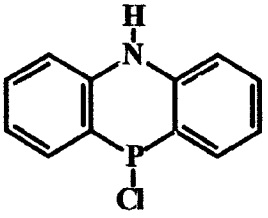
126



127

6.2 14 Hückel Electrons: A Phosphenium Center in an Anthracenic Framework

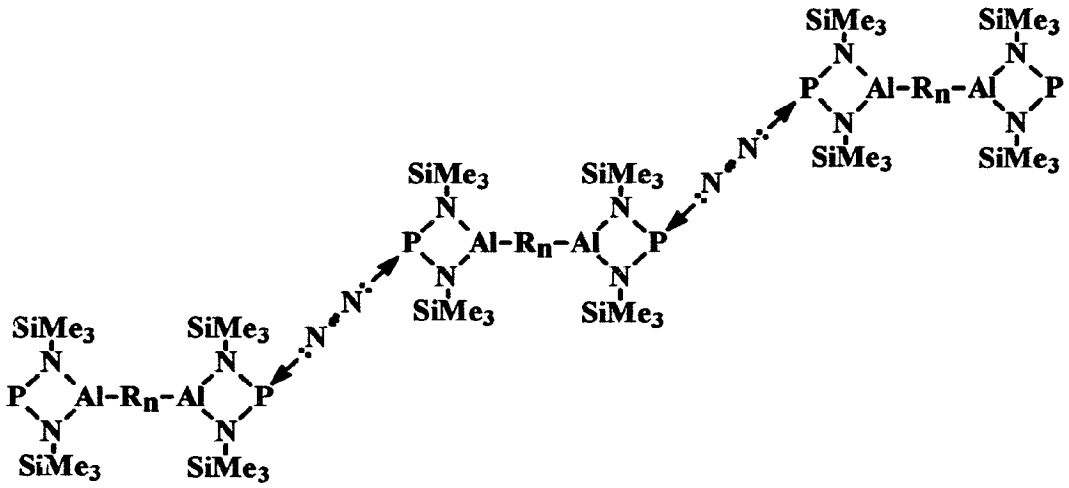
The stability of phosphenium centers in a naphthalenic framework (**56**, **58-61**) is attributed to a Hückel number of π-electrons (*vide supra*). Phosphenium centers in an anthracenic framework have yet to be characterized but should be stable on account of 14 π electrons (4n+2) delocalized over the structure. Compound **128**[130] is a possible precursor for this study.



128

6.3 Phosphenium Species as "Building Blocks" to Polymers

This work has demonstrated the ability to link two neutral phosphenium species **69** via a bidentate diamine (complexes **98-100**). Formation of oligomers or polymers as shown in **129** is envisaged through the association of diphosphenium units but unfortunately such bifunctional acids have yet to be synthesised.



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Chapter 7 Experimental

7.1 The Handling of Air Sensitive Reagents

Due to the air and moisture sensitivity of most reagents and products employed in this work, appropriate steps were taken to keep them in a pristine state. The reader is referred to a recent description of the equipment and techniques currently used by the Burford laboratory in dealing with air sensitive reagents.[131]

7.2 General Procedures

Diisopropylamine, phosphorus trichloride and N,N'-dimethylethylenediamine were purified by dynamic vacuum distillation while chlorodi-*tert*-butylphosphine, chlorodiisopropylphosphine, 2,3-dimethyl-1,3-butadiene, chlorodimethylphosphine and chlorodiethylphosphine were distilled under static vacuum. Gallium trichloride, aluminium trichloride, quinuclidine and 1,4-diazabicyclo[2.2.2]octane (DABCO) were sublimed *in vacuo* (dynamic). Adamantyl azide, sodium tetraphenylborate, butyllithium, sulfur, triphenylphosphine, 1,1,1,3,3,3-hexamethyldisilazane, selenium, tellurium and chlorodiphenylphosphine were used without purification. $(^{i}Pr_2N)_2PCl$,[132] $\overline{NMeCH_2CH_2NMePCl}$,[133] $(Me_3Si)N{=}PN(SiMe_3)_2$[134] and $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ [15] were prepared according to the literature. Tetrahydrofuran, 1,4-dioxane, toluene and benzene were dried at reflux over sodium metal and benzophenone. Triethylamine, N,N,N',N'-tetramethylethylenediamine, acetonitrile and n-hexanes were refluxed over CaH_2. Similarly 1,2-dichloroethane, 1,1,2,2-tetrachloroethane and 1,2-dichlorobenzene were dried at reflux over P_2O_5 while dichloromethane, chloroform and the deuterated

derivatives were dried at reflux over P_2O_5 and CaH_2. All solvents were stored in evacuated bulbs.

$^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR solution spectra were recorded at the Atlantic Region Magnetic Resonance Center on samples sealed in evacuated Pyrex tubes using a Bruker AC-250 (250.13MHz for ^1H, 62.89MHz for ^{13}C, 101.26MHz for ^{31}P). Solution ^{11}B NMR and solid state ^{31}P CP-MAS NMR spectra were obtained on a Bruker AMX-400 (400.13MHz for ^1H, 161.98MHz for ^{31}P and 128.38MHz for ^{11}B). Solid state spectra are referenced to solid $NH_4H_2PO_4$ which has a chemical shift of +0.81 ppm relative to 85% H_3PO_4 and each CP-MAS NMR experiment was carried out at several sample spinning frequencies from 4.0 to 10.0kHz. All solution chemical shifts are reported at room temperature in ppm relative to external standards, 85% H_3PO_4 for ^{31}P, $BH_3{\cdot}Et_2O$ for ^{11}B and $SiMe_4$ for ^1H and ^{13}C. Melting points were recorded on a Fisher-Johns apparatus. Infrared spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510P FT-IR spectrometer. X-ray crystallographic analyses were performed by Dr. T.S. Cameron and Mr. P.K. Bakshi at the DALX Crystallography Center with the use of Rigaku AFC5R or Enraf-Nonius CAD-4 diffractometers.

7.3 Specific Procedures

7.3.1 Preparation of $[\overline{N(Me)CH_2CH_2N(Me)P}][GaCl_4]$: A solution of $\overline{N(Me)CH_2CH_2N(Me)P}Cl$ (1.7 g, 11 mmol) in CH_2Cl_2 (5 mL) was added to a solution

of $GaCl_3$ (2.0 g, 11 mmol) in CH_2Cl_2 (8 mL) and stirred for 5 hrs. The ^{31}P NMR spectrum of the reaction mixture showed a single signal at 269 ppm. Slow removal of solvent *in vacuo* (static) resulted in the precipitation of a white crystalline solid which was characterized as 1,3-dimethyl-1,3-diaza-2-phospholidinium tetrachlorogallate (2.4 g, 7.1 mmol, 62%); m.p. 95-97°C.

Anal. Calcd. C, 14.6; H, 3.1; N, 8.5%; Anal. Found C, 14.7; H, 3.1; N, 8.4%

IR (cm^{-1}): 1356(s), 1310(m), 1253(s), 1204(s), 1143(s), 1077(m), 1036(s), 1013(s), 964(s), 849(m), 742(s), 593(s), 492(m), 382(s), 325(s).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 269; $^{13}C\{^1H\}$, 35.3 [d, $^2J_{PC}$ = 19 Hz], 56.0 [d, $^2J_{PC}$ = 9 Hz]; ^1H, 3.25 [d, $^3J_{PH}$ = 11.6 Hz, 6H], 4.03 [d, $^3J_{HH}$ = 4.4 Hz, 4H].

X-ray: monoclinic, space group $P2_1$, a = 6.489(3) Å, b = 13.893(5) Å, c = 7.066(5) Å, β = 92.58(5)°, V = 636.3 $Å^3$, Z = 2, D_{calcd} = 1.715 Mg m^{-3}, μ =30.86 cm^{-1}, R_w = 0.0516.

7.3.2 Preparation of $[(^iPr_2N)_2P][GaCl_4]$: A solution of $(^iPr_2N)_2PCl$ (1.02 g, 3.75 mmol) in CH_2Cl_2 was added to a solution of $GaCl_3$ (0.64 g, 3.6 mmol) in CH_2Cl_2 (total 30 mL) and gave a clear yellow solution within seconds. A single signal at 313 ppm was observed in the ^{31}P NMR spectrum of the reaction mixture. After stirring for approximately 3 hrs, half of the solvent was removed *in vacuo* (dynamic) and the resulting precipitate was recrystallized from the warmed solution. Pale yellow crystals (two crops) were characterized as bis(diisopropylamino)phosphenium tetrachlorogallate (1.22 g, 2.75 mmol, 76%); m.p. 127.5-128.5°C.

Anal. Calcd: C, 32.5; H, 6.4; N, 6.3%; Anal. Found C, 32.7; H, 6.4; N, 6.3%

IR (cm^{-1}): 1399(s), 1377(s), 1337(m), 1300(m), 1209(s), 1172(sh), 1163(sh), 1135(br), 1060(s), 1038(s), 925(s), 884(w), 859(w), 835(w), 620(w), 549(m), 529(m), 375(s), 331(sh), 305(w), 281(w), 256(w), 248(w).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 313; $^{13}C\{^1H\}$, 25.2 [d, $^3J_{PC}$ = 8 Hz], 55.2; ^1H, 1.52 [d, $^3J_{HH}$ = 6.7 Hz, 24H], 4.20 [d of sept, $^3J_{PH}$ = 2.6 Hz, $^3J_{HH}$ 6.7 Hz, 4H].

X-ray: tetragonal, space group $I4_1cd$, a = 20.014(4) Å, b = 20.014(4) Å, c = 21.466(6) Å, V = 8598(6) Å, Z = 16, D_{calcd} = 1.3684 Mg m^{-3}, μ =18.45 cm^{-1}, R_w = 0.0640.

Approx. solubility in CH_2Cl_2: 0.03 g/mL. An NMR study has shown that $[(^iPr_2N)_2P][GaCl_4]$ is stable in a CH_2Cl_2 solution at room temperature for a period exceeding one year. A solution containing a two-fold excess of $(^iPr_2N)_2PCl$ with $GaCl_3$ in CH_2Cl_2 gave a single broad peak at 225 ppm in the ^{31}P NMR spectrum at room temperature, which is assigned to a chloride exchange process between the phosphine and the phosphenium cation.

7.3.3 Preparation of $[(^iPr_2N)_2P][BPh_4]$: A solution of $(^iPr_2N)_2PCl$ (0.54 g, 2.0 mmol) in CH_2Cl_2 (~10 mL) was added to a suspension of $NaBPh_4$ (0.68 g, 2.0 mmol) in CH_2Cl_2 (~10 mL) and stirred for 1 hr. A single signal at 284 ppm was observed in the ^{31}P NMR spectrum of the reaction mixture. The resulting yellow solution was separated from the white precipitate through a sintered glass frit, and a fraction of the solvent was removed *in vacuo* (dynamic) until a yellow precipitate was observed. A

layer of hexane (~10 mL) was distilled onto the mixture and the solution was warmed to redissolve the solid. Removal of the volatiles *in vacuo* (static) within 3 hrs resulted in yellow crystalline plates, which were washed with fresh hexane and characterized as bis(diisopropylamino)phosphenium tetraphenylborate (0.46 g, 1.0 mmol, 82%); d.p. above 114°C.

Anal. Calcd. C, 78.5; H, 8.8; N, 5.1%; Anal. Found C, 78.4; H, 8.8; N, 5.0%

IR (cm^{-1}): 1937(w), 1883(w), 1815(w), 1759(w), 1701(w), 1673(w), 1648(w), 1582(s), 1562(w), 1481(s), 1430(s), 1400(sh), 1390(sh), 1347(s), 1306(m), 1268(m), 1203(s), 1182(m), 1157(s), 1132(s), 1104(s), 1066(m), 1046(s), 1028(s), 947(sh), 932(s), 884(w), 848(m), 813(w), 747(s), 707(s), 628(m), 610(s), 545(m), 527(m), 492(w), 466(m), 350(w), 307(w), 266(w), 256(w).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 308; $^{13}C\{^1H\}$, 25.0 [d, $^3J_{PC}$ = 8 Hz], 55.2, 164.4, 136.3, 125.6, 121.8; ^1H, 1.27 [d, $^3J_{HH}$ = 6.8 Hz, 24H], 3.92 [d of sept, $^3J_{PH}$ = 2.0 Hz, $^3J_{HH}$ = 6.7 Hz, 4H], 6.94 [m] 7.08 [m], 7.46; ^{11}B, -7.0.

X-ray analysis was not possible due to the decomposition of the crystals in the X-ray beam.

7.3.4 Preparation of $\overline{N(Me)CH_2CH_2N(Me)P(Ph)}$-$BPh_3$: A solution of $\overline{N(Me)CH_2CH_2N(Me)PCl}$ (0.16 g, 1.0 mmol) in CH_2Cl_2 was added quickly to a suspension of $NaBPh_4$ (0.37 g, 1.1 mmol) in CH_2Cl_2 (total CH_2Cl_2 7 mL) and stirred for 12 hrs. The resulting precipitate was separated from the solution by decantation. A single signal at 80 ppm was observed in the ^{31}P NMR spectrum of the reaction

mixture. Slow removal of the solvent *in vacuo* (static) yielded crystals of 2-phenyl-1,3-dimethyl-1,3-diazaphospholidine-triphenylboron (0.23 g, 0.52 mmol, 49%); m.p. 168-173°C.

Chemical analyses not performed.

IR (cm^{-1}): 1960(w), 1891(w), 1816(w), 1588(w), 1335(m), 1304(w), 1255(m), 1229(w), 1206(m), 1198(m), 1164(m), 1128(s), 1100(s), 1069(w), 1035(s), 1002(w), 976(w), 937(s), 862(m), 849(sh), 803(w), 751(sh), 743(s), 715(s), 704(s), 697(sh), 686(sh), 635(m), 619(m), 609(m), 526(s), 487(m), 462(m), 438(m), 283(w), 229(w).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 82; $^{13}C\{^1H\}$, 34.9 [d, $^2J_{PC}$ = 7 Hz], 52.1, 125.9, 126.9, 128.3, 131.0, 131.8, 136.7; ^1H, 2.07 [d, $^3J_{PH}$ = 10.8 Hz, 6H], 2.98 [m, 2H], 3.15 [m, 2H], 7.30 [m, 20H]; ^{11}B, 0.2.

X-ray: triclinic, space group $P\bar{1}$, a = 9.710(1) Å, b = 14.962(2) Å, c = 9.610(2) Å, α = 105.45(1)°, β = 113.59(1)°, γ = 92.73(1)°, V = 1214.3 $Å^3$, Z = 2, D_{calcd} = 1.193 Mg m^{-3}, μ =1.26 cm^{-1}, R_w = 0.0422.

7.3.5 ^{31}P NMR study of $[(^iPr_2N)_2P][BPh_4]$ in CH_2Cl_2 and $CHCl_3$: Equimolar mixtures (0.3 mmol) of $(^iPr_2N)_2PCl$ and $NaBPh_4$ in three different solvent systems (1 mL) were treated in an ultrasonic bath and examined by ^{31}P NMR spectroscopy at 2 hr intervals. Observations are presented as ^{31}P NMR chemical shifts (ppm) with relative signal heights in parentheses.

CH_2Cl_2: 2 hrs: 312

4 hrs: 312 (100), 338 (5) + minor peaks

6 hrs: 312 (100), 58 (20), 45 (25) and 13 (20) + minor peaks

8 hrs: 13 + minor peaks

^{11}B NMR, -7.0 characteristic of BPh_4^-

$CHCl_3$: 2 hrs: 150 (100) + minor peaks

4 hrs: 162 (100), 62 (15), 59 (20) + minor peaks

6 hrs: 172 (100), 62 (20), 59 (30) + minor peaks

8 hrs: 153 (100), 62 (35) 59 (55) + minor peaks

24 hrs: 145 + minor peaks

^{11}B NMR, -7.0

$CH_2Cl_2/CHCl_3$ (~1:1): 2 hrs: 217 (100), 59 (5), 16 (5)

4 hrs: 226 (100), 59 (15), 16 (10) + minor peaks

6 hrs: 218 (100), 59 (50), 45 (20), 16 (25) + minor peaks

8 hrs: 196 (50), 59 (100), 45 (55), 16 (35) + minor peaks

24 hrs: 169 (50), 59 (100) + minor peaks

Similar activity was observed with 1,2-dichloroethane, 1,1,2,2-tetrachloroethane and 1,2- dichlorobenzene. Isolation was not attempted, however, a recurring signal at ~59 ppm is assigned to the $[(^iPr_2N)_2P(Cl)CH_2Cl][BPh_4]$ addition product (*vide infra*).

7.3.6 Isolation of $[(^iPr_2N)_2P(Cl)CH_2Cl][BPh_4]$: In one experiment, a solution of $(^iPr_2N)_2PCl$ (0.27 g, 1.0 mmol) in CH_2Cl_2 was added quickly to a mixture of $NaBPh_4$ (0.34 g, 1.0 mmol) in $CHCl_3$ (1:1 CH_2Cl_2:$CHCl_3$). After 10 days slow removal of solvent from the orange solution *in vacuo* (static) gave 20-30 small rectangularly

shaped crystals, which were characterized by X-ray crystallography as chlorobis(diisopropylamino)chloromethylphosphonium tetraphenylborate. Other attempts (5) to isolate this material were unsuccessful yielding only crystals of $[^iPr_2NH_2][BPh_4]$ identified by X-ray analysis.[135]

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 57; ^1H, 7.40 [m], 4.45 [d, $^2J_{PH}$ = 2.6 Hz, 2H], 3.93 [m, 4H], 1.41 [m].

X-ray: monoclinic, space group $P2_1/n$, a = 10.049(3) Å, b = 21.794(3) Å, c = 16.391(3) Å, β = 92.78(2)°, V = 3585(1) Å^3, Z = 4, D_{calcd} = 1.177 Mg m^{-3}, μ =2.50 cm^{-1}, R_w = 0.0569.

7.3.7 Reaction of $[(^iPr_2N)_2P][GaCl_4]$ with N_3Ad: A solution of N_3Ad (0.08 g, 0.5 mmol) in CH_2Cl_2 was added rapidly to a yellow solution of $[(^iPr_2N)_2P][GaCl_4]$ (0.22 g, 0.50 mmol) in CH_2Cl_2 (total 30 mL) and the mixture was stirred for ~72 hours. The ^{31}P NMR spectrum of the reaction mixture showed a dominant signal at 38 ppm assigned to $(^iPr_2N)_2P(Cl)NAd{\cdot}GaCl_3$ [based on the derivative $(^iPr_2N)_2P(Cl)NPh{\cdot}AlCl_3$, $\delta^{31}P$ = 51 ppm][48] co-existing with some unreacted phosphenium cation at 315 ppm. Isolation was not attempted.

7.3.8 Reaction of $[(^iPr_2N)_2P][AlCl_4]$ with S_8: A suspension of excess S_8 (0.05 g, 1 mmol) in a CH_2Cl_2 solution (0.5 mL) of $[(^iPr_2N)_2P][AlCl_4]$ (0.15 g, 0.37 mmol) was monitored over 3 weeks by ^{31}P NMR spectroscopy. The appearance of a single peak at 62 ppm was assigned to the previously reported $(^iPr_2N)_2P(Cl)S{\cdot}AlCl_3$.[95]

7.3.9 Reaction of $[(^iPr_2N)_2P][BPh_4]$ with N_3Ad: A solution of $[(^iPr_2N)_2P][BPh_4]$ (0.06 g, 0.1 mmol) in CH_2Cl_2 was added quickly to a solution of N_3Ad (0.02 g, 0.1 mmol) in CH_2Cl_2 (3 mL total) and gave a yellow solution that was stirred for 1 hour. The ^{31}P NMR spectrum of the reaction mixture showed multiple products including dominant peaks at 36, 33 and 5 ppm, although the ^{11}B NMR gave a single signal at -6.8 ppm indicating that $[BPh_4]^-$ was unchanged. Isolation or structural elucidation of the products was not attempted.

7.3.10 Reaction of $(^iPr_2N)_2P(Cl)N$-Ph with $NaBPh_4$: A sample of $(^iPr_2N)_2P(Cl)NPh$ (0.08 g, 0.2 mmol) was dissolved in CH_2Cl_2 (5 mL) and added rapidly to a suspension of $NaBPh_4$ (0.08 g, 0.2 mmol) in CH_2Cl_2 (5 mL). The solution was stirred for 24 hours and during that time the mixture turned light yellow. The ^{31}P NMR spectrum showed only unreacted starting material at -8 ppm.[48]

7.3.11 Reaction of $[(^iPr_2N)_2P][BPh_4]$ with S_8: A yellow solution of $[(^iPr_2N)_2P][BPh_4]$ (0.11 g, 0.20 mmol) in CH_2Cl_2 was added quickly to a suspension of S_8 (0.01 g, 0.04 mmol) in CH_2Cl_2 (6 mL total). The solution was stirred for 1 hour and then slightly heated. The ^{31}P NMR spectrum of the reaction mixture showed a multitude of products after one day although two peaks were dominant. One unidentified signal was observed at 86 ppm and the other peak at 69 ppm is assigned to the thiophosphoryl chloride $(^iPr_2N)_2P(Cl)S$.[95] The corresponding ^{11}B NMR spectrum

showed only one signal at -6.8 ppm indicating BPh_4^- as the only boron species in solution. Attempts at isolating the products gave a white crystalline solid which did not have a ^{31}P NMR signal.

7.3.12 ^{31}P NMR Study of Reactions between $[(^iPr_2N)_2P][A]$ and 2,3-Dimethyl-1,3-butadiene, [A] = $[GaCl_4]$ or $[BPh_4]$: In two similar experiments, $[(^iPr_2N)_2P][A]$ (0.02 mmol) in CH_2Cl_2 (1 mL) was added to 2,3-dimethyl-1,3-butadiene (1.4 mmol) in an NMR tube. A single signal at 67 ppm in the ^{31}P NMR spectra was assigned to the previously reported cycloaddition product.[51]

7.3.13 Reaction of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ with S_8 and Preparation of $[\overline{N(SiMe_3)AlCl_2N(SiMe_3)PS}]_2$: A solution of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.61 g, 2.0 mmol) in toluene (10 mL) was added quickly to a suspension of S_8 (0.03 g, 1 mmol) in toluene (5 mL) and formed a white precipitate within minutes. After 12 hours stirring at room temperature the solution was decanted, the solid was washed twice by back-distillation and all volatiles removed *in vacuo* (dynamic). The white powder was contaminated with a small amount of elemental sulfur (0.26 g, ~76%). ^{31}P NMR spectra of the crude material showed a single signal at -18 ppm in CH_2Cl_2 and at -17 ppm in the ^{31}P CP-MAS NMR spectrum. Recrystallization from CH_2Cl_2 gave a 68% recovery of colourless crystals characterized as the dimer bis(spiro)tricyclodialuminatetraazadithiadiphosphetane. m.p. 174.5-179.0°C.

Anal. Calcd. C, 21.5; H, 5.4; N, 8.3%; Anal. Found C, 21.2; H, 5.4; N, 8.4%.

IR (cm^{-1}): 1258(s), 1147(m), 1108(s), 848(s), 776(s), 739(s), 695(w), 661(w), 647(m), 617(m), 603(w), 533(s), 443(s), 378(w), 343(w).

NMR (ppm in CH_2Cl_2):$^{31}P\{^1H\}$, -18, solid state $^{31}P\{^1H\}$ CP-MAS isotropic NMR, -17.

Approximate solubility in CH_2Cl_2: 6 mg/mL.

X-ray: monoclinic, space group $P2_1/n$, a = 6.599(3) Å, b = 12.602(2) Å, c = 20.070(2) Å, β = 96.02(2)°, V = 1659.8(8) $Å^3$, Z = 2, D_{calcd} = 1.342(6) Mg m^{-3}, μ = 7.80 cm^{-1}, R_w = 0.035.

When the reaction mixture was stirred at room temperature for a period of two weeks, a reaction involving toluene gave a product ($\delta^{31}P$ = 56 ppm) which was isolated as a crystalline solid (0.24 g, 0.6 mmol, 37%) and characterized by X-ray analysis as 2-benzyl-4,4-dichloro-2-trimethylsilylamino-3-trimethylsilyl-1,3,2,4-thiaazaphosphalumetidine.

IR (cm^{-1}): 3313(m), 2722(w), 1953(w), 1602(w), 1587(w), 1493(m), 1411(w), 1258(s), 1187(w), 1130(w), 1070(sh), 1050(s), 979(s), 912(s), 880(sh), 846(s), 829(sh), 809(s), 777(s), 758(s), 699(s), 673(m), 647(m), 612(w), 595(m), 551(s), 531(s), 508(s), 487(s), 439(w), 417(m).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 55; $^{13}C\{^1H\}$, 130.0, 129.9, 129.5, 128.5, 46.9, 2.2, 1.2; ^1H, 0.24 [6H], 0.31 [6H], 2.48 [1H], 3.51 [m, 2H], 7.36 [m, 5H].

X-ray: monoclinic, space group $P2_1/n$, a = 12.694(2) Å, b = 12.275(3) Å, c = 15.541(3) Å, β = 107.95(1)°, V = 2303.8(8) $Å^3$, Z = 4, D_{calcd} = 1.232 Mg m^{-3}, μ = 5.755 cm^{-1}, R_w = 0.0551.

7.3.14 Reaction of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ with Se and Te: A solution of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (3.0 g, 10 mmol) in CH_2Cl_2 (5 mL) was added to a suspension of elemental Se (0.08 g, 1 mmol) in CH_2Cl_2 (5 mL). The heterogeneous mixture was stirred for 4 days as the presence of a green precipitate increased with time. The solution was decanted and the crude solid (traces of Se present) isolated as a light green powder (yield not determined) which was assigned to $[\overline{N(SiMe_3)AlCl_2N(SiMe_3)PSe}]_2$ on the basis of ^{31}P NMR spectroscopy. Further attempts at characterization were not conducted.

NMR (ppm in CH_2Cl_2, note: poor solubility): $^{31}P\{^1H\}$, -63. Solid state $^{31}P\{^1H\}$ CP-MAS isotropic NMR, -57.

Addition of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ to elemental Te showed no reaction, only $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ was observed in the ^{31}P NMR spectrum at 380 ppm.

7.3.15 ^{31}P NMR study of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ in CH_2Cl_2 and $CHCl_3$: In two similar experiments, $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.03 g, 0.1 mmol) was dissolved in CH_2Cl_2 (4 mL) or $CHCl_3$ (4 mL), respectively, and the solutions were monitored by ^{31}P NMR spectroscopy. Slow reaction in $CHCl_3$ (half-life of approximately one month) was observed with the appearance of a signal at 37 ppm assigned to $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P(Cl)(CHCl_2)}$. No reaction was observed with CH_2Cl_2.

7.3.16 Preparation of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$·Quinuclidine: A solution of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.91 g, 3.0 mmol) in toluene (10 mL) was quickly added to a solution of quinuclidine (0.33 g, 3.0 mmol) in toluene (10 mL) and stirred for 10 min. The ^{31}P NMR spectrum of the reaction mixture showed a single peak at 208 ppm. The solvent was reduced to approximately 1 mL to which 1 mL of n-hexanes was added. The resulting precipitate was heated back into solution and crystals of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$·Quinuclidine were obtained by cooling the solution to -30°C (0.58 g, 1.4 mmol, 47%). m.p. 82.5-85.0°C.

Anal. Calcd. C, 37.7; H, 7.5; N, 10.1%; Anal. Found C, 37.5; H, 7.6; N, 10.1%.

IR (cm^{-1}): 1484(m), 1403(w), 1350(m), 1318(m), 1250(s), 1207(m), 1088(s), 1045(sh), 988(s), 907(m), 845(s), 762(s), 738(s), 687(s), 640(s), 625(m), 580(s), 503(s), 446(w), 359(w), 346(m), 337(w), 309(w), 277(w), 259(w).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 205 (sample slowly reacts further within 2 days to multiple products); $^{13}C\{^1H\}$, 2.9, 21.5, 25.1, 45.7; ^1H, 0.18 [18H], 1.81 [m, 6H], 2.03 [m, 1H], 2.90 [t, $^3J_{HH}$ = 7.7 Hz, 6H]; solid state $^{31}P\{^1H\}$ CP-MAS isotropic NMR, 203.

X-ray: monoclinic, space group $P2_1/n$, a = 6.900(9) Å, b = 19.442(8) Å, c = 17.258(9) Å, β = 96.85(8)°, V = 2298(4) $Å^3$, Z = 4, D_{calcd} = 1.198 Mg m^{-3}, μ = 4.91 cm^{-1}, R_w = 0.0611.

7.3.17 Preparation of $[\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}]_2$DABCO: A solution of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.30 g, 1.0 mmol) in toluene (10 mL) was added over 5 min to a solution of DABCO (0.06 g, 0.5 mmol) in toluene (5 mL). The ^{31}P NMR

spectrum of the reaction mixture showed a single peak at 313 ppm. The slightly turbid solution was filtered and slow removal of solvent yielded clear colourless crystals of $[\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}]_2$DABCO (0.14 g, 0.19 mmol, 38%). m.p. decomposition above 130°C.

Anal. Calcd. C, 30.1; H, 6.7; N, 11.7%; Anal. Found C, 29.4; H, 6.6; N, 11.3%.

IR (cm^{-1}): 1408(w), 1324(m), 1254(s), 1086(s), 1052(m), 988(s), 936(sh), 849(s), 785(sh), 762(s), 744(sh), 691(m), 672(sh), 642(m), 623(sh), 580(s), 514(s), 487(sh), 444(w), 416(w), 354(m), 341(w), 326(w), 307(w), 263(w), 252(w).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 282 ppm (sample slowly reacts further with ~ 2 days to multiple products); $^{13}C\{^1H\}$, 2.3, 45.5; ^1H, 0.23 [36H], 2.91 [12H]; solid state $^{31}P\{^1H\}$ CP-MAS isotropic NMR, 246, 243, 239, 235.

X-ray: triclinic, space group $P\bar{1}$, a = 15.558(9) Å, b = 17.160(7) Å, c = 15.507(7) Å, α = 95.92(4)°, β = 90.09(4)°, γ = 111.81(3)°, V = 3819(3) $Å^3$, Z = 4, D_{calcd} = 1.250 Mg m^{-3}, μ = 5.8 cm^{-1}, R_w = 0.1424.

7.3.18 Preparation of $[\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}]_2$TMEDA: A solution of TMEDA (0.33 g, 2.8 mmol) in toluene (30 mL) was quickly added to a solution of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (1.71 g, 5.64 mmol) in toluene (15 mL). The mixture was stirred for 15 min and a small amount of white precipitate was filtered from the clear solution. ^{31}P NMR spectrum of the solution showed a single signal at 285 ppm. Clear colourless crystals identified as $[\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}]_2$TMEDA were obtained by concentrating the solution *in vacuo* (0.99 g, 1.4 mmol, 49%). m.p. 91.0- 93.5°C.

Anal. Calcd. C, 29.9; H, 7.3; N, 11.6%; Anal. Found C, 30.1; H, 7.1; N, 11.7%

IR (cm^{-1}): 1476(sh), 1404(s), 1351(w), 1336(w), 1324(w), 1267(sh), 1249(s), 1199(w), 1174(w), 1113(sh), 1095(s), 1014(sh), 1003(s), 943(m), 864(sh), 848(s), 787(s), 756(s), 742(s), 689(s), 641(s), 623(m), 579(s), 506(s), 458(sh), 410(m), 390(sh), 354(m), 313(m), 268(w).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 293 (broad and sample slowly reacts further within 3 days to multiple products); $^{13}C\{^1H\}$, 2.2, 44.2; ^1H, 0.24 [36H], 2.44 [12H], 2.76 [4H]; solid state $^{31}P\{^1H\}$ CP-MAS isotropic NMR, 234.

X-ray: triclinic, space group $P\bar{1}$, a = 10.622(3) Å, b = 11.580(4) Å, c = 9.194(5) Å, α = 105.22(4)°, β = 95.90(4)°, γ = 63.56(2)°, V = 977.1(7) $Å^3$, Z = 1, D_{calcd} = 1.228 Mg m^{-3}, μ =5.69 cm^{-1}, R_w = 0.0471.

7.3.19 ^{31}P NMR studies of *Quinuclidine* with $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$:

(a) Excess $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$: Approximately 1 mL of toluene was distilled into an NMR tube containing quinuclidine (0.02 g, 0.15 mmol) and a 2-fold excess of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.10 g, 0.30 mmol). $^{31}P\{^1H\}$ NMR (ppm in toluene): Very broad signals at 375 and 207, presumably the free $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ and complexed $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$·Quinuclidine respectively; two days later, 376 [100%], 198 [23%] unassigned.

(b) Excess quinuclidine: Approximately 1 mL of toluene was distilled into an NMR tube containing $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.10 g, 0.30 mmol) and a 2-fold excess of quinuclidine (0.07 g, 0.60 mmol). $^{31}P\{^1H\}$ NMR (ppm in toluene), 207 assigned to

$\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$·Quinuclidine; two days later, 207 [100%], 198 [8%] unassigned.

7.3.20 ^{31}P NMR studies of DABCO with $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$:

(a) Equimolar: Approximately 1 mL of toluene was distilled into an NMR tube containing DABCO (0.04 g, 0.3 mmol) and an equimolar amount of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.10 g, 0.30 mmol). $^{31}P\{^1H\}$ NMR (ppm in toluene): 215 assigned to $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$·DABCO; two days later, 215[100%], 199 [80%] unassigned.

(b) Excess DABCO: Approximately 1 mL of toluene was distilled into an NMR tube containing $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.10 g, 0.30 mmol) and a 2-fold excess of DABCO (0.08 g, 0.6 mmol). $^{31}P\{^1H\}$ NMR (ppm in toluene), 214 assigned to $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$·DABCO; two days later, 215 [100%], 199 [29%] unassigned.

7.3.21 ^{31}P NMR studies of TMEDA with $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$:

(a) Excess $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$: A toluene solution of TMEDA (0.10 g, 0.90 mmol) was quickly added to a 5-fold excess of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (1.36 g, 4.50 mmol) in toluene (6 mL total). $^{31}P\{^1H\}$ NMR (ppm in toluene): 375 [100%] assigned to free $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$, 187 [32%] unassigned, 206 [13%] unassigned, and multiple doublets between 100-10 ppm.

(b) Excess TMEDA: A sample of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.09 g, 0.3 mmol) was partially dissolved in TMEDA (0.5 mL). $^{31}P\{^1H\}$ NMR (ppm in TMEDA): 226 [100%] assigned to $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$·TMEDA, 22 [46%] unassigned, and multiple peaks from 200-0 ppm.

7.3.22 Preparation of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$·THF: A solution of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.91 g, 3.0 mmol) dissolved in THF (10.28 g) was stirred for 14 hrs at room temperature. Slow removal of solvent *in vacuo* (static) over 3 hrs yielded a white solid (0.93 g). The solid was quickly washed with cold n-hexanes to give a white solid speculatively characterized as $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$·THF (0.64 g).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 180 (sample reacts further within hours to multiple products including a systems of doublets at 138 and 68 ppm, $^2J_{PP}$ = 53 Hz); $^{13}C\{^1H\}$, 72.2, 25.7, 3.2; ^1H, 4.16 [4H], 2.00 [4H], 0.11 [m]; solid state $^{31}P\{^1H\}$ CP-MAS isotropic NMR, 195, 192 and an impurity at 69.

In one experiment, further reaction of the mixture lead to the isolation of colourless crystals of $[(THF)_4AlCl_2][AlCl_4]$ identified by comparison of the crystallographic cell parameters to literature values as shown in the table below.[114]

Parameters	this work	literature
space group	$P2_1/n$	$P2_1/n$
a, Å	9.101(7)	9.023(2)
b, Å	39.486(30)	39.134(9)
c, Å	15.399(10)	15.319(5)
β, °	91.08(6)	91.22(3)
cell vol, $Å^3$	5532(8)	5408
Z	8	8
no. of reflcns collcd	5530	4507
no. of reflcns obsd	1402	2548
no. of variables	305	215
GOF	1.99	1.08
R	0.084	0.096
R_w	0.101	0.088

7.3.23 Preparation of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$·1,4-dioxane: A solution of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.96 g, 3.2 mmol) dissolved in 1,4-dioxane (11.98 g) was stirred for 21 hrs at room temperature. Slow removal of solvent *in vacuo* (static) over 5 hrs yielded a white solid (0.90 g) which was quickly washed with cold n-hexanes. The white solid is speculatively assigned to the ring opened complex Me_3SiNP(1,4-dioxane)$N(AlCl_2)SiMe_3$ (0.59 g).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 184 (sample slowly reacts further within hours to multiple products including a system of doublets at 137 and 35 with $^2J_{PP}$ = 53 Hz) with the presence of free $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$, 380; $^{13}C\{^1H\}$, 68.7, 3.5, 1.4, 0.2; ^1H, 4.19 [8H], 0.28 [18H], 0.16 [9H], 0.12 [9H]; solid state $^{31}P\{^1H\}$ CP-MAS isotropic NMR, 169,167,165 and $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ at 382.

7.3.24 Reactions of Chlorophosphines with $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$: Solutions of the respective phosphines in CH_2Cl_2 were added stoichiometrically to solutions of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ in CH_2Cl_2.

69 g (mmol)	R_3P g (mmol)	CH_2Cl_2 mL	$^{31}P\{^1H\}$ NMR	Isolation attempts
0.40 (1.3)	Me_2PCl 0.13 (1.3)	20	69 & -21 [d, $^1J_{PP}$ = 345 Hz] + minor products	oil
0.22 (0.7)	Et_2PCl 0.09 (0.7)	10	68 & 6 [d, $^1J_{PP}$= 362 Hz]	oil
0.18 (0.6)	$^iPr_2PCl$ 0.09 (0.6)	10	380 [76%], 136[100%], 115 & 14 [d, $^1J_{PP}$= 443 Hz, 5%] + minor products	oil
0.15 (0.5)	Ph_3P 0.13 (0.5)	2	38, -6	not attempted

The acid-base complexes $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}\cdot R_2PCl$ are formed when R = Me or Et; however, there is no reaction of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ with $^iPr_2PCl$ or Ph_3P.

7.3.25 NMR Studies of $\overbrace{N(SiMe_3)AlCl_2N(SiMe_3)P}$ with Triethylamine: Solutions of triethylamine in CH_2Cl_2 were added in various ratios to solutions of $\overbrace{N(SiMe_3)AlCl_2N(SiMe_3)P}$ in CH_2Cl_2.

69 g (mmol)	NEt_3 g (mmol)	CH_2Cl_2 mL	$^{31}P\{^1H\}$ NMR	Isolation attempts
0.59 (1.9)	0.20 (1.9)	15	366 [100%], 150 & 36 [d, $^2J_{PP}$ = 46 Hz, 90%] + minor products	yellow oil
0.37 (1.2)	0.61 (6.0)	10	149 [100%], 35 [99%], 19 [48%] + minor products	yellow oil
0.19 (0.6)	0.03 (0.3)	10	373 [100%], 150 & 36 [d, $^2J_{PP}$ =50Hz, 20%] + minor products	yellow oil

7.3.26 Reaction of $\overbrace{N(SiMe_3)AlCl_2N(SiMe_3)P}$ with Acetonitrile: In one experiment, an orange solid (0.06 g) was obtained from the reaction of $\overbrace{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.36 g, 1.2 mmol) in MeCN (5.28 g).

$^{31}P\{^1H\}$ NMR (ppm in CD_2Cl_2): 150 [d, $^2J_{PP}$ = 53 Hz], 36 [d, $^2J_{PP}$ = 53 Hz]; $^{13}C\{^1H\}$, 0.4 [apparent t, $^3J_{PC}$ = 3 Hz], 2.5 [d, $^3J_{PC}$ = 5 Hz], 3.1 [d, $^3J_{PC}$ = 10 Hz]; ^1H, 0.24 [d, $^4J_{PH}$ = 1.8 Hz, 9H], 0.26 [m, 18H], 0.31 [d, $^4J_{PH}$ = 1.1 Hz, 9H]. Preliminary assignments include two distinct $RN(SiMe_3)P$- fragments and two equivalent -P-$N(SiMe_3)P'$- fragments.

7.3.27 Preparation of $[Me_2P(GaCl_3)PMe_2Cl][GaCl_4]$: Me_2PCl (0.56 g, 5.8 mmol) in CH_2Cl_2 (10 mL) was added to $GaCl_3$ (1.02 g, 5.8 mmol) in CH_2Cl_2 (10 mL). Removal of solvent *in vacuo* (static) gave a white crystalline solid [1.52 g, 96%] which was recrystallized from n-hexanes (5 mL) and benzene (10 mL) and characterized as 2-chloro-1,1,2,2-tetramethyl-1-phosphino-2-phosphonium-gallium trichloride complex tetrachlorogallate [0.48 g, 1.8 mmol, 33%] m.p. 78-81°C.

Anal. Calcd. C, 8.8; H, 2.2%; Anal. Found C, 8.7; H, 2.2%

IR (cm^{-1}): 1297(s), 1167(w), 1156(w), 955(s), 931(m), 922(m), 903(s), 892(s), 868(w), 837(w), 777(w), 757(w), 688(w), 573(s), 461(w), 411(s), 367(s).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 98 [d, $^1J_{PP}$ = 332 Hz], 57 [s, <5%], -31 [d, $^1J_{PP}$ = 332 Hz]; $^{13}C\{^1H\}$, 16.5 [d of d, $^1J_{PC}$ = 39.1 Hz, $^2J_{PC}$ = 5.7 Hz], 7.4 [d of d, $^1J_{PC}$ = 18.6 Hz $^2J_{PC}$ = 4.3 Hz]; ^1H, 2.54 [d of d, $^2J_{PH}$ = 11.0 Hz, $^3J_{PH}$ = 4.6 Hz, 6H], 1.69 [d of d, $^2J_{PH}$ = 23.9 Hz, $^3J_{PH}$ = 4.0 Hz, 6H]; Solid state $^{31}P\{^1H\}$ CP-MAS isotropic NMR: 84 [d, $^1J_{PP}$ = 154 Hz], -16 [broad].

X-ray: monoclinic, space group $P2_1/c$, a = 10.227(2) Å, b = 13.504(3) Å, c = 13.968(4) Å, β = 91.39(2)°, V = 1928(1) $Å^3$, Z = 4, D_{calcd} = 1.878 Mg m^{-3}, μ =40.40 cm^{-1}, R_w = 0.1107.

7.3.28 Preparation of $[Me_2PPMe_2Cl][GaCl_4]$: Me_2PCl (0.32 g, 3.4 mmol) in CH_2Cl_2 (10 mL) was added to $GaCl_3$ (0.29 g, 1.7 mmol) in CH_2Cl_2 (5 mL). Removal of solvent *in vacuo* (static) gave a white solid identified as 2-chloro-1,1,2,2-tetramethyl-1-phosphino-2-phosphonium tetrachlorogallate [crude yield: 0.51 g, 84%] m.p.

236-246°C.

IR (cm^{-1}): 1410(s), 1297(s), 1169(w), 1151(w), 1104(w), 960(s), 929(s), 888(s), 871(sh), 835(w), 777(m), 662(w), 550(s), 500(w), 426(m), 368(s), 309(w).

NMR (ppm in CD_2Cl_2): $^{31}P\{^1H\}$, 99 [d, $^1J_{PP}$ = 340 Hz], -32 [d, $^1J_{PP}$ = 341 Hz], 57 [s, <5%]; $^{13}C\{^1H\}$, 16.5 [d of d, $^1J_{PC}$ = 38.2 Hz, $^2J_{PC}$ = 5.7 Hz], 7.7 [d of d, $^1J_{PC}$ = 21.0 Hz, $^2J_{PC}$ = 4.8 Hz]; ^1H, 2.55 [d of d, $^2J_{PH}$ = 11.3 Hz, $^3J_{PH}$ = 4.4 Hz, 6H], 1.65 [d of d, $^2J_{PH}$ = 24.3 Hz, $^3J_{PH}$ = 4.9 Hz, 6H], Solid state $^{31}P\{^1H\}$ CP-MAS isotropic NMR: 99 [d, $^1J_{PP}$ = 331 Hz], 57 [s, <10%], -36 [d, $^1J_{PP}$ = 331 Hz].

7.3.29 NMR Solution Studies of Reactions Involving Me_2PCl with $GaCl_3$ (1 mL of CD_2Cl_2):

(a) Me_2PCl (0.06 g, 0.7 mmol) and $GaCl_3$ (0.12 g, 0.68 mmol): $^{31}P\{^1H\}$, 96 [d, $^1J_{PP}$ = 311 Hz], 57 [s, <5%], -28 [d, $^1J_{PP}$ = 311 Hz]; ^1H, 2.59 [d of d, $^2J_{PH}$ = 11.3 Hz, $^3J_{PH}$ = 4.7Hz, 6H], 1.75 [d of d, $^2J_{PH}$ = 22.7 Hz, $^3J_{PH}$ = 2.1 Hz, 6H]; all representative of $[Me_2PPMe_2Cl]^+$.

(b) Me_2PCl (0.07 g, 0.7 mmol) and $GaCl_3$ (0.26 g, 1.5 mmol): $^{31}P\{^1H\}$, 89 [d, $^1J_{PP}$ = 219 Hz], 56 [s, <5%], -16 [d, $^1J_{PP}$ = 219 Hz]; ^1H, 2.90 [d of d, $^2J_{PH}$ = 11.6 Hz, $^3J_{PH}$ = 5.0 Hz, 6H], 2.15 [d of d, $^2J_{PH}$ = 17.5 Hz, $^3J_{PH}$ = 6.3 Hz, 6H]; all representative of $[Me_2P(GaCl_3)PMe_2Cl]^+$.

(c) Me_2PCl (0.10 g, 1.1 mmol) and $GaCl_3$ (0.10 g, 0.53 mmol): $^{31}P\{1H\}$, 99 [d, $^1J_{PP}$ = 340 Hz], 57 [s, <5%], -33 [d, $^1J_{PP}$ = 340 Hz]; ^1H, 2.50 [d of d, $^2J_{PH}$ = 11.1 Hz, $^3J_{PH}$ = 4.4 Hz, 6H], 1.53 [d of d, $^2J_{PH}$ = 24.2 Hz, $^3J_{PH}$ = 4.6 Hz, 6H]; all representative of

$[Me_2PPMe_2Cl]^+$.

7.3.30 NMR Study of Et_2PCl with $GaCl_3$:

(a) Et_2PCl (0.06 g, 0.5 mmol) in CD_2Cl_2 (1 mL) was added to solid $GaCl_3$ (0.09 g, 0.5 mmol): $^{31}P\{^1H\}$, 101 [d, $^1J_{PP}$ = 240 Hz], 79 [s, <10%], 72 [s, <10%], 0 [d, $^1J_{PP}$ = 240 Hz]; $^{13}C\{^1H\}$, 23.9 [d, $^1J_{PC}$ = 27 Hz], 21.9 [d, $^1J_{PC}$ = 17 Hz], 14.3, 9.3 [d, $^2J_{PC}$ = 6 Hz], 7.5 [d, $^2J_{PC}$ = 8 Hz], 6.9; ^1H, 3.05 [m, 4H], 2.59 [m, 4H], 1.59 [m, 12H] assigned as $[Et_2PPEt_2Cl]^+$.

(b) Et_2PCl (0.11 g, 0.90 mmol) in CH_2Cl_2 (1 mL) was added to solid $GaCl_3$ (0.49 g, 2.7 mmol): $^{31}P\{^1H\}$, 100 [d, $^1J_{PP}$ = 237 Hz], 79 [s, <10%], 72 [s, <10%]. 0 [d, $^1J_{PP}$ = 240 Hz] assigned as $[Et_2PPEt_2Cl]^+$.

(c) Et_2PCl (0.90 g, 7.0 mmol) in CH_2Cl_2 (1 mL) was added to solid $GaCl_3$ (0.62 g, 3.5 mmol): $^{31}P\{^1H\}$, 101 [d, $^1J_{PP}$ = 263 Hz], 79 [s, <10%], 72 [s, <10%], 0 [d, $^1J_{PP}$ = 267 Hz] assigned as $[Et_2PPEt_2Cl]^+$.

7.3.31 NMR Studies of Ph_2PCl with $GaCl_3$:

(a) Ph_2PCl (0.11 g, 0.5 mmol) in CD_2Cl_2 (1 mL) was added to solid $GaCl_3$ (0.09 g, 0.5 mmol): $^{31}P\{^1H\}$, 73 [d, $^1J_{PP}$ = 393 Hz], 41 [s, <10%], 1 [d, $^1J_{PP}$ = 391 Hz]; $^{13}C\{^1H\}$, 137.1, 135.6 [m], 133.4 [m], 130.9 [m]; ^1H, 7.65 [m]. $\delta^{31}P$ = 73 and 1 ppm is assigned to $[Ph_2PPPh_2Cl]^+$ and $\delta^{31}P$ = 41 ppm is assigned to $Ph_2PCl{\cdot}GaCl_3$.

(b) Ph_2PCl (0.13 g, 0.6 mmol) in CH_2Cl_2 (1 mL) was added to solid $GaCl_3$ (0.31 g, 1.8 mmol): $^{31}P\{^1H\}$, 41; $^{13}C\{^1H\}(CD_2Cl_2)$, 139.3, 134.0 [d, $^2J_{PC}$ =14 Hz], 132.1 [d, $^3J_{PC}$

= 15 Hz], 114.7 [d, $^1J_{PC}$ = 91 Hz]; ^1H, 7.95 [m], assigned to $Ph_2PCl{\cdot}GaCl_3$.

(c) Ph_2PCl (0.17 g, 0.8 mmol) in CH_2Cl_2 (1 mL) was added to solid $GaCl_3$ (0.07 g, 0.4 mmol): $^{31}P\{^1H\}$, 73 [d, $^1J_{PP}$ = 393 Hz], 41 [s, <10%], 0 [d, $^1J_{PP}$ = 393 Hz]. Assignments are as in (a).

7.3.32 NMR Studies of $^i Pr_2PCl$ with $GaCl_3$:

(a) $^i Pr_2PCl$ (0.04 g, 0.2 mmol) in CD_2Cl_2 (0.5 mL) was added to solid $GaCl_3$ (0.04 g, 0.2 mmol): $^{31}P\{^1H\}$, 91 [s broad, 100%] assigned to $^i Pr_2P(Cl){\cdot}GaCl_3$, 86 [s, 56%] assigned to $[^i Pr_2P(Cl)H][CHCl_2{\cdot}GaCl_3]$; $^{13}C\{^1H\}$, 29.1 [d, $^1J_{PC}$ = 11 Hz], 26.6 [d, $^1J_{PC}$ = 33 Hz], 17.3 [d, $^2J_{PC}$ = 2 Hz], 17.0 [d, $^2J_{PC}$ = 2 Hz], 16.4 [d, $^2J_{PC}$ = 3 Hz], 15.6 [d, $^2J_{PC}$ = 4 Hz]; ^1H, 7.28 [d of t, $^1J_{PH}$ = 517.1 Hz, $^3J_{HH}$ = 4.5 Hz], 3.07 [m], 2.86 [m], 1.61 [d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 11.0 Hz], 1.52 [d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ unresolved], 1.51 [d of d, $^3J_{HH}$ and $^3J_{PH}$ unresolved], 1.44 [d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 3.4 Hz].

(b) $^i Pr_2PCl$ (0.05 g, 0.3 mmol) in CD_2Cl_2 (0.5 mL) was added to solid $GaCl_3$ (0.16 g, 0.9 mmol): $^{31}P\{^1H\}$, 91 [s broad, 43%], 87 [s, 100%]; $^{13}C\{^1H\}$, 33.6, 29.1 [d, $^1J_{PC}$ = 11 Hz], 26.6 [d, $^1J_{PC}$ = 33 Hz], 17.2 [d, $^2J_{PC}$ = 2 Hz], 16.9 [d, $^2J_{PC}$ = 2 Hz], 16.4 [d, $^2J_{PC}$ = 3 Hz], 15.5 [d, $^2J_{PC}$ = 4 Hz]; ^1H, 7.25 [d of t, $^1J_{PH}$ = 516.4 Hz, $^3J_{HH}$ = 4.7 Hz, 1H], 3.06 [d of d of q of q, $^3J_{HH}$ = 7.0 Hz, $^2J_{PH}$ = 1.5 Hz, $^3J_{PH}$ = 4.3 Hz, 2H], 2.85 [d of q of q, $^3J_{HH}$ = 7.0 Hz, $^2J_{PH}$ = 2.1 Hz, 2H], 2.83 [1H], 1.61 [d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 11.0 Hz, 6H], 1.51 [d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ unresolved, 6H], 1.49 [d of d, $^3J_{HH}$ and $^3J_{PH}$ unresolved, 6H], 1.43 [d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 3.3 Hz, 6H]. Assignments are as in (a).

(c) $^{i}Pr_2PCl$ (0.07 g, 0.5 mmol) in CH_2Cl_2 (1 mL) was added to solid $GaCl_3$ (0.04 g, 0.2 mmol): $^{31}P\{^{1}H\}$, 115 [d, $^{1}J_{PP}$ = 445 Hz, <5%], 92 [s broad, 100%], 86 [s, 17%], 14 [d, $^{1}J_{PP}$ = 445 Hz, <5%]. Assignments are as in (a) with the addition of the complex $[^{i}Pr_2PP^{i}Pr_2Cl]^{+}$assigned to the doublets at $\delta^{31}P$ = 115 and 14 ppm.

7.3.33 **Preparation of $^{i}Pr_2PCl{\cdot}GaCl_3$:** A solution of $^{i}Pr_2PCl$ (0.47 g, 3.1 mmol) in CH_2Cl_2 (5 mL) was added to a solution of $GaCl_3$ (0.54 g, 3.1 mmol) in CH_2Cl_2 (5 mL) and stirred for 12 hrs. Removal of solvent *in vacuo* (dynamic) gave a solid (0.89 g, 87%) which was recrystallized (from 0.44 g) twice from a mixture of CH_2Cl_2:10 n-hexanes and characterized as the diisopropylchlorophosphine-gallium trichloride adduct[136] (0.26 g, 0.78 mmol, 51%). m.p. 77.5-83.0°C.

IR (cm^{-1}): 1312(w), 1291(w), 1274(w), 1244(m), 1160(m), 1100(m), 1080(m), 1065(m), 1027(m), 977(sh), 966(w), 932(m), 899(w), 877(m), 773(w), 679(w), 651(m), 567(s), 506(w), 463(w), 389(s), 373(sh), 352(s), 320(w), 298(w).

NMR (ppm in CD_2Cl_2): $^{31}P\{^{1}H\}$, 91; $^{13}C\{^{1}H\}$, 28.7 [d, $^{1}J_{PC}$ = 10.5 Hz], 17.2 [d, $^{2}J_{PC}$ = 2.9 Hz], 16.3 [d, $^{2}J_{PC}$ = 2.9 Hz]; ^{1}H, 2.77 [d of q of q, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HH}$ = 7.1 Hz, $^{2}J_{PH}$ = 2.6 Hz, 2H], 1.48 [d of d, $^{3}J_{HH}$= 7.1 Hz, $^{3}J_{PH}$ = 8.3 Hz, 6H], 1.41 [d of d, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{PH}$ = 5.0 Hz, 6H].

X-ray: monoclinic, space group C_c, a = 13.508(5) Å, b = 7.531(4) Å, c = 27.397(8) Å, β = 92,24(3)°, V = 2784(1) $Å^3$, Z = 12, D_{calcd} = 2.352 Mg m^{-3}, μ = 42.20 cm^{-1}, R_w = 0.0667.

7.3.34 NMR Studies of $^tBu_2PCl$ with $GaCl_3$:

(a) $^tBu_2PCl$ (0.03 g, 0.2 mmol) in CH_2Cl_2 (1 mL) was added to solid $GaCl_3$ (0.03 g, 0.2 mmol): $^{31}P\{^1H\}$, 101 [s broad, 100%], 96 [s, 44%]; $^{13}C\{^1H\}(CD_2Cl_2)$, 42.0 [d, $^1J_{PC}$ = 1 Hz], 39.5 [d, $^1J_{PC}$ = 22 Hz], 27.8 [d, $^2J_{PC}$ = 4 Hz], 26.5 [d, $^2J_{PC}$ = 3 Hz]; ^1H 6.92 [d, $^1J_{PH}$ = 500.3 Hz, 1H], 1.62 [d, $^3J_{PH}$ = 21.4 Hz, 9H], 1.56 [d, $^3J_{PH}$ = 18.6 Hz, 9H]. $\delta^{31}P$ = 101 ppm was assigned to $^tBu_2PCl{\cdot}GaCl_3$ and $\delta^{31}P$ = 96 ppm was assigned to $[^tBu_2P(Cl)H]^+$.

(b) $^tBu_2PCl$ (0.02 g, 0.1 mmol) in CH_2Cl_2 (1 mL) was added to solid $GaCl_3$ (0.06 g, 0.3 mmol): $^{31}P\{^1H\}$, 102 [s broad, 100%], 96 [s, 13%]. Assignment is as in (a)

(c) $^tBu_2PCl$ (0.12 g, 0.7 mmol) in CH_2Cl_2 (1 mL) was added to solid $GaCl_3$ (0.06 g, 0.3 mmol): $^{31}P\{^1H\}$, 148 [s broad, 100%], 101 [s broad, 100%], 95 [s, 24%]. Assignments are as in (a) with the additional assignment of the peak at $\delta^{31}P$ = 148 ppm to free $^tBu_2PCl$.

7.3.35 Reaction of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}{\cdot}Et_2PCl$ with $GaCl_3$: A solution of $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}$ (0.54 g, 1.8 mmol) in CH_2Cl_2 (5 mL) was quickly added to a solution of Et_2PCl (0.22 g, 1.8 mmol) in CH_2Cl_2 (5 mL). After stirring for 1 hr at room temperature, the solution was concentrated to 5 mL and a solution of $GaCl_3$ (0.31 g, 1.8 mmol) in CH_2Cl_2 (5 mL) was slowly added to the mixture. The reaction was stirred for 20 hrs at room temperature. A sample of the reaction mixture was investigated by ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$(ppm in CH_2Cl_2): 32 [d, $^1J_{PP}$ = 76 Hz], 9 [s broad] + minor products. Upon cooling the sample to -80°C, the peak

resolution improved to give signals at 30 [d, $^1J_{PP}$ = 69 Hz] and 8 [d,$^1J_{PP}$ = 69 Hz] which is attributed to complexation of $GaCl_3$ to the phosphino site of the adduct $\overline{N(SiMe_3)AlCl_2N(SiMe_3)P}\cdot Et_2PCl$. Attempts at isolation gave an oil.

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136. Supplementary material available from Dr. Neil Burford at Dalhousie University, Halifax, NS, B3H 4J3, Canada.