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**New Nitrogen-Phosphorus Chemistry Dependent on
the 2,4,6-Tri-*tert*-Butylphenyl Substituent**

by

Jason A. C. Clyburne

Submitted in partial fulfilment of the requirements

for the degree of Doctor of Philosophy

at

Dalhousie University

Halifax, Nova Scotia

March, 1995

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For Alison

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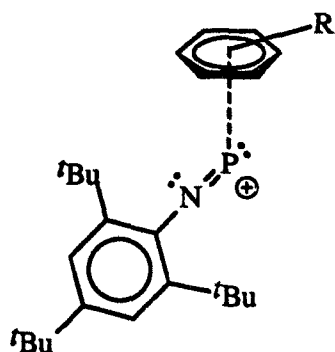
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Abstract

Large, sterically demanding groups have facilitated preparation of many compounds containing low coordinate environments for main group elements. Assessment of strain energy for molecules containing main group elements in low coordinate environments indicates that thermodynamic stability with respect to oligomers and structural alternatives involving higher coordination numbers is imposed by large substituents. These results help rationalize some of the observations made in recent years.

The phosphoazonium cation $[\text{Mes}^*\text{NP}]^+$ ($\text{Mes}^* = 2,4,6\text{-tri-}i\text{-tert-butylphenyl}$) is a



phosphorus analogue of the diazonium cation, and its reaction with hydridic bases results in the formation of aminophosphenium cations. A mechanism is proposed, and the first example of an oxyphosphenium cation is reported. The first arene complexes of phosphorus (shown in figure) have been isolated and comprehensively characterized,

arene = benzene, toluene, or mesitylene and they represent stable models of π -complex
anion = $[\text{GaCl}_4]^-$ or $[\text{Ga}_2\text{Cl}_7]^-$ intermediates in electrophilic aromatic substitution.

Spectroscopic studies indicate that the coordination geometries observed in the solid are maintained in solution.

A convenient synthesis of rare monomeric trihalogenophosphine imides ($\text{Mes}^*\text{N}=\text{PX}_3$) is described, and attempts to prepare stable methylenephosphonium cations have resulted in the discovery an unprecedented ring expansion reaction for methylenephosphoranes. The factors governing the structure of SbCl_3 arene complexes are discussed.

List of Abbreviations Used

Ad	adamantyl
avg.	average
bp.	boiling point
Bu	butyl, C ₄ H ₉
CP	cross polarization
Et	ethyl, C ₂ H ₅
FT	Fourier Transform
HOMO	highest occupied molecular orbital
IR	infrared
LUMO	lowest unoccupied molecular orbital
MAS	magic angle spinning
Me	methyl, CH ₃
Mes	2,4,6-trimethylphenyl, C ₆ H ₂ Me ₃
Mes*	2,4,6-tri- <i>tert</i> -butylphenyl, C ₆ H ₂ (<i>tert</i> -Bu) ₃
MHz	megahertz
mp.	melting point
NA	not available
NMR	nuclear magnetic resonance
ppm	parts per million
Ph	phenyl, C ₆ H ₅
Pr	propyl, C ₃ H ₇
Py	pyridine, NC ₅ H ₅
TMS	tetramethylsilane, SiMe ₄

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

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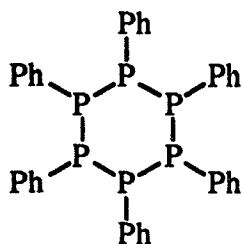
the writing of this thesis. When not in the lab, we crossed the country, paddled the lakes in Mazurka (a red canoe), toured the highways of Eastern Canada in Eudromedaries (a blue 1981 Volvo), played and marched with the Halifax 33rd Pipes and Drums, danced Irish Ceili style, and enjoyed fresh coffee from Robin's Donuts. I would like to thank J., G. and F. Sherwood for providing creature comforts to a graduate student.

Lillian and Hilda (LSC) make the best coffee on campus, a fuel too often needed.

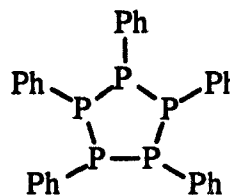
Chapter 1 Introduction

Compounds containing either multiple bonds or electron deficient sites are considered to be low coordinate, and as such offer great synthetic potential *via* addition or coordination reactions. High reactivity and structural simplicity make these species ideal molecular building blocks, and this capacity is best illustrated by the established chemistry of alkenes, alkynes, carbenes, and aromatic compounds.¹

The *p*-block elements of the second row, which include carbon, are unique because of the relative ease with which they engage in multiple ($\sigma + \pi$) bonding. In contrast, much of the chemistry of the heavier *p*-block elements shows a preference for σ bond formation; multiple bonds are rare.² Perhaps the most striking comparison is between azobenzene, ($\text{PhN}=\text{NPh}$) and its heavier congener, phosphobenzene ($\text{PhP}=\text{PPh}$). Early studies by Michaelis and Köhler reported formation of $\text{PhP}=\text{PPh}$ *via* direct combination of PhPCl_2



1.1



1.2

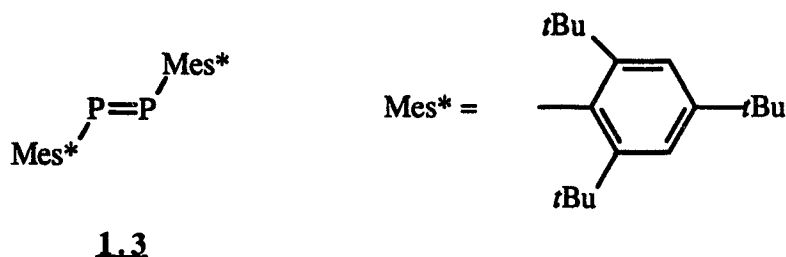
and PhPH_2 .³ It was later shown by cryoscopic techniques⁴ and X-ray crystallographic studies⁵ that the products of this reaction were cyclic polyphosphines **1.1** and **1.2**.

Despite numerous synthetic difficulties (*i. e.*, tendency to oligomerize, high reactivity, and air and moisture sensitivity), compounds containing stable (*vide infra*) $p_\pi - p_\pi$ bonds between heavy elements have been prepared and characterized.⁶ Common to

all of these molecules are large, sterically demanding substituents which “protect” the reactive low coordinate site. This thesis shows that for low coordinate main group element environments, thermodynamic stability with respect to alternatives with higher coordination is imposed by large substituents.

1.1 2,4,6-Tri-*tert*-butylphenyl (Mes*)

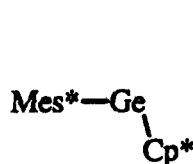
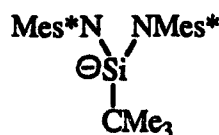
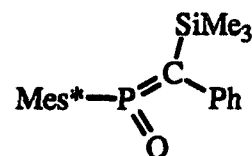
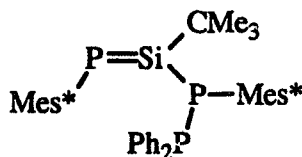
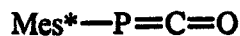
The first comprehensively characterized phosphobenzene (diphosphene **1.3**) was synthesized in 1981 by the reaction of Mes*PCl₂ and magnesium in THF.⁷ This paper introduced the new sterically demanding group, 2,4,6-tri-*tert*-butylphenyl (Mes*, supermesityl), as the substituent on the first molecule containing a 3p_π - 3p_π bond. Since



then, the Mes* group has played a central role in the chemistry of compounds containing elements with low coordination numbers.⁸

Most elements adopt novel bonding environments with the Mes* substituent. For example, compounds of the Group 13 elements (B, Al, Ga, and In) with a Mes* substituent typically exist as three coordinate monomers.⁹ Lower coordination numbers (*i. e.*, one and two) have been observed for Group 14 (C, Si, Ge, Sn, Pb) and Group 15 (N, P, As, Sb, Bi) elements with examples such as germylene **1.4**,¹⁰ silaamidide **1.5**,¹¹ persistent radicals Mes*O,¹² iminophosphines (*vide infra*), diphosphene Mes*P=PMes*,^{7,13} phospharsene Mes*P=AsMes*,^{14,13} phosphastibene

Mes*P=SbMes*,¹³ diarsene Mes*As=AsMes*,¹⁵ phosphalkyne Mes*CP,¹⁶ arsaalkyne Mes*CA,¹⁷ methylenexophosphorane **1.6**,¹⁸ phosphasilene **1.7**,¹⁹ phosphaketene

**1.4****1.5****1.6****1.7****1.8****1.9**

1.8,²⁰ and phosphallene **1.9**.²¹ Finally, the stable iodoselenide Mes*SeI represents a unique molecule containing a single Se-I bond.²²

Other bulky substituents employed in a similar manner include 2,6-di-*tert*-butylphenyl,²³ 2,6-di-*tert*-butyl-4-methylphenyl,²⁴ adamantyl,²⁵ 1,2,3,4,5-pentamethylcyclopentadienyl,²⁶ tris(trimethylsilyl)methyl,²⁷ and the recently reported 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl group.²⁸ Mes* is the most common due to its low cost, availability, and ease of derivatization *via* bromination, lithiation, and nitration.

1.2 The Chemistry of Mes*N-P

Iminophosphines (R-P=N-R) represent one of the most extensive series of compounds containing dicoordinate phosphorus,²⁹ and they are observed to dimerize in the absence of sterically demanding substituents.³⁰ The most interesting and synthetically versatile iminophosphine is Mes*NPCl.³¹ First reported in 1988, this compound has

played an important role in many of the recent developments in the chemistry of iminophosphines and phosphorus chemistry in general. The most obvious synthetic potential of Mes*NPCL is nucleophilic substitution of chloride ion with lithium reagents.³² In addition, this compound has been part of investigations into the chemistry of iminophosphines with transition metal complexes,³³ alkynes,³⁴ and alkyl azides.³⁵

More interesting is the phosphoazonium cation [Mes*NP]⁺, which is obtained by halide ion abstraction from Mes*NPCL.³¹ Also known as the iminophosphenium cation, this cation is isoelectronic to the diazonium cation and the analogy implies a diverse chemistry. Consistently, the phosphoazonium cation is extremely reactive.

1.3 The Report

The chemistry of Mes*N-P fragments plays a central role in this thesis, which begins in Chapter 2 with an assessment of the thermodynamic consequences of large substituents bound to low coordinate main group centers. Chapter 3 describes the oxidation of Mes*NPX (X = Cl, Br, I) with halogens (Cl₂, Br₂, I₂), as well as a novel reaction between Mes*NPCL and [CPh₃][BF₄]. Chapter 4 explores the analogy between diazonium and phosphoazonium cations. A brief analysis of the coordination chemistry of main group elements is presented to introduce the first examples of arene complexes of phosphorus. Structural and spectroscopic features of five arene complexes [Mes*NP-arene]⁺ are reported. These compounds represent stable models of π -complex intermediates in electrophilic aromatic substitution reactions. The reactivity of [Mes*NP]⁺ with simple hydridic bases establishes the chemical similarity between diazonium and phosphoazonium cations. The preparation and spectroscopic characterization of the first oxyphosphenium cation is described. Chapter 5 focuses on the chemistry of methylenephosponium cations and includes an unprecedented rearrangement of a phosphorus ylide. Chapter 6 describes the factors governing the coordination chemistry of

SbCl₃ with arenes. A proposal for further research is presented, highlighting the synthetic versatility of main group element cations, particularly [Mes*NP]⁺.

Note: In many cases, trivial compound names are used in preference to the IUPAC nomenclature. This is to be consistent with much of the established literature and to help the reader easily appreciate structural comparisons.

Chapter 2 Stability of Low Coordinate Environments for Main Group Elements: Theoretical and Experimental Considerations

Stability is a relative term and refers to the reluctance of a system to adjust to another energy state. There are two general types of stability: thermodynamic and kinetic. A thermodynamically stable molecule is of lower absolute energy than any other structural arrangement. A kinetically stable molecule has alternative structures of lower energy; however, access to these alternatives is prevented by an activation barrier which is insurmountable under normal conditions, such as room temperature. For a synthetic chemist, a realistic criterion for a stable molecule is isolation and storage in pure form without decay for indefinite periods of time, although shelf lifetimes of several years are more realistic. It is important to assess the thermodynamic and kinetic factors contributing to the stability of a compound in order to predict both structure and reactivity.

There has been much discussion concerning the role played by bulky substituents in the stability of low coordinate environments for main group elements. It is generally thought that large groups hinder the approach of molecules which, under normal circumstances, would oligomerize or undergo other reactions. As early as 1984, Cowley proposed that the stability of disilenes ($R_2Si=SiR_2$) and diphosphenes ($RP=PR$) may also involve a significant thermodynamic component (*i.e.*, an oligomer possessing large groups may be thermodynamically unstable with respect to monomers containing multiple bonds).^{6, 36}

Despite extensive use of large substituents in main group element chemistry, there has been no attempt to assess the thermodynamic effects of these bulky groups. This study examines these effects using molecular mechanics calculations on a series of model compounds. These results have been extrapolated to iminophosphines and other low coordinate main group element environments.

2.1 Thermodynamic Consequences of Steric Crowding

For all elements of the *p*-block other than those of the second row (B-Ne), examination of single and multiple bond energies reveals that the energy of two σ bonds is much greater than that of a σ and π bond (a double bond).² Consistent with this, iminophosphines can dimerize in the absence of large substituents *via* [2 + 2] cycloaddition, giving P₂N₂ rings. Although bond energy stabilization is maximized with formation of σ bonds, there is a concomitant increase in strain energy due to steric interactions between substituents and ring strain for four membered rings.

Calculation of strain energy for these cyclic oligomers is restricted by the large number of atoms involved and the presence of heavy elements. To appreciate the size of the calculation required, the [2 + 2] dimer of Mes*P=NMes* has a molecular formula of C₇₂H₁₁₆N₂P₂, 192 atoms in total. Such a calculation is clearly beyond the scope of most *ab initio* methods. Semi-empirical molecular mechanics packages such as PCModel³⁷

Table 2.1: PCModel calculated absolute strain energies (kJ/mol) for tetra-substituted (all *trans*) cyclobutane rings and the corresponding *trans*-alkene.

	cyclobutane	2 x <i>t</i> -alkene
R = H	110	≈ 0
R = Me	100	≈ 0
R = <i>t</i> Bu	190	10
R = Ph	290	200
R = Mes	360	300
R = Mes*	1200	660

using the MM2 force field can handle large numbers of atoms; however, parameters are not available for P-N systems. Nevertheless, a model involving various disubstituted alkenes and corresponding tetra-substituted cyclobutanes can assess the

magnitude of strain energy due to unavoidable steric crowding. The calculated strain energy for these molecules, reported to two significant figures, is presented in Table 2.1.

Minimum strain energies are obtained for alkenes and cyclobutanes with all substituents in the *trans* configuration. The strain energy calculated for cyclobutane compares well with the literature value (110 kJ/mol) and is primarily due to bond bending

to make the ring.³⁸ The calculated strain energies for the larger substituents include this energy, but also incorporate repulsions which result from non-bonded interactions (*i. e.*, steric crowding). For large substituents, this factor dominates the calculated strain energy. Strain energies are also calculated for cyclohexane rings, which, unsubstituted, can be considered strain-free.³⁹ This is not true for hexa-substituted rings with Me, Ph, Mes,

Table 2.2: Enthalpy of dimerization (kJ/mol) calculated for substituted alkenes incorporating strain energy.

R	ΔH
H	-30
Me	-40
<i>t</i> Bu	40
Ph	-40
Mes	-80
Mes*	400

*t*Bu, and Mes*⁴⁰ groups in the equatorial positions, which have calculated strain energies of 50, 320, 450, 1300, and 3500 kJ/mol, respectively. The calculated values are consistent with other sterically crowded hydrocarbons such as *cis*-1,2-di-*tert*-butylethylene (46 kJ/mol), tri-*tert*-butylethylene (130 kJ/mol) and the unknown tetra-*tert*-butylethene (250 kJ/mol).⁴¹ Cyclo- $C_4H_4Mes^*_4$ and $Mes^*CH=CHMes^*$ are also unknown; however, highly strained molecules can be prepared, such as *t*-butyl substituted tetrahedrane which has an estimated strain

energy of ≈ 550 kJ/mol.⁴²

The calculated data show a rapid increase of strain energy with increased steric bulk of the substituent, and this trend is evident for both alkenes and cyclobutanes. The effect is more pronounced in the cyclobutane rings. Estimates of $\Delta H_{\text{dimerization}}$ (Table 2.2) for the alkenes incorporating strain energy are calculated using carbon-carbon bond strengths (C-C 340 kJ/mol, C=C 610 kJ/mol),⁴³ and the following expression:

$$\Delta H_{\text{dimerization}} \approx (\sum \Delta H_{C=C} + \text{strain}_{\text{alkene}}) - (\sum \Delta H_{C-C} + \text{strain}_{\text{cyclobutane}})$$

Most important, the dimerization of $Mes^*CH=CHMes^*$ is estimated to be 400 kJ/mol endothermic. That is, the alkene is thermodynamically stable with respect to dimerization.

Extrapolation of these values to the heavier main group elements is enlightening. Specifically for P-N systems, bond energy considerations provide a convenient assessment of the thermodynamic stability of these compounds. The simplest cyclic

diazadiphosphetidine P_2N_2 ring **2.2** has four P-N bonds which account for 920 kJ/mol (4×230 kJ/mol P-N),⁴⁴ whereas for iminophosphine **2.1** the energy due to P=N bonds is 810 kJ/mol (2×405 kJ/mol P=N).⁴⁵ Therefore, with small substituents, iminophosphines are thermodynamically unstable with respect to dimerization by 110 kJ/mol (Figure 2.1). Values for strain energy in the P_2N_2 ring are not available; however, it is probable that this value is between the strain energy calculated for cyclobutane (110 kJ/mol) and that for cyclo- P_4H_4 (28 kJ/mol).⁴⁶

Internuclear distances are larger for phosphorus-containing compounds, and consequently the strain energy due to steric interactions is decreased. Nevertheless, the strain energy will be comparable since C-C (1.47-1.53 Å)⁴⁷ and P-N (1.59-1.77 Å)⁴⁸ bond lengths are similar. An estimate for the strain energy in P-N systems is difficult, although a conservative estimate is approximately half the value calculated for the organic model. Bond energy and strain considerations predict that Mes*-substituted iminophosphines are thermodynamically stable with respect to dimerization by 160 kJ/mol. With reference to Figure 2.1, iminophosphine **2.4** is thermodynamically stable with respect to its dimeric alternative **2.3**.

Entropy considerations ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$) have not been discussed since dissociation reactions are generally entropically favoured.⁴⁹ With large groups, both components of ΔG° favour multiply bonded systems. Kinetic factors, such as the energy of activation, can prevent reaction, but the relative energy between alternative structures remains unchanged. In the absence of kinetic factors (*i. e.*, barriers to reaction are overcome), compounds will adopt the lowest energy structure.

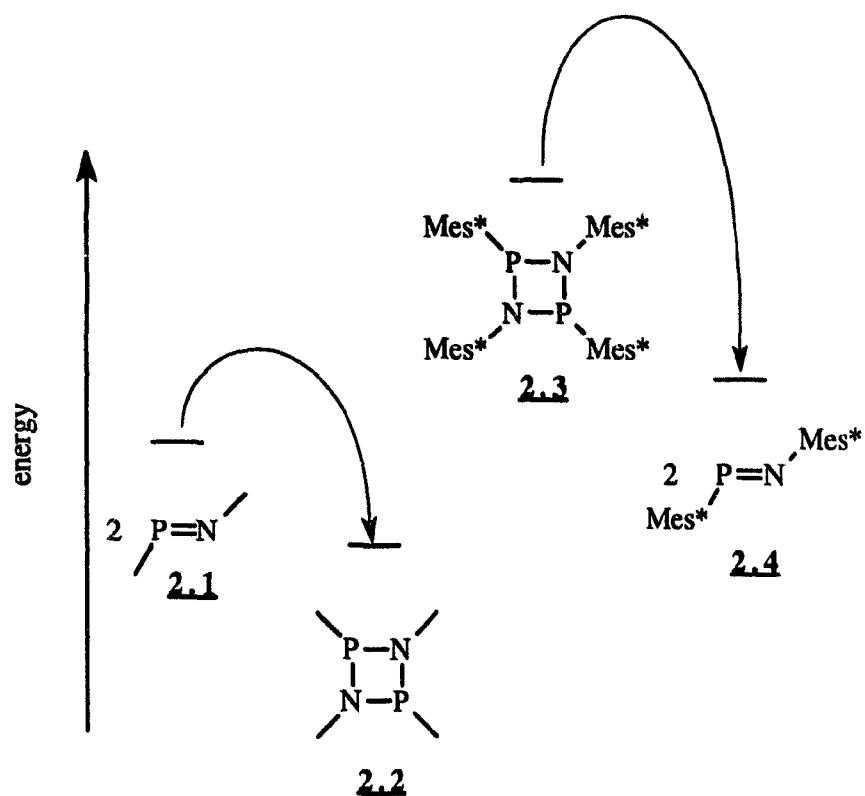
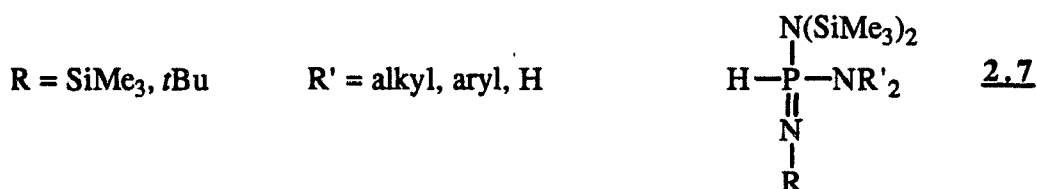
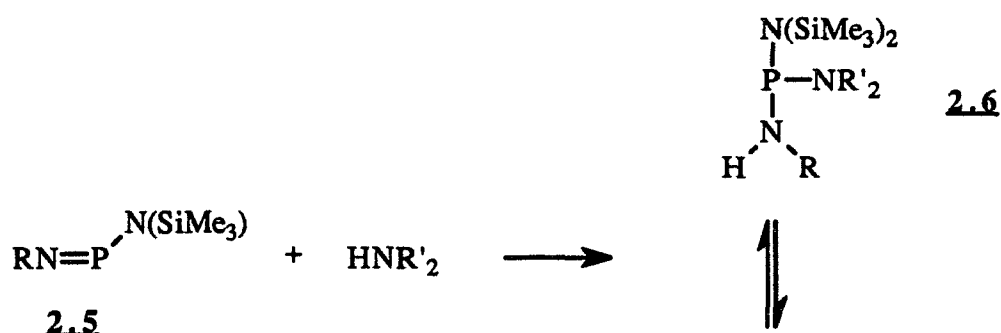


Figure 2.1: Schematic representation of the thermodynamic consequences of sterically demanding substituents on the stability of iminophosphines. The substituents on **2.1** and **2.2** are small, such as H or Me.

2.2 Experimental Support for Thermodynamic Consequences of Steric Crowding⁵⁰

The consequences of steric shielding are expressed in addition as well as dimerization reactions of P-N systems. Dicoordinate environments for phosphorus are generally considered unstable with respect to compounds having higher coordination



R = SiMe₃, *t*Bu

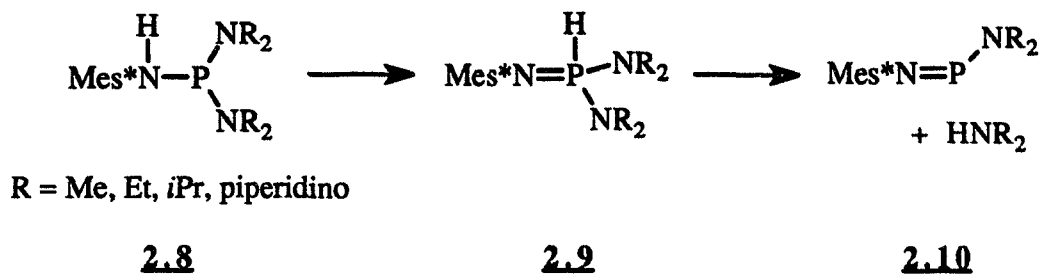
R' = alkyl, aryl, H

(2.1)

numbers (*vide supra*).⁴⁵ Consistently, iminophosphines **2.5** readily undergo addition reactions with primary or secondary amines [Equation 2.1], giving three or four coordinate phosphorus compounds, **2.6** and **2.7**, respectively.^{51, 52} These species adopt an equilibrium in which tautomer stability is dependent upon the substituents.⁵³

Dr. Simon Mason⁵⁴ showed that bis(dialkylamino)phosphine chlorides, (NR₂)₂PCl, react quantitatively with Mes*N(H)Li to give the corresponding trisaminophosphines **2.8**. These coordinatively saturated molecules (*i. e.*, three single bonds) spontaneously eliminate a molecule of secondary amine giving iminophosphines **2.10** via a tetracoordinate intermediate **2.9** [Equation 2.2]. This suggests thermodynamic preference for the dicoordinate phosphine over the tri- and tetracoordinate alternatives.

This situation is schematically represented in Figure 2.2. Slower rates of elimination of amine from **2.8** result with increasingly large NR₂ groups (*i. e.*, a kinetic barrier).



(2.2)

Phenylaminophosphines such as (PhNH)₃P have been reported to decompose on heating *via* amine elimination.⁵⁵ Based on the observations with sterically crowded trisaminophosphines **2.8**, it is conceivable that amine eliminations from phenylaminophosphines proceed through iminophosphine intermediates; however, without large substituents, these intermediates are thermodynamically unstable with respect to oligomeric alternatives that are reminiscent of cyclic polyphosphines **1.1** and **1.2**.

Sterically imposed thermodynamic stability with respect to oligomers is illustrated by numerous molecules containing multiple bonds between heavy elements, such as diphosphenes (R-P=P-R) and disilenes (R₂Si=SiR₂). Another system where strain concepts are applicable is the Lewis acid-base adducts of R₃E (E = Al, Ga, In) compounds. It has been said that sterically demanding groups decrease the acidity of R₃E acids, but no explanation is offered.⁵⁶ Recognizing that steric repulsion between substituents in a trigonal planar arrangement is less than that in a tetrahedral environment, adducts of R₃E Lewis acids (R = a large substituent) may be thermodynamically unstable with respect to the free acid and base.

Iodoselenides (R-SeI) are thermodynamically unstable with respect to I₂ and a

diselane -Se-Se- ($\Delta H = -1.3$ kJ/mol).⁵⁷ The iodo selenide, Mes*SeI, is unique since it is the only example of a neutral molecule with a stable Se-I bond.²² This compound is considered kinetically stable;⁵⁷ however, Mes*SeI is clearly thermodynamically stable with respect to I₂ and Mes*Se-SeMes* since these species adopt an equilibrium with Mes*SeI in benzene solution, the major component being Mes*SeI ($K \approx 10^2$ mol²/L²).²² The origin of the thermodynamic stability is likely the release of strain energy from Mes*Se-SeMes*.

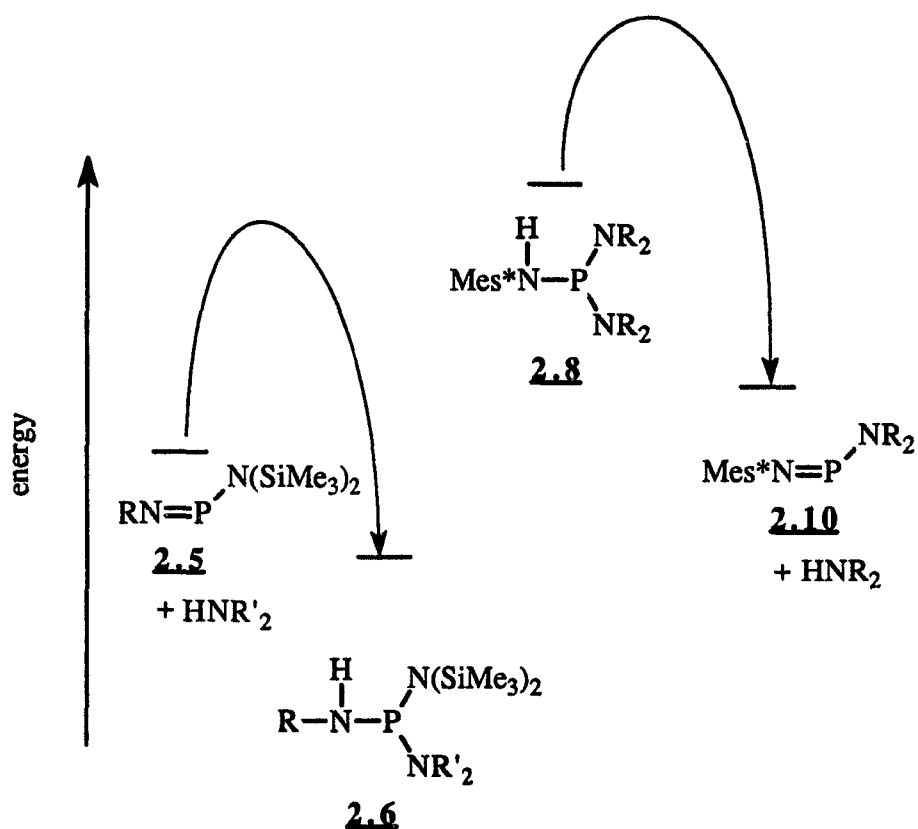
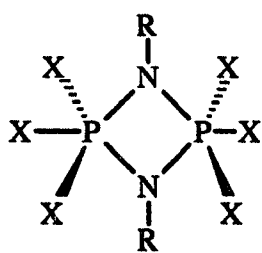


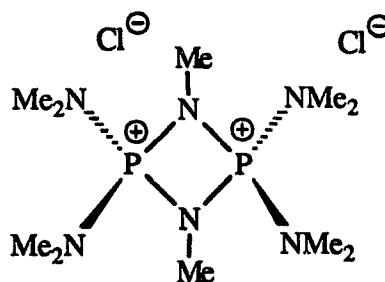
Figure 2.2: Schematic representation of the thermodynamic consequences of sterically demanding substituents on the addition of amines to iminophosphines.

Chapter 3 Monomeric Trihalogenophosphine Imides⁵⁸

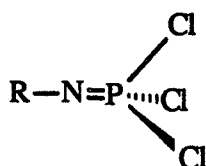
Trichlorophosphine imides (chlorophosphazenes) have been extensively studied,⁵⁹ and they typically adopt four-membered cyclic dimeric structures in both the solid state and in solution. As such they are categorized as cyclodiphosphazane⁷, and, depending on the substituents on nitrogen and phosphorus, may be covalent **3.1**⁶⁰ or ionic **3.2**.⁶¹ Hundreds of derivatives have been reported⁶² and yet, surprisingly, only two⁶³ examples



3.1



3.2



3.3a: R = C(Cl)(CCl₃)₂

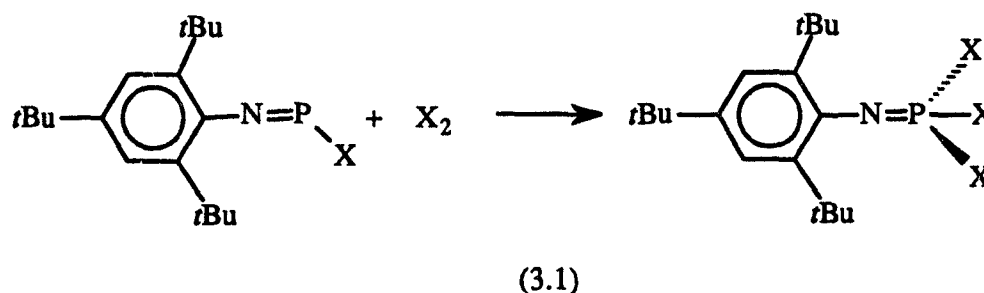
3.3b: R = C(CF₃)₃

of monomeric trihalogenophosphine imides, **3.3a**⁶⁴ and **3.3b**,⁶⁵ have been confirmed by structural studies. The Mes* substituent provides a unique opportunity to easily prepare monomeric compounds of the form Mes*NPX₃, which are useful synthons by virtue of their potential for substitution and elimination.

3.1 Synthesis of Mes*NPCL₃ and Mes*NPBr₃

Preliminary observations⁶⁶ had shown that Mes*NPCL reacts with chlorine in CH₂Cl₂ to give the corresponding trichlorophosphine imide, Mes*NPCL₃ [Equation. 3.1].

The compound was isolated from the reaction solids by vacuum sublimation, and its identity was determined by ^{31}P NMR, elemental analysis, and a single crystal X-ray structure which established its monomeric nature. ^{31}P NMR studies of the reaction mixtures indicated the presence of at least five other phosphorus containing compounds in



solution, with $\text{Mes}^*\text{NPCl}_3$ representing only 35% (by integration) of the mixture. In addition to the generation of multiple reaction products, the isolated yield of $\text{Mes}^*\text{NPCl}_3$ was less than 20 mg.

(Dichloroiodo)benzene, which is readily prepared by direct combination of Cl_2 with iodobenzene in cold (0°C) CH_2Cl_2 , reacts quickly and quantitatively (as shown by ^{31}P NMR) with Mes^*NPCl to form $\text{Mes}^*\text{NPCl}_3$. Iodobenzene, the only by-product of the reaction, is easily removed under vacuum. $\text{Mes}^*\text{NPCl}_3$ can be purified by either vacuum sublimation or recrystallization from hexanes or pentanes. ^{31}P NMR studies indicate that $\text{Mes}^*\text{NPCl}_3$ is not formed by the Kirsanov reaction [$\text{Mes}^*\text{NH}_2 + \text{PCl}_5$].⁵⁹

In contrast to the reaction of Mes^*NPCl with Cl_2 , $\text{Mes}^*\text{NPBr}_3$ is generated quantitatively by the reaction of Mes^*NPBr with Br_2 in hexane, and red crystals of $\text{Mes}^*\text{NPBr}_3$ can be isolated in high yield. NMR studies of Mes^*NPI and I_2 indicate that no reaction occurs (Mes^*NPI_3 not formed), reflecting the decreasing oxidizing power of the halogens with increasing atomic number (*vide infra*). Attempts to prepare the corresponding trifluoride, Mes^*NPF_3 , *via* halide exchange of $\text{Mes}^*\text{NPCl}_3$ with SbF_3 and

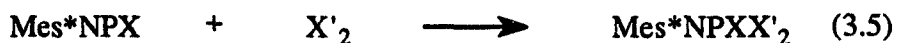
CsF were unsuccessful, and the starting material remained unchanged. No reaction is observed between Mes*NPCL₃ and SbPh₃.

3.2 Reactions of Iminophosphine Halides With Molecular Halogens

Reactions involving the iminophosphine halides, Mes*NPX (X = Cl, Br, I), with halogens (PhICl₂, Br₂, and I₂) have been comprehensively assessed by ³¹P NMR spectroscopy, and most derivatives of Mes*NPX_nX'_{3-n} have been identified. For example, the reaction mixture of Mes*NPCL with Br₂ exhibits ³¹P NMR signals assigned to Mes*NPCL₃ (-96 ppm), Mes*NPBrCl₂ (-136 ppm), Mes*NPBr₂Cl (-183 ppm) and Mes*NPBr₃ (-236 ppm). These compounds crystallize as a mixture of crystals from which a single crystal of Mes*NPBr₃ was isolated and characterized by an X-ray study. Chemical analyses of the recrystallized bulk sample are consistent with a mixture in the relative ratios revealed in the solution ³¹P NMR spectrum of the sample. The chlorine rich reaction products Mes*NPBrCl₂ (20% by integration) and Mes*NPCL₃ (trace) observed in the reaction mixture are accounted for by a mechanism involving a halide exchange process. Other combinations of Mes*NPX and dihalogens X'₂ reveal similar product mixtures.

Reactions of I₂ with Mes*NPCL and Mes*NPBr are an exception. Independent of stoichiometry, reaction of Mes*NPCL and I₂ produces Mes*NPCL₂I (-211 ppm), of which several crystals have been isolated and characterized by X-ray crystallography. The remaining reaction products are a halide exchanging mixture of Mes*NPCL and Mes*NPI whose average chemical shift is dependent upon the stoichiometry. Reaction mixtures containing Mes*NPCL and trace I₂ give a signal at $\approx$ 150 ppm, close to that of Mes*NPCL (139 ppm in C₆D₆),³¹ whereas reaction mixtures with an excess of I₂ give a signal at $\approx$ 200 ppm, close to that of Mes*NPI (218 ppm in C₆D₆).³¹ Reaction of Mes*NPBr with I₂ produces a single signal at 170 ppm which has been assigned to an exchanging mixture of

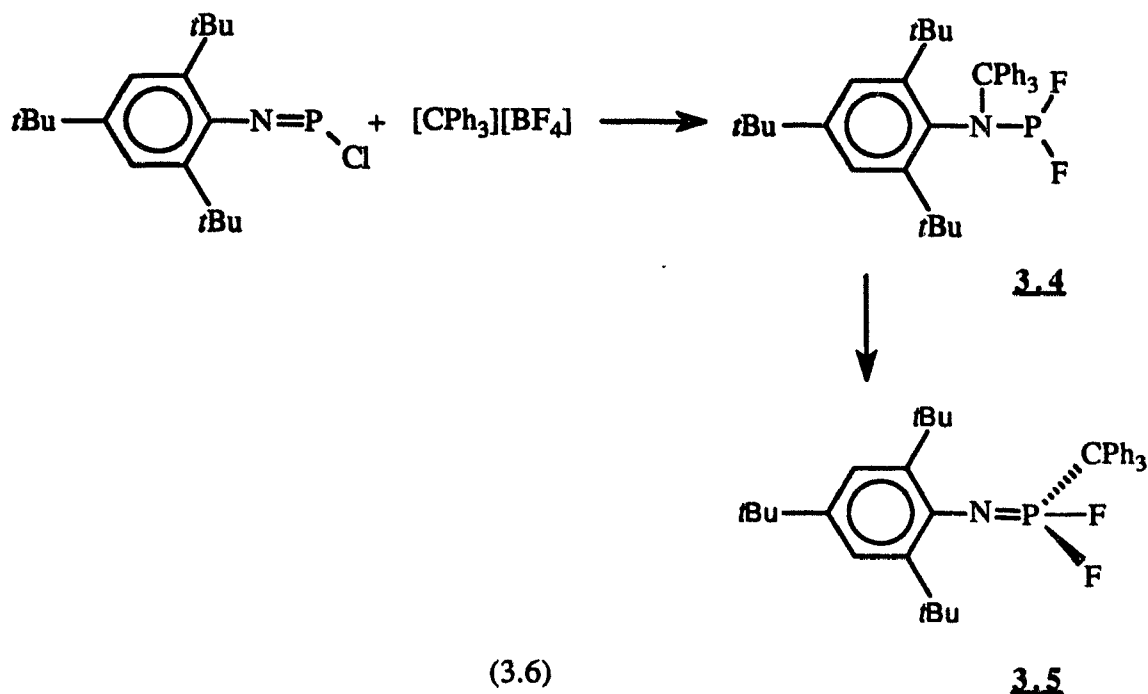
Mes*NPBr and Mes*NPI. Mixtures of Mes*NPBr and Mes*NPI also show an average signal (159 ppm), indicating an exchange process which presumably takes place *via* the phosphoazonium cation, [Mes*NP]⁺, or perhaps *via* trihalide anion formation, [X'₂X]⁻. Mixtures of Mes*NPCl₃ and Mes*NPBr₃ do not show evidence for halide exchange, even after one month. On this basis, formation of the mixed halides likely involves halide exchange at the monohalide followed by oxidation of the resulting monohalides by the now mixed dihalogens. These reactions are summarized below [Equations 3.2 - 3.5]:



A reaction process involving halide exchange accounts for the formation of Mes*NPCl₂I from the reaction of Mes*NPCl + I₂, but does not account for the absence of the diiodo or triiodo trihalides, Mes*NPI₂X and Mes*NPI₃. This may be due to either the low reduction potential of iodine (+0.620 V, *cf.*, Br₂, +1.078 V; Cl₂, +1.360 V),⁶⁷ or to the increase in steric demands of the halogen (Covalent radii: 0.99 Å, Cl; 1.14 Å, Br; 1.33 Å, I).⁶⁷

3.3 Formation of a Phosphine Imide by the Reaction of Mes*NPCl with [Ph₃C][BF₄]⁶⁸

Reaction of Mes*NPCl with AlCl₃ produces the phosphoazonium cation, [Mes*NP]⁺,³¹ however, combination of Mes*NPCl with stoichiometric quantities of [Ph₃C][BF₄] in CH₂Cl₂/hexanes solution results in the quantitative formation of aminodifluorophosphine **3.4**. Structural assignment for this compound is based on ³¹P



NMR data (146 ppm, $^1J_{\text{PF}}$ 1105 Hz), which is typical of other aminodifluorophosphines:

$\text{R}(\text{TMS})\text{N}-\text{PF}_2$, $^{69}\text{R} = \text{Ad}$ (165 ppm, $^1J_{\text{PF}}$ 1208 Hz), Mes (151 ppm, $^1J_{\text{PF}}$ 1225 Hz).

Compound **3.4** could not be isolated in pure form as it readily isomerizes to the difluoroalkylphosphine imide **3.5**, a rearrangement which is reminiscent of an Arbuzov-type reaction.⁷⁰ This isomerization is likely driven by the steric crowding at the nitrogen center in **3.4**. Solution studies indicate that **3.5** is formed in excess of 90 % yield, and can be isolated readily from the reaction mixtures as light yellow block crystals.

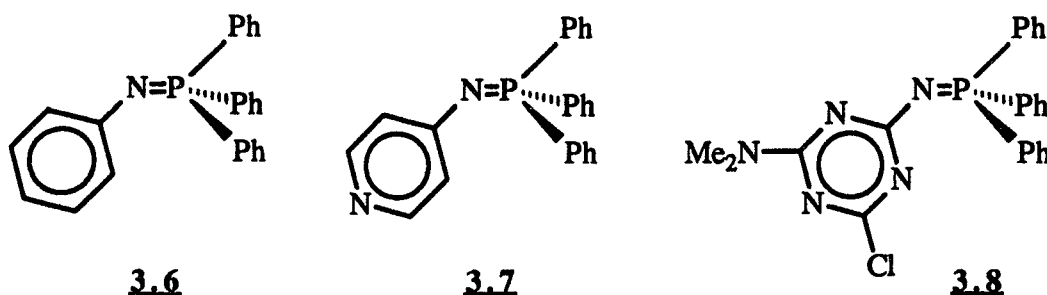
3.4 Structural Features of Monomeric Trihalogenophosphine Imides

The solid state structures of $\text{Mes}^*\text{NPCl}_3$, $\text{Mes}^*\text{NPBr}_3$ and $\text{Mes}^*\text{NPF}_2(\text{CPh}_3)$ have been determined by X-ray crystallography. ORTEP views are presented in Figures 3.1-3.3. The crystal structure of $\text{Mes}^*\text{NPCl}_2\text{I}$ has also been determined and confirms the covalent monomeric arrangement; however, disorder prevents accurate assessment of bond

lengths and angles. Significant intermolecular contacts are not observed in the structures of Mes*NPCl₃, Mes*NBr₃, and Mes*NPF₂(CPh₃).

The molecules all exhibit unusually large angles at the nitrogen center [Mes*NPCl₃, 160.9(3)°; Mes*NBr₃, 160.1(9)°; Mes*NPF₂(CPh₃), 156.3(3)°]. Similarly, a wide angle at nitrogen is also observed for Mes*N=P(Cl)(NEt₂)₂ (161.5(2)°).⁵⁰ For comparison, monomeric triarylphosphine imides (ArNPAR₃) have geometries at the nitrogen center that are in accord with the VSEPR model. The C-N-P bond angles in **3.6**,⁷¹ **3.7**,⁷² and **3.8**

73



(130.4(3)°, 128.6(3)°, and 121°, respectively) are typical of other phosphine imides. Many derivatives of the iminato ligand (R₃PN⁻) are known for the transition metals, and these exhibit a wide range of angles for the metal-bound nitrogen center (130-177°).⁷⁴ The wider angles are rationalized in terms of P-N and N-M π -interactions and *sp* hybridization at the nitrogen center. The phosphorus centers in Mes*NPCl₃ and Mes*NBr₃ are distorted

Table 3.1: Selected bond lengths (Å) and angles (°) for three phosphine imides.			
	Mes*NPCl ₃	Mes*NBr ₃	Mes*NPF ₂ (CPh ₃)
PN	1.467(4)	1.46(1)	1.475(4)
NC _{Mes} *	1.410(4)	1.45(1)	1.431(5)
C _{Mes} *-N-F	160.9(3)	160.1(9)	156.3(3)

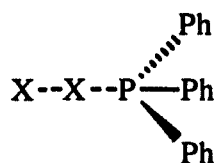
from a tetrahedral geometry, and they exhibit close to C_{3v} symmetry with the narrow angle for X-

P-X of 100°, which can be compared to the Cl-P-Cl angle in OPCl₃ (103.3°).⁷⁵

The P-N bonds for these Mes* substituted phosphine imides are consistently short (Mes*NPCl₃, 1.467(4) Å; Mes*NBr₃, 1.46(1) Å; Mes*NPF₂(CPh₃), 1.475(4) Å); and

are much shorter than often observed for other phosphazenes. For example, the P-N bonds in the arylphosphine imides are **3.6**, **3.7**, and **3.8** are 1.602(3) Å, 1.574(2) Å, and 1.622(5) Å, respectively. The Mes* substituted phosphine imide Mes*N=P(Cl)(NEt₂)₂ also has a short P=N bond (1.492(2) Å).⁵⁰ The P-N bond in Mes*NPCl₃ represents one of the shortest P-N bonds reported to date and is comparable to the P-N bond observed for the phosphoazonium cation, [Mes*NP]⁺, 1.475(8) Å.³¹ This molecule is considered to contain a P-N triple bond.^{76,77}

MacAuliffe has recently shown that the solid state structures of diiodo- and dibromophosphoranes adopt linear 'spoke' structures **3.9** involving tetracoordinate phosphorus centers, rather than the expected pentacoordinate arrangement.⁷⁸ The linear spoke arrangement is not observed for the phosphine imides, with the preferential adoption of tetracoordinate environments for phosphorus rather than a three coordinate trigonal planar geometry. The tricoordinate phosphonium center has been demonstrated to be thermodynamically unstable with respect to other structural alternatives (*vide infra*).



3.9

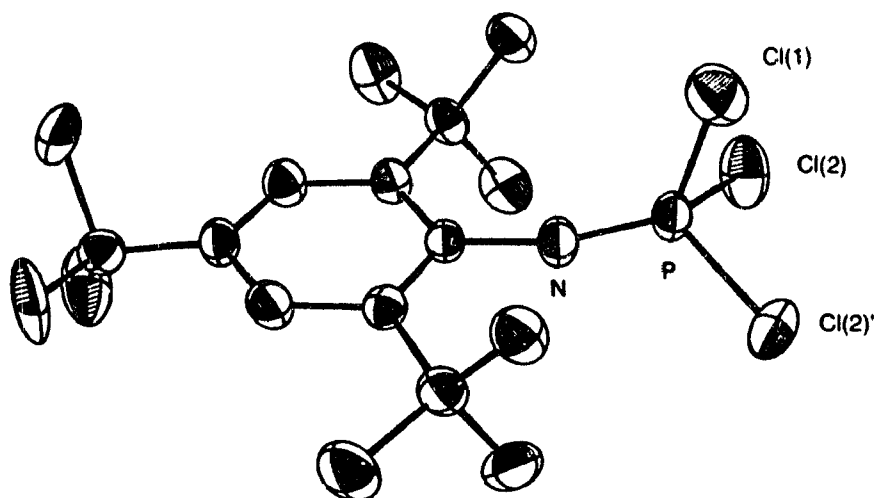


Figure 3.1: ORTEP view of Mes*NPCl₃ (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity. Important bond lengths (Å) and angles (°): P-N 1.467(4), P-Cl(1) 2.017(1), P-Cl(2) 2.004(1), N-C_{Mes*} 1.410(4), C_{Mes*}-N-P 160.9(3), Cl(1)-P-Cl(2) 100.71(5), N-P-Cl(1) 118.9(2), N-P-Cl(2) 116.69(9).

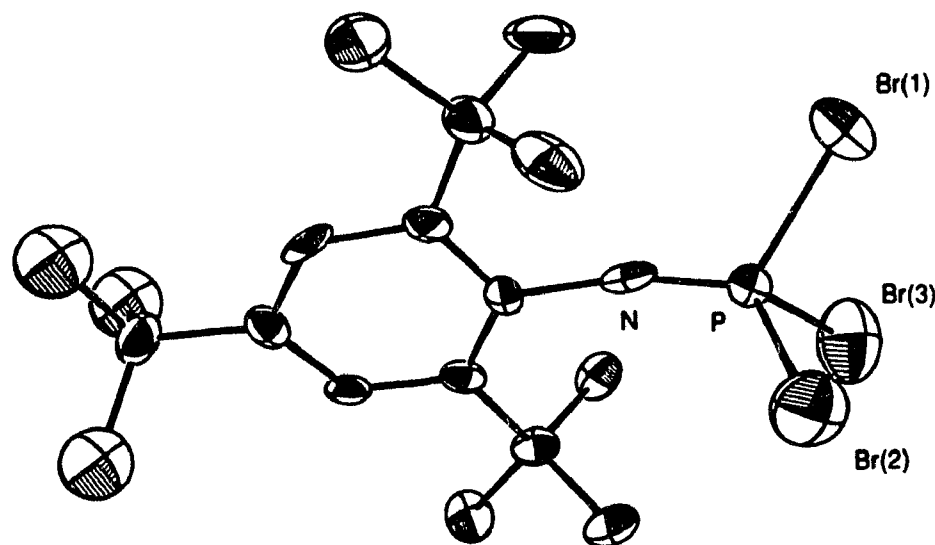


Figure 3.2: ORTEP view of Mes*NPBr₃ (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity. Important bond lengths (Å) and angles (°): P-N 1.46(1), P-Br(1) 2.165(4), P-Br(2) 2.171(4), P-Br(3) 2.148(4), N-C_{Mes*} 1.45(1), C_{Mes*}-N-P 160.1(9), Br(1)-P-Br(2) 101.8(2), Br(1)-P-Br(3) 100.8(2), Br(2)-P-Br(3) 100.2(2), N-P-Br(1) 117.2(5), N-P-Br(2) 118.5(4), N-P-Br(3) 115.4(4).

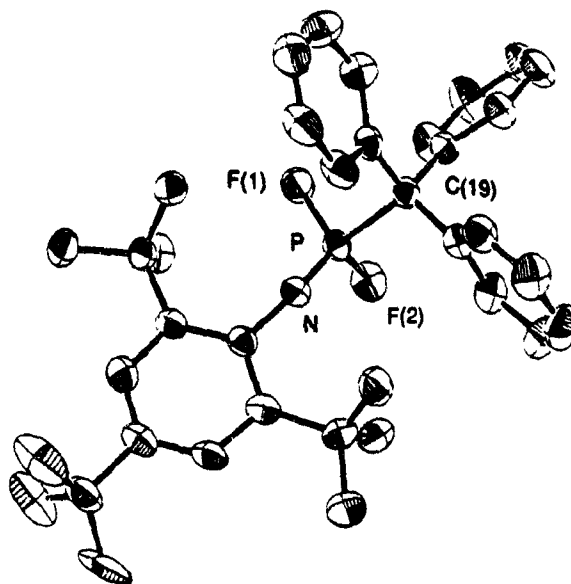


Figure 3.3: ORTEP view of Mes*NPF₂(CPh₃) (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity. Important bond lengths (Å) and angles (°): P-N 1.475(4), P-C(19) 1.847(4), P-F(1) 1.557(3), P-F(2) 1.562(3), C_{Mes}-N 1.563(3), P-N-C_{Mes} 156.3(3), F(1)-P-F(2) 96.97(15), F(1)-P-N 117.7(2), F(1)-P-C(19) 99.3(2), F(2)-P-N 114.9(2), F(2)-P-C(19) 104.8(2), N-P-C(19) 119.7(2).

3.5 Steric and Electronic Control of Geometries at Nitrogen

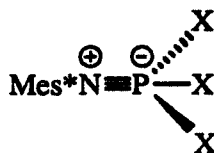
Trihalogenophosphine imides typically dimerize (*vide supra*); however, dimerization of Mes*NPX₃ derivatives is not anticipated since the dimeric alternatives should possess a large strain energy due to steric interactions. That is, the monomeric Mes*NPX₃ derivatives are thermodynamically stable with respect to dimerization.

Large bond angles at nitrogen and short P-N bonds are evident in Mes*NPCl₃, Mes*NPBr₃, and Mes*NPF₂(CPh₃). For comparison, the P-N bond length of Mes*NPCl₃ is significantly shorter and the C-N-P angle is substantially larger than those in the only other examples of monomeric trichlorides **3.3a** [1.504(2) Å and 144.6(2)°] and **3.3b** [1.505(3) Å and 142.9(3)°].

In all cases, Mes* substituted iminophosphines and phosphine imides possess

short P-N bonds, and this is likely due to steric enforcement of linearity. For example, the P-N bond in the parent iminophosphine chloride, Mes*NPCl,³¹ is 1.495(4) Å and there is only a small, yet significant, shortening of the P-N bond for any of the Mes* substituted phosphine imides.

The short P-N bond and large C-N-P angle for Mes*NPCl₃, Mes*NBr₃, and Mes*NPF₂(CPh₃) implies *sp* hybridization at the nitrogen center. Two factors that can affect the bond length are the extent of π bonding between the atoms, as well as the hybridization of the atoms engaged in the bond. It is difficult to assess the extent of the shortening of the P-N bond due to enhanced π bonding, and how much is due to the sterically enforced *sp* hybridization at the nitrogen center. This problem has been addressed in the case of P-P bond shortening in diphosphenes (RP=PR) and diphosphines (R₂P-PR₂).⁷⁹ Another factor to consider is the ionic bonding contribution to the P-N bond which has been illustrated for monomeric aluminum aryloxides, where the lack of a significant rotation barrier around the O-Al bond suggests that π bonding is minimal.⁸⁰ The shortness of the O-Al bonds in these compounds may be explained by a significant ionic contribution to the bond, noting that a large electronegativity difference exists between oxygen and aluminum (Pauling scale: O, 3.44; Al, 1.61, diff. 1.83).⁶⁷ The electronegativity of nitrogen and phosphorus are comparable (Pauling scale: N, 3.04; P, 2.19; diff. 0.85),⁶⁷ and it is questionable if there is a significant ionic contribution to the short P-N bonds observed. It is tempting to conclude that the P-N triple bond model **3.10**



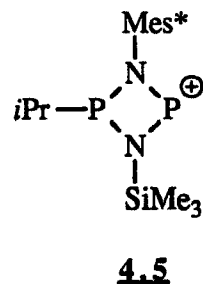
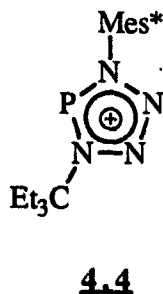
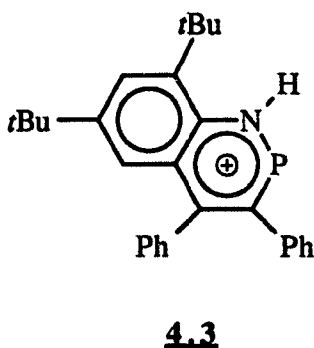
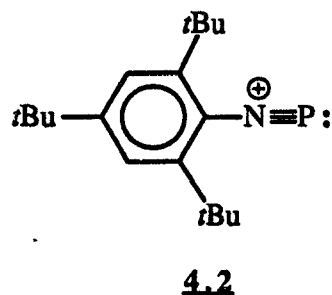
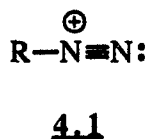
3.10

is a significant resonance contributor to the electronic structure with P-N π -interaction enhanced in the presence of electronegative substituents.

Chapter 4 The Chemistry of the Phosphoazonium Cation

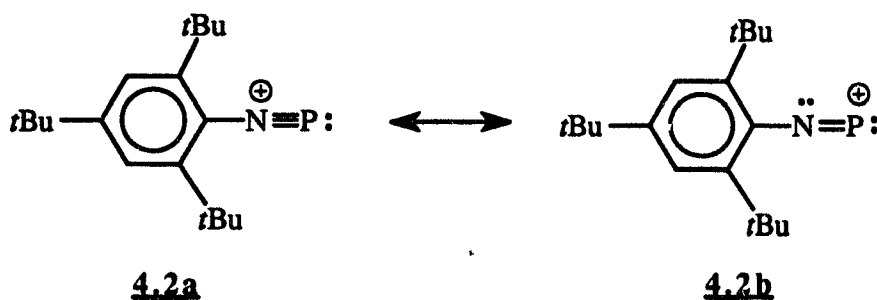
The diazonium cation **4.1** is one of the most versatile functional groups in organic chemistry.⁸¹ The phosphoazonium cation ($R = \text{Mes}^*$ **4.2**) can be considered a derivative of **4.1**, representing a formal replacement of the terminal nitrogen atom by a phosphorus atom. Numerous derivatives of the diazonium cation have been isolated; however, only one example of a phosphoazonium cation **4.2** has been isolated.³¹ Recently, $[\text{MeNP}]^+$ and $[\text{MeNAs}]^+$ have been observed in the gas phase.⁸²

The chemistry of **4.2** is still in its infancy and includes reactions with diphenylacetylene,⁸³ alkyl azides, and iminophosphines;⁸⁴ each giving cyclic phosphonium



cations **4.3**, **4.4**, and **4.5**, respectively. The iminophosphine, $\text{Mes}^*\text{NPCp}^*$, exhibits ring whizzing in the solid state and can be viewed as an η^1 complex of the phosphoazonium cation and the Cp^* anion.⁸⁵

Recent theoretical studies indicate that loss of N₂ from **4.1** should occur much easier than loss of PN from **4.2** (methyl cation affinity for N₂ and PN are 180 and 420 kJ/mol respectively).⁷⁶ In addition, calculation of the charge distribution for these cations suggests that whereas **4.1** is the best resonance structure for the diazonium cation, the charge for phosphoazonium is localized on the terminal phosphorus atom. That is, resonance structure **4.2b** dominates over **4.2a**. The phosphoazonium cation offers a unique electron deficient, coordinatively unsaturated phosphorus center as a potential coordination site which is exploited for the first time in this study. By way of introduction



to the coordination chemistry of **4.2**, some general aspects of the coordination chemistry of main group elements are presented.

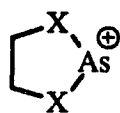
4.1 Coordination Chemistry of the Main Group Elements

The coordination chemistry of the metallic elements,⁸⁶ including those from the *s* and *p* blocks,⁸⁷ is well established. These compounds are structurally diverse with many types of ligands attached to the metal centers. The coordination chemistry of the lighter main group elements is not as extensive.

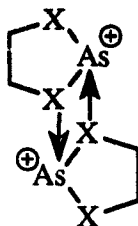
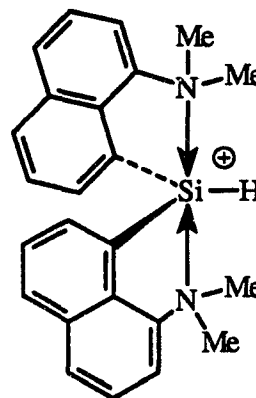
The concept of coordination chemistry is simply described: an electron deficient species (a Lewis acid) reacts with an electron rich species (a Lewis base) to form a coordinate covalent bond. This acid-base adduct, or complex, can be neutral, as in the case

of $\text{Et}_2\text{O} \rightarrow \text{BF}_3$, or charged (a complex ion), as in the anionic species $[\text{GaCl}_4]^-$. Other examples of anionic complex ions include $[\text{I}_3]^-$, $[\text{SF}_5]^-$ and $[\text{PCl}_6]^-$. These represent σ complexes of halide ions coordinated to non-metal acids (I_2 , SF_4 , and PCl_5 , respectively). Cationic species include oxonium and sulfoxonium cations, $[\text{Me}_3\text{O}]^+$ and $[\text{Me}_3\text{S}]^+$, which are complexes between Me_2E ($\text{E} = \text{O}$ or S) and $[\text{Me}]^+$. The iodine cation $[\text{Py}_2\text{I}]^+$ can be considered as a complex between two pyridine molecules and $[\text{I}]^+$.⁸⁸

A recent focus of synthetic inorganic chemistry has been the preparation of cations containing elements in low coordination environments. Species such as phosphonium,⁸⁹ silylium,⁹⁰ and arsenium⁹¹ cations have been prepared, and their potential as coordination sites is being studied.

**4.6a**

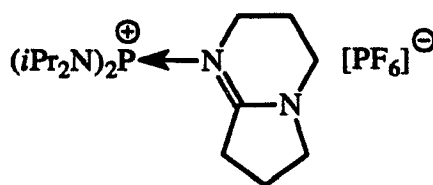
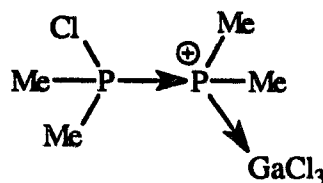
$\text{X} = \text{N}(\text{Me}), \text{S}$

**4.6b****4.7**

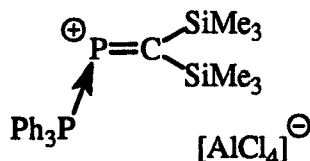
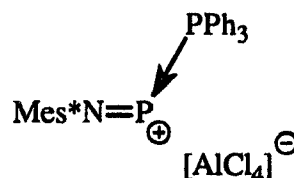
The most spectacular examples of *p*-block σ -complex ions are the dimeric arsenium cations **4.6a**, which exist in the solid state as complex ions **4.6b**, with mutual donor/acceptor interactions ($\text{S} \rightarrow \text{As}$ or $\text{N} \rightarrow \text{As}$) evident in each unit.⁹¹ The σ -complex of the silylium cation, $[\text{RCN} \rightarrow \text{Si}(\text{iPr})_3]^+$, has been characterized by NMR spectroscopy,⁹² and, more recently, a novel pentacoordinate silicon cation **4.7** has been prepared.⁹³

Several σ -complexes of phosphorus cations have been reported. The Lewis acidity

of phosphonium cations was first demonstrated in 1976 with the spectroscopic characterization of $[R_3P \rightarrow PR_2]^+$ complexes in solution;⁹⁴ however, the first comprehensively characterized examples of σ -complexes of phosphonium cations are the DBN and DBU complexes of $[(iPr_2N)_2P]^+$ **4.8**.⁹⁵ The cation **4.9** has been described as a

**4.8****4.9**

complex demonstrating the ability of a Lewis base (Me_2PCl) to induce coordination from the prototypical phosphonium cation $[Me_2P]^+$ to a second Lewis acid ($GaCl_3$).⁹⁶ Most interesting is the donor stabilized methylenephosphonium cation **4.10**.⁹⁷ The report of this cation is perhaps one of the best examples of base stabilization, a concept whereby

**4.10****4.11**

extremely reactive, electron deficient compounds are isolated as their Lewis base adducts.⁹⁸ Surprisingly, only one σ -complex of the phosphazonium cation **4.11** with a neutral ligand has been reported; characterized only by ^{31}P NMR spectroscopy.⁹⁹

π -Complexes are somewhat rare for the main group element cations. There are a

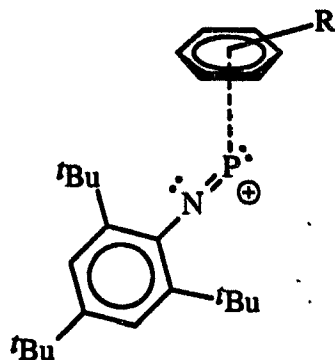
number of main group element cations which engage π -ligands, such as pentamethylcyclopentadienide (Cp^*),¹⁰⁰ as in $[\text{Cp}^*_2\text{As}]^+$,¹⁰¹ which may be considered a non-metal analogue of the metallocenes (*e. g.*, ferrocene). Examples of η^6 -arene complexation to the heavier *p*-block metals and metalloids are also well established.¹⁰² Examples include a series of complexes involving substituted benzenes coordinated to group 15 trihalides (EX_3 ; E = As, Sb, Bi; X = Cl, Br, I) (*vide infra*) and cationic centers such as Ga (I),¹⁰³ In (I)¹⁰⁴, Sn (II)¹⁰⁵, Pb (II).¹⁰⁶ An example of a bismuthenium cation, $[\text{Me}_6\text{C}_6\text{---BiCl}_2][\text{AlCl}_4]$, has been reported.¹⁰⁷ The classical benzene---dihalogen complexes,¹⁰⁸ referred to as charge transfer complexes, represent examples of π -complexes to neutral non-metal elements. Noticeably absent from the list of elements (cationic or neutral) which form arene complexes is phosphorus, despite extensive studies into its chemistry.¹⁰⁹

4.2 Identification of the First Arene Complexes of Phosphorus¹¹⁰

The phosphoazonium cation, $[\text{Mes}^*\text{NP}]^+$, was first prepared as the $[\text{AlCl}_4]^-$ salt, and X-ray analysis showed the presence of toluene in the crystal lattice. Described as a solvate, the formula was reported as $[\text{Mes}^*\text{NP}][\text{AlCl}_4] \cdot \text{C}_7\text{H}_8$.³¹ Reactions of $\text{Mes}^*\text{NP}\text{Cl}$ with a stoichiometric quantity of GaCl_3 in toluene quantitatively generate $[\text{Mes}^*\text{NP-toluene}][\text{GaCl}_4]$ with a ^{31}P NMR chemical shift of 78 ppm. X-ray analysis of crystalline $[\text{Mes}^*\text{NP-toluene}][\text{GaCl}_4]$ clearly reveals the presence of a significant contact between the cation, $[\text{Mes}^*\text{NP}]$, and the arene, toluene. Stoichiometric studies of $\text{Mes}^*\text{NP}\text{Cl}$ with GaCl_3 in toluene indicate that with a two-fold excess of GaCl_3 , a compound with a ^{31}P NMR chemical shift of 91 ppm is formed. Attempts to isolate this compound are made difficult because the reaction mixtures generally separate into oily layered solutions, but crystalline material forms in high yield upon standing overnight. This material has been characterized as $[\text{Mes}^*\text{NP-toluene}][\text{Ga}_2\text{Cl}_7]$, and structural analysis of this compound reveals a much closer association of the arene with the phosphoazonium

cation than that found for [Mes*NP-toluene][GaCl₄].

Five compounds of the general form [Mes*NP-arene][anion] **4.12** have been isolated and characterized: two gallate salts, [Mes*NP-benzene][GaCl₄] and



arene = benzene, toluene, or mesitylene
anion = GaCl₄ or Ga₂Cl₇

4.12

[Mes*NP-toluene][GaCl₄], and three digallate salts, [Mes*NP-benzene][Ga₂Cl₇], [Mes*NP-toluene][Ga₂Cl₇], and [Mes*NP-mesitylene][Ga₂Cl₇]. Observation of a single signal in the ³¹P NMR spectra of the reaction mixtures indicates a quantitative reaction in each case. The gallate salts are susceptible to loss of the arene from the solid,¹¹¹ and under dynamic vacuum (24 hours at 10⁻³ Torr) benzene and toluene are quantitatively removed as shown by IR and NMR spectroscopy and elemental analysis. In contrast, the digallate salts remain unchanged under vacuum over long periods of time (>60 hours).

4.3 Structural Features of Arene Complexes of the Phosphoazonium Cation

Each salt **4.12** is composed of discrete ions with tetrahedral geometry observed for [GaCl₄]⁻ and typical structural parameters for the previously described [Ga₂Cl₇]⁻ anion.¹¹²

The salt [Mes*NP-toluene][GaCl₄] is isostructural to the original report of [Mes*NP-toluene][AlCl₄].³¹ The cation in each case is [Mes*NP]⁺, and shows the structural features anticipated for the cation (Table 4.1), such as the linear C_{Mes}*-N-P

Table 4.1: Important bond lengths (Å), bond angles (°), and contact distances (Å) for arene complexes of the phosphoazonium cation. P---arene measured to the centroid of the arene ring.				
Compound	P-N	P-N-Mes*	P---Arene	P---Cl
[Mes*NP-benzene][GaCl ₄]	1.484(7)	175.5(7)	3.0012(6)	3.083(4) 3.389(4) 3.429(4)
[Mes*NP-toluene][GaCl ₄]	1.529(15)	177.0(13)	3.038(13)	3.139(9) 3.237(8) 3.474(8)
[Mes*NP-benzene][Ga ₂ Cl ₇]	1.463(5)	178.5(4)	2.820(4)	3.395(3) 3.570(3)
[Mes*NP-toluene][Ga ₂ Cl ₇]	1.464(9)	178.7(8)	2.767(7)	3.487(4) 3.584(4)
[Mes*NP-mesitylene][Ga ₂ Cl ₇]	1.471(6)	175.7(5)	2.687(4)	3.513(4) 3.805(4)

fragment with extremely short P-N bonds, irrespective of the anion or the coordinated arene.

Of particular interest is the local coordination sphere around the cation. Each compound displays a number of close contacts between the phosphorus center, the anion, and the arene. In the gallate salts the cation interacts with two anions, having phosphorus to chlorine contacts (P---Cl) as short as 3.083(4) Å. The digallate salts adopt an ion pair arrangement with the closest contacts (P---Cl) at 3.395(3) Å. Complete listings of the anion---P contacts are presented in Table 4.1. The contacts are all substantially longer than typical covalent P-Cl bonds found in PCl₃ (2.043 Å) and [PCl₆]⁻ (2.14 Å),¹¹³ or than in the covalent compounds Mes*NPCl (2.142(4) Å)³¹ and Mes*NPCl₃ (2.017(1) and 2.004(1) Å).⁵⁸ The interactions are significantly shorter than the anion-cation contacts observed in other salts of phosphorus cations. For example, the closest P---Cl contacts for

the diaminophosphenium cations **4.13** and **4.14** are 3.867(6) Å and 3.548(1) Å, respectively.¹¹⁴ These cation-anion contacts are often observed in salts of non-metal cations, and have been interpreted as donations from the anion to the cation.¹¹⁵ They do not appear to affect the structural features of the cation.¹¹⁶ Differences in contact distance can be rationalized in terms of the relative acidic character of the phosphorus centers. The positive charge in diaminophosphenium cations in **4.13** and **4.14** can, by virtue of π -resonance, be delocalized over three atomic centers (Figure 4.1); whereas, for the

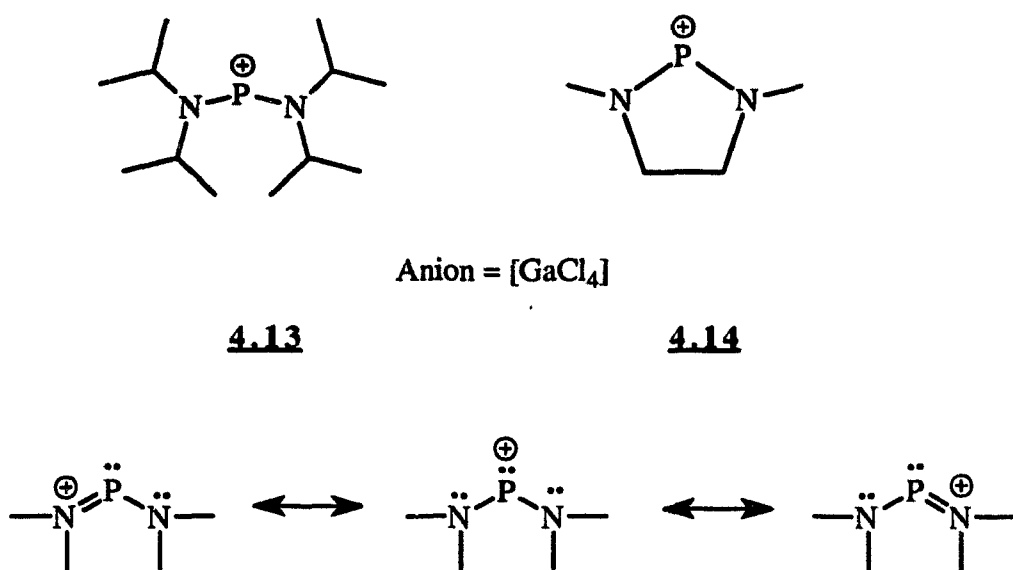


Figure 4.1: Lewis structures illustrating charge delocalization for diaminophosphenium cations.

phosphoazonium cation there is only one adjacent nitrogen to engage in delocalization.

Significant changes occur in the local coordination geometry of the phosphoazonium cation upon changing the anion. Shown in Figures 4.2 and 4.3 are crystallographic views of [Mes*NP-benzene]⁺ with two different anions; [GaCl₄]⁻ and [Ga₂Cl₇]⁻. In the case of the gallate salt, three close cation-anion contacts are evident

between the phosphorus center and the chlorine centers of two anions, as well as the P---arene contact. This results in a distorted trigonal bipyramidal geometry for the local coordination sphere of the phosphorus center which is illustrated by Cl(1)a and Cl(4)b occupying axial positions, and Cl(2)a, N(1) and benzene occupying equatorial positions. The larger digallate anion affords one less P---Cl contact to the phosphorus center; thus the local coordination sphere for the phosphorus center is a distorted tetrahedron.

For all salts the arene is best described as hexa-hapto bound (η^6) to the phosphorus center, with the arene carbon atoms equidistant from phosphorus, and the largest angle deviation from 90° between the phosphorus center, the arene centroid, and a carbon center of the arene, is $6.2(8)^\circ$. Two trends are evident in the data presented in Table 4.1: the P---arene_{centroid} distance is shorter in the digallate salts; and the P---arene_{centroid} distance decreases for the three digallate salts (benzene > toluene > mesitylene), in accord with the π -donor capabilities of the arene. This is surprising due to the substantial increase in steric demands of the ligand as the number of alkyl groups on the arene is increased. The benzene units in [Mes*NP-benzene][GaCl₄]⁻ and [Mes*NP-benzene][Ga₂Cl₇]⁻ are each structurally identical to free benzene,¹¹⁷ and there are no obvious distortions from planarity of the arene in any of the structures. The maximum deviations from planarity are: benzene [GaCl₄]⁻, 0.0029 Å; [Ga₂Cl₇]⁻, 0.005 Å; toluene [GaCl₄]⁻, 0.033 Å; [Ga₂Cl₇]⁻, 0.028 Å; and mesitylene [Ga₂Cl₇]⁻, 0.014 Å. Also, the P---Cl contacts increase in length as the P---arene_{centroid} distances decrease. Elongation of the P---Cl contacts can be rationalized in two ways: steric interactions restrict close approach of the anion; or arene coordination reduces the electrostatic attraction between phosphorus and the chlorine centers of the anion.

4.4 Spectroscopic Features of Arene Complexes of the Phosphoazonium Cation

The observed solid state features, specifically the change in the local coordination sphere of phosphorus with different anions and the variation of the P---arene interaction

Table 4.2: Comparison of IR data (cm^{-1}) for the arene in [Mes*NP-arene] complexes to the free arene.

Compound	Coordinated Arene	Free Arene
[Mes*NP-benzene][GaCl ₄]	1979	1960
	1842	1815
[Mes*NP-toluene][GaCl ₄]	weak and broad	1943
		1860
		1803
		1735
[Mes*NP-benzene][Ga ₂ Cl ₇]	1981	1960
	1849	1815
[Mes*NP-toluene][Ga ₂ Cl ₇]	1971	1943
	1892	1860
	1842	1803
	1787	1735
[Mes*NP-mesitylene][Ga ₂ Cl ₇]	1813	1759
	1784	1713
	1759	

with different arenes, produce significant spectroscopic differences with respect to the free arene. The FT-IR spectra of the salts are complex; however, overtone and combination bands in the 2000-1750 cm^{-1} region corresponding to the C-H out-of-plane deformations¹¹⁸ are well separated from other bands in the spectra. These bands are distinctive for the

arene (see Table 4.2), and their significant shifts with respect to those of the pure (free) arene¹¹⁹ are further evidence for interaction between the arene and the phosphorus center.

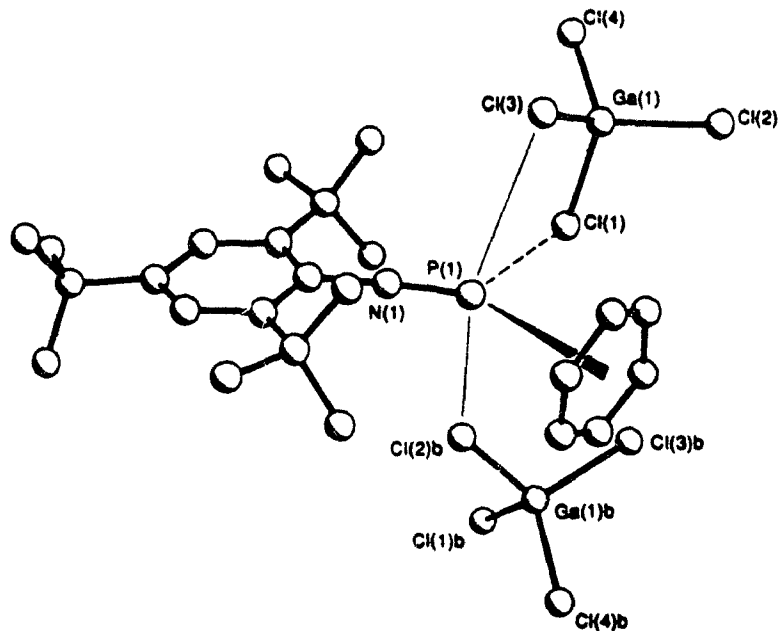


Figure 4.2: PLUTO view of [Mes*NP-benzene][GaCl₄] illustrating the distorted trigonal bipyramidal local coordination sphere around phosphorus.

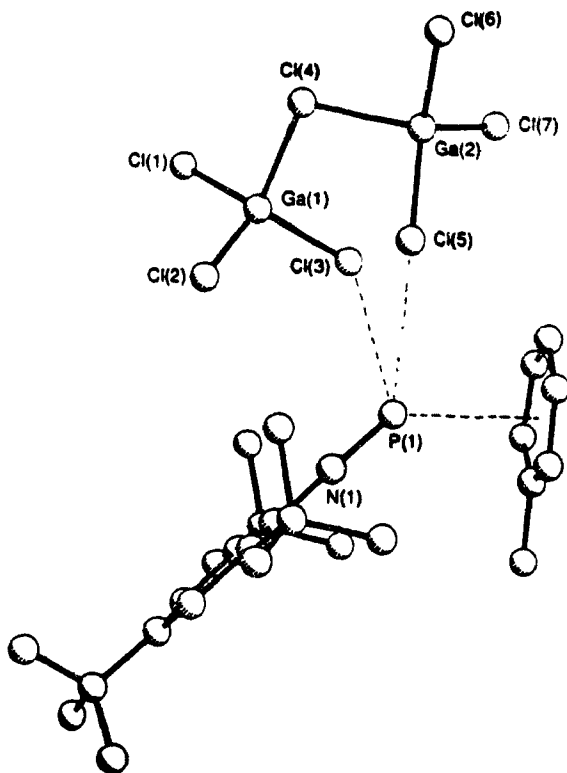


Figure 4.3: PLUTO view of [Mes*NP-benzene][Ga₂Cl₇] illustrating the distorted tetrahedral local coordination sphere around phosphorus.

Solution NMR spectra have been obtained for all salts (Table 4.3), both in the corresponding arene and in CD_2Cl_2 . ^{31}P NMR chemical shifts for the salts seem to be independent of the solvent, but there is a significant chemical shift difference (as large as 15 ppm) between the gallate and digallate salts. In general, the solution chemical shifts are

Table 4.3: ^{31}P NMR data for arene complexes of the phosphoazonium cation (ppm).

Compound	In Arene	In CD_2Cl_2	In Solid
$[\text{Mes}^*\text{NP}][\text{GaCl}_4]$	–	76	63
$[\text{Mes}^*\text{NP-benzene}][\text{GaCl}_4]$	78	76	NA
$[\text{Mes}^*\text{NP-toluene}][\text{GaCl}_4]$	78	76	79 ¹¹¹
$[\text{Mes}^*\text{NP-benzene}][\text{Ga}_2\text{Cl}_7]$	93	93	90
$[\text{Mes}^*\text{NP-toluene}][\text{Ga}_2\text{Cl}_7]$	91	95	89
$[\text{Mes}^*\text{NP-mesitylene}][\text{Ga}_2\text{Cl}_7]$	91	91	NA

consistent with those observed in the solid state. The arene free salt $[\text{Mes}^*\text{NP}][\text{GaCl}_4]$ reacts slowly with dichloromethane; however, spectra obtained within minutes

of sample preparation have a similar ^{31}P chemical shift (76 ppm) as those of the benzene and toluene complexes. This is in contrast to the ≈ 15 ppm difference observed between $[\text{Mes}^*\text{NP}][\text{GaCl}_4]$ and $[\text{Mes}^*\text{NP-toluene}][\text{GaCl}_4]$ in the solid state spectra, and suggests that solvation of the arene free salt involves a significant interaction with dichloromethane, which has an effect comparable to that of the coordinated arene. It is interesting to note that the nature of the anion has a dramatic effect on the ^{31}P chemical shift, supporting the existence of substantial ion pairing in solution.¹¹⁴

The coordinated arenes of the complexes in dichloromethane solution exhibit deshielding of the ^{13}C and ^1H nuclei (Table 4.4) with respect to those of the pure arene.¹²⁰

Table 4.4: Solution ^{13}C and ^1H NMR chemical shifts (δ , ppm, CD_2Cl_2) of the arenes in [Mes*NP-arene] complexes.

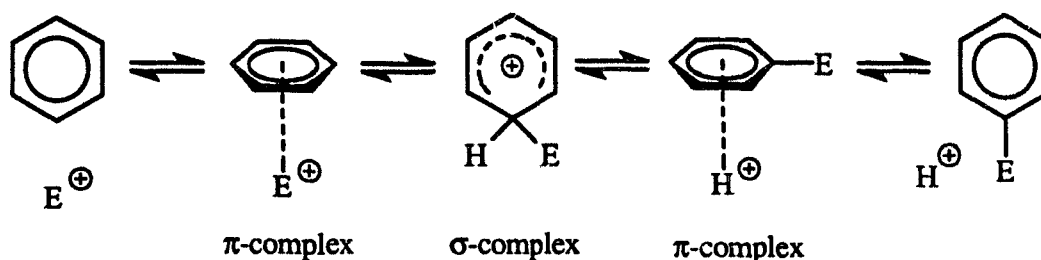
Compound	^{13}C NMR	^1H NMR
[Mes*NP-benzene][GaCl ₄]	128.7	7.38
[Mes*NP-toluene][GaCl ₄]	C ₂ 132.4	7.56-7.47
	C ₃ 131.4	(multiplet)
	C ₄ 128.1	7.49 Max
	CH ₃ 22.0	CH ₃ 2.48
[Mes*NP-benzene][Ga ₂ Cl ₇]	132.6	7.80
[Mes*NP-toluene][Ga ₂ Cl ₇]	C ₂ 134.4	7.76-7.66
	C ₃ 133.1	(multiplet)
	C ₄ 130.0	7.69 Max
	CH ₃ 22.3	CH ₃ 2.56
[Mes*NP-mesitylene][Ga ₂ Cl ₇]	131.1	7.21
	CH ₃ 21.6	CH ₃ 2.42
benzene	128.5	7.23
toluene	C ₂ 129.3	7.04 Max
	C ₃ 128.5	CH ₃ 2.29
	C ₄ 125.7	
	CH ₃ 21.4	
mesitylene	127.4	6.69
	CH ₃ 21.2	CH ₃ 2.23

This deshielding of the arene unit would be anticipated if the P---arene coordination observed in the solid state is retained in CD_2Cl_2 solution. The results support maintenance of arene coordination in solution, and the deshielding of the arene for [Mes*NP-benzene][Ga₂Cl₇] (^{13}C , 128.7, ^1H 7.38) and [Mes*NP-benzene][GaCl₄] (^{13}C ,

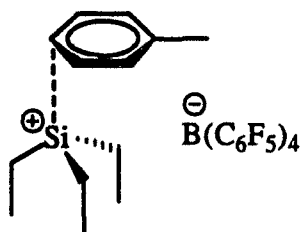
132.6, ^1H 7.80) is consistent with the P---arene_{centroid} distances observed in the solid state, 3.0012(6) Å and 2.820(4) Å, respectively.

4.5 Isolable π -Complexes as Models for Intermediates in Electrophilic Aromatic Substitution¹²¹

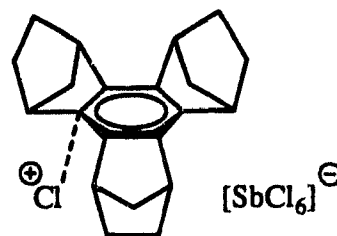
The electrophilic aromatic substitution reaction is one of the most important reactions in organic chemistry, and its mechanism has fascinated chemists for decades.¹²² There are a number of intermediates proposed in this mechanism [Equation 4.1]. Kinetic



studies first demonstrated the existence the σ -complex intermediate (also known as the Wheland intermediate).¹²³ Numerous examples of stable σ -complexes have been characterized spectroscopically,¹²⁴ and recently, two arene σ -complexes (**4.15**^{125, 126} and **4.16**)¹²⁷ have been isolated and characterized by X-ray crystallography. Furthermore, Olah *et al.*, have shown that solutions of **4.15** treated with strong bases ultimately produce phenylsilanes which can be rationalized as products of electrophilic



4.15

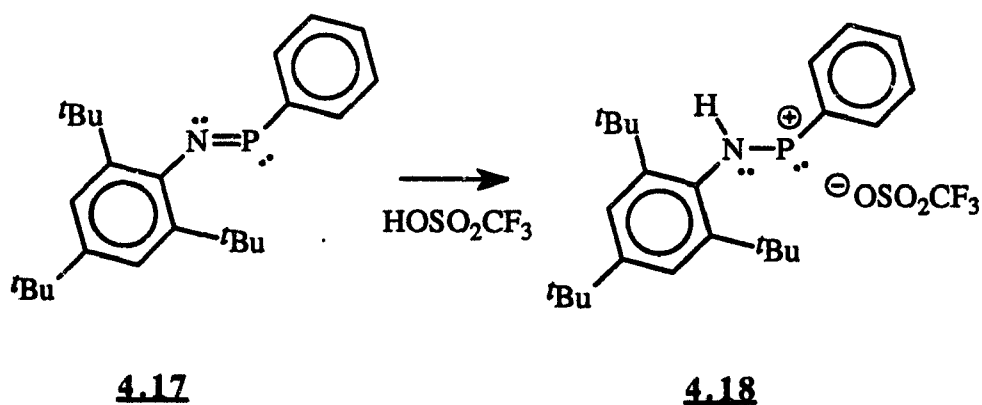


4.16

aromatic substitution.¹²⁸ This observation confirms the description of these compounds as stable Wheland intermediates.

A π -complex intermediate was proposed for the electrophilic aromatic substitution reaction by Dewar.¹²⁹ Kinetic data supporting the formation of π -complex intermediates was provided by Olah, who defined the complex as "an electrophile interacting with the aromatic substrate with little deformation of the latter in the transition state."¹³⁰ In other words, the electrophile is in weak association with the arene. A rate determining formation of π -complex intermediates has been disputed,¹³¹ and evidence for such systems is limited.

The arene (benzene, toluene and mesitylene) complexes of the phosphoazonium cation, [Mes*NP-arene], exhibit hexahapto (η^6) association of the arene with the phosphorus center and represent models of π -complex intermediates in electrophilic aromatic substitution. A careful examination of the literature also reveals a number of other structures which have been overlooked in this context. For example, arenes have been found to form π -complexes with the nitrosyl cation, [NO]⁺, which are reported to have much greater stability than the group 15 trihalide (*i. e.*, SbCl₃) complexes (*vide infra*).¹³²



(4.2)

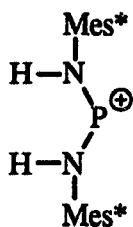
The arene complexes of the phosphoazonium cation, [Mes*NP-arene]⁺, provide

excellent models of π -complex intermediates in electrophilic aromatic substitution. The kinetic stability of the arene coordination complexes of the phosphoazonium cation $[\text{Mes}^*\text{NP-arene}]^+$ with respect to addition products is implied by the fact that reaction of the phenyliminophosphine **4.17**¹³³ with trifluoromethanesulfonic acid (HOSO_2CF_3) [Equation 3.2] quantitatively generates a compound with a ^{31}P NMR shift of 187 ppm. This signal is assigned to the aminophenylphosphenium cation **4.18**. This demonstrates the relative thermodynamic stability of the complexes with respect to the electrophilic addition product, or other possible structural arrangements. Phenylsilanes, in contrast, react when treated with strong acid to generate an arene and a silane (protodesilylation).¹³⁴ The presence of the large Mes^* substituent may render the σ -complex thermodynamically unstable with respect to the π -complex, thus facilitating the isolation of these intermediates.

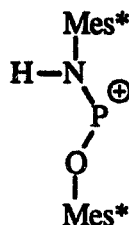
The complexes, $[\text{Mes}^*\text{NP-arene}]^+$, offer important comparisons with the recently reported silicon complex $[\text{Et}_3\text{Si-toluene}]^+$. The salt, $[\text{Et}_3\text{Si-toluene}][\text{B}(\text{C}_6\text{F}_5)_4]$,^{125,126} contains a formally cationic silicon center bound to a toluene molecule in an $\eta^1 \pi$ -coordination⁹⁰ or as a σ -complex¹³⁵ and is viewed as an example of a stabilized Wheland intermediate.⁹⁰ The dramatic differences in coordinative strength and hapticity (E-arene distance, $\text{Si} \cdots \text{C} = 2.18(1) \text{ \AA}$ in $[\text{Et}_3\text{Si-}\eta^1\text{-toluene}]^+$ ^{125,126} $\text{P} \cdots \text{C}_{\text{avg.}} = 3.31(3) \text{ \AA}$ for $[\text{Mes}^*\text{NP-}\eta^6\text{-toluene}][\text{GaCl}_4]$; $\text{P} \cdots \text{C}_{\text{avg.}} = 3.080(3) \text{ \AA}$ for $[\text{Mes}^*\text{NP-}\eta^6\text{-toluene}][\text{Ga}_2\text{Cl}_7]$) are related to the relative acidities of the cationic centers. While the silicon center of $[\text{Et}_3\text{Si}]^+$ **4.15** is truly electron deficient with the only possible resonance provided by hyperconjugation with the α -H's of the ethyl substituents, the phosphoazonium cation, $[\text{Mes}^*\text{NP}]$, can be described as the iminiumphosphine **4.2a**; isoelectronic to the phosphalkynes RCP.¹³⁶ In view of the significantly shorter $\text{Si} \cdots \text{toluene}$ interaction observed in the crystal structure of $[\text{Et}_3\text{Si-toluene}][\text{B}(\text{C}_6\text{F}_5)_4]$,^{125,126} spectroscopic features for the coordinated arene in the solid state, such as IR, should have alerted the researchers to the significance of the interaction.

4.6 Reaction of the Phosphoazonium Cation with Hydridic Bases

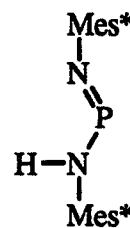
The phosphoazonium cation reacts rapidly and quantitatively with hydridic bases resulting in formal insertion of the P-N moiety into H-N and H-O bonds. For example, reaction of $[\text{Mes}^*\text{NP}]^+$ with Mes^*NH_2 in CH_2Cl_2 gives the symmetrical phosphonium



4.19



4.20



4.21

cation **4.19**. The structure of this molecule is established by spectroscopic techniques and is confirmed by an X-ray crystal structure. Similarly, ^{31}P NMR studies of the reaction of $[\text{Mes}^*\text{NP}]^+$ with Ph_2NH show rapid formation of the phosphonium cation $[\text{Mes}^*\text{N}(\text{H})\text{PNPh}_2]^+$ (249 ppm). Reaction of $[\text{Mes}^*\text{NP}]^+$ with Mes^*OH produces a single phosphorus-containing species with a ^{31}P NMR shift of 290 ppm. The bright yellow microcrystalline powder from this reaction is characterized by elemental analysis, IR, and solution and solid state NMR as the first aryloxy-substituted phosphonium cation **4.20**.

4.7 Structural and Spectroscopic Features of Two New Phosphonium Cations

The structure of **4.19** exhibits the structural features typical of other aminophosphonium centers (Figure 5.1).¹¹⁴ The phosphorus atom of **4.19** exhibits two contacts with the anion, $[\text{GaCl}_4]^-$ ($\text{P} \cdots \text{Cl}$ 3.854(2) Å), as well as hydrogen bonding with each $[\text{GaCl}_4]^-$ with two $\text{H} \cdots \text{Cl}$ bonds (2.52 Å). As illustrated in Figure 4.4, each $[\text{GaCl}_4]^-$ exhibits four-fold coordination with two $\text{P} \cdots \text{Cl}$ contacts and two $\text{H} \cdots \text{Cl}$ contacts.

Spectroscopic data are consistent with the structures of **4.19** and **4.20**. For example, characteristic IR absorptions for N-H (ν_{NH} **4.19** 3175 cm⁻¹, **4.20** 3120 cm⁻¹) and [GaCl₄]⁻ are evident. Also, ¹H NMR data confirm the symmetric nature of **4.19** and display a distinct N-H resonance at 9.94 ppm. ¹H NMR data for **4.20** is consistent with the formation of an aminoxyphosphenium cation with a broad N-H resonance at 10.9 ppm.

Solid state ³¹P CP-MAS NMR data show large chemical shift anisotropy (span = Ω = $\delta_{11} - \delta_{33}$) characteristic for phosphonium¹³⁷ and related carbene sites.¹³⁸ Figures 4.6 and Figure 4.7 show, respectively, a ³¹P CP static powder spectrum and a ³¹P CP-MAS

powder spectrum for **4.19**.

Chemical shift tensors for

4.19 and **4.20** are presented

in Table 4.5. Included in this

table are chemical shift tensors

which have been calculated by

Dr. Klaus Eichele and Prof.

Rod Wasylishen for model

Table 4.5: Experimental and calculated phosphorus chemical shift tensors (in ppm) of aminophosphenium and iminophosphine centers (R = Mes*).

Compound	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω
RNH-P=NR	281	628	124	90	538
[RNH-P-NHR] ⁺	281	624	167	51	573
[RNH-P-OR] ⁺	308	670	124	124	546
H ₂ N-P=NH	301	815	58	31	784
[H ₂ N-P-NH ₂] ⁺	242	623	136	-32	655
[H ₂ N-P-OH] ⁺	268	692	59	54	638

compounds H₂NP=NH, [H₂NPNH₂]⁺, and [H₂NP⁺OH]⁺. These values are in good

agreement with the observed Mes* substituted compounds. Also note that the chemical

shift anisotropy of **4.19** is similar to that of its conjugate base, Mes*N(H)PNMes*

4.21.¹³⁹ It is obvious that the formal positive charge at phosphorus is not reflected in

the ³¹P chemical shift, contrary to popular understanding.¹⁴⁰ The effect of charge on ³¹P

chemical shifts is readily appreciated when one considers the chemical shift of 328 ppm for

the bare phosphorus nucleus P¹⁵⁺.¹⁴¹ It is also interesting to note that **4.19** has similar

structural features to **4.21**, and these include N-P-N, 103.8(5)°; P-N, 1.633(8) Å; and

P=N, 1.573(8) Å.

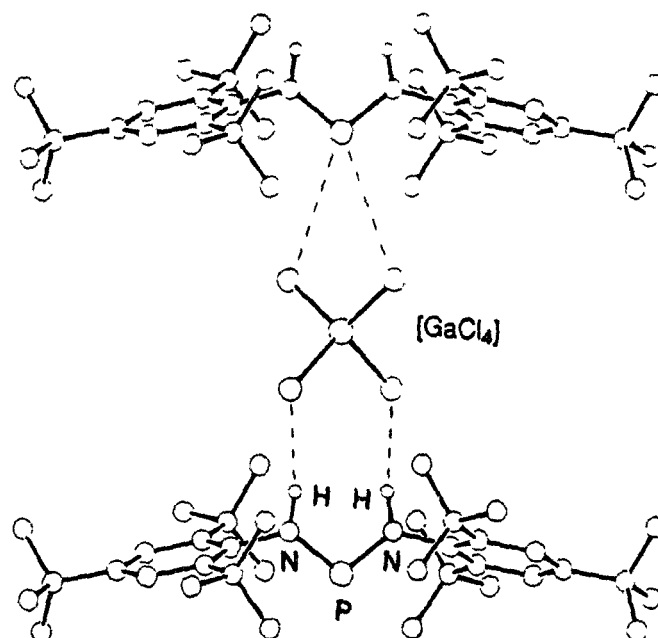


Figure 4.4: PLUTO view of $[\text{Mes}^*\text{N}(\text{H})\text{PN}(\text{H})\text{Mes}^*][\text{GaCl}_4]$ **4.19** showing two cations and one anion. The hydrogen atoms (except N-H) have been omitted for clarity. Important bond lengths ($\text{\AA}$) and angles ($^\circ$): N-P 1.613(3), N- C_{Mes^*} 1.473 (4), N-P-N 104.2(2), P-N- C_{Mes^*} 126.6(2).

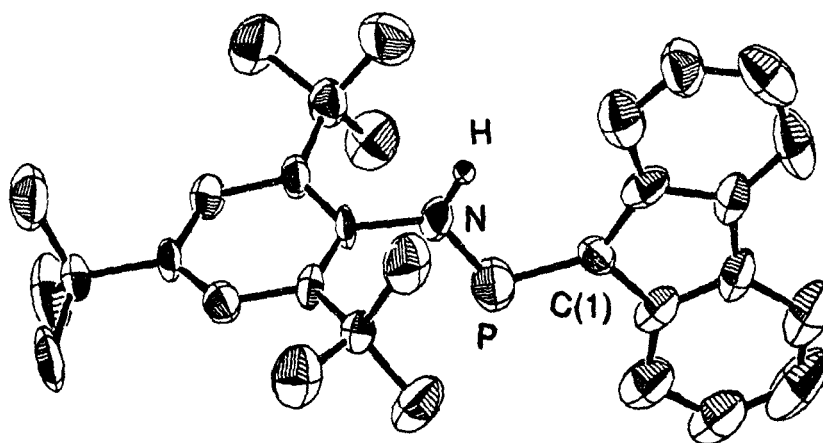


Figure 4.5: ORTEP view of $\text{Mes}^*\text{N}(\text{H})\text{P}=\text{fluorenylidene}$ **4.22** (50 % probability ellipsoids). The hydrogen atoms (except N-H) have been omitted for clarity. Important bond lengths ($\text{\AA}$) and angles ($^\circ$): P-C(1) 1.706(7), P-N 1.639(6), N- C_{Mes^*} 1.458(8), N- C_{Mes^*} 1.458(8), N-P-C(1) 109.9(4), P-N- C_{Mes^*} 121.2(5).

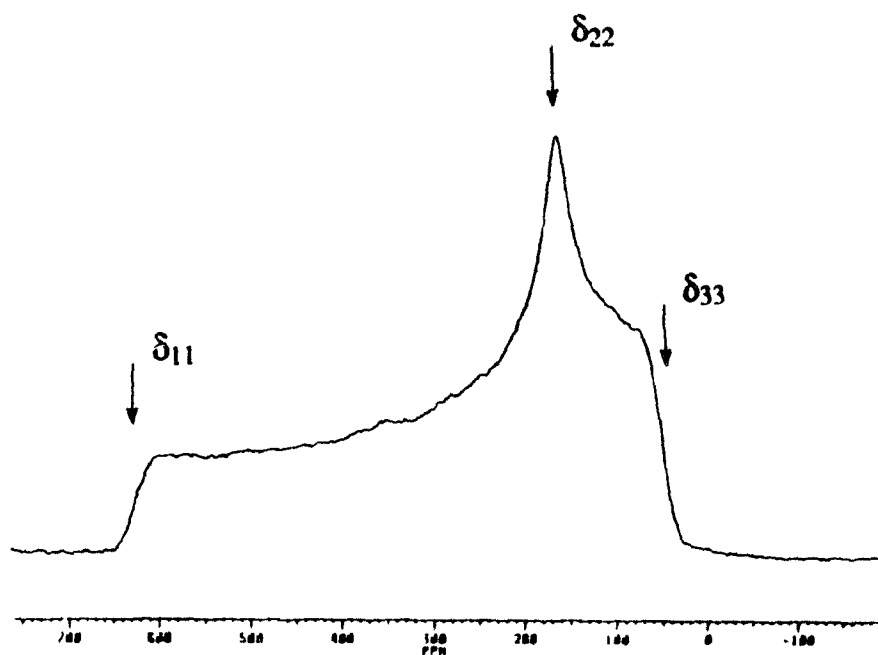


Figure 4.6: ^{31}P CP NMR spectrum for a static powder sample of $[\text{Mes}^*\text{N}(\text{H})\text{PN}(\text{H})\text{Mes}^*]$ **4.19** obtained on an MSL-200 spectrometer.

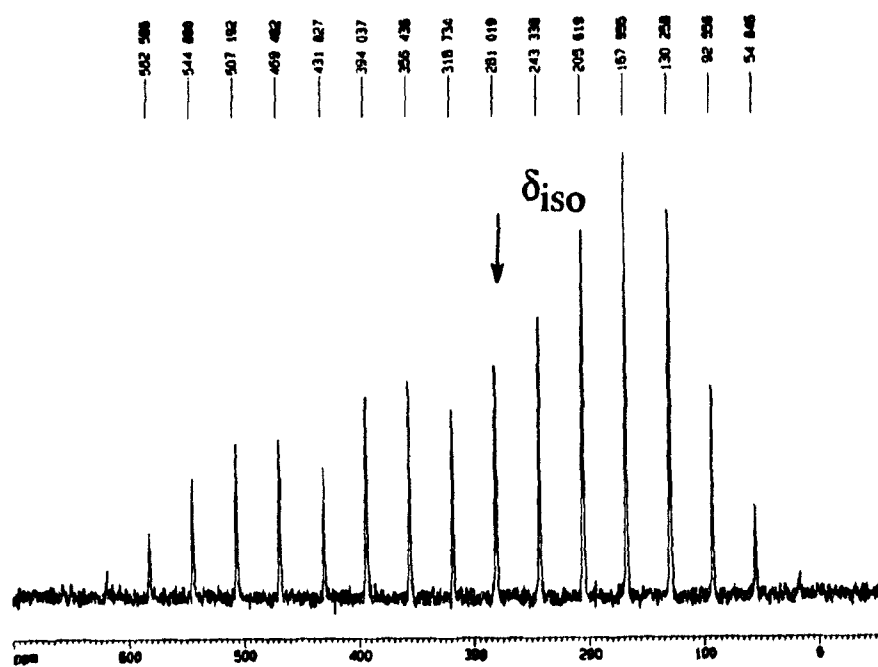
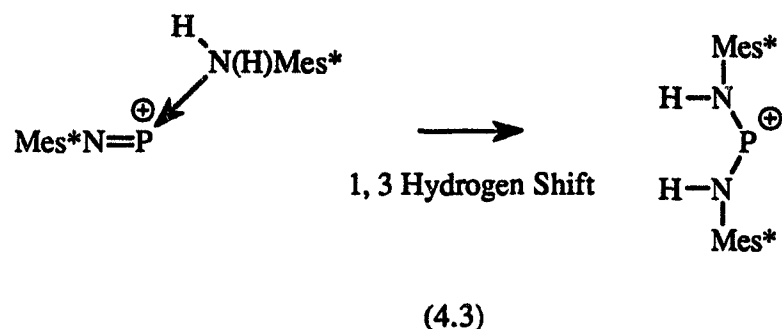


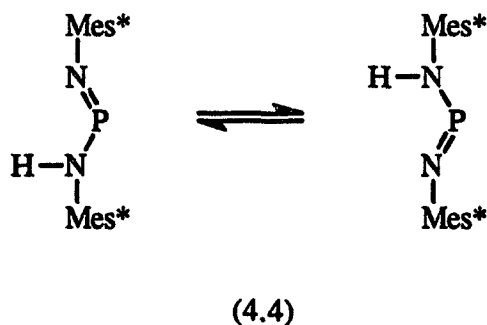
Figure 4.7: ^{31}P CP-MAS NMR spectrum for a spinning (6103 Hz) powder sample of $[\text{Mes}^*\text{N}(\text{H})\text{PN}(\text{H})\text{Mes}^*]$ **4.19** obtained on an Bruker AMX 400 spectrometer.

4.8 Proposed Mechanism For Phosphoazonium Cation Insertion Reactions

Formation of cations **4.19** and **4.20** represents a formal insertion of the NP group into the N-H and O-H bonds of the hydridic bases. Given the demonstrated ability of the



phosphoazonium cation to form complexes with both σ and π donors, a mechanism is proposed [Equation 4.3] involving a σ -coordination complex, followed by a 1, 3 hydrogen shift from the base to the imino-nitrogen center. 1, 3 hydrogen shifts,^{142,143} as well as related silyl shifts,¹⁴⁴ have been documented for neutral iminophosphines, but are usually facilitated by an external base or heating, except in the case of $\text{Mes}^*\text{N(H)PNMes}^*$.¹⁴⁵ A slow tautomerism had previously been observed *via* Nuclear Overhauser Effects for

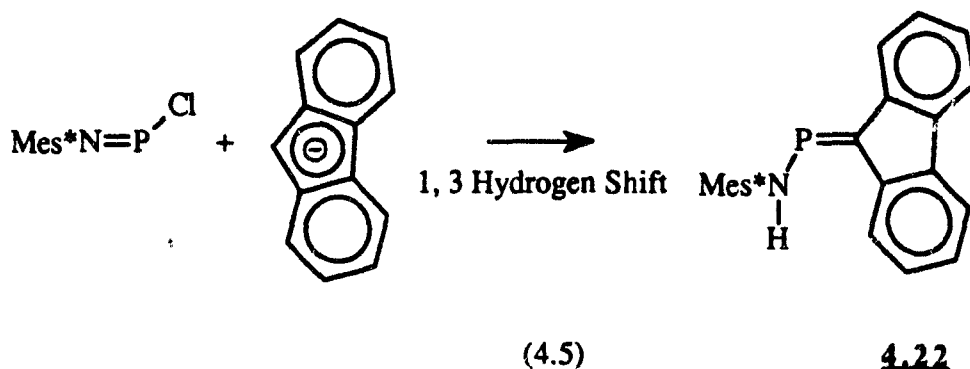


$\text{Mes}^*\text{N(H)PNMes}^*$ [Equation 4.4], and this is confirmed *via* ^{15}N -labelled experiments.

$\text{Mes}^*^{15}\text{NPCl}$ reacts with LiN(H)Mes^* in ether (0 °C), and isolation of the reaction product

after only twenty minutes in solution indicates a 1:1 mixture of two isotopomers, $\text{Mes}^*\text{N}(\text{H})\text{P}^{15}\text{NMes}^*$ and $\text{Mes}^*^{15}\text{N}(\text{H})\text{PNMes}^*$, as characterized by IR ($\nu^{15}\text{N-H}$ 3338 and $\nu^{14}\text{N-H}$ 3344 cm^{-1}) and ^{31}P and ^{15}N NMR spectroscopy. The rapid equilibration of these two isotopomers suggests that the prototropic tautomerization [Equation 4.4] has a low kinetic barrier.

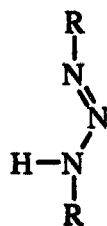
The reaction of Mes^*NPCl with fluorenyllithium [Equation 4.5] results in the quantitative formation of the aminophosphaalkene **4.22**, which illustrates the prevalence of the 1, 3 hydrogen shift for dicoordinate phosphorus systems. The structure of the



phosphaalkene $\text{Mes}^*\text{N}(\text{H})-\text{P}=\text{fluorenylidene}$ is confirmed by the distinct $\nu_{\text{N-H}}$ absorption in the IR spectrum at 3413 cm^{-1} and the corresponding doublet in the ^1H NMR at 6.85 ($^2J_{\text{PH}} = 11$ Hz). An X-ray crystal structure of this molecule is shown in Figure 4.5.

The well established reaction of a diazonium cation with a 1° or 2° amine to give a triazene⁸¹ **4.23** likely involves a similar reaction pathway [Equation 4.3]; however, since these reactions are typically performed in protic media (*e. g.*, water or alcohol), isolation of the intermediate nitrenium cations may not be possible. The cationic intermediates may be deprotonated in these solvents to give the observed triazenes. Indeed, the 1, 3 hydrogen shift observed for $\text{Mes}^*\text{N}(\text{H})\text{PNMes}^*$ is analogous to tautomerisms well established for triazenes **4.23**.⁸¹

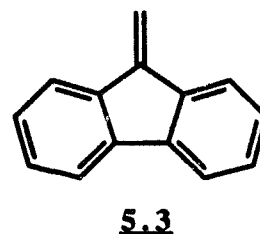
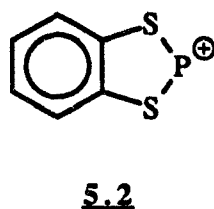
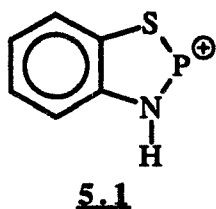
These results show the synthetic versatility of the insertion of [Mes*NP]⁺ into element-H bonds to generate new phosphonium cations. For example, this strategy provides the first example of a cationic N-P-O framework, in spite of numerous examples of neutral oxy-substituted iminophosphines.¹⁴⁶



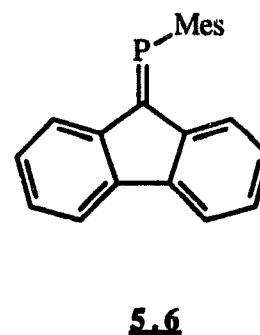
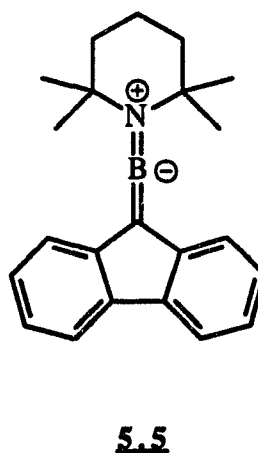
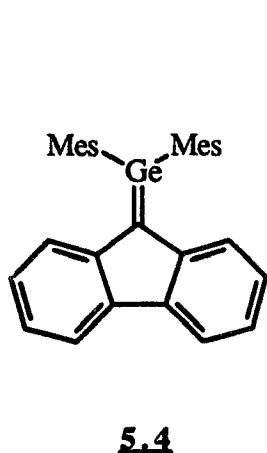
4.23

Chapter 5 Fluorenylidene Methylene phosphonium Cations

Sterically demanding groups can stabilize multiple bonds between heavy elements *via* thermodynamic destabilization of alternative structures (*vide supra*). In contrast, the stability of phosphonium cations **5.1** and **5.2** results from the incorporation of the low

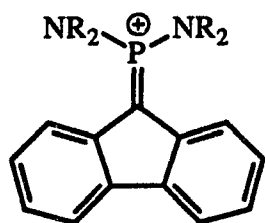
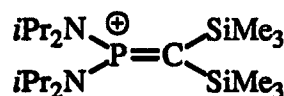


coordinate phosphorus center within a Hückel 10 π -electron system.¹⁴⁷ The fluorenylidene unit **5.3** is an attractive substituent for the development of new bonding environments, as it offers both steric and electronic stabilizing features. Consequently, it has been used to prepare the first methylenegermane **5.4**,¹⁴⁸ and also novel boron **5.5**¹⁴⁹ and phosphorus compounds **5.6**.¹⁵⁰



On the basis of spectroscopic data, the first methylenephosphonium cation **5.7** was

proposed as the result of halide abstraction from a fluorenylidene substituted phosphorane.¹⁵¹ These conclusions have been refuted after comparison with a structurally characterized methylenephosphonium cation **5.8**.¹⁵² Tricoordinate phosphonium cations are isoelectronic to alkenes and are of theoretical interest.¹⁵³ It is surprising that very little chemistry of these compounds has been explored, and much of our knowledge of these species is dominated by the fact that they are thermodynamically unstable with respect to

**5.7****5.8**

intramolecular electrocyclic ring closure,¹⁵⁴ covalent alternatives,¹⁵⁵ or other decomposition pathways.¹⁵⁶

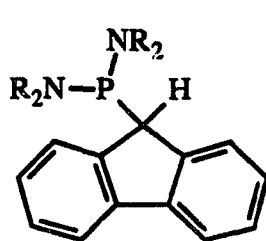
5.1 Precursors to Methylenephosphonium Cations

Preparation of chlorophosphoranes involves a two step reaction sequence beginning with a chlorophosphine $[R_2N]_2P-Cl$, $R = iPr$, and $R = Et$. Reaction of fluorenyllithium with the $[iPr_2N]_2P-Cl$ and $[Et_2N]_2P-Cl$ generates the fluorenyl-phosphorus bond giving fluorenyl phosphines **5.9a** and **5.9b**, respectively. The reactions proceed quantitatively in ether solution (0 °C), and crystalline $[iPr_2N]_2P$ -fluorenyl **5.9a** is readily obtained from hexane solution.

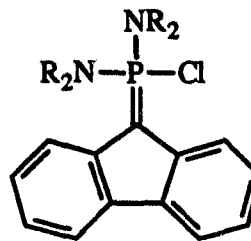
The structure of **5.9a** is shown in Figure 5.1 and contains a severely disordered phosphorus atom. This disorder is modelled with two phosphorus positions. The carbon

C(1) of the fluorenyl fragment is tetrahedral and the P-C bond length is 1.99(7) Å.

Unfortunately, the disorder in the molecule does not allow for meaningful comparison with other P-C bonds such as in PMe_3 (1.85 Å),¹⁵⁷ and related pentamethylcyclopentadienyl-



5.9a R = *i*Pr
5.9b R = Et

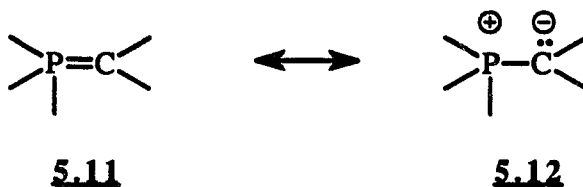


5.10a R = *i*Pr
5.10b R = Et

phosphorus compounds such as $\text{Cp}^*\text{P}=\text{PCp}^*$ 1.893(7) Å and 1.883(7) Å,¹⁵⁸ and $[\text{Cp}^*\text{-P-N(H)-}i\text{Bu}][\text{AlCl}_4]$ 1.990(2) Å.¹⁵⁹ Although in each case the Cp^* substituted compounds exhibit ring whizzing as shown by NMR spectroscopy in both solution and the solid state, the structures show attachment of the phosphorus atom to a single distorted tetrahedral carbon center of the Cp^* ring; indicating of a monohapto (η^1) interaction. Recognizing fluorenyl as a derivative of Cp^* , **5.9a** can be viewed as an intimate-ion pair coordination complex between the fluorenyl anion and the diaminophosphenium cation, $[(i\text{Pr}_2\text{N})_2\text{P}]$. The ^{31}P NMR chemical shift for **5.9a** (71 ppm) is substantially upfield from that of the free cation $[(i\text{Pr}_2\text{N})_2\text{P}][\text{GaCl}_4]$ ^{31}P 313 ppm,¹¹⁴ but is consistent with the DBU complex $[(i\text{Pr}_2\text{N})_2\text{P} \leftarrow \text{DBU}][\text{PF}_6]$ 108 ppm.¹⁶⁰

The phosphines **5.9a** and **5.9b** react quantitatively with CCl_4 to yield the chlorophosphoranes **5.10a** and **5.10b**. An ORTEP view of **5.10a** is shown in Figure 5.2 and illustrates the anticipated steric crowding. This crowding is manifest in CD_2Cl_2 solution with ^1H and ^{13}C NMR spectra, indicating two distinct types of *i*Pr- groups. This implies restricted rotation around the P-N bonds. Similarly, **5.10b** exhibits a single resonance for the Et groups at room temperature; however, this resonance broadens on

cooling, suggesting a barrier to rotation around the P-N bond. The P=C bond is short, 1.698(7) Å, and is typical of other methylenephosphoranes such as *t*Bu₂(Cl)P=CPh₂, 1.673 (5) Å, 1.667 (5) Å,¹⁵⁶ 1.668(5) Å; Ph₃P=C(cyclopropyl), 1.696(6) Å;¹⁶¹ *i*Pr₃P=CMe₂ 1.731(3) Å.¹⁶²



Two reasonable Lewis structures can be drawn to represent methylenephosphoranes, **5.11** (*ylene*) and **5.12** (*ylide*). There has been much controversy concerning their relative contributions; however, most experimental and theoretical data supports the dominance of the *ylide* form, with little participation of the *ylene* form.¹⁶³ X-ray crystal structures of methylenephosphoranes indicate slightly distorted tetrahedral environments for phosphorus (*sp*³), and in the case of compounds which lack substituents on carbon to engage in delocalization, the carbon centers are pyramidal. The shortness of the P-C bond can be attributed to electrostatic attraction between phosphorus and carbon. The upfield ¹³C chemical shifts of the carbon centers are consistent with carbanionic character.¹⁶⁴ Caution should therefore be taken where methylenephosphoranes are illustrated in the *ylene* form. For the purposes of chemical reactivity the dipolar *ylide* form is more appropriate.

The ylidic carbon center in **5.10a** is planar, consistent with other Cp and Cp* substituted phosphoranes; thus suggesting that the resonance structure **5.13a** is important.

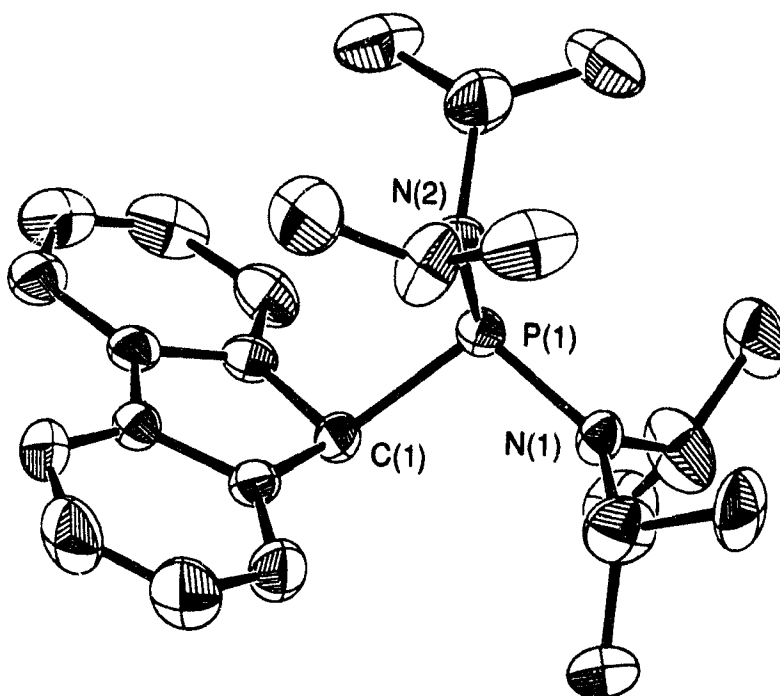


Figure 5.1: ORTEP view of $[iPr_2N]_2P$ -fluorenyl (**5.9h**) (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity.

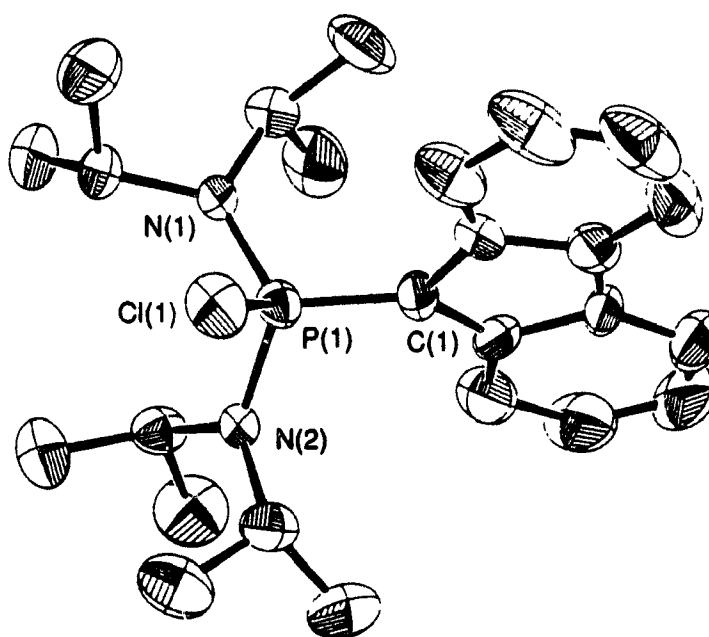
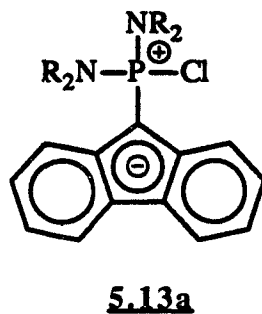


Figure 5.2: ORTEP view of $[iPr_2N]_2P(Cl)=$ fluorenylidene (**5.10h**) (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity. Important bond lengths (Å) and angles (°): P(1)-C(1) 1.698(7), P(1)-Cl(1) 2.085(3), P(1)-N(1) 1.634(6), P(1)-N(2) 1.668(5), Cl(1)-P(1)-N(1) 102.9(2), Cl(1)-P(1)-N(2) 104.4(2), Cl(1)-P(1)-C(1) 107.3(3), N(1)-P(1)-N(2) 111.4(3), N(1)-P(1)-C(1) 117.3(3), N(2)-P(1)-C(1) 112.1(3).

in the extremely large $^1J_{PC}$ values (**5.10a**, 201 Hz; **5.10b**, 205 Hz), which are among the largest yet observed for methylenephosphoranes.¹⁶³



The chlorine atom of the phosphorane **5.10a** is almost in the plane defined by the fluorenylidene substituent [Cl-P-C₁-C₂ 151.5(6)[°]; Cl-P-C₁-C₈ -33.7(7)[°]]. Such an arrangement precludes interaction between the π framework of the fluorenylidene moiety and the σ^* orbital of the P-Cl bond, and as a result, the P-Cl bond in **5.10a** is short (2.085(3) Å). It is argued that hyperconjugation accounts for the long P-Cl bonds in *t*Bu₂(Cl)P=CPh₂, 2.195(2) Å, 2.228(2) Å, and 2.235(2) Å¹⁵⁶ where even weak Lewis acids, such as SnCl₂, can effect halide ion abstraction to give methylenephosphonium cations.

X-ray structures of three fluorenyl and fluorenylidene compounds provide an opportunity to assess the ligand for different coordination environments at phosphorus (Figure 5.3). The bond alternation observed in fluorene **5.14**¹⁶⁵ arises from the presence of a saturated C(1), whereas in the “naked” fluorenyl anion **5.15**¹⁶⁶ the 14 π -electron delocalized framework results in shorter bonds for bridging C(1). Based on these data, **5.9a** is best viewed as a fluorenyl ligand with a saturated C(1) center, whereas **5.10a** and **5.16** have delocalized fluorenylidene rings.

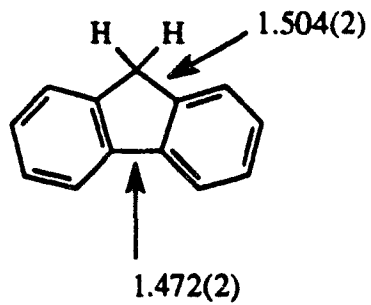
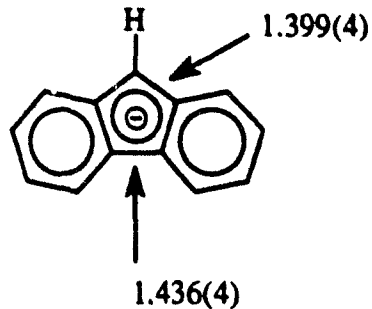
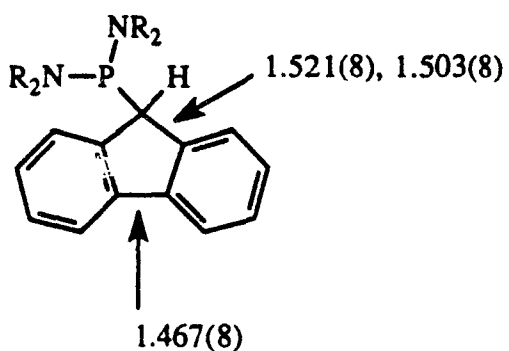
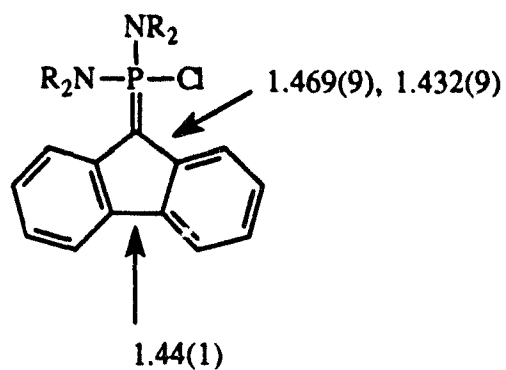
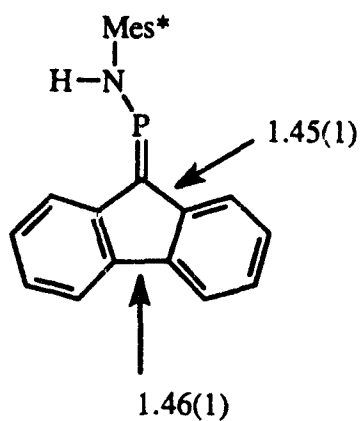
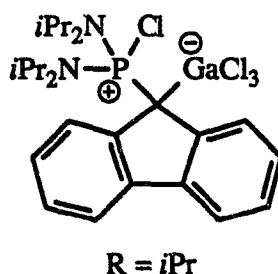
**5.14****5.15****5.9a****5.10a****5.16**

Figure 5.3: Comparison of three fluorenyl phosphorus derivatives with fluorene and the fluorenyl anion. Distances are in Å.

5.2 Ring Expansion Isomerism of a Fluorenylidenephosphonium Cation

Methylenephosphorane **5.10a** reacts rapidly with a stoichiometric amount of GaCl_3 in CH_2Cl_2 to give a single phosphorus containing species with a ^{31}P NMR chemical shift of 71 ppm. This material has a very low solubility in benzene and can be quantitatively precipitated. It has not been possible to recrystallize this material because of its facile isomerization (*vide infra*). ^1H and ^{13}C NMR data are not informative; however, it is



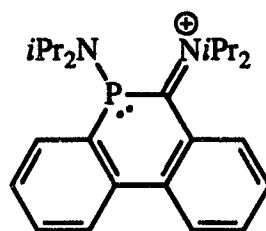
5.17a

reasonable to speculate on the formation of a coordination complex involving a carbon-gallium coordinate bond, **5.17a**, similar to those reported for other ylide/Lewis acid adducts.¹⁶⁷ The complex can be viewed as a zwitterionic fluorenylphosphonium derivative with the fluorenyl C-H replaced by C- GaCl_3 . Formation of this covalent complex is in contrast to the ionic structure observed for $[\text{tBu}_2\text{P}=\text{C}(\text{SiMe}_3)_2][\text{AlCl}_4]$ (^{31}P NMR 130 ppm).¹⁶⁸ Similarly, **5.10b** reacts with GaCl_3 in CH_2Cl_2 to give a single phosphorus-containing species with a chemical shift of 71 ppm.

Further support for the formation of the Lewis acid adduct is provided by the reaction of **5.10b** with HOSO_2CF_3 . The reaction is quantitative and produces a compound whose solution NMR spectra are consistent with the formation of $[(\text{Et}_2\text{N})_2\text{P}(\text{Cl})\text{-fluorenyl}][\text{OSO}_2\text{CF}_3]$. For example, the magnitude of $^1\text{J}_{\text{PC}}$ (79 Hz) and ^{13}C multiplicity analysis of this carbon center are in accord with the protonation of the

ylidic carbon to give a phosphonium cation.¹⁶⁹ Indeed, the *ylide* resonance structure **5.12** would predict that electrophilic attack by GaCl₃ would occur on the *ylidic* carbon in preference to halide ion abstraction from a phosphonium center.

The GaCl₃ complex **5.17a** is soluble in polar solvents such as CH₂Cl₂, but reacts giving a red solution with a single ³¹P NMR signal at 21 ppm. The reaction is complete within eight hours. The formation of this red solution was noted in the original report; however, characterization of the compound was not attempted.^{151, 170} Slow removal of solvent produces a red crystalline material, which is isolated in high yield and characterized as 9-di-*i*-propylamino-10-di-*i*-propyliminium-9, 10-dihydro-9-phosphaphenanthrene tetrachlorogallate **5.18**. The presence of a C=N bond is clearly revealed in the IR



5.18

spectrum with a strong absorption at 1582 cm⁻¹,¹⁷¹ as well as a distinct signal in the ¹³C NMR spectrum at 213.9 ppm (d, ¹J_{PC} = 89 Hz). A crystallographic view of the cation is shown in Figure 5.4.

The salt **5.18** is isomeric to the zwitterionic fluorenyl-phosphonium-GaCl₃ complex **5.17a**. No intermediates are observed in low temperature ³¹P NMR studies; nevertheless, isomerization of the neutral fluorenylphosphonium in polar solvents implicates the formation of a polar intermediate, possibly the tetrachlorogallate salt of the methylenephosphonium cation **5.7a**. A proposed mechanism is presented Figure 5.5. Solutions of **5.17b** in CH₂Cl₂ do not isomerize and remain unchanged for periods of several months. Attempts to isolate the reaction products from these solutions result in the

formation of an oily material. The stability of **5.17b**, in contrast to the facile isomerization of **5.17a**, suggests that the reaction is driven by the release of steric stresses in the fluorenyl-phosphonium- GaCl_3 complex due to the increased steric demands of the *N*-alkyl groups (*i. e.*, *i*Pr vs Et).

The quantitative rearrangement is unique in terms of the nature of the bonds broken and formed, and further demonstrates the thermodynamic instability of the tricoordinate phosphonium environment. Ring expansions *via* Beckman rearrangements have been reported for fluorenone oximes.¹⁷² In addition, such an isomerization is unprecedented in the chemistry of phosphorus ylides despite extensive research.¹⁷³

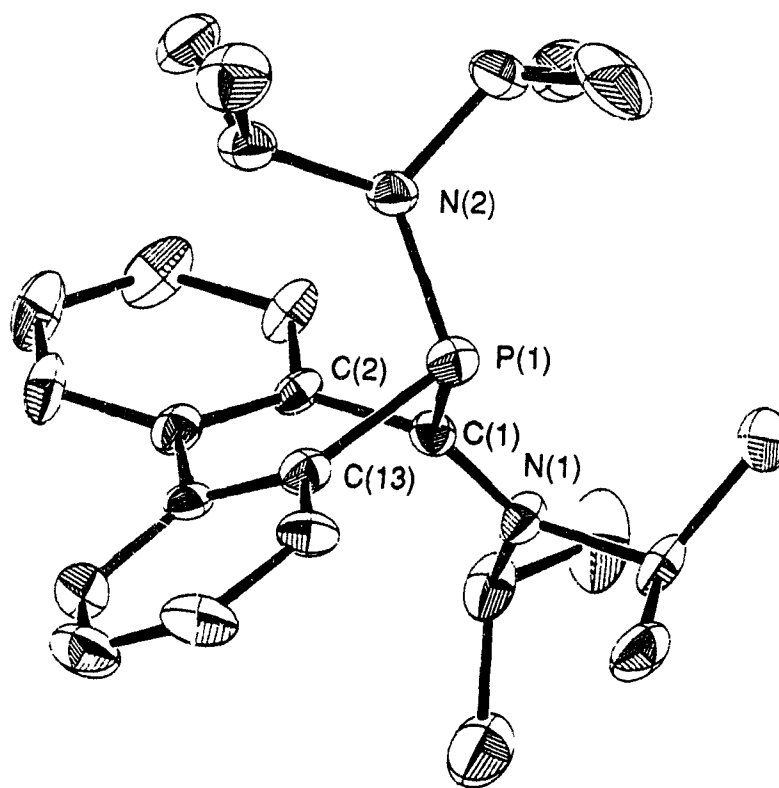


Figure 5.4: ORTEP view of 9-di-*i*-propylamino-10-di-*i*-propyliminium-9,10-dihydro-9-phosphaphenanthrene **5.18** (50% probability ellipsoids). The hydrogen atoms have been omitted for clarity. Important bond lengths (Å) and angles (°) P(1)-N(2) 1.667(6), P(1)-C(1) 1.905(8), P(1)-C(13) 1.822(8), N(1)-C(1) 1.305(9), N(2)-P(1)-C(1) 105.6(3), N(2)-P(1)-C(13) 105.0(3), C(1)-P(1)-C(13) 88.8(3), Σ angles at N(1) 359.9(6), Σ angles at N(2) 359.2(5), Σ angles at C(1) 359.8(6).

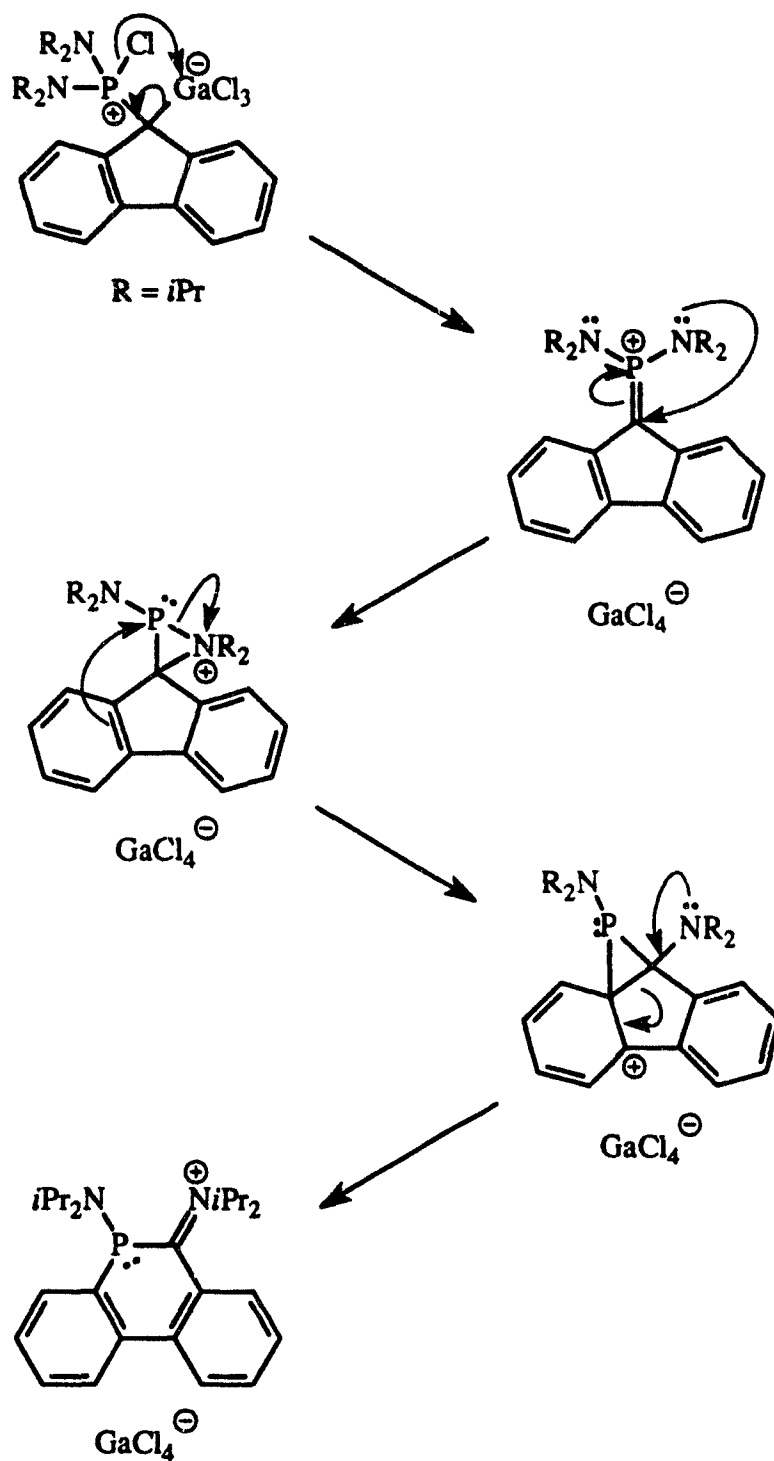
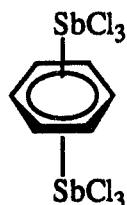


Figure 5.5: Proposed mechanism for the isomerization of **5.17a**.

Chapter 6 Bis-Arenes as Four Site Donors to Antimony Trichloride

A general feature of arene complexes of the heavier *p*-block elements is structural diversity. Variations include the hapticity of the metal---arene interaction, and the metal:arene ratio (*i. e.*, sandwich, half sandwich, and inverse sandwich structures). The limited data on *p*-element---arene complexes indicate that many elements prefer the inverse sandwich arrangement with an arene donor sandwiched by two acceptors.¹⁷⁴ Despite an extensive study by Schmidbaur,¹⁷⁵ it is still not clear which factors govern the structure and stoichiometry of these complexes. In addition, the *p*-element---arene interaction is weak because of the lack of σ donor/ π acceptor synergism, generally associated with transition metal complexes. For the *p*-elements, *d* core electrons are not available for back-bonding.¹⁷⁶

One of the most extensively studied series of main group element arene complexes are the arene complexes of the antimony trihalides (Menshutkin complexes),¹⁷⁷ but this class is often extended to include all arene complexes of EX_3 ($E=As, Sb, Bi, X=Cl, Br, I$). "Half sandwich" and "inverse sandwich" **6.1** complexes of neutral aromatic hydrocarbons and SbX_3 ($X=Cl, Br, I$), are readily prepared.



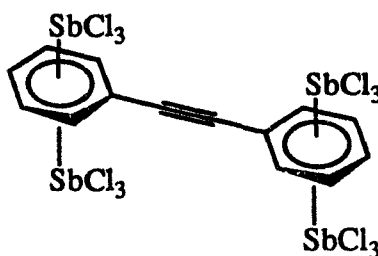
6.1

Most of the arene ligands examined to date have been monoarenes (*i.e.*, single arene donors such as benzene¹⁷⁸ and various alkylated benzenes).^{179,180} There appears to be no obvious reason for the 1:2 or 1:1 stoichiometries that are observed. Poly-arenes

which have been examined include naphthalene,¹⁸¹ phenanthrene,¹⁸² and pyrene (SbBr₃).¹⁸³ A few examples are known with bifunctional arene donors that do not contain fused rings, including biphenyl,¹⁸⁴ 9,10-dihydroanthracene (SbBr₃),¹⁸⁵ and diphenylamine;¹⁸⁶ however, maximum coordinating ability of the arenes in such species has not been realized (*i. e.*, not all arene rings of the poly-arene engage two SbCl₃ molecules). For example, biphenyl forms 2 SbCl₃:biphenyl despite potential for engaging four molecules of SbCl₃.

6.1 Preparation of 4 SbCl₃:Bis-Arene Complexes

Crystalline adducts of SbCl₃ with the general form 4 SbCl₃:bis-arene are readily prepared with bis-arenes diphenylacetylene **6.2**, *trans*-stilbene and bibenzyl. Direct



6.2

combination of the bis-arene with four equivalents of SbCl₃ in CH₂Cl₂ solution produces the adducts in high yield as analytically pure compounds.

A macroscopic characteristic of the 4 SbCl₃:bis-arene complexes is their beautiful

Table 6.1: Comparison of melting points (°C) for 4 SbCl₃:bis-arene complexes. N.B: mp. SbCl₃ 73 °C.

Arene	Complex	Pure Bis-arene
diphenylacetylene	76-78	59-61
<i>trans</i> -stilbene	101-103	122-124
bibenzyl	78-79	50-53

crystalline form (clear plates, some as large as 10 mm x 10 mm x 2 mm) which are readily soluble in CH₂Cl₂ and significantly less soluble in hexane. The complexes acquire a light green color upon

exposure to moist air; however, they are stable when stored under dry nitrogen. The complexes have been characterized by melting points (Table 6.1), which are sharp and distinctly different from the original starting materials. As pure compounds, both SbCl_3 and the bis-arenes are volatile and are conveniently purified by vacuum sublimation. The 4 SbCl_3 :bis-arene complexes remain unchanged after evacuation (ca. 10^{-3} Torr) for 24 hours as shown by elemental analysis.

One of these complexes (bibenzyl) was originally described in an abstract;¹⁸⁷ however, this report was brief, consisting only of cell parameters and the space group of the complex. Full description of the sample preparation and an interpretation of the crystallographic data has not been published. This report also mentions a 2 SbCl_3 :bis-arene complexes (*t*-stilbene and bibenzyl) as well as reference to the “instability” of a 4:1 bibenzyl complex.

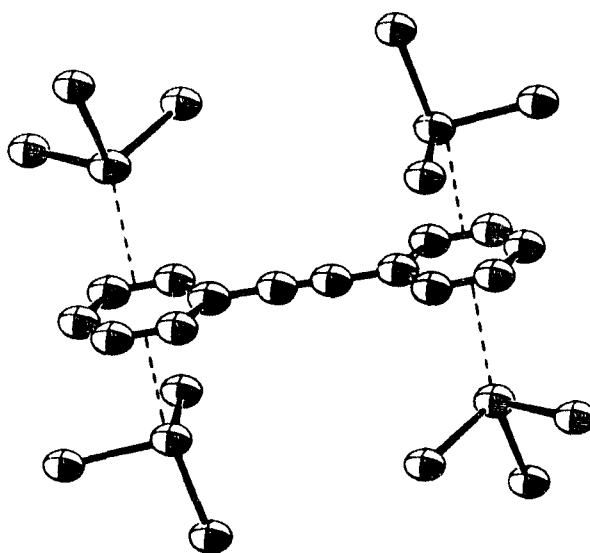


Figure 6.1: ORTEP view of the 4 SbCl_3 :diphenylacetylene complex (50% probability ellipsoids). The hydrogen atoms on the arene rings have been omitted for clarity.

6.2 Solid State and Spectroscopic Features of 4 SbCl₃:Bis-Arene Complexes

IR spectra are consistent with the complexes containing monosubstituted arenes, with two strong bands corresponding to C-H out-of-plane vibrations between 770-730 and

Table 6.2: IR data (cm⁻¹) for bis-arenes and 4 SbCl₃:bis-arene complexes.

diphenyl acetylene	complex	<i>t</i> -stilbene	complex	bibenzyl	complex
1953s	1974w	1950w	1966w	1945w	1974w
1886s	1913w	1875w	1899w	1870w	1894w
1830s	1854w	1818w	1854w	1811w	1840w
1763s	1798w	1751w	1775w	1750w	1761w
756s	780s	763s	779s	758w	785s
689s	692s	688s	704s	699w	720s

720-680 cm⁻¹. More importantly, these peaks are shifted in the complexes compared to those bands in the pure solid arenes (Table 6.2). Significant

shifts of combination and overtone bands of the C-H out-of-plane deformations are also observed.

No significant differences were observed between the ¹³C and ¹H NMR spectra of the complexes and the pure arenes, in accord with earlier studies on the SbCl₃:hexaethylbenzene 1:1 complex.¹⁸⁰ This complex does not show significant changes for the

Table 6.3: Comparison of Sb-arene and Sb---C_{arene} distances (min.-max.) (Å) for 4:1 SbCl₃:arene complexes. Sb-arene measured to the centroid of the arene.

Compound	Sb-centroid (Å)	Sb---C _{arene} (Å)
2 SbCl ₃ :Benzene	3.22, 3.30	
4 SbCl ₃ :bibenzyl	3.21(1), 3.36(1)	3.36(3)-3.79(3)
4 SbCl ₃ : <i>t</i> -stilbene	3.24(1), 3.35(1)	3.38(3)-3.80(3)
4 SbCl ₃ :diphenylacetylene	3.284(3), 3.385(3)	3.418(8)-3.840(8)

NMR of the arene; however, it exhibits rapid exchange with excess hexaethylbenzene. Crystals of the complexes were

obtained by slow solvent removal from CH₂Cl₂/hexane solution. The three structures belong to the same space group (P1), and are isotypical. Views of the diphenylacetylene

and *t*-stilbene complexes are presented in Figures 6.1-6.2. In all cases, the molecular structures of the 4:1 SbCl₃:arene complexes consist of corrugated layers of SbCl₃, with

Table 6.4: Sb-Cl bond lengths and Sb---Cl contact distances (Å) for SbCl ₃ :arene complexes.				
Compound	Sb(1)-Cl	Sb(1)---Cl	Sb(2)-Cl	Sb(2)---Cl
2 SbCl ₃ :Benzene	2.353(2)	3.449(2)	2.357(2)	3.502(2)
	2.347(2)	3.401(2)	2.340(2)	3.802(2)
	2.380(2)	3.968(2)	2.378(2)	4.047(2)
4 SbCl ₃ :Bibenzyl	2.311(8)	3.499(8)	2.335(7)	3.408(7)
	2.359(6)	3.804(7)	2.352(9)	3.661(8)
	2.381(9)	3.933(7)	2.361(8)	4.002(7)
4 SbCl ₃ : <i>t</i> -Stilbene	2.347(7)	3.588(8)	2.343(7)	3.441(7)
	2.360(7)	3.799(8)	2.355(7)	3.572(7)
	2.367(8)	3.878(8)	2.371(7)	3.923(9)
4 SbCl ₃ :Diphenylacetylene	2.345(2)	3.401(2)	2.334(2)	3.622(3)
	2.352(2)	3.519(3)	2.358(2)	3.788(3)
	2.378(2)	3.862(3)	2.372(2)	3.813(3)
SbCl ₃	2.304(2)	2 x 3.457(1)		
	2 x 2.368(1)	3.609(2)		
		2 x 3.736(1)		

each molecule of SbCl₃ coordinated to one ring of the bis-arene. The result is a sandwich with alternating organic and inorganic layers.

The Sb---arene distance as well as the range of Sb---C_{arene} contacts are presented in Table 6.3. An interesting feature is the trend in Sb---arene distance with changes in the arene donor. The bibenzyl complex exhibits the shortest interaction with SbCl₃, whereas the diphenylacetylene adduct engages in the longest coordination. A possible explanation may be the simple concept that *sp*³ hybridized alkyl substituents are electron donating and enhance the interaction with SbCl₃. In contrast, *sp* hybridized carbon substituents (alkynes) are electron withdrawing. It should be noted, that the effect on the Sb---arene distance is small.

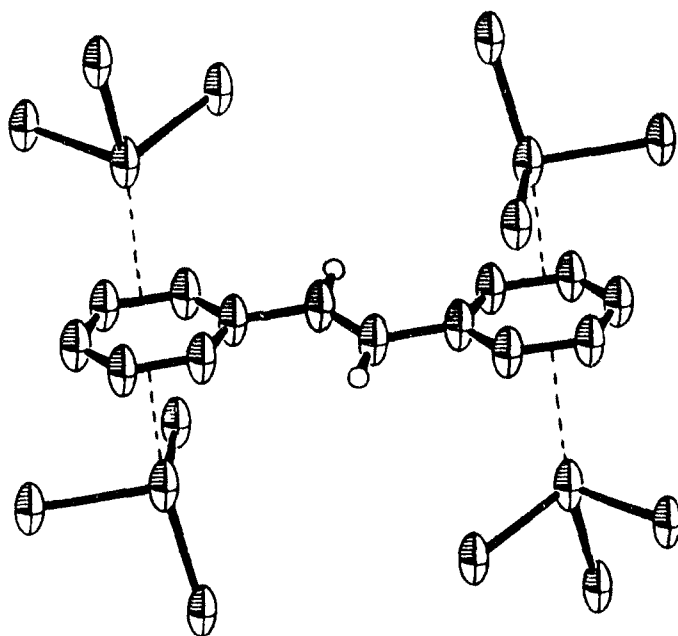


Figure 6.2: ORTEP view of the 4:1 SbCl₃:*t*-stilbene complex (50% probability ellipsoids). The hydrogen atoms on the arene ring have been omitted for clarity.

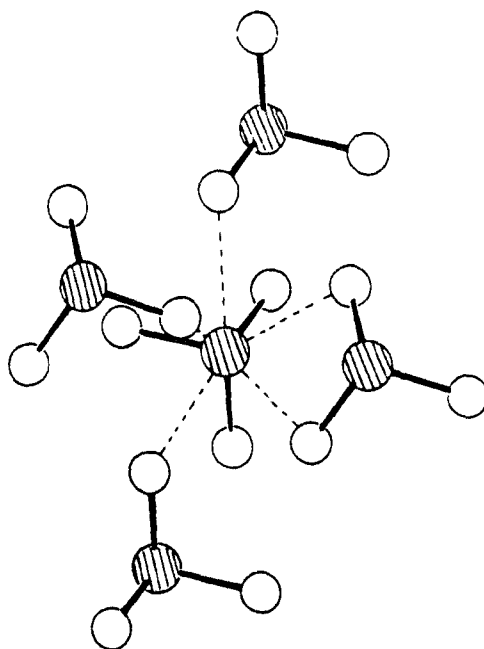


Figure 6.3: PLUTO view of SbCl₃ illustrating the local coordination environment for antimony. Antimony atoms are shaded.

It is informative to compare the crystal structures of SbCl_3 ¹⁸⁸ with those of the 4:1 SbCl_3 :bis-arene complexes. The structure of SbCl_3 (Figure 6.3) clearly shows that each antimony center achieves a coordination number of eight with three Sb-Cl bonds and five Sb---Cl contacts. Each SbCl_3 in the 4:1 SbCl_3 :bis-arene complexes exhibits a coordination number of seven, with the aromatic ring occupying the axial position of a distorted pentagonal bipyramid. Sb-Cl bond lengths and Sb---Cl contacts for the 4:1 SbCl_3 :bis-arene complexes, as well as for 2SbCl_3 :benzene, are presented in Table 6.4. The organic layers of the complex adopt an arrangement in which all of the arene rings are coplanar and parallel.

6.3 Factors Governing the Structure of SbCl_3 :Arene Complexes

As noted earlier, the array of structures observed for the SbCl_3 -arene complexes, so far, has appeared to be unpredictable. The 4:1 complexes offer a new insight into factors

Table 6.5: Comparison of crystallographic data for 2 SbCl_3 :benzene and 4 SbCl_3 : <i>t</i> -stilbene.		
Compound	2 SbCl_3 :benzene	4 SbCl_3 : <i>t</i> -stilbene
System	triclinic	triclinic
Space group	P1	P1
Z	2	2
<i>a</i> /Å	8.211(1)	8.363(3)
<i>b</i> /Å	11.83(2)	11.950(3)
<i>c</i> /Å	8.165(1)	8.099(3)
α /°	94.00(1)	95.44(3)
β /°	108.55(1)	109.15(3)
γ /°	94.22(1)	96.28(3)
<i>V</i> /Å ³	746.4(2)	752.6(4)

which govern the structure of these complexes. The prototypical

SbCl_3 :arene complex is the 2:1 SbCl_3 :benzene,¹⁸⁹ which is isomorphic to the 4:1 SbCl_3 :bis-arene complexes (Table 6.5).¹⁷⁸

The structures consist of corrugated layers of antimony trichloride with alternating layers of arene molecules. Packing

diagrams of the 2:1 SbCl_3 :benzene

complex¹⁹⁰ and the 4:1 SbCl_3 :*t*-stilbene complex are shown in Figure 6.4 and Figure 6.5, respectively.

The bis-arenes of the 4:1 SbCl_3 :bis-arene complexes (bis-arene= bibenzyl, *t*-stilbene, and diphenylacetylene) exhibit maximum donating ability (*i. e.*, each arene ring coordinates to a molecule of SbCl_3) and this is in contrast to other examples of SbCl_3 :bis-arene complexes. Structural studies of SbCl_3 complexes of naphthalene,¹⁸¹ phenanthrene,¹⁸² biphenyl,¹⁸⁴ and diphenylamine¹⁸⁶ reveal that only two molecules of SbCl_3 are engaged by the bis-arene despite potential for four-fold coordination. Alternating inorganic and organic layers are evident in the structures of these complexes, with SbCl_3 involved in extensive Sb---Cl interactions as seen in the 2 SbCl_3 :benzene complex. The longest arene-arene tether for these complexes is one atom long and the distance between adjacent arene rings is too short to incorporate another molecule of SbCl_3 without disturbing the SbCl_3 layer. Therefore, the maximum donating ability of the arene cannot be achieved. The complexes of the bis-arenes diphenylacetylene, *t*-stilbene and bibenzyl contain a two carbon tether between each arene ring. This distance between arene rings is sufficient to allow four molecules of SbCl_3 to interact with the bis-arene while maintaining the Sb---Cl contacts evident in solid SbCl_3 . Attempts to prepare a 4:1 SbCl_3 :bis-arene complex with diphenylbutadiyne were unsuccessful, and it is possible that the four carbon tether may be too long to facilitate formation of poly- SbCl_3 layers.

SbCl_3 forms a variety of coordination complexes with alkylated benzenes, and it is again likely that the establishment of Sb---Cl contacts is important. Formation of SbCl_3 chains and layers with six and seven coordinate antimony centers are common in these complexes. In cases of extreme steric crowding where formation of poly- SbCl_3 is prevented, alternate modes of coordination are adopted to maintain the key Sb---Cl contacts. For example, hexamethylbenzene forms a complex with 2 SbCl_3 molecules, but the solid state structure does not reveal layers of SbCl_3 molecules as seen in the case of 4:1 SbCl_3 :bis-arene complexes.¹⁹¹ Rather, tetrameric units are formed, perhaps to maintain high coordination at the antimony center. Hexaethylbenzene, which is substantially more

sterically crowded, forms a 1:1 complex.¹⁸⁰ The antimony center is located directly above the centroid of the arene, with a centroid---SbCl₃ contact 2.96 Å and no evident Sb---Cl contacts. This distance is substantially shorter than those observed in other complexes, such as 4:1 SbCl₃:*t*-stilbene (3.255(1) and 3.315(1) Å) and 2:1 SbCl₃:hexamethylbenzene (3.15 and 3.13 Å).¹⁹¹ Without the Sb---Cl interactions which result upon formation of inorganic layers, an isolated SbCl₃ could be significantly more acidic than an SbCl₃ antimony center engaged with other SbCl₃ molecules. This could enhance the Sb---arene interaction. The single strong interaction with one SbCl₃ may prevent coordination of the arene by a second molecule of SbCl₃. It is interesting to note that 2 AsBr₃:hexaethylbenzene has been isolated, indicating significant differences between the coordination complexes of arsenic and antimony trihalides.¹⁹²

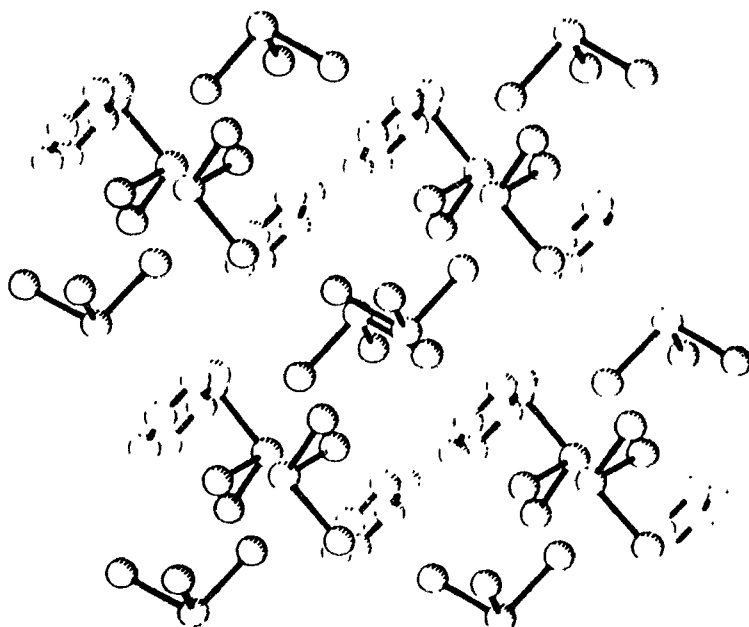


Figure 6.4: Packing diagram of the 2:1 SbCl₃:benzene complex illustrating the alternating layers of SbCl₃ and arenes.

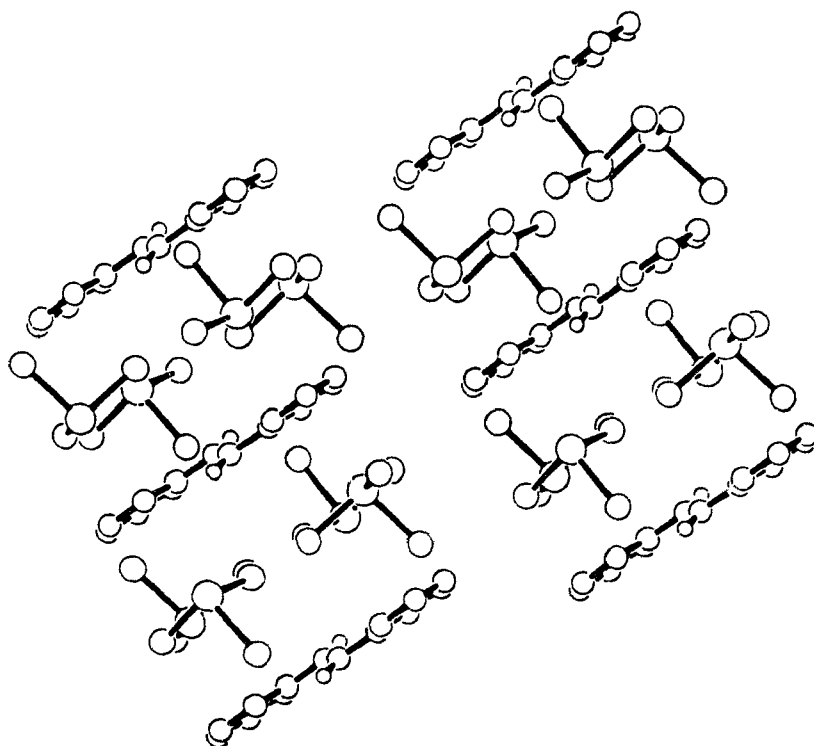


Figure 6.5: Packing diagram of the 4:1 SbCl₃:*l*-stilbene complex illustrating the alternating layers of SbCl₃ and arenes.

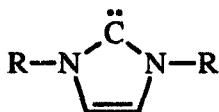
Chapter 7 Future Work

The full extent of the coordination chemistry of main group element cations has not been realized, and future work should focus on the examination of common ligands, such as PR_3 , NR_3 , R_2CO , etc., as potential donors to these cations. Bidentate ligands should also be examined. These reactions will not be described; however, more exciting and perhaps more synthetically challenging investigations will be proposed.

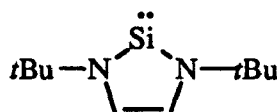
In addition to synthetic studies, calculations of strain energies should continue for other systems containing main group elements in low coordinate environments, such as the Lewis base adducts of R_3E ($\text{E} = \text{B}, \text{Al}, \text{Ga}, \text{and In}$).

7.1 Novel Ligands with Interesting Cations

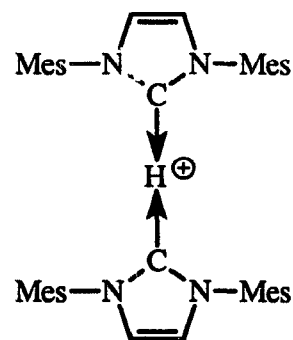
σ -Complexes of the main group element cations are well established with donors such as amines and phosphines (*vide supra*). Further investigations into the preparation and reactivity of these complexes are in progress.¹⁹³ There are other, perhaps more interesting, ligands available. Possible novel ligands include CO, alkynes, nucleophilic



7.1



7.2

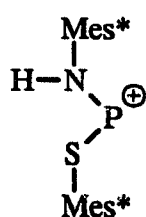
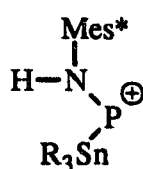
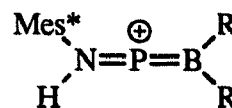


7.3

carbenes **7.1** and silylenes **7.2**. The rich potential of the stable carbenes is perhaps best illustrated by the recent characterization of **7.3**.

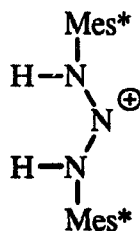
7.2 Synthesis of New Phosphorus Cations

The quantitative insertion of $[\text{Mes}^*\text{NP}]^+$ into E-H bonds provides a unique approach to phosphorus cations which have previously eluded synthesis. Particularly promising are reactions of $[\text{Mes}^*\text{NP}]^+$ with Mes^*SH , R_3SnH , and R_2BH to form novel phosphorus cations **7.4**, **7.5**, and **7.6**.

**7.4****7.5****7.6**

7.3 Nitrenium Cations

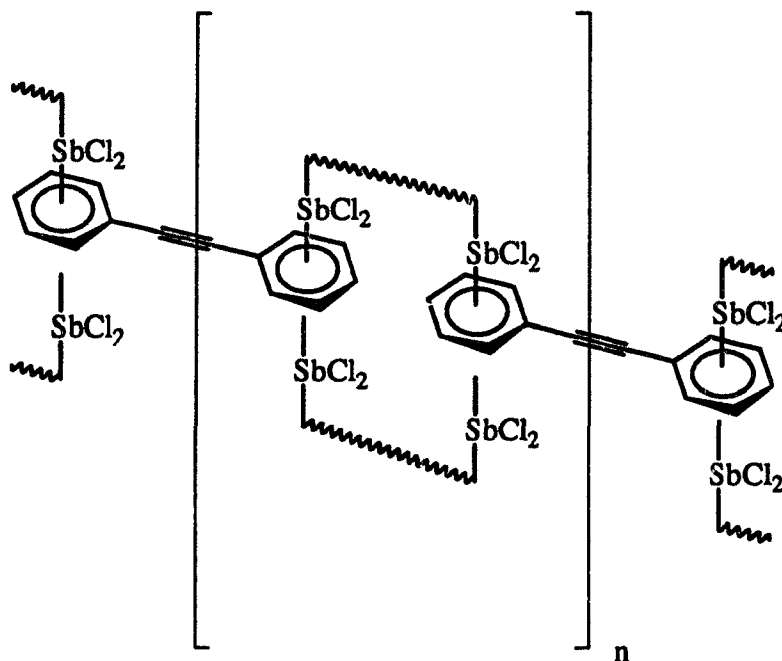
The diazonium cation $[\text{Mes}^*\text{NN}]^+$ should be prepared and characterized. This key molecule could yield stable π complexes analogous to those described in Chapter 4 for the

**7.7**

phosphoazonium cation. Isolation of the nitrenium cation **7.7** should then be realized using the 1, 3 hydrogen shift reaction.

7.4 Polymers Based on the SbCl_3 ---Arene Interaction

Preparation of polymers containing transition metals in the backbone are being examined by a number of research groups;¹⁹⁴ however, analogous *p*-block



7.8

metalloid---arene interactions have not yet been exploited in terms of their potential for the preparation of such novel oligomers and polymers. Recognizing the ease with which SbCl_3 forms arene complexes, preliminary investigations should be attempted to examine the potential of polymer preparation using the Sb ---arene interaction.

The polymer **7.8** is no different than any other polymer. Nylon 6,6 is a copolymer of hexanedioic acid (bifunctional acid) and 1,6-hexanediamine (bifunctional base) with the resulting polymer formed by amide bonds. The requirements for the polymer using the Cl_3Sb ---arene interaction are analogously simple. Unfortunately, bifunctional acids $\text{Cl}_2\text{Sb}(\text{R})\text{-SbCl}_2$ are not readily available.

Chapter 8 Experimental

8.1 Handling Air Sensitive Reagents

Cationic main group elements in low coordination environments are extremely reactive, and special apparatus and techniques are required to handle these air and moisture sensitive compounds. Over the past 8 years, our lab has developed a convenient system for handling such sensitive compounds. The reactors which are used to prepare the compounds are referred to as bridges, and their design and use has been described.¹⁹⁵ All reactions, with the exception of the preparation of Mes*NPCl, were performed in three bulb bridges equipped with two reaction bulbs and an NMR tube.

Before use, the empty bridge was placed under dynamic vacuum for a minimum of 1 hour (ca. 10^{-3} Torr) and was flame dried with a Bunsen burner for 10 minutes. It was then allowed to slowly cool to room temperature. Solid starting materials were prepared for use by exposure to dynamic vacuum (10^{-3} Torr) for a minimum period of 30 minutes. Their purity was assessed by melting point and/or NMR spectroscopy. Solid reagents were introduced into the bridge inside a nitrogen-filled drybox. Liquid starting materials were distilled before use and degassed using the standard freeze-pump-thaw technique. Liquid reagents with low volatility were introduced into the bridge inside a polyethylene glove bag, which had been flushed three times with dry nitrogen. Volatile reagents and solvents were vacuum distilled into the bridge on the vacuum line.

8.2 General Procedures

Phosphorus trichloride (Aldrich) and arsenic trichloride (BDH) were vacuum distilled and stored in evacuated bulbs. Triethylamine was distilled from CaH_2 and degassed. Trimethylsilylbromide and trimethylsilyliodide were vacuum distilled. Iodobenzene (Aldrich) and bromine (Fisher) were distilled from P_2O_5 . Gallium trichloride, antimony trichloride (both Aldrich), and iodine (BDH) were sublimed under vacuum.

Chlorine (Matheson) was used as supplied. Sodium tetrafluoroborate, 2,4,6-tri-*tert*-butylaniline, 2,4,6-tri-*tert*-butylphenol, triphenylphosphine, 2,6-dimethylphenol, diphenylamine, pentachlorothiophenol, trifluoromethanesulphonic acid, diphenylacetylene, fluorene, bibenzyl, triphenylcarbenium tetrafluoroborate, triphenylcarbenium hexafluorophosphate, and stilbene (Aldrich) were used as supplied. Dichloromethane was dried over P_2O_5 and CaH_2 . Toluene, benzene, tetrahydrofuran, and ether were dried over $Ni/benzophenone$. Pentane and hexane were dried over CaH_2 and degassed. All solvents were stored in evacuated bulbs. Deuterated solvents were dried over P_2O_5 or CaH_2 . Mes^*NPCl was prepared using a variation of the literature procedure (*vide infra*).³¹ $C_6H_5ICl_2$,¹⁹⁶ Mes^*NPBr ,³¹ and Mes^*NPI ³¹ were prepared following literature procedures. All solids were manipulated in Vacuum/Atmospheres or MBraun dryboxes containing an atmosphere of 99.998% prepurified nitrogen, which was constantly circulated through water and oxygen scavenging trains. Reactions were performed in evacuated bridges unless otherwise indicated. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany. IR spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510P FT-IR spectrometer. Solution NMR spectra were recorded on either a Bruker AC250 or Bruker AMX400 spectrometer in 5 mm evacuated flame sealed Pyrex tubes. Chemical shifts are reported in ppm relative to TMS (1H and ^{13}C), $^{15}NH_3$ (^{15}N) or 85% H_3PO_4 ($^{31}P\{^1H\}$). 1H and ^{13}C spectra were calibrated to the internal solvent signal. Variable temperature NMR studies involved equilibrium times of ten minutes at each temperature. Solid state ^{13}C and ^{31}P CP MAS NMR spectra were recorded on a Bruker AMX 400 spectrometer in 3 mm zirconium oxide spinners. Spinning rates are given in parentheses after the isotropic chemical shift. Crystals suitable for crystallography were obtained as described for each compound and mounted in Pyrex capillaries in a drybox. Structures were solved by Dr. T. Stanley Cameron, Dr. S. Sereda, P. Bakshi,

K. Robertson, or Dr. John F. Richardson. X-ray crystallographic data were collected on Rigaku AFC5R (TSC) or Enraf-Nonius CAD-4 (JFR) diffractometers with graphite-monochromated Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$ or $\lambda = 0.70926 \text{ \AA}$, respectively). Full details on the data collection and structure solution procedures used are available from the references as indicated in the appropriate discussion section for each compound. Part of the work described below was performed with students as part of their honours degree. Acknowledgement to these people is made where appropriate.

Cautionary Note: Many phosphorus compounds are toxic and possibly carcinogenic. Alkylolithium reagents are pyrophoric. Handle with care.

8.3 Specific Procedures

Preparation of 2,4,6-Tri-*tert*-butylphenyliminophosphine chloride: In a bridge equipped with a porous frit, PCl₃ (17.0 g, 124 mmol) was condensed over a solution of Et₃N (15.0 g, 149 mmol), pentane ($\approx 50 \text{ mL}$), and 2,4,6-tri-*tert*-butylaniline (3.60 g, 13.8 mmol). The reaction mixture was stirred for one week and the solution became bright red with copious precipitation of Et₃NHCl. The precipitate was filtered and washed several times by repeated back distillations of the solvent mixture. Volatiles were removed *in vacuo* and the red solid was sublimed twice under dynamic vacuum ($\approx 10^{-3}$ Torr) at 60-70°C. The red crystalline solid was characterized as 2,4,6-tri-*tert*-butylphenyliminophosphine chloride, Mes*NPCL (2.90 g, 8.90 mmol, 65%), mp. 93-93.5°C.

IR: 1601s, 1271s, 1246s, 1246s, 1221s, 1200m, 1137m, 1060w, 927m, 879s, 763s, 651w, 497w, 410vs

NMR (CH₂Cl₂): ³¹P{¹H}, 131.

Under similar experimental conditions, AsCl₃ was used in place of PCl₃ in an attempt to

prepare the arsenic analogue, Mes*NA₃Cl. These reaction conditions yielded a dark precipitate which was not characterized.

Preparation of Mes*NPCl₃: A solution of Mes*NPCl (0.33 g, 1.0 mmol) in CH₂Cl₂ ($\approx$ 10 mL) was added to a slurry of PhICl₂ (0.32 g, 1.2 mmol) in CH₂Cl₂ ($\approx$ 10 mL) over a period of 30 minutes. The solvent was removed *in vacuo* and the residue was recrystallized twice from hexane to give yellow crystals characterized as Mes*NPCl₃ (0.20 g, 0.50 mmol, 50%), mp. 148-149°C.

Elemental Anal. Calcd: C, 54.49; H, 7.37; N, 3.53; Cl, 26.81%.

Found: C, 54.39; H, 7.24; N, 3.49; Cl, 26.70%.

IR: 1605m, 1530s, 971w, 922w, 888w, 879m, 768m, 658m, 648m, 530s, 448m.

NMR: (CD₂Cl₂): ³¹P{¹H}, -96 ppm; ¹H, 1.30 (s, 9H), 1.46 (s, 18H), 7.30 (d ⁵J_{PH} = 3.0 Hz, 2H); ¹³C, 31.8 (s), 32.4 (s), 32.9 (s), 35.7 (s), 122.3 (s), 124.1 (s), 142.4 (d, J_{PC} = 7.6 Hz), 145 (d J_{PC} = 3.8 Hz); ³¹P CP-MAS -103 small impurity at -73 (4000, 7000).

Reaction Mixture: ³¹P{¹H} NMR spectra of the reaction mixtures contained a single signal at -96 ppm.

X-ray: monoclinic, space group *Cm*, *a* = 11.960(3) Å, *b* = 14.696(2) Å, *c* = 5.954(2) Å, β = 97.71(2) Å, *V* = 1037.1 Å³, *Z* = 2, *D*_{calcd} = 1.27 g cm⁻³, μ = 5.2 cm⁻¹, 100*R*_w = 4.7 (JFR).

Preparation of Mes*NPBr₃: Bromine (0.15 g, 0.93 mmol) in hexane ($\approx$ 5 mL) was added to a solution of Mes*NPBr (0.33 g, 0.91 mmol) in hexane ($\approx$ 5 mL). After stirring at room temperature for 5 minutes, the solvent was removed *in vacuo* and the solids were recrystallized from a minimum amount of warm hexane giving orange/red crystals. These crystals were characterized as Mes*NPBr₃ (0.34 g, 71%), mp. 161.5-163 °C.

Elemental Anal. Calcd: C, 40.78; H, 5.51; N, 2.64 %.

Found: C, 41.07; H, 5.72; N, 2.57 %.

IR: 1601m, 1504s, 923w, 881w, 513s, 487m, 446s, 425m.

NMR: (CD₂Cl₂): ³¹P{¹H}, -236; ¹H, 1.30 (s, 9H), 1.46 (s, 18H), 7.30 (d, ⁵J_{PH} = 3.0 Hz, 2H); ¹³C, 31.8 s, 32.4 s, 32.9 s, 35.7 s, 122.3 s, 124.1 s, 142.4 (d, J_{PC} = 7.6 Hz), 145.0 (d, J_{PC} = 3.8 Hz).

Reaction mixture: ³¹P{¹H} NMR spectra of the reaction mixture showed a single signal at -236 ppm.

X-ray: monoclinic, space group *P2₁/c*, *a* = 18.841(8) Å, *b* = 9.480(4) Å, *c* = 12.186(5) Å, *β* = 98.00(3) Å, *V* = 2155.3 Å³, *Z* = 4, *D_{calcd}* = 1.63 g cm⁻³, *μ* = 56.4 cm⁻¹, 100*R_w* = 7.4 (JFR).

Reaction of Mes*NPCL with Br₂: Bromine (0.32 g, 2.0 mmol) in pentane (≈ 15 mL) was added to a solution of Mes*NPCL (0.52 g, 1.6 mmol) in pentane (≈ 15 mL). After stirring at room temperature for 12 hours 50% of the solvent was removed *in vacuo* and the solid that formed was warmed back into solution. Slow cooling to room temperature resulted in the formation of orange/red crystals; which were characterized as a mixture of Mes*NPBr₃, Mes*NPBr₂Cl and Mes*NPBrCl₂ (total recovered mass 0.62 g) mp. range 172-184°C. A single crystal of Mes*NPBr₃ was isolated from this mixture and characterized by X-ray crystallography (*vide supra*). Calculated composition based on the integrated ratios observed in the ³¹P{¹H} NMR spectrum of the solids: -236 (40) Mes*NPBr₃, -183 (50) Mes*NPBr₂Cl, -136 (10) Mes*NPBrCl₂. (Derek P. Gates)

Elemental Anal. Calcd: C, 43.3; H, 5.9 %.

Found: C, 43.2; H, 5.7 %.

Reaction Mixture: ³¹P{¹H} NMR spectra of the reaction mixture indicated formation of five products: -236 (40) Mes*NPBr₃, -213 (minor), -182 (40) Mes*NPBr₂Cl,

-162 (minor), -136 (10) Mes*NPCl₂I.

Reaction of Mes*NPCl with I₂: A slurry of I₂ (0.28 g, 1.1 mmol) in pentane ($\approx$ 30 mL) was added to a solution of Mes*NPCl (0.70 g, 2.2 mmol) in pentane ($\approx$ 20 mL).

After stirring overnight at room temperature, slow removal of the solvent *in vacuo* resulted in the precipitation of orange/red needle crystals which were isolated in very low yield and characterized as Mes*NPCl₂I, mp. 124-130°C (sublimes). (Derek P. Gates)

Elemental Anal. Calcd: C, 44.28; H, 5.99; N, 2.87 %.

Found: C, 44.62, H, 5.86, N, 2.74 %.

IR: 1598s, 1476s, 924w, 880m, 527s, 507m, 480s, 431m.

NMR: (CD₂Cl₂): ³¹P{¹H}, -211; ¹H, 1.30 (s, 9H), 1.46 (s, 18H), 7.30 (d ⁵J_{PH} = 3.0 Hz, 2H); ¹³C, 31.8 (s), 32.4 (s), 32.9 (s), 35.7 (s), 122.3 (s), 124.1 (s), 142.4 (d, J_{PC} = 7.6 Hz), 145 (d J_{PC} = 3.8 Hz).

Reaction mixture: -211 Mes*NPCl₂I, 200-160 Mes*NPCl and Mes*NPI broad (δ varies depending upon the stoichiometry. With excess I₂, δ = 200, with trace I₂, δ = 164, average signal due to exchange.

X-ray: monoclinic, space group *P*2₁/*n*, *a* = 9.903(3) Å, *b* = 11.638(3) Å, *c* = 19.734(5) Å, β = 103.34(2) Å, *V* = 2213.0 Å³, *Z* = 4, *D*_{calcd} = 1.47 g cm⁻³, μ = 17.5 cm⁻¹, 100*R*_w = 10.2 (JFR).

NMR Studies: The reactions listed below were examined by combining the reactants in equimolar amounts in pentanes and obtaining a ³¹P{¹H} NMR spectrum of the reaction mixture. The results are presented as the chemical shifts (ppm) of the observed signals with their relative integration given as percentages, in parentheses, followed by the assignment for each signal.

Mes*N⁺PBr with PhICl₂: -96 (10) Mes*N⁺PCl₃, -135 (70) Mes*N⁺PBrCl₂, -183 (20) Mes*N⁺PBr₂Cl.

Mes*N⁺PBr with I₂: 177 (>90) Mes*N⁺PBr and Mes*N⁺NPI average due to exchange.

Mes*N⁺NPI with PhICl₂: 220 (1) PCl₃, 158 (40) Mes*N⁺NPI and Mes*N⁺NPI average due to exchange, -96 (10) Mes*N⁺PCl₃, -211 (40) Mes*N⁺PCl₂I.

Mes*N⁺NPI with Br₂: 227 (100) PBr₃.

Mes*N⁺NPI with I₂: No reaction.

Mes*N⁺PBr with Mes*N⁺NPI: 159 (100) average signal due to exchange.

Mes*N⁺PCl₃ with Mes*N⁺PBr₃: No reaction.

Mes*N⁺PCl₃ with Ph₃Sb: no reaction in CH₂Cl₂.

Mes*N⁺PCl₃ with SbF₃: no reaction in CH₂Cl₂.

Reaction of Mes*N⁺PCl with [Ph₃C][BF₄]: Mes*N⁺PCl (0.41 g, 1.26 mmol) in ≈ 10 mL of 3:1 CH₂Cl₂/hexane was added over a period of 10 minutes to a solution of [Ph₃C][BF₄] (0.42 g, 1.28 mmol) in ≈ 10 mL of a similar solvent mixture. The solution turned bright yellow after 10 minutes and slow removal of solvent yielded yellow crystals which were characterized as Mes*N⁺PF₂CPh₃ (0.56 g, 0.98 mmol, 78%), mp. 157.0-158.5 °C.

Elemental anal: Calcd: C, 77.73; H, 7.76; N, 2.45 %.

Found C, 76.53; H, 8.34; N, 2.59 %.

IR: 3055s, 3035s, 1530s, 1494s, 1295m, 1272m, 1247m, 1215m, 1193m, 1135m, 1083m, 1083m, 1035m, 945m, 922m, 915m, 899m, 879m, 854m, 828s, 818s, 775m, 769m, 762m, 741s, 697s, 643m, 624m, 521s, 487m, 457m.

NMR: (CD₂Cl₂): -38 ppm (triplet; ¹J_{PF}: 1221 Hz), ¹H and ¹³C NMR spectra were very complex and poorly resolved due to splitting with the PF₂ unit.

Reaction Mixture: ³¹P{¹H} NMR studies of [Ph₃C][BF₄] with Mes*N⁺PCl in

CH_2Cl_2 /hexane solution indicate immediate quantitative formation of a signal at 146 ppm (triplet; $^1J_{\text{PF}} = 1105$ Hz) which then decays over three days to give a signal at -38 ppm (triplet; $^1J_{\text{PF}} = 1221$ Hz) in a solution yield of > 90%.

X-ray: triclinic, space group $P\bar{L}$, $a = 13.728(3)$ Å, $b = 23.808(5)$ Å, $c = 10.125(2)$ Å, $\alpha = 95.69(1)^\circ$, $\beta = 101.37(1)^\circ$, $\gamma = 91.62(2)^\circ$, $V = 3224$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.178$ gcm⁻³, $\mu = 1.17$ cm⁻¹, $100R_w = 4.98$ (TSC).

Preparation of [Mes*NP-benzene][GaCl₄]: A solution of GaCl₃ (0.21 g, 1.2 mmol) in benzene (≈ 15 mL) was added over a period of ≈ 5 minutes to a stirred solution of Mes*NP-Cl (0.38 g, 1.2 mmol) in benzene (≈ 15 mL) giving a bright yellow solution. Solvent was removed *in vacuo* overnight to yield a yellow powder which was characterized as [Mes*NP][GaCl₄]. Recrystallization from benzene through repeated cycles of warming to ≈ 60 °C and slow cooling to room temperature gave [Mes*NPC₆H₆][GaCl₄], dp. ≈ 90 °C. Elemental analysis was not obtained.

IR: 1979w, 1842w, 1597s, 1267m, 1245m, 1134m, 1066m, 1033m, 927w, 886s, 764m, 699s, 674s, 393s, 361s, 263m.

NMR: (CD_2Cl_2): $^{31}\text{P}\{^1\text{H}\}$, 76; ^1H , 7.47 (d, $^5J_{\text{PH}} = 2$ Hz, 2H), 1.56 (s 18H), 1.33 (s, 9H) [Mes*], 7.38 (s, 6H) [benzene]; ^{13}C , 123.8 (d, $^4J_{\text{PC}} = 3$ Hz), 30.9 (s), 30.1 ppm (d, $^5J_{\text{PC}} = 2$ Hz) [Mes*], 128.7 ppm (s) [benzene], quaternary carbon nuclei not observed.

Reaction mixture: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixture showed a single signal at 71 ppm.

X-Ray: orthorhombic, space group $Pbca$, $a = 24.948(4)$, $b = 20.195(4)$, $c = 11.953(3)$ Å, $V = 6022(4)$ Å³, $Z = 8$, $D_{\text{calcd}} = 1.279(1)$ gcm⁻³, $\mu = 13.32$ cm⁻¹, $100R_w = 4.19$ (TSC).

Benzene is quantitatively removed from the crystals under dynamic vacuum for 24 hours to

give [Mes*NP][GaCl₄] as characterized by IR and elemental analysis; dp. 122-3.5 °C

Elemental Anal. Calcd: C, 43.07; H, 5.82; N, 2.79 %.

Found: C, 43.02; H, 5.79; N, 2.97 %.

IR: 1594s, 928m, 885m, 842m, 763m, 693m, 650w, 474w, 464m, 401s, 373s, 360s, 261m.

NMR: (CD₂Cl₂): ³¹P{¹H}, 76; ¹H, 7.46 (d, ⁵J_{PH} = 2 Hz, 2H), 1.54 (s, 18H), 1.31 (s, 9H); ³¹P CP-MAS NMR, 63 ppm (4000, 7000 Hz).

Preparation of [Mes*NP-toluene][GaCl₄]: A solution of GaCl₃ (0.08 g, 0.47 mmol) in toluene (≈ 2 mL) was added over ≈ 5 minutes to a stirred solution of Mes*NP-Cl (0.15 g, 0.47 mmol) in toluene (≈ 2 mL) giving a yellow solution. Solvent was removed *in vacuo* to give a yellow powder which was recrystallized from a minimum amount of toluene to give [Mes*NPC₇H₈][GaCl₄], dp. 157-160°C. Elemental analysis was not obtained.

IR: 1594w, 1267m, 1243w, 1133m, 886m, 762w, 722m, 699m, 674w, 400s, 368s, 266s.

NMR: (CD₂Cl₂): ³¹P{¹H}, 76; ¹H, 7.36 (s, 2H), 1.45 (s, 18H), 1.28 (s, 9H) [Mes*], 7.56 - 7.47 (multiplet, 5H), 2.48 (s, 3H) [toluene]; ¹³C, 123.7 (d ⁵J_{PC} = 3 Hz), 30.6, 29.4 [Mes*], 132.4, 131.4, 128.1, 22.0 [toluene], quaternary carbon nuclei not observed.

Reaction mixture: ³¹P{¹H} NMR spectra of the reaction mixture showed a single signal at 78 ppm.

X-ray: orthorhombic, space group *Pbca*, *a* = 25.006(9), *b* = 20.358(8), *c* = 12.126(5) Å, *V* = 6173(8) Å³, *Z* = 8, *D*_{calcd} = 1.278(2) gcm⁻³, *μ* = 13.01 cm⁻¹, 100*R*_w = 7.60 (TSC).

Toluene is quantitatively removed from the crystals under dynamic vacuum for 24 hours to

give [Mes*NP][GaCl₄].

IR: 1596s, 928m, 887m, 842m, 764m, 694m, 464m, 402s, 373s, 362s.

NMR reactions involving Mes*NPCL with 0.5 equivalents of GaCl₃ in toluene show a single ³¹P{¹H} shift of 112 ppm. NMR reactions involving Mes*NPCL with 4 equivalents of GaCl₃ in toluene show a single ³¹P{¹H} shift of 92 ppm.

Preparation of [Mes*NP-benzene][Ga₂Cl₇]: A solution of GaCl₃ (0.41 g, 2.3 mmol) in benzene (≈ 10 mL) was added over a period of ≈ 5 minutes to a stirred solution of Mes*NPCL (0.38 g, 1.2 mmol) in benzene (≈ 10 mL). Upon standing for ≈ 5 minutes a small amount of yellow oil formed under a bright yellow solution. Solvent was removed *in vacuo* to yield a yellow powder which was recrystallized from benzene in hexane (75 % v/v) with repeated cycles of warming to ≈ 60 °C and slow cooling to room temperature to give [Mes*NPC₆H₆][Ga₂Cl₇] (0.71 g, 0.95 mmol, 82%), mp. 78-81 °C.

Elemental Anal. Calcd: C, 38.12; H, 4.67; N, 1.85 %.

Found: C, 37.97; H, 4.47; N, 1.89 %.

IR: 1981w, 1849w, 1597m, 1268m, 1135m, 1068m, 1025w, 986w, 929w, 887m, 763w, 700s, 400s, 367s, 265s.

NMR: (CD₂Cl₂): ³¹P{¹H}, 93; ¹H, 7.40 (s, 2H), 1.48 (s, 18H), 1.30 (s, 9H) [Mes*], 7.80 (s, 6H) [benzene]; ¹³C, 124.0, 30.6, 29.3 [Mes*], 132.6 [benzene], quaternary carbon nuclei not observed. ³¹P{¹H} CP-MAS NMR, 90 (3000, 7000 Hz). ¹³C{¹H} CP-MAS NMR 129.4 ppm [benzene].

Reaction mixture: ³¹P{¹H} NMR spectra of the reaction mixture showed a single signal at 93 ppm.

X-ray: triclinic, space group *P* $\bar{1}$, *a* = 11.579(2), *b* = 16.350(3), *c* = 11.085(3) Å, α = 90.74(2), β = 118.00(2), γ = 73.53(2)°, *V* = 1759(1) Å³, *Z* = 2, *D*_{calcd} = 1.428(1) gcm⁻³, μ = 21.23 cm⁻¹, 100*R*_w = 3.86 (TSC).

Preparation of [Mes*NP-toluene][Ga₂Cl₇]: Mes*NPCl (0.34 g, 1.1 mmol) in toluene ($\approx$ 30 mL) was added over a period of $\approx$ 5 minutes to a stirred solution of GaCl₃ (0.38 g, 2.1 mmol) in toluene ($\approx$ 30 mL). An orange oil formed on removal of the solvent *in vacuo*. Fresh toluene ($\approx$ 25 mL) was distilled onto this oil and yellow orange crystals formed upon standing overnight. Solvent was decanted from the crystalline material which was washed with hexanes and characterized as [Mes*NPC₇H₈][Ga₂Cl₇] (0.65 g, 80%), mp. 87.5-89 °C.

Elemental Anal. Calcd: C, 38.99; H, 4.84; N, 1.82 %.

Found: C, 38.72; H, 5.01; N, 1.81 %.

IR: 1971w, 1892w, 1842w, 1787w, 1594m, 1266s, 1244m, 1134m, 1067m, 887s, 764m, 419s, 401s, 362s, 263s.

NMR: (CD₂Cl₂): ³¹P{¹H}, 95; ¹H, 7.42 (s, 2H), 1.50 (s, 18H), 1.31 (s, 9H) [Mes*], 7.76 - 7.66 (multiplet, 5H), 2.56 ppm (s, 3H) [toluene]; ¹³C, 124.0, 30.6, 29.4 [Mes*], 134.2, 133.1, 130.0, 22.3 [toluene], quaternary carbon nuclei not observed. ³¹PCP-MAS NMR 89 (3137, 4045 Hz).

Reaction mixture: ³¹P{¹H} NMR spectra of the reaction mixture showed a single signal at 91 ppm.

X-ray: triclinic, space group *P* $\bar{1}$, *a* = 11.571(4), *b* = 16.335(5), *c* = 11.326(3) Å, α = 91.47(4)°, β = 117.87(2)°, γ = 105.34(3)°, *V* = 1797(1) Å³, *Z* = 2, *D*_{calcd} = 1.423(1) g cm⁻³, μ = 20.80 cm⁻¹, 100*R*_w = 4.64 (TSC).

Preparation of [Mes*NP-mesitylene][Ga₂Cl₇]: Mes*NPCl (0.35 g, 1.1 mmol) in mesitylene ($\approx$ 7 mL) was added to a solution of GaCl₃ (0.38 g, 2.2 mmol) in mesitylene ($\approx$ 3 mL) and a yellow oil formed under a clear yellow solution. Hexanes ($\approx$ 10 mL) was distilled onto this solution giving a light yellow precipitate, which was isolated by decantation and recrystallized from a warm solution of hexane/mesitylene (20/80). Two

crops of crystals were isolated and characterized as [Mes*NP(mesitylene)][Ga₂Cl₇] (total yield 0.76 g, 0.97 mmol, 90 %). mp. 105-7 °C.

Elemental Anal. Calcd: C, 40.63; H, 5.18; N, 1.75 %.

Found: C, 38.38; H, 5.54; N, 1.71 %.

IR: 1813w, 1784w, 1759w, 1589m, 1302m, 1265m, 1243m, 1219m, 1194m, 1134m, 885m, 856m, 762m, 676m, 407s, 367m, 360m, 265m.

NMR: (CD₂Cl₂): ³¹P{¹H}, 91; ¹H, 7.41 (d, ⁵J_{PH} = 2 Hz, 2H), 1.50 (s, 18H), 1.30 (s, 9H) [Mes*], 7.21 (s, 3H), 2.42 (s, 9H) [mesitylene]; ¹³C, 123.8 (s), 31.0 (s), 30.3 (s) [Mes*], 131.1 (s), 21.6 (s) [mesitylene] (Quaternary carbons not reported).

Reaction mixture: ³¹P{¹H} NMR spectra of the reaction mixture showed a single signal at 91 ppm.

X-ray: triclinic, space group *P*1, *a* = 12.119(3) Å, *b* = 16.575(4) Å, *c* = 11.309(3) Å, *α* = 93.22(2)°, *β* = 115.62(2)°, *γ* = 107.64(2)°, *V* = 1905(1) Å³, *Z* = 2, *D*_{calcd} = 1.391(1) gcm⁻³, *μ* = 19.64 cm⁻¹, 100*R*_w = 4.50 (TSC).

Protonation Reaction of Mes*NP-Ph: A blue solution of Mes*NP-Ph (0.61 mmol), prepared *in situ* by the reaction of Mes*NP-Cl with NaBPh₄ in CH₂Cl₂ (≈ 10 mL) was added to a solution of HOSO₂CF₃ (0.61 mmol) in CH₂Cl₂ (≈ 10 mL). A ³¹P NMR spectrum of the yellow reaction mixture showed a single signal at 187 ppm assigned to [Mes*N(H)P-Ph][SO₃CF₃].

Preparation of Mes*N(H)P=fluorenylidene: A solution of fluorenyl lithium in ether (0 °C, 30 ml) was prepared by reacting fluorene (0.51 g, 3.07 mmol) with BuLi (1.9 ml, 1.6 M BuLi, 3.04 mmol) for 30 minutes and was added to a stirred solution of Mes*NP-Cl (1.02 g, 3.14 mmol) in ether (0 °C). The solution was allowed to warm to room

temperature and the volatiles were removed *in vacuo* and the solids were recrystallized from hexane giving orange crystals characterized as Mes*N(H)P=fluorenylidene (0.55 g, 1.22 mmol, 39 %), dp. 207-9 °C.

Elemental anal. Calcd: C, 81.72; H, 8.41; N, 3.07 %.

Found: C, 81.54; H, 8.50; N, 3.31 %.

IR: 3413m, 1597m, 1308s, 1268s, 1217s, 1115s, 1026m, 1004m, 920s, 904s, 881 s, 762s, 739s, 650m, 620m, 412m. IR spectrum unchanged after 20 minutes in moist air.

NMR (CD₂Cl₂): ³¹P{¹H} 256; ¹H 7.92-7.79 and 7.39-7.21 (8H, aromatic), 7.49 (s, 2H), 6.85 (d, 11 Hz, 1H), 1.34 (s, 18H), 1.36 (s, 9H); ¹³C 127.3 (d, 3Hz), 126.8 (s), 126.6 (d, 5 Hz), 125.5 (d, 5 Hz), 123.8 (s), 123.2 (d, 4 Hz), 120.1 (s), 118.1 (d, 21 Hz), 33.54 (s), 33.48 (s), 31.4 (s) quaternary carbons not observed.

Reaction mixture: ³¹P{¹H} NMR spectrum of the reaction mixture indicated immediate (5 minutes) quantitative formation of Mes*N(H)P=fluorenylidene in solution.

X-ray: monoclinic, space group *P*2₁/*c*, *a* = 9.586(8) Å, *b* = 24.25(2) Å, *c* = 11.77(1) Å, β = 101.38(8)°, *V* = 2678(8) Å³, *Z* = 4, *D*_{calcd} = 1.13 gcm⁻³, μ = 1.161 cm⁻¹, 100*R*_w = 4.75 (TSC).

Preparation of [Mes*N(H)PN(H)Mes*][GaCl₄]: A solution of Mes*NH₂ (0.13 g, 0.51 mmol) in ≈ 20 mL of CH₂Cl₂ was added over ≈ 20 minutes to a stirred solution of [Mes*NP][GaCl₄] (0.26 g, 0.51 mmol) in ≈ 25 mL of CH₂Cl₂. The solution slowly turned light yellow/orange, and with stirring turned light yellow in four hours. Solvent was removed *in vacuo*, and the solids recrystallized from CH₂Cl₂ to give pale yellow crystals of crystallographic quality characterized as [Mes*N(H)PN(H)Mes*][GaCl₄] (0.25 g, 0.32 mmol, 64 %), mp. 152-153.5 °C.

Elemental anal. Calcd: C, 56.94; H, 7.43; N, 3.69 %.

Found: C, 56.79; H, 7.69; N, 3.57 %.

IR: 3175sb, 1599m, 1419m, 1396m, 1319m, 1271m, 1242m, 1212s, 1178m, 1103s, 981s, 881s, 694m, 651w, 389s, 376s, 362s.

NMR (CD_2Cl_2): $^{31}\text{P}\{^1\text{H}\}$ 272; ^1H 9.94 (d, $^2J_{\text{PH}} = 14$ Hz, 2H), 7.54 (s, 4H), 1.57 (s, 36H), 1.32 (s, 18H); ^{13}C 125.0 (s), 34.1 (s), 31.2 (s), 31.4 (s) quaternary carbons not observed. Solid state ^{31}P CP MAS 281 ppm (4000, 6000).

Reaction mixture: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture indicated immediate (5 min.) quantitative formation of $[\text{Mes}^*\text{N}(\text{H})\text{PN}(\text{H})\text{Mes}^*][\text{GaCl}_4]$ in solution.

X-ray: monoclinic, space group $C2/c$, $a = 24.931(2)$ Å, $b = 10.198(4)$ Å, $c = 16.444(?)$ Å, $\beta = 93.32(1)^\circ$, $V = 4172(8)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.215$ gcm⁻³, $\mu = 9.769$ cm⁻¹, $100R_w = 3.27$ (TSC).

Reaction of $[\text{Mes}^*\text{NP}][\text{GaCl}_4]$ with Mes^*OH : A solution of Mes^*OH (0.19 g, 0.72 mmol) in ≈ 10 mL of CH_2Cl_2 was added over ≈ 10 minutes to a stirred solution of $[\text{Mes}^*\text{NP}][\text{GaCl}_4]$ (0.36 g, 0.71 mmol) in ≈ 20 mL of CH_2Cl_2 . The solution slowly turned light yellow. Solvent was removed *in vacuo*, and the solids recrystallized from CH_2Cl_2 to give a bright yellow microcrystalline solid characterized as $[\text{Mes}^*\text{N}(\text{H})\text{POMes}^*][\text{GaCl}_4]$ (0.45 g, 0.70 mmol, 98 %), m.p. 160-163 °C.

Elemental anal. Calcd: C, 56.57; H, 7.78; N, 1.83 %.

Found: C, 56.00; H, 7.75; N, 1.89 %.

IR: 120sb, 1599m, 1418s, 1318m, 1305m, 1245m, 1219m, 1207m, 1165m, 1066s, 997s, 881s, 805w, 756m, 737m, 649w, 379s, 361s.

NMR: (CD_2Cl_2): $^{31}\text{P}\{^1\text{H}\}$ 296; ^1H 10.9 (broad, 1H), 7.59 (s, 2H), 7.48 (s, 2H), 1.60 (s, 18H), 1.58 (s, 18H), 1.40 (s, 9H), 1.32 (s, 9H); ^{13}C 125.6 (s), 125.3 (s), 34.4 (s), 33.7 (s), 31.3 (s), 31.2 (s) quaternary carbons not observed. Solid state

^{31}P CP MAS 305.7, 302.7 ppm (5000, 8000).

Reaction mixture: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture indicated immediate (5 minutes) quantitative formation of a species with a chemical shift of 296. On standing, a bright yellow powder precipitates.

Reaction of $[\text{Mes}^*\text{NP}][\text{GaCl}_4]$ with $\text{C}_6\text{Cl}_6\text{SH}$: A solution of $\text{C}_6\text{Cl}_6\text{SH}$ (0.20 g, 0.71 mmol) in ≈ 20 mL of CH_2Cl_2 was added over ≈ 10 minutes to a stirred solution of $[\text{Mes}^*\text{NP}][\text{GaCl}_4]$ (0.35 g, 0.71 mmol) in ≈ 50 mL of CH_2Cl_2 . The solution turned bright yellow with copious precipitation of a light yellow solid which was extremely insoluble. Solvent was decanted and the solids washed with CH_2Cl_2 to give a bright yellow powder (0.42 g) dec. $> 225^\circ\text{C}$.

IR: 1592m, 1334s, 1303s, 1210w, 1164w, 494s, 463s, 378s, 364s.

NMR: Solid state ^{31}P CP MAS 366 (4000, 8000) weak signal. ^1H and ^{13}C not obtained because of the extreme insolubility of the compound.

Reaction mixture: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture showed quantitative formation of a species with a chemical shift of 360 ppm, but the peak was broad due to the formation of copious precipitate in the NMR tube.

NMR Studies: Reactions of $\text{Mes}^*\text{N}=\text{P}-\text{N}(\text{H})\text{Mes}^*$ with CH_3I in CH_2Cl_2 and in neat solution showed only a single peak at 270 ppm $[\text{Mes}^*\text{N}=\text{P}-\text{N}(\text{H})\text{Mes}^*]$. No reaction was observed between $\text{Mes}^*\text{N}=\text{P}-\text{N}(\text{H})\text{Mes}^*$ or $\text{Mes}^*\text{N}(\text{H})\text{P}$ -fluorenylidene with CCl_4 . $\text{Mes}^*\text{N}=\text{P}-\text{N}(\text{H})\text{Mes}^*$ reacts slowly with $[\text{CPh}_3][\text{GaCl}_4]$ to give a single species with a chemical shift of 15 ppm. There was no immediate reaction between Mes^*NPCI and $[\text{CPh}_3][\text{GaCl}_4]$, but after one week a multitude of species were formed, from which a single crystal of $[\text{Mes}^*\text{N}(\text{H})\text{PN}(\text{H})\text{Mes}^*][\text{GaCl}_4]$ was isolated. Reaction mixtures containing $[\text{Mes}^*\text{NP}][\text{GaCl}_4]$ with Et_2O , THF, and NEt_3 in CH_2Cl_2 all exhibited

quantitative formation of Mes*NPCl (132 ppm). Reaction mixtures containing equimolar amounts of [Mes*NP][GaCl₄] and Ph₃P in CH₂Cl₂ exhibited quantitative formation of Mes*NPCl (132 ppm) and Ph₃P→GaCl₃ (-6 ppm). [Mes*NP][GaCl₄] with 2,6-dimethylphenol gave a single phosphorus containing species with a chemical shift of 27 ppm (soluble in hexanes). [Mes*NP][GaCl₄] with Ph₂NH gave a single species with a ³¹P NMR shift of 249 ppm.

Reaction of Mes*¹⁵NPCl with LiHNMes*: A sample of ¹⁵N labelled Mes*N=P-N(H)Mes* was prepared by the reaction of Mes*¹⁵NPCl with LiHMes* in ether (0°C). Solvent was removed rapidly (20 minutes) *in vacuo*, and the light orange solids were washed with hexanes and characterized as a mixture of Mes*N(H)P=¹⁵NMes* and Mes*¹⁵N(H)P=NMes*.

IR: 3344m, 3337m, 1599m, 1421s, 1303m, 1274s, 1241m, 1217m, 1114m, 888m, 879m, 768w, 523w.

NMR: ³¹P, 269.9 (d, ¹J_{15N-P} 87 Hz), 269.8 (d, ¹J_{15N-P} 69 Hz); ¹⁵N-{H}, 307.7 (d, ¹J_{15N-P} 68 Hz), 139.6 (d, ¹J_{15N-P} 88 Hz) ¹J_{15N-H} 85 Hz.

Preparation of [iPr₂N]₂P-fluorenyl: Fluorenyllithium was prepared by slow addition of 4.8 ml of 1.6 M butyllithium in hexane solution to fluorene (1.27 g, 7.64 mmol) in 30 ml of ether (0°C). The solution turned bright yellow and was stirred for 30 minutes, and then was added over ≈ 10 minutes to a stirred solution (0 °C) of [iPr₂N]₂P-Cl in ≈ 30 ml of ether. The solution was warmed to room temperature and became colorless with precipitation of LiCl. Volatiles were removed *in vacuo*, the resulting solids were extracted and recrystallized from hexanes. The pink crystals were characterized as [iPr₂N]₂P-fluorenyl (2.78 g, 7.02 mmol, 92%), mp. 120-2 °C.

Elemental Anal. Calcd: C, 75.72; H, 9.40; N 7.06 %.

Found: C, 75.80; H, 9.37; N 6.89 %.

IR: 1343m, 1297s, 1192m, 1175s, 1155m, 1117m, 1092m, 1018m, 948s, 865m, 529m, 520s.

NMR: (CD₂Cl₂): ³¹P{¹H}, 71; ¹H: 7.86-7.27 (8H, aromatic); 4.34 (s, 1H); 3.58-3.35 (multiplet, 4H); 1.17 (d, ³J_{HH} = 7 Hz, 12H); 0.77 (d, ³J_{HH} = 7 Hz, 12H); ¹³C: 126.7 (s), 126.5 (s), 126.3 (s), 119.7(s), 57.4 (d, ¹J_{PC} = 35 Hz), 48.9 (d, ²J_{PC} = 13 Hz), 24.1 (d, ³J_{PC} = 7 Hz), 23.9 (d, ³J_{PC} = 7 Hz), quaternary carbons not reported.

Reaction Mixture: ³¹P{¹H} NMR spectrum of the reaction mixture indicated quantitative formation of [iPr₂N]₂P-fluorenyl in solution.

X-ray: monoclinic, space group *P*2₁/*n*, *a* = 15.710(5) Å, *b* = 9.66(1) Å, *c* = 15.93(2) Å, β = 91.48(6) Å, *V* = 2417(7) Å³, *Z* = 4, *D*_{calcd} = 1.089 g cm⁻³, μ = 1.210, 100*R*_w = 4.8 (TSC).

NMR Reactions of [iPr₂N]₂P-fluorenyl with [Ph₃C][BF₄] indicate quantitative formation of a species with a ³¹P signal at 27.5 ppm. This species decays quantitatively to give a fluorinated species at 154 ppm (t, ¹J_{PF} = 1194 Hz). In one reaction, as single crystal of Ph₃C-fluorenyl was isolated and characterized by X-ray crystallography.

Preparation of [Et₂N]₂P-fluorenyl: Prepared in the same fashion as [iPr₂N]₂P-fluorenyl. Elemental analysis not obtained, yield 1.27 g, 3.78 mmol, 50 %, mp. 121-3 °C.

IR: 1939w, 1901w, 1373w, 1345w, 1290s, 1189s, 1010s, 904s, 791m, 776m, 688m, 661m, 636m, 504m, 476w, 427w, 411w.

NMR (CD₂Cl₂): ³¹P{¹H} 95 ppm; ¹H: 7.82-7.24 (8H, aromatic); 4.75 (d, ²J_{PH} = 4 Hz, 1H), 3.31-3.18 (multiplet, 8H); 1.14 (t, ³J_{HH} = 7 Hz, 12H) ¹³C: 126.8, 126.6, 126.4, 119.7, 47.6 (d, ¹J_{PC} = 21 Hz), 44.1 (d, ²J_{PC} = 17 Hz), 14.6 (d, ³J_{PC} = 4

Hz), quaternary carbons not reported.

Preparation of $[iPr_2N]_2P(Cl)=fluorenylidene$: $[iPr_2N]_2P$ -fluorenyl (1.4 g, 3.6 mmol) was dissolved in ≈ 20 ml of pentanes. CCl_4 (≈ 1 mL) was poured into this solution and the clear solution was allowed to stand for two days at room temperature during which time yellow block crystals began to form. The supernatant solution was decanted from the crystalline material and the crystals washed with a small amount of pentanes. All volatiles were removed *in vacuo* and the solid was characterized as $[iPr_2N]_2P(Cl)=fluorenylidene$ (0.47 g, 1.09 mmol, 30%). A second crop of crystals was obtained (0.83 g) by recrystallization of the supernatant solids from pentanes/ CCl_4 (30:1) on standing for three days. Total yield of $[iPr_2N]_2P(Cl)=fluorenylidene$ 1.3 g, 3.0 mmol, 83 %; mp. 207-9 °C (dec.)

Elemental Anal. Calcd: C, 69.67; H, 8.42; N, 6.50 %.

Found: C, 69.88; H, 8.38; N, 6.45 %.

IR: 1609m, 1588m, 1553m, 1420m, 1322m, 1299s, 1278s, 1193s, 1167s, 1148s, 1118s, 1111s, 889m, 875m, 855m, 753s, 694s, 642m, 599m, 558s, 542s, 536s, 525m, 503m, 469s, 452m, 425m.

NMR: (CD_2Cl_2): $^{31}P\{^1H\}$: 53 ppm; 1H (298 K): 8.33-7.31 ($H_{aromatic}$, 8H), 3.84-3.60 (multiplet, 4H), 1.02 (d, $^3J_{HH} = 7$ Hz, 12H), 0.98 (d, $^3J_{HH} = 7$ Hz, 12H); ^{13}C (213 K): 140.7 (d, $J_{PC} = 21$ Hz), 139.5 (d, $J_{PC} = 19$ Hz), 130.7 (d, $J_{PC} = 18$ Hz), 130.0 (d, $J_{PC} = 19$ Hz), 122.8 (d, $J_{PC} = 29$ Hz), 119.1 (d, $J_{PC} = 58$ Hz), 118.2 (d, $J_{PC} = 68$ Hz), 117.0 (d, $J_{PC} = 20$ Hz), 66.3 (d, $^1J_{PC} = 201$ Hz), alkyl region is broad. At 293 K aryl region is broad, but alkyl region is sharp: 66.3 (d, $^1J_{PC} = 201$ Hz), 50.0 (d, $J_{PC} = 4$ Hz), 24.2 (d, $J_{PC} = 4$ Hz), 23.4 (d, $J_{PC} = 4$ Hz).

Reaction Mixture: $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture containing copious amounts of crystalline $[iPr_2N]_2P(Cl)=fluorenylidene$ indicated no presence of

starting material in solution or other phosphorus containing compounds.

X-ray: monoclinic, space group $P2_1/c$, $a = 8.69(1) \text{ \AA}$, $b = 16.24(1) \text{ \AA}$, $c = 17.16(2) \text{ \AA}$, $\beta = 96.0(1)^\circ$, $V = 2409(8) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 1.188 \text{ g cm}^{-3}$, $\mu = 2.351$, $100R_w = 4.5$ (TSC).

[Et₂N]₂P(Cl)=fluorenylidene: [Et₂N]₂P-fluorenyl (1.07 g, 3.14 mmol) was dissolved in 25 mL of hexanes. CCl₄ ($\approx 1 \text{ mL}$) was to the solution with immediate formation of a yellow precipitate. All volatiles were removed *in vacuo* and the solid was recrystallized from benzene and characterized as [Et₂N]₂P(Cl)=fluorenylidene (1.10 g, 2.93 mmol, 90%) mp. 103-4 °C. Elemental analyses not obtained.

IR: 1610m, 1588m, 1557w, 1421s, 1356s, 1326s, 1289s, 1234m, 1203s, 1153s, 1115m, 1095m, 1061s, 1035s, 1022s, 892m, 788s, 753s, 704s, 675s, 597w, 528s, 504m, 453m, 422m, 365w, 332w.

NMR (CD₂Cl₂): ³¹P{¹H}: 58; ¹H: 8.09-7.09 (8H aromatic), 3.52-3.20 (multiplet, 8H), 1.29 (t, J_{HH} = 7 Hz, 12H); ¹³C: 124.4 (s), 119.7 (s), 118.7 (s), 117.8(s), 64.5 (d, ¹J_{PC} = 205 Hz) 40.8 (d, ²J_{PC} = 5 Hz), 13.5 (d, ³J_{PC} = 2 Hz). Alkyl peaks become broad on cooling.

Preparation of [iPr₂N]₂P(Cl)=fluorenylidene-GaCl₃ complex: A solution of [iPr₂N]₂P(Cl)=fluorenylidene (0.21 g, 0.47 mmol) in benzene ($\approx 20 \text{ mL}$) was added to a stirred solution of GaCl₃ (0.085 g, 0.47 mmol) in benzene ($\approx 20 \text{ mL}$) in a 10 °C bath. A white precipitate formed immediately and the solvent was decanted from the solid which was washed by back-distillation. The volatiles were removed *in vacuo* and the white powder was characterized as [iPr₂N]₂P(Cl)=fluorenylidene-GaCl₃ complex: mp. 105 °C (dec.).

IR: 1305m, 1195m, 1165m, 1149m, 1140m, 1110m, 994s, 972s, 942m, 799m, 740s,

681m, 606m, 558m, 540s, 366s, 359s, 345s.

NMR (CD_2Cl_2 , -80°C): $^{31}\text{P}\{^1\text{H}\}$ 71; ^{13}C and ^1H were obtained but peaks were poorly resolved and difficult to interpret due to facile isomerization.

Reaction Mixture: ^{31}P NMR reactions in benzene indicate quantitative precipitation of the complex with no starting material remaining in solution.

Isomerisation of the $[\text{iPr}_2\text{N}]_2\text{P}(\text{Cl})=\text{fluorenylidene-GaCl}_3$ Complex:

$[\text{iPr}_2\text{N}]_2\text{P}(\text{Cl})=\text{fluorenylidene-GaCl}_3$ was prepared as described above using (GaCl_3 : 0.14 g, 0.79 mmol, ≈ 30 mL benzene; $[\text{iPr}_2\text{N}]_2\text{P}(\text{Cl})=\text{fluorenylidene}$: 0.34 g, 0.77 mmol, ≈ 30 mL benzene). The resulting white powder of $[\text{iPr}_2\text{N}]_2\text{P}(\text{Cl})=\text{fluorenylidene/GaCl}_3$ complex was then dissolved in (≈ 40 mL) $\text{CH}_2\text{Cl}_2/\text{pentanes}$ (75/25). Slow removal of solvent overnight yielded light pink crystals characterized as 9-di-*i*-propylamino-10-di-*i*-propyliminium-9, 10-dihydro-9-phosphaphenanthrene tetrachlorogallate (0.39 g, 0.64 mmol, 83%) mp. $166-7^\circ\text{C}$.

Elemental Anal. Calcd: C, 49.46; H, 5.98; N, 4.61 %.

Found: C, 49.23; H, 6.08; N, 4.54 %.

IR: 1582s, 1195s, 1167s, 1138s, 1113s, 1017s, 964s, 874m, 785m, 758s, 738s, 687m, 678m, 517m, 489m, 456m, 372s.

NMR: (CD_2Cl_2 , -80°C): $^{31}\text{P}\{^1\text{H}\}$ 22; ^1H 8.03-7.17 (8H, aromatic), 4.79 (multiplet, 1H), 4.42 (multiplet, 1H), 3.22 (multiplet, 1H), 2.74 (multiplet, 1H), 2.01 (d, $^3J_{\text{HH}} = 6.4$ Hz), 1.52 (d, $^3J_{\text{HH}} = 6.1$ Hz), 1.44 (d, $^3J_{\text{HH}} = 6.8$ Hz), 1.39 (d, $^3J_{\text{HH}} = 6.0$ Hz), 1.07 (d, $^3J_{\text{HH}} = 5.9$ Hz), 0.97 (d, $^3J_{\text{HH}} = 5.9$ Hz), 0.48 (d, $^3J_{\text{HH}} = 5.7$ Hz), -0.04 (d, $^3J_{\text{HH}} = 6.0$ Hz) total integration 24H; ^{13}C 213.9 (d, $^1J_{\text{PC}} = 89$ Hz, C=N), ^{13}C NMR complex and not fully resolved and assigned.

Reaction Mixtures: $^{31}\text{P}\{^1\text{H}\}$ NMR reactions of $[\text{iPr}_2\text{N}]_2\text{P}(\text{Cl})=\text{fluorenylidene/GaCl}_3$ complex in CH_2Cl_2 indicate quantitative isomerisation. NMR reactions with

$[\text{iPr}_2\text{N}]_2\text{P}(\text{Cl})=\text{fluorenylidene}$ and GaCl_3 in CH_2Cl_2 solution indicate quantitative formation of $[\text{iPr}_2\text{N}]_2\text{P}(\text{Cl})=\text{fluorenylidene}/\text{GaCl}_3$ which isomerizes quantitatively to give 9-di-*iso*-propylamino-10-di-*iso*-propyliminium-9, 10-dihydro-9-phosphaphenanthrene tetrachlorogallate.

X-ray: monoclinic, space group $P2_1/n$, $a = 9.884(3)$ Å, $b = 21.189(4)$ Å, $c = 14.639(4)$ Å, $\beta = 95.12(2)$ Å, $V = 3054(2)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.320$ g cm⁻³, $\mu = 13.18$, $100R_w = 3.7$ (TSC).

NMR reactions of $[\text{Et}_2\text{N}]_2\text{P}(\text{Cl})=\text{fluorenylidene}$ and GaCl_3 in CH_2Cl_2 solution indicate quantitative formation of $[\text{Et}_2\text{N}]_2\text{P}(\text{Cl})=\text{fluorenylidene}/\text{GaCl}_3$ ($^{31}\text{P}\{^1\text{H}\}$ 72) which does not isomerize (stable for 1 month).

NMR reactions of $[\text{Et}_2\text{N}]_2\text{P}(\text{Cl})=\text{fluorenylidene}$ with HOSO_2CF_3 in CD_2Cl_2 indicate quantitative formation of $\{[\text{Et}_2\text{N}]_2\text{P}(\text{Cl})\text{-fluorenyl}\}\{\text{OSO}_2\text{CF}_3\}$: NMR ^{31}P 72 ppm; ^1H 7.92-7.33 (8H, aromatic), 5.74 (d, $^2J_{\text{PH}} = 18$ Hz, 1H), 3.17-2.93 (m, 8H), 0.97 (t, $^3J_{\text{HH}} = 7$ Hz, 12H); ^{13}C : 130.7(d, $J_{\text{PC}} = 3$ Hz), 128.7(d, $J_{\text{PC}} = 4$ Hz), 127.1 (d, $J_{\text{PC}} = 4$ Hz), 121.6 (d $J_{\text{PC}} = 2$ Hz), 50.4 (d, $^1J_{\text{PC}} = 89$ Hz), 42.1 (s), 12.5 (s), 12.4 (s) (no change after one month). ^{13}C multiplicity analysis (JMOD) is consistent with the assignment. Reaction of $[\text{iPr}_2\text{N}]_2\text{P}(\text{Cl})=\text{fluorenylidene}$ with HOSO_2CF_3 in CH_2Cl_2 have a single ^{31}P signal at 71 ppm (no change after one month).

Preparation of 4 SbCl_3 :Diphenylacetylene Complex: Diphenylacetylene (0.39 g, 2.19 mmol) in ≈ 25 ml of hexanes was added dropwise over a period of 10 minutes to a solution of antimony trichloride (1.98 g, 8.68 mmol) in ≈ 25 ml CH_2Cl_2 . Solvents were removed from the clear solution *in vacuo* over a three hour period, during which clear, shiny plates formed. The crystalline material was recrystallized from 50/50 CH_2Cl_2 /hexanes, and the clear plate crystals were placed under dynamic vacuum for thirty minutes and characterized as $\text{C}_{14}\text{H}_{10}\text{Sb}_4\text{Cl}_{12}$ (2.02 g, 1.85 mmol, 85 %), mp. 76-78 °C.

Elemental Anal. Calcd: C, 15.42; H, 0.92 %.

Found: C, 15.48; H, 0.96 %.

IR: 1974w, 1913w, 1854w, 1798w, 780s, 692s.

NMR (CD_2Cl_2): ^1H : 7.56-7.35 (10H, aromatic); ^{13}C : 132.0, 129.0, 128.9, quaternary carbons not observed.

X-ray: triclinic, space group $P\bar{1}$, $a = 8.379(2)$ Å, $b = 11.965(3)$ Å, $c = 8.122(1)$ Å, $\alpha = 95.51(2)^\circ$, $\beta = 110.37(1)^\circ$, $\gamma = 94.69(2)^\circ$, $V = 754.0(3)$ Å³, $Z = 1$, $D_{\text{calcd}} = 2.402$ g cm⁻³, $\mu = 46.51$ cm⁻¹, $100R_w = 2.90$ (TSC).

Preparation of 4 SbCl_3 :*t*-Stilbene Complex: *t*-Stilbene (0.55 g, 3.05 mmol) in $\approx$ 15 ml of hexanes was added dropwise to a solution of antimony trichloride (2.80 g, 12.27 mmol) in $\approx$ 15 ml CH_2Cl_2 over a period of 10 minutes. Solvents were removed from the clear solution *in vacuo* over a three hour period, during which clear, shiny plates formed. The crystalline material was recrystallized from 50/50 CH_2Cl_2 /hexanes, and the clear plate crystals were placed under dynamic vacuum for thirty minutes and characterized as $\text{C}_{14}\text{H}_{12}\text{Sb}_4\text{Cl}_{12}$ (3.05 g, 2.79 mmol, 91 %), mp. 101-103 °C.

Elemental Anal. Calcd: C, 15.39; H, 1.11 %.

Found: C, 15.24; H, 1.11 %.

IR: 1966w, 1899w, 1845w, 1775w, 779s, 704s.

NMR (CD_2Cl_2): ^1H : 7.54-7.23 (10H, aromatic), 7.13 (s, 2H); ^{13}C : 129.2, 129.0, 128.2, 127.0, quaternary carbons not observed.

X-ray: triclinic, space group $P\bar{1}$, $a = 8.363(3)$ Å, $b = 11.950(3)$ Å, $c = 8.099(3)$ Å, $\alpha = 95.44(2)^\circ$, $\beta = 109.15(3)^\circ$, $\gamma = 96.28(2)^\circ$, $V = 752.6(4)$ Å³, $Z = 1$, $D_{\text{calcd}} = 2.411$ g cm⁻³, $\mu = 46.15$ cm⁻¹, $100R_w = 8.39$ (TSC).

Preparation of 4 SbCl₃:Bibenzyl Complex: Bibenzyl (0.71 g, 3.90 mmol) in $\approx$ 40 ml of hexanes was added dropwise to a solution of antimony trichloride (3.58 g, 15.69 mmol) in $\approx$ 20 ml CH₂Cl₂ over a period of 10 minutes. Solvents were removed from the clear solution *in vacuo* over a three hour period, during which clear, shiny plates formed. The crystalline material was recrystallized from 50/50 CH₂Cl₂/hexanes, and the clear plate crystals were placed under dynamic vacuum for thirty minutes and characterized as C₁₄H₁₄Sb₄Cl₁₂ (3.94 g, 3.60 mmol, 92 %), mp. 78-79 °C.

Elemental Anal. Calcd: C, 15.36; H, 1.29 %.

Found: C, 15.57; H, 1.37 %.

IR: 1974w, 1894w, 1840w, 1761w, 785s, 720s.

NMR (CD₂Cl₂): ¹H: 7.30-7.18 (10H, aromatic), 2.92 (s, 4H); ¹³C: 129.0, 128.8, 126.4, 38.1, quaternary carbons not observed.

X-ray: triclinic, space group *PL*, $a = 8.384(2)$ Å, $b = 11.950(4)$ Å, $c = 8.103(2)$ Å, $\alpha = 94.81(3)^\circ$, $\beta = 108.64(2)^\circ$, $\gamma = 97.42(3)^\circ$, $V = 756.0(4)$ Å³, $Z = 1$, $D_{\text{calcd}} = 2.404$ gcm⁻³, $\mu = 45.94$ cm⁻¹, $100R_w = 7.34$ (TSC).

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