Investigations of Phosphenium Insertion into Phosphorus-Phosphorus Bonds

by

Dane A. Knackstedt

Submitted in partial fulfilment of the requirements
for the degree of Master of Science

at

Dalhousie University
Halifax, Nova Scotia
April 2011

DALHOUSIE UNIVERSITY

DEPARTMENT OF CHEMISTRY

The undersigned hereby certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "INVESTIGATIONS OF PHOSPHENIUM INSERTION INTO PHOSPHORUS-PHOSPHORUS BONDS" by Dane A. Knackstedt in partial fulfillment of the requirements for the degree of Master of Science.

Dated: April 25th, 2011

Supervisor: ______________________________

Readers: ______________________________

____

____

DALHOUSIE UNIVERSITY

DATE: April 25th, 2011

AUTHOR: Dane A. Knackstedt

TITLE: Investigations of Phosphenium Insertion into Phosphorus-Phosphorus Bonds

DEPARTMENT OR SCHOOL: Department of Chemistry

DEGREE: MSc CONVOCATION: October YEAR: 2011

Signature of Author

Table of Contents

List of Tables……………………………………………………………...……………vii

List of Figures…………………………………..……………………………viii

Abstract…………………………………………………………………..……....xii

List of Abbreviations and Symbols Used…………………………………………xiii

Acknowledgements……………………………………………………….……xv

Chapter 1: Introduction

1.1: Carbon and Phosphorus……..……………………………………………1

1.2: Oxidation States and Nomenclature…………………………………….2

1.3: Neutral Polyphosphines………………………………………………5

1.4: Anionic Polyphosphines……………………………………………10

1.5: Cationic Polyphosphines……………………………………………14

1.5.1: Acyclic Polyphosphorus Cations…………………………..14

1.5.2: Cationic Phosphorus Clusters……………………………..20

1.5.3: Cyclic Polyphosphorus Cations…………………………...22

1.6: Phosphenium Cations………………………………………………….24

1.7: Summary and Outlook……..………………………………………….25

Chapter 2: Studies on 1,3-diphosphino-2-phosphonium cations

2.1: Introduction…………………………………………………………27

2.2: Results and Discussion……………………………………………...29

2.3: Summary, outlook and conclusions…………………………………31

Chapter 3: Expansion of known Cyclotriphosphinophosphonium Ions

3.1: Introduction……………………………………………………………32

3.2: Results and Discussion…………………………………………………...35

3.3: Controlled Isomerization of $({}^{t}BuP)_3$ to $({}^{t}BuP)_4$……………………………..42

3.4: Summary, Outlook and Conclusions……..………………………………44

Chapter 4: 2-Phosphino-1,3-diphosphonium Ion Derivatives

4.1: Introduction……………………………………………………………45

4.2: Results and Discussion…………………………………………………...46

4.3: Summary, Outlook and Conclusions………..……………………………54

Chapter 5: Summary, Proposed Future Directions and Preliminary Results

5.1: Summary………………………………………………………………55

5.2: In series *catena*-phosphorus coordination complexes and subsequent derivitization…………………………………………………………...55

5.3: Hypervalent phosphorus compounds……………………………………..57

5.4: Diphosphenes as precursors to phosphinophosphonium compounds…………………………………………………………..…60

5.5: Melt reactions towards new cyclophosphinophosphonium cations………………………...60

5.6: Non-symmetric diphosphines and diphospholes as mediators of novel *catena*-phosphorus chemistry……………………………………………62

5.7: Perfluorinated phosphorus compounds as precursors for novel cationic phosphorus frameworks…………………………………………………..64

5.8: Ligand stabilization of Phosphorus(V) cations……………………………..68

Chapter 6: Experimental

6.1: General Procedures……………………………………………………….69

6.2: Preparation and Characterization of Compounds…………………………...70

Appendix A: Details on the modified synthesis and purification of tetramethyldiphosphine (Me_2P-PMe_2)……………………………………………...…76

Appendix B: Crystallographic Tables……………………………………….…..79

References…………………………………………………………………..……81

List of Tables

Table 1.0 – Comparison of selected atomic properties for carbon, phosphorus and silicon……………………………………………………………………...1

Table 1.1 – Examples of common synthetic routes to cyclopolyphosphines……………10

Table 3.0 – $^{31}P\{^{1}H\}$ NMR Parameters for [**3.4(Ph$_2$)**][GaCl$_4$], [**3.4(Ph$_2$)**][OTf], and [**3.4(^{t}Bu(Cl)**][GaCl$_4$]…………………………………………………………42

Table 4.0 – $^{31}P\{^{1}H\}$ NMR parameters at 101.3 MHz for derivatives of the 2-phosphino-1,3-diphosphonium framework adapted from thesis by Y. Carpenter.[82] Coupling constants are derived by iterative fitting of the spectra at 298K and 101.3 MHz…………………………………..…..………………………49

Table 4.1 – Selected relevant bond lengths and angles in the solid state structures of the dications in characterized acyclic 2-phosphino-1,3-phosphonium triflates **4.1**[OTf]$_2$. Table adapted from thesis by Y. Carpenter.[82]…..……..….52

List of Figures

Figure 1.0 – Oxidation of phosphorus (III) to phosphorus (V) and its isolobal relationship to carbon……………………………………..……………2

Figure 1.1 – Various phosphorus environments…………………………….……………4

Figure 1.2 – Allotropic forms of phosphorus. White (left), Red (middle) and black (right)…………………………………...…………………….………….6

Figure 1.3 – Disproportionation of diphosphine to generate triphosphine………………..7

Figure 1.4 – General scheme towards linear phosphorus hydrides………………………7

Figure 1.5 – Synthesis of Li_3P_7..10

Figure 1.6 – Degenerate Cope rearrangement observed for P_7^{3-}………………………...11

Figure 1.7 – P_{16}^{2-} as a decomposition product of P_7^{3-}…………………………………....11

Figure 1.8 – Synthetic route to saturated cyclopolyphosphides…………………………12

Figure 1.9 – Unsaturated cyclopolyphosphides; P_4^{2-} (left), P_5^- (middle) and P_6^{4-} (right)..13

Figure 1.10 – Unsaturated tri (left) and tetra (right) phosphorus frameworks resulting from alkali silanide degradation of P_4……………………………….………..14

Figure 1.11 – Lewis (left) and dative (right) models for cationic phosphorus frameworks…………………………………………………………...15

Figure 1.12 – Alkylation of a diphosphene produces an unsaturated cationic phosphorus framework……………………………………………………15

Figure 1.13 – Examples of acyclic (left) and polycyclic (middle and right) diphosphonium frameworks……………………………………………....16

Figure 1.14 – Lewis (right) and dative (left) models of monocationic triphosphorus frameworks…………………………………………………………...16

Figure 1.15 – Protonation and subsequent ligand substitution of aminophosphenes leads to unsaturated triphosphorus monocations ………...………………..17

Figure 1.16 – Proposed mechanism for the reductive coupling of 2,3-diphosphino-1,4-diphosphonium frameworks……………………………..…………19

Figure 1.17 – Ligand displacement of 2,3-diphosphino-1,4-diphosphonium cation by a donor (Do)……………….……………………………………………19

Figure 1.18 – Examples of tethered 2,3-diphosphino-1,4-diphosphonium cations……...20

Figure 1.19 – Functionalization of P_4 by $[DippNPCl]_2$ and $GaCl_3$………………………22

Figure 1.20 – 2,4-cyclodiphosphino-1,3-diphosphonium (left), 3,4-cyclodiphosphino-1,2-diphosphonium (right)……………………..………………………..23

Figure 1.21 – Resonance delocalization of positive charge in diaminophosphenium cations………………………………………………………………...24

Figure 2.0 – Phosphenium cation stabilized by a tertiary phosphine (top) and diphosphine (bottom)……..……………………………………………27

Figure 2.1 –A_2B spin system of $[Me_2P\text{-}PMe_2\text{-}PMe_2][OTf]$ ($^{31}P\{^1H\}$ NMR)[59]…………28

Figure 2.2 – Diphosphines with substituents of varying steric bulk……………………..29

Figure 2.3 –Proposed mechanism for the insertion of phosphenium cations into diphosphines…………………………………………………………....30

Figure 2.4 – Reaction scheme describing low temperature experiments targeted at elucidating phosphenium cation insertion into diphosphines ……………..31

Figure 3.0 –Generation of a four phosphorus monocation by direct oxidation (left) and by phosphenium insertion (right). Vertices without a label are assumed to be phosphorus. All other unlabelled points are alkyl/aryl substituents……………………………………………………………....32

Figure 3.1 – Cationic and neutral *cyclo*-phosphorus compounds………………………..35

Figure 3.2 – $^{31}P\{^1H\}$ NMR spectrum of [**3.4**(**Ph$_2$**)][$GaCl_4$] with experimental (top) and iterative simulated spectrum (inverse)……………………….………..36

Figure 3.3 – ORTEP plot of the molecular structure of the cation [**3.4**(**Ph$_2$**)**]**$^+$ in [**3.4**(**Ph$_2$**)][$GaCl_4$]. Thermal ellipsoids with 50% probability (hydrogen atoms and counteranions are omitted for clarity)…………………………37

Figure 3.4 – Reaction of $[^tBuPCl]^+$ with $(^tBuP)_4$ to produce [**3.4**(***t*****Bu(Cl)**)][$GaCl_4$]…….39

Figure 3.5 – $^{31}P\{^1H\}$ NMR spectrum of [**3.4**(***t*****Bu(Cl)**)][$GaCl_4$]…………………………39

Figure 3.6 – Proposed mechanism rationalizing empirical results………………………41

Figure 3.7 – Proposed intermediates in the isomerisation of $(^tBuP)_3$ to $(^tBuP)_4$…...……43

Figure 4.0 – Lewis (left) and delocalized (right) models for the triphosphenium framework reported by Schmidpeter and co-workers in 1982……………..45

Figure 4.1 – Synthesis of a 2-phosphino-1,3-diphosphonium cation by alkylation (top) and by direct synthesis (bottom)……………………………...…………46

Figure 4.2 – Lewis (left column) and dative (right column) representations of **4.1** and **4.2**, respectively..…………………………………………...………46

Figure 4.3 – Lewis model, highlighting the P-E interaction (E = C, N, H)…….…..……51

Figure 4.4 – ORTEP representations of the solid state structure of the cation in (left to right; top to bottom): **4.1(Me)[OTf]$_2$**, **4.1(Cy)[OTf]$_2$**, **4.1(^{t}Bu)[OTf]$_2$** and **4.1(N^{i}Pr$_2$)[OTf]$_2$**. Hydrogen atoms and counterions omitted for clarity. Thermal ellipsoids shown at the 50% probability level. Unlabelled atoms are carbon atoms. Relevant parameters are listed in Table 4.1…….…………………………………………………...……53

Figure 5.0 – 'In-Series' coordination of dimethylphosphenium to gallium trichloride…55

Figure 5.1 – Dative (left) and covalent (right) models for 1-phosphino-2,3-diphosphonium framework (R = C_6F_5, CF_3)……………………………56

Figure 5.2 – Generation of a 1,4-diphosphino-2,3-diphosphonium framework by TMSCl elimination…………………………………………...………....56

Figure 5.3 – $[(CF_3)_2P\text{-}PMe_3][OTf]$ **(3a)** as Lewis (left) and coordination (right) models……………………………………………………..….57

Figure 5.4 – 2-phosphinide-1,3-diphosphonium as proposed product of $[(CF_3)_2P\text{-}PMe_3][OTf]$ with PMe_3……………………………………….58

Figure. 5.5 – Proposed product of $[(CF_3)_2P\text{-}PMe_3][OTf]$ with a bidentate phosphine….58

Figure 5.6 – Amphoteric reactivity of neutral coordination complexes………………...59

Figure 5.7 – Representation of potential reactivity of diphosphenes with respect to phosphenium cations……………………………………………………60

Figure 5.8 – Lewis structure of tetraphenyldiphosphole………………………………...63

Figure 5.9 – Lewis model of various branched *catena*-phosphorus cations……………64

Figure 5.10 – Proposed S_N2 mechanism for the insertion of phosphenium cations into phosphorus rings……………………………………………………………...65

Figure 5.11 – Proposed neutral coordination complex (A) and metathesized products (B)……………………………………………………………………..66

Figure 5.12 – ^{31}P NMR spectrum of a reaction mixture containing Me_2PCl and $Me_2P-P(C_6F_5)_2$………………………………………………………………..67

Abstract

Despite many drawn parallels between carbon and phosphorus, the development of *catena*-phosphorus chemistry is superficially explored when compared to carbon. This lack of progression is especially highlighted for cationic phosphorus frameworks, as neutral and anionic phosphorus frameworks have been studied to a much greater extent. This stresses cationic *catena*-phosphorus frameworks as important molecules for an improved understanding of fundamental phosphorus chemistry. Recent advancements in synthetic methods demonstrate that phosphorus frameworks of this type are viable target molecules. Furthermore, the precedence of a variety of new cationic *catena*-phosphorus frameworks by such methods exemplify their versatility. Here, novel 1,3-diphosphino-2-phosphonium $[R_2P\text{-}PR_2\text{-}PR_2]^+$, 2-phosphino-1,3-diphosphonium $[R_3P\text{-}PR\text{-}PR_3]^+$ and *cyclo*-triphosphinophosphonium $[R_2P(RP)_3]^+$ cations have been isolated and characterized in order to study the insertion of phosphenium cations into the phosphorus-phosphorus bonds of *catena*-phosphines.

List of Abbreviations and Symbols Used

^{1}H	Proton
^{31}P	Phosphorus-31
^{13}C	Carbon-13
$\{^{1}H\}$	Proton decoupled
Å	angstrom (10^{-10} m)
^{t}Bu	Tertiary butyl
Calcd	Calculated
Cy	Cyclohexyl
d	Doublet (NMR)
D.p.	Decomposition point
dq	Doublet of quintet
ds	Doublet of septet
FT	Fourier transform
Hz	hertz
IR	Infrared
J	Joule
m	Multiplet
M^{I}	Alkali metal
Me	Methyl
Mes	2,4,6-Trimethylphenyl
Mes*	2,4,6-Tri-tertbutylphenyl
M.p.	Melting point
$^{n}J_{AB}$	n-bond coupling constant between nuclei A and B
NMR	Nuclear magnetic resonance
OTf	Trifluoromethanesulfonate (Triflate)
Ph	Phenyl
ppm	Parts per million
^{i}Pr	Isopropyl

R	Organic substituent
Ph_f	Perfluorophenyl (C_6F_5)
s	Singlet
t	Triplet
THF	Tetrahydrofuran
TMS	Trimethylsilyl
X	Halogen or general anion
δ	Chemical shift

Acknowledgements

I would first like to thank Dr. Neil Burford for his supervision, guidance and encouragement in the time I’ve been at Dalhousie University. Furthermore, I would like to thank my committee members, Drs. Mark Stradiotto, Kevin Grundy and Jim Pincock for providing helpful classes and discussion. Notes of thanks are also extended to past and present members of the Burford research group (Saurabh Chitnis, Lauren Doyle, Eamonn Conrad, Yuen-ying Carpenter, Elizabeth MacDonald, Janet Pickup, Cheryl Saunders, Adam Dyker, Michael Holthausen and Jan Weigand), administrative staff in the Department of Chemistry (Cheryl Stanton, Giselle Andrews, Deanna Wentzell, Sean Hartwell and Cheryl Coolen), machine shop gurus (Mike Boutillier and Rick Conrad), Mike Lumsden and Jurgen Mueller.

Finally, I would like to thank my family and friends for their loving support throughout this academic pursuit.

Chapter 1: Introduction

1.1: Carbon and Phosphorus

Catenation, or the ability of an element to generate stable homo-atomic bonds, is an eminent feature of carbon. In studying the fundamental conditions under which carbon frameworks catenate, chemists have developed empirically based theories that allow for the systematic assembly of large, complex carbon frameworks, often with useful applications in material science.[1] While phosphorus also displays the ability to catenate, there has been much less progress in its development. This is surprising, given that carbon is arguably more similar to phosphorus than its nearest congener. For example, the electronegativities of carbon and phosphorus ($\chi_C = 2.5$; $\chi_P = 2.2$) are closer in magnitude than carbon and silicon ($\chi_{Si} = 1.90$).[2] Of course, electronegativities alone are not sufficient in predicting the potential reactivity of an element. However, the coupling of many atomic properties, such as electron affinity and ionization energy help to illuminate a clearer picture of an atom's physical properties, and thus, potential similarities between two atoms. These properties are summarized in Table 1.0.

Element	Pauling Electronegativity	Electron Affinity (kJmol^{-1})	1st Ionization Energy (kJmol^{-1})	Covalent Radius (Å)
Carbon	2.55	122	1086	0.77
Phosphorus	2.19	72	1012	1.10
Silicon	1.90	134	786	1.17
$\Delta_{C\text{-}P}$	**0.36**	50	**74**	**0.33**
$\Delta_{C\text{-}Si}$	0.65	**12**	300	0.40

Table 1.0 – Comparison of selected atomic properties for carbon, phosphorus and silicon

A differentiating feature between carbon and phosphorus is the number electrons in the valence shell. With phosphorus being in group 15, it has one more electron in the valence shell than carbon, and is traditionally seen as three or five coordinate, whereas carbon most often has four interactions. By removing an electron from phosphorus, however, it has the same number of valence electrons as carbon, and so cationic phosphorus may be considered isolobal to neutral carbon as it also has atomic orbitals of similar symmetry and energy (Figure 1.0).

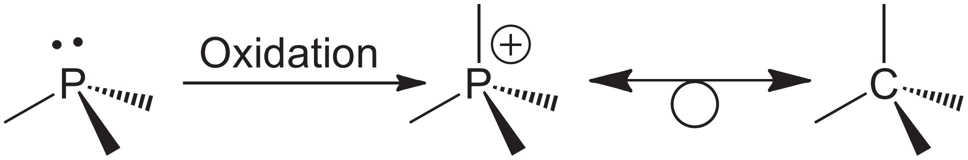


Figure 1.0 – Oxidation of phosphorus (III) to phosphorus (V) and its isolobal relationship to carbon.

Owing to the common ability to catenate, the isolobal relationship and similar atomic properties, cationic phosphorus is highlighted as a foundation for which higher ordered frameworks with potentially useful properties may be derived. However, this development of cationic phosphorus chemistry as a basis for new materials and technology is precluded by a lack of understanding in the fundamentals related to the structure and bonding of such frameworks.

1.2: Oxidation States and Nomenclature

Oxidation States

When discussing the reactivity, as well as coordination schemes of many transition metal complexes, it is often imperative to assess the oxidation state of the metal. By assigning neutral ligands as non-contributing factors to the metal's oxidation state, and by treating anionic ligands such as hydrogen atoms or alkyl frameworks as contributing a negative charge to the complex, one may assign the oxidation state of the metal. This can be accomplished by balancing the negative charges contributed by the ligands, with a positive metal charge. Despite parallels between metal-ligand complexes and main group analogues, the same methodology for assigning oxidation states is not as consistent when considering the latter. For example, PCl_3 is often referred to as phosphorus (III) chloride, which indicates that phosphorus is in the third oxidation state, or having an overall 3+ charge localized on the phosphorus atom. Similarly, PCl_5 suggests phosphorus being in the fifth oxidation state and having a 5+ charge localized on phosphorus. However, for analogues of these two compounds that have less electronegative substituents, such as hydrogen, designation of oxidation states becomes much more ambiguous. In the example of PH_3, the electronegativities for phosphorus (2.19) and hydrogen (2.20) are almost identical, suggesting that the molecular electron density is no longer localized on the subsituents of phosphorus, but instead spread throughout the molecule evenly. As such, designation of phosphorus being in the third oxidation state no longer holds true, given that a 3+ charge is no longer confined to the phosphorus atom.

While some transition metals do have similar electronegativities to adjacent atoms in ligands, assumptions can be made based on the fact that the majority of transition metals are lower in electronegativity. Furthermore, analysis of oxidation states for transition metal complexes is useful for mechanistic insight, among other considerations. Assessment of oxidation states for these purposes is not as prevalent for main group reactivity. This, coupled with the inconsistency of oxidation state designation for main group compounds, is why formal oxidation states will not be considered in the present document, except when discussing reaction schemes such as reductive coupling.[3,4]

Nomenclature:

There are a number of bonding environments observed for phosphorus. As such, standard methods of naming compounds are used for consistency when discussing different phosphorus environments. Despite the need for such regularity, instances have arisen where more than one name is used for one particular bonding environment. For this reason, the following nomenclature will be used throughout this document.

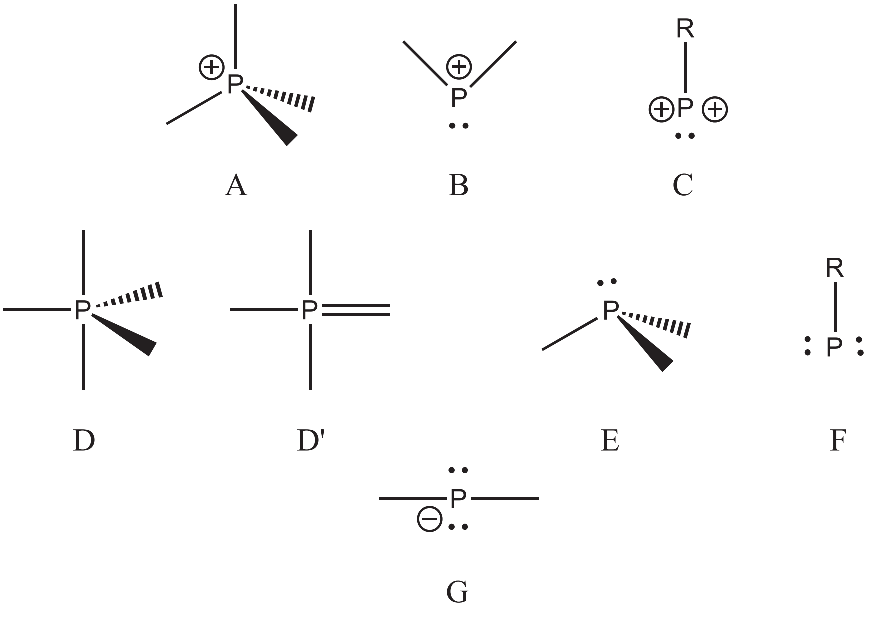


Figure 1.1 – Various phosphorus environments

Phosphonium (A): Four coordinate phosphorus with a +1 charge.

Phosphenium (B): Two coordinate phosphorus with a lone pair and a +1 charge.

Phosphinidinium (C): Single coordinate phosphorus center with one lone pair and a 2+ charge.

Phosphorane (D, D'): Neutral five (D) or four (D') coordinate phosphorus center.

Phosphine (E): Neutral three coordinate phosphorus center with a lone pair.

Phosphinidine (F): Neutral single coordinate phosphorus center with two lone pairs.

Phosphide (G): Two coordinate phosphorus with two lone pairs and a -1 charge.

1.3: Neutral Polyphosphines

Possibly the best known examples of neutral polyphosphines are the natural allotropes. Natural allotropes have three distinct divisions, although as many as eleven variations,[5] in addition to instances of phosphorus nanorods,[6] have been reported. White phosphorus exhibits four phosphorus centers in a strained tetrahedron, imposing bond angles of 60°. For this reason, it is the most reactive among the phosphorus allotropes. Both black and red phosphorus can be generated by heating white phosphorus to varying degrees, with black phosphorus being kinetically inert and red phosphorus being an intermediate in the conversion of white phosphorus to black. The most commonly known variety of red phosphorus is referred to as Hittorf's phosphorus, which is composed of interlocking phosphorus chains. Black phosphorus, on the other hand, displays an array of puckered six-membered rings, which stack on one another to generate sheets that have similar electrical conductivity as graphite (Figure 1.2).

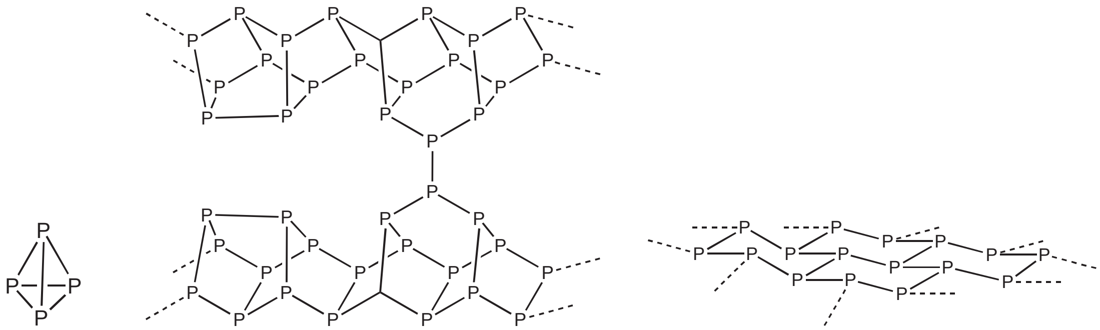


Figure 1.2 – Allotropic forms of phosphorus. White (left), red (middle) and black (right)

Instances of neutral phosphorus clusters that do not occur naturally also exist, although isolation of such compounds is limited to a single example. Heptaphosphine (P_7H_3) has been isolated by the methanolysis of $(Me_3Si)_3P_7$ at -40°, however, characterization has been restricted to NMR studies, as it is amorphous in the solid state.[7]

The simplest neutral polyphosphine contains only one phosphorus-phosphorus linkage and hydrogen as a substituent ($H_2P\text{-}PH_2$). Due to rapid decomposition, however, characterization is limited to mass spectrometry or Raman studies. High yields of polyphosphorus hydrides (P_nH_{n+2}) are achieved by reacting Ca_3P_2 with degassed water at 0°C under reduced pressure, which separates the reactive and volatile diphosphine from the reaction mixture as it is generated. Initially, it was thought that P_nH_{n+2} compounds for $n > 2$ would not be sufficiently stable under accessible conditions to observe, given that diphosphine is so unstable in a wide variety of conditions. However, a number of other phosphorus hydride chains ($n = 3\text{-}9$) have been isolated either as a decomposition product of diphosphine, or as a fraction of the reaction of Ca_3P_2 with degassed water. Triphosphine ($H_2P\text{-}PH\text{-}PH_2$), for example, can be found along with phosphine gas (PH_3), as a disproportionation product of $H_2P\text{-}PH_2$ when exposed to light or heat, according to Figure 1.3.

$$2P_2H_4 \rightarrow P_3H_5 + PH_3$$

Figure 1.3 – Disproportionation of diphosphine to generate triphosphine

Variable amounts of tetraphosphine ($H_2P\text{-}(PH)_2\text{-}PH_2$) can also be obtained by thermal reactions of liquid diphosphine and triphosphine. Similarly, pentaphosphine ($H_2P\text{-}(PH)_3\text{-}PH_2$) can be observed by mild thermolysis reactions of diphosphine and triphosphine. This trend can be generalized in Figure 1.4, where polyphosphine hydride open chains can be observed up to lengths of seven phosphorus atoms long, albeit chain lengths of 5-7 are generated with much more difficulty than shorter ones.

$$P_xH_{x+2} + P_yH_{y+2} \rightarrow P_{(x+y)}H_{(x+y)+2}$$

Figure 1.4 – General scheme towards linear phosphorus hydrides

As the number of phosphorus atoms in the chain increases, linear chains become progressively more difficult to isolate due to longer chains being thermodynamically less stable than smaller chains or to structural isomers ($n \geq 4$).[8]

Linear polyphosphines containing akyl and aryl substituents in place of hydrogen are significantly more stable which allows for facile isolation, extensive characterization and thus, greater availability for use in further synthesis compared to polyphosphosphine hydrides. A large part of the stability is attributed to the alkyl or aryl substituents, which serve as kinetic stabilizers by reducing molecular motion. However, synthetic methods to these polyphosphines generally limit chain lengths to four phosphorus atoms, after which there is a tendency for these molecules to cyclize. The simplest examples of acyclic organo-polyphosphines are diphosphines, triphosphines, and linear tetraphosphines, although a branched tetraphosphine can be obtained in the reaction of tris(trimethylstannyl)phosphine and three equivalents of chlorodiphenylphosphine. Typically, *catena*-phosphines of this type undergo disproportionation, which is why development of iso-tetraphosphines have been limited to this example.

The discovery of neutral polyphosphorus rings has been much slower compared to the acyclic analogues, despite the fact that the first cyclophosphine was described more than 130 years ago by Kohler and Michaelis. However, advancement in instrumentation as well as laboratory techniques have facilitated the development and characterization of four basic ring frameworks containing trivalent phosphorus $(RP)_n$ ($n = 3$-6; R = H or an organic substituent). When R is hydrogen, larger rings ($n = 10$) have been detected by mass spectrometry as a thermolysis byproduct of H_2P-PH_2, although isolation of such rings has been elusive.

Synthetic strategies to polyphosphorus rings vary and can be classified into two categories: Those that generate a specific ring size, or those that generate mixtures of rings. For the set of reactions that generate a mixture of ring sizes, the distribution of products depends on which ring size is most thermodynamically favoured. This is largely dependent on the size of the substituent. For example, the more strained $(RP)_3$ rings are generated preferentially when R = ^{t}Bu, despite its large strain energy. This is because the bulky substituents provide steric shielding of the P_3 skeleton and reduce rates of oligomerization to larger ring sizes. The employment of larger supermesityl[12] or terphenyl[13-14] substituents exemplify the effect that bulky groups have on oligomerization, as they facilitate the generation of organo-diphosphenes (RP=PR) by hindering adjacent molecular interactions. The preference for generating low coordinate diphosphenes when bulky substituents are present is supported by calculations that show alkenes with bulky substituents are thermodynamically more favourable than their cyclobutane analogues.[15] Larger rings $(RP)_n$ (n = 5) are favoured for less bulky R groups such as methyl, ethyl or phenyl as there is less steric shielding, therefore, higher rates of oligomerization to larger, less strained rings.[7]

Synthetic strategies to such cyclopolyphosphines usually involve either the reduction of the corresponding dichloroorganophosphine with mono- or divalent metals (lithium, sodium, magnesium, mercury), or the dehydrohalogenation of a mono-substituted organophosphine (RPH_2) and dichloroorganophosphine ($RPCl_2$), as summarized in table 1.1.[7]

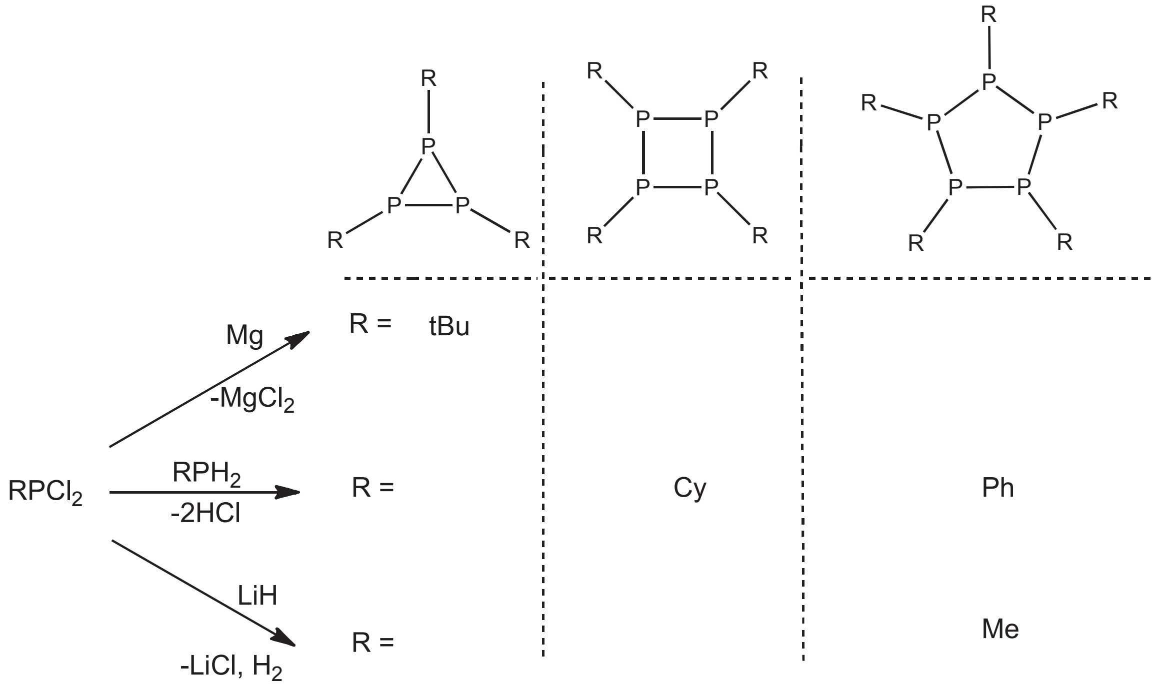


Table 1.1 – Examples of common synthetic routes to cyclopolyphosphines

1.4: Anionic Polyphosphines

Similar to neutral polyphosphines, anionic polyphosphines can be classified into three major categories: clusters, acyclic and cyclic. Anionic clusters are generated by reacting diphosphine (H_2PPH_2) with reducing alkali metals. The reaction of diphosphine with *n*-butyllithium or lithium dihydrogen phosphide in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) at -20°C, for example, facilitates the generation of lithium heptaphosphide (Li_3P_7), as well as PH_3 according to figure 1.5.[8]

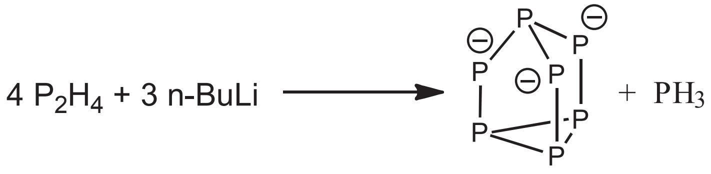


Figure 1.5 – Synthesis of Li_3P_7

It has been noted to be structurally fluxional via a degenerate Cope rearrangement and can be described by two equivalent forms (Figure 1.6).[16]

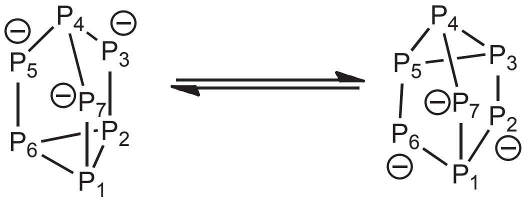


Figure 1.6 – Degenerate Cope rearrangement observed for P_7^{3-}

Anionic phosphorus clusters systems such as this, however, are unstable at room temperature and often decompose to larger polyphosphide complexes, that can be described as two P_7^- fragments, joined by a common two-atom linker (Figure 1.7).

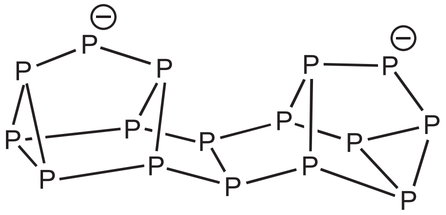


Figure 1.7 – P_{16}^{2-} as a decomposition product of P_7^{3-}

Hexadecaphosphide (P_{16}^{2-}) is generated with greater ease and yield, however, by the reaction of white phosphorus with $LiPH_2$[17], sodium[18] or $LiP(SiMe_3)_2$[19]. By altering stoichiometric conditions, it is even possible to isolate larger polyphosphide complexes. Specifically, P_{21}^{3-} can be isolated in pure form as a lithium salt in the aforementioned manner and can be viewed as having a P_7 cluster flanked by two P_7 terminal groups. This trend continues in describing P_{26}^{4-}, which is described as having alternating P_2, P_3^- fragments being terminated by P_7^-. An interesting ion that deviates slightly from this trend is P_{19}^{3-}, which consists of two P_7 fragments joined by a five-membered ring. The joining five-membered ring forces an open structure that has little steric shielding. As a result, P_{19}^{3-} is very reactive, which prevents its full characterization. This is consistent with studies that show it to be a reactive intermediate in the conversion of white phosphorus (P_4) to partial structures of Hittorf's phosphorus.[16]

Instances where saturated cyclic phosphorus anions are isolable are limited when compared to neutral cyclic polyphosphines. This is largely due to the preference of P-P bonds in cyclophosphines to be reduced over P-C bonds in the presence of alkali metals, resulting in acyclic polyphosphides.

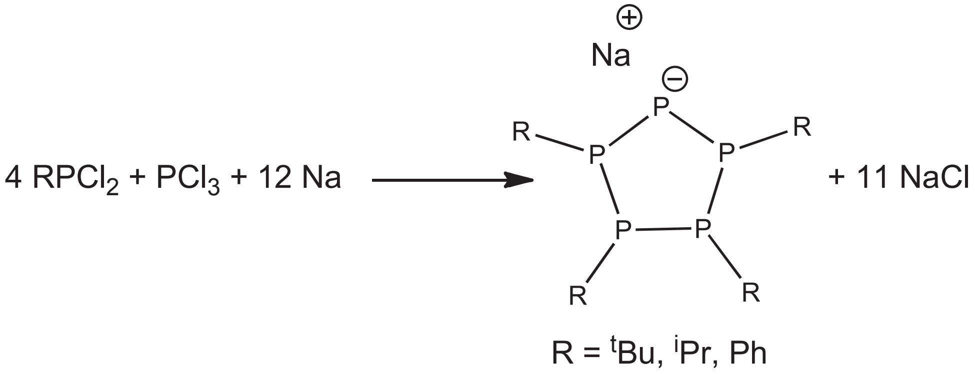


Figure 1.8 – Synthetic route to saturated cyclopolyphosphides

As a remedy, the use of PCl_3 facilitates the generation Na_3P, which then reacts with $RPCl_2$, making it possible to generate four or five membered polyphosphides (Figure 1.8).[20]

Other cyclic phosphorus anions of notable mention are P_4^{2-}, P_5^- and P_6^{4-} (Figure 1.9), which have been shown to function as a building blocks in several organometallic complexes, coordinating in η^4, η^5, and η^6 fashions, respectively. It is important that the former two anions have been shown to have aromatic character, which parallels their role to aromatic carbon rings in organometallic coordination complexes.[21] However, P_6^{4-} has been noted to be unstable in solution, as it disproportionates to a complex mixture of phosphides and hydrogen (poly)phosphides.

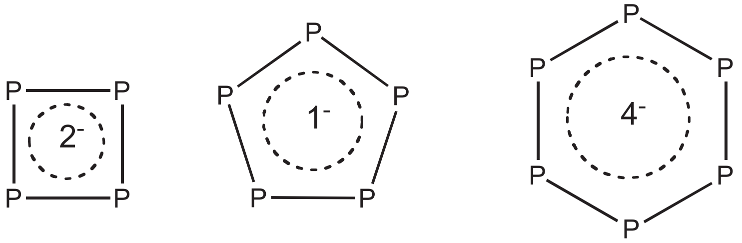


Figure 1.9 – Unsaturated cyclopolyphosphides; P_4^{2-} (left), P_5^- (middle) and P_6^{4-} (right)

Acyclic polyphosphides can be generated by reducing cyclopolyphosphines which are, themselves, obtained by the reduction of dichlorophosphines. Nevertheless, with appropriate stoichiometric equivalents, a number of di, tri and tetra phosphorus dianions have successfully been isolated from the direct combination of sodium metal and the respective dichlorophosphine, or similar procedure.[22, 23] Furthermore, unsaturated polyphosphorus anions (Figure 1.10) can be produced by the nucleophilic degradation of P_4 by alkali silanides. The resulting unsaturated tri and tetra phosphorus frameworks both exhibit terminal silyl functionalities, as well as formal negative charge(s) at the 3 position (former example) or 1 and 4 position (latter example).[24]

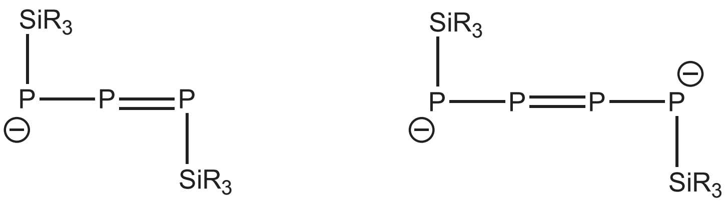


Figure 1.10 – Unsaturated tri (left) and tetra (right) phosphorus frameworks resulting from alkali silanide degradation of P_4

1.5: Cationic Polyphosphines

1.5.1: Acyclic Polyphosphorus Cations:
Two-Phosphorus Frameworks

The simplest cationic polyphosphine can be described as a phosphinophosphonium cation, where there is a formally neutral, three coordinate phosphorus center linked directly to a cationic four coordinate phosphorus center. Phosphinophosphonium cations were intitially proposed as products from the reaction of chlorophosphines with $AlCl_3$,[25, 26] or from the reaction of a diphosphine with alkylating agents,[27] however, the proposed connectivity has only recently been affirmed.[28] Cationic molecules of this type can be described using a Lewis model, where there is a covalent interaction between the two adjacent phosphorus centers; however, a dative model is much more representative of the chemistry that these complexes exhibit. By envisaging a phosphinophosphonium cation as a phosphine-stabilized phosphenium cation, the phosphine may be considered a ligand, coordinating to the Lewis acidic phosphenium center. The introduction of a stronger donor affords displacement of the original ligand, which exemplifies the donor-acceptor properties of these complexes and parallels the type of chemistry seen for many transition metal complexes. Not only can this idea be used for *catena*-phosphorus frameworks, but it also has been extrapolated as a general synthetic method towards other cationic inter-pnictogen frameworks.[29]

Figure 1.11 – Lewis (left) and dative (right) models for cationic phosphorus frameworks

Unsaturated cationic frameworks represent another class of compounds obtainable through alkylation of molecules containing a P-P bond. Specifically, Mes*P=PMes* reacts with MeOTf to give an unsaturated P-P framework (Figure 1.12).[30] However, while this shows that diphosphenes (RP=PR) react with alkylating agents in a similar manner to diphosphines (R_2P-PR_2), a phosphine-stabilized phosphenium model is not accurate in describing the bonding.[31]

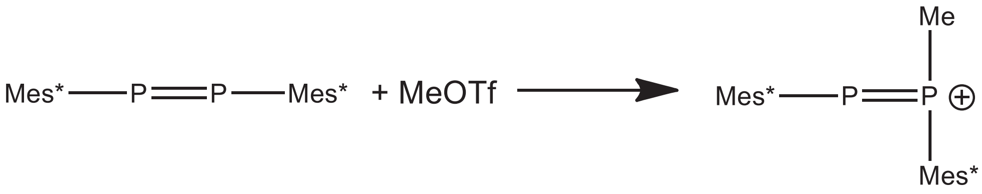


Figure 1.12 – Alkylation of a diphosphene produces an unsaturated cationic phosphorus framework

Diphosphonium cations where two four-coordinate, cationic phosphorus centers are directly linked (Figure 1.13) were originally observed as a by-product for reactions of red phosphorus with alkyl iodides.[32] However, such examples were only superficially characterized due to poor yields. High yielding routes to diphosphonium cations allowed for much more thorough characterization although, initially, this required distinctive polycyclic frameworks as kinetic stabilizers.[33-35] It is only recently that diphosphonium derivatives have been synthesized in the absence of polycyclic frameworks and is accomplished by alkylation of Me_2P-PMe_2,[36] or by employment of sterically bulky amine substituents.[37]

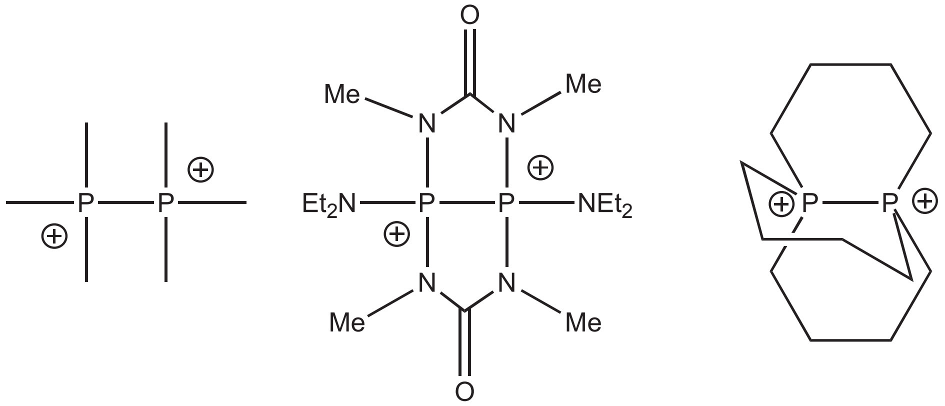


Figure 1.13 – Examples of acyclic (left) and polycyclic (middle and right) diphosphonium frameworks

Tri-Phosphorus Frameworks

Ligand displacement by a phosphine is an effective method for generating a number of phosphino-phosphonium cation derivatives. Thus, a natural progression for this synthetic method involves ligand displacement using diphosphines, where a phosphorus-phosphorus linkage is already present. Coordination of a diphosphine to phosphenium cations is, therefore, an efficient method to generate 1,3-diphosphino-2-phosphonium frameworks (Figure 1.14).

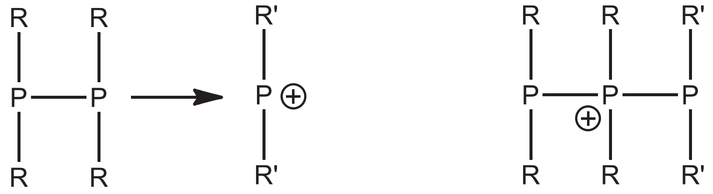
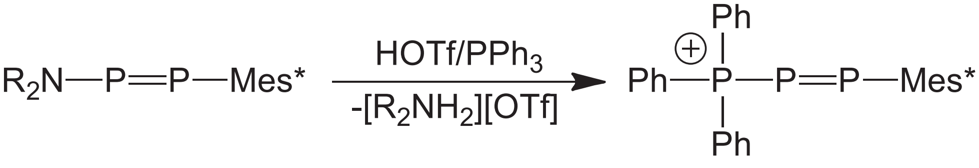


Figure 1.14 – Lewis (right) and dative (left) models of monocationic triphosphorus frameworks

The reaction of diphosphines (R = Me, Ph) with various phosphenium centers leads to insertion of the phosphenium cation into the P-P linkage, rather than terminal stabilization of the phosphenium center by the diphosphine, as one might expect.[38] However, the phosphenium inserted product is only distinguishable when using phosphenium cations whose substituents differ from those of the diphosphine. For example, in an analogous reaction of I_2P-PI_2 with PI_3 and $AgAl[OC(CF_3)_3]_4$ where $[I_2P$-PI_2-$PI_2][OC(CF_3)]_4$ is produced, the mechanistic pathway is undefined, as the products for both a phosphenium-inserted and end-on stabilized pathways are identical.[39] Other diphosphino-phosphonium complexes of this type have been reported, however, the reactivity is either more complex,[40] or doesn't exemplify the versatility of phosphine stabilized phosphenium centers.[41]

Monocationic tri-phosphorus cations can also be obtained by the selective protonation of nitrogen and subsequent ligand substitution of aminodiphosphenes in the presence of triphenylphosphine (Figure 1.15),[42] by the reduction of PCl_3 with $SnCl_2$ in the presence of a stabilizing phosphine,[43] or by the chelation of a bidentate ligand to PI_3.[44]



R = ^{i}Pr, Cy, or 2,2,4,4-tetramethylpiperdine

Figure 1.15 – Protonation and subsequent ligand substitution of aminophosphenes leads to unsaturated triphosphorus monocations

The methodology of using a halide abstractor and chlorophosphines to generate phosphenium centers can be expanded to dichlorophosphines, where up to two chlorine atoms may be removed. Doing so generates phosphinidinium cations, or single coordinate phosphorus centers with a formal 2+ charge that are stabilized by two adjacent phosphine interactions.[45] These compounds are referred to as 2-phosphino-1,3-diphosphonium cations using a Lewis model and can alternatively be prepared by the alkylation of unsaturated three-phosphorus cations.

Tetra-Phosphorus Frameworks

The same methodology used to produce 2-phosphino-1,3-diphosphonium cations has been shown to be an effective route towards 2,3-diphosphino-1,4-diphosphonium frameworks by alteration of reactant stoichiometry. Although mechanistic insight is speculative, it is suggested that these dicationic complexes are synthesized by reductive coupling of chlorophosphinophosphonium cations.[4] Initially, the reaction of TMSOTf with a dichlorophosphine ($RPCl_2$) and tertiary phosphine (PR_3) generates a chlorophosphinophosphonium cation $[R_3P\text{-}PRCl]^+$. Next, an additional equivalent of the tertiary phosphine reduces $[R_3P\text{-}PRCl]^+$ to produce $[R_3P^+\text{-}P^-R]$ which stabilizes an $[R'PCl]^+$ ion through donation of a lone pair of electrons. An additional halide abstraction and phosphine stabilization results in the four phosphorus, dication shown in Figure 1.16.

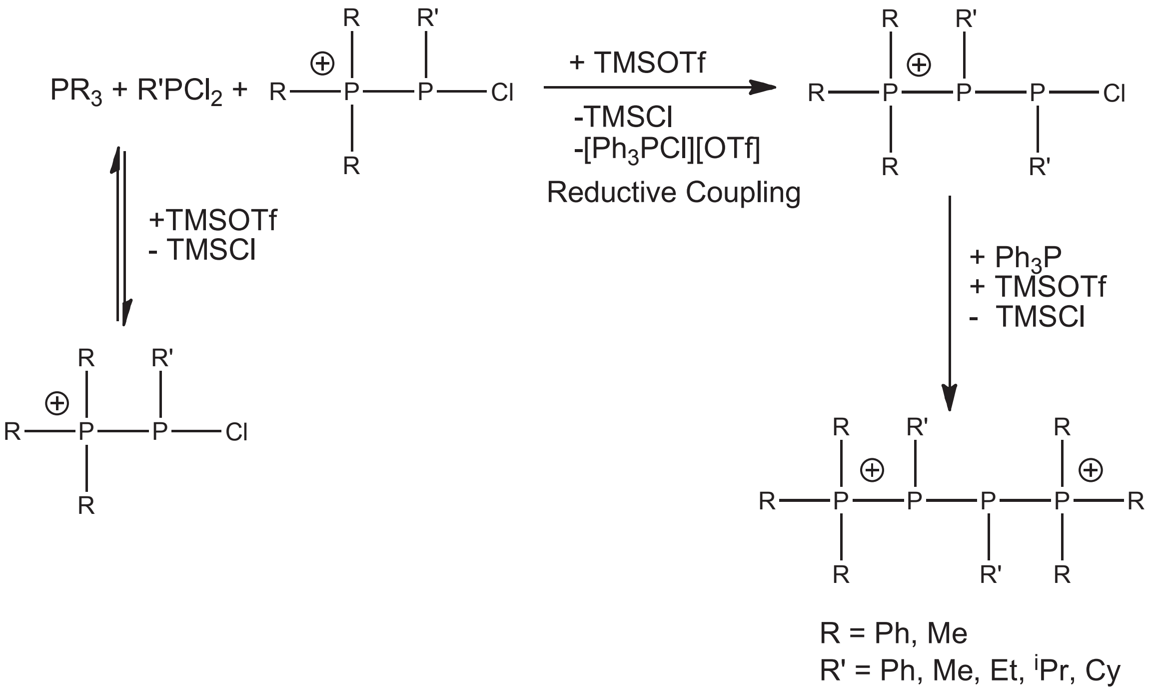


Figure 1.16 – Proposed mechanism for the reductive coupling of 2,3-diphosphino-1,4-diphosphonium frameworks

Similar to other phosphino-phosphonium compounds, 2,3-diphosphino-1,4-diphosphonium frameworks may be described as two adjacent phosphenium centers, each stabilized by a phosphine ligand. This model helps to explain their susceptibility to ligand displacement in the presence of a stronger donor, which is observed for a number of derivatives of the type [R_3P-PR-PR-PR_3] (Figure 1.17).[3, 4]

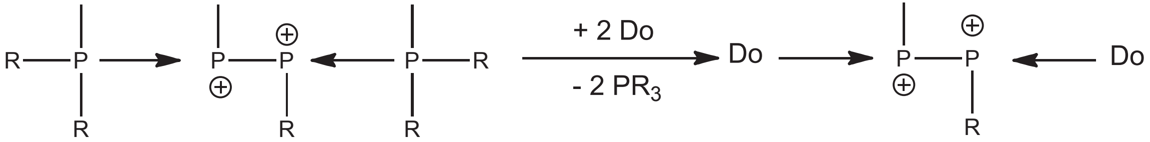
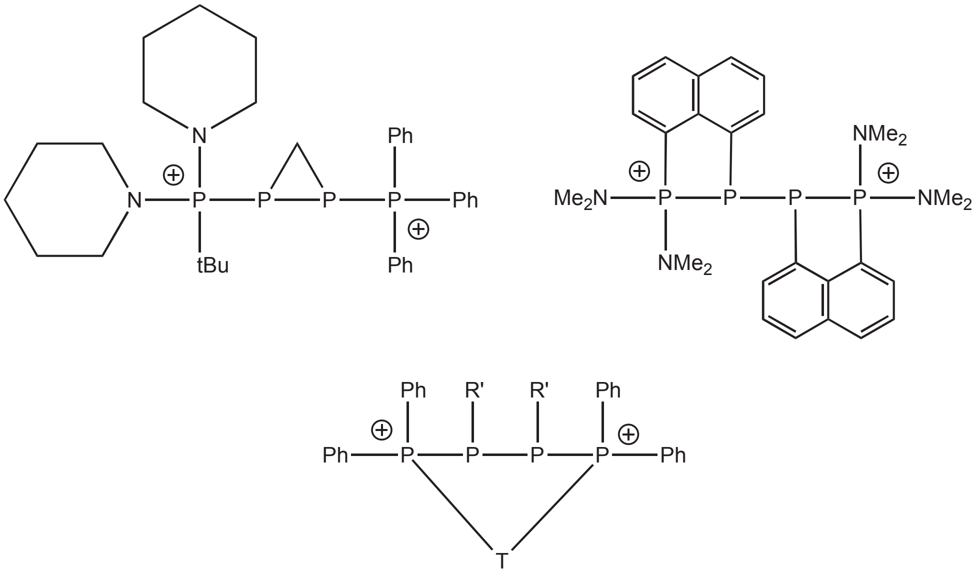


Figure 1.17 – Ligand displacement of 2,3-diphosphino-1,4-diphosphonium cation by a donor (Do)

Indeed, a number of derivatives featuring a phosphorus backbone of this type have been reported. However, a characteristic difference is that the majority of these frameworks require a tethering carbon chain (Figure 1.18).[35,46,47]

A unique example of a cationic tetraphosphorus framework is generated from the ring opening reaction of [(^{t}BuP)$_3$Me][OTf] with PMe$_3$ or PPhMe$_2$.[48] Acyclic 2,3,4-triphosphino-1-phosphonium cations are afforded largely due to the unique reactivity imposed by the strained (^{t}BuP)$_3$ skeleton.



T = (CH$_2$)$_n$ (n = 1, 2, 4), etc.
R' = Et, Ph

Figure 1.18 – Examples of tethered 2,3-diphosphino-1,4-diphosphonium cations

1.5.2: Cationic Phosphorus Clusters:

In contrast to neutral or anionic polyphosphorus clusters, the chemistry of cationic polyphosphorus clusters has only recently been developed. In fact, to date there have been only three reports of cationic phosphorus clusters, with the oldest having been reported within the last decade. This not only epitomizes the degree to which cationic phosphorus chemistry is underdeveloped, but it also validates its novelty. Interestingly, all instances of cationic phosphorus clusters involve the activation of white phosphorus with phosphenium cations. Krossing and co-workers initially reported the insertion of an in-situ prepared dihalophosphenium (PX_2^+) into the tetrahedron of white phosphorus, producing the binary cage with general formula $P_5X_2^+$.[49] Using a non-oxidizing, weakly coordinating counterion of type $[Al(OR)_4]$ (OR = polyfluorinated aliphatic alkoxide), they were able to successfully isolate the phosphorus rich cage. Weigand and co-workers, on the other hand, employed a molten mixture of P_4, Ph_2PCl and $GaCl_3$ in varying stoichiometries to sequentially activate the P_4 tetrahedron up to three times, generating cationic clusters with charges of +1, +2 and +3, respectively.[50] It was noted, however, that the highly charged clusters display an instability in solution, as well as in a basic medium (i.e. presence of Cl^- ions), which is remedied by a solventless approach, as well as by altering the reaction medium to one that is Lewis acidic (Ga_2Cl_7). Later, Weigand and co-workers demonstrated that the activation of P_4 by means of a phosphenium cation could allow for its diverse functionalization. Specifically, it was shown that $[DippNPCl]_2$ could be effectively considered $[DippNP]_2^{2+}$ in the presence of $GaCl_3$ and react with up to two equivalents of P_4 to produce $[DippNP(P_4)]_2^{2+}$ (Figure 1.19).[51] These instances are effective in demonstrating the possibility of utilizing P_4 as a building block for larger phosphorus clusters.

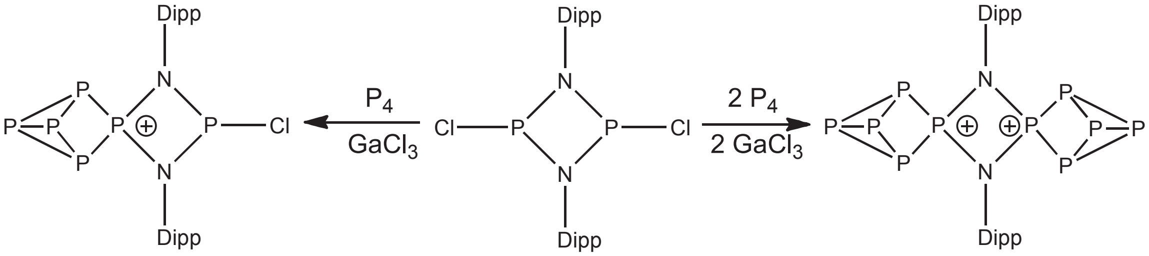


Figure 1.19 – Functionalization of P_4 by $[DippNPCl]_2$ and $GaCl_3$

1.5.3: Cyclic Polyphosphorus Cations:

Cyclo-tri- and tetraphosphinophosphonium cations had initially been proposed on the basis of elemental analysis of compounds produced from the reaction of organo-cyclotriphosphines with either CCl_4 or MeI.[52-54] However, these structures have only recently been confirmed in the solid state as triflate salts. Alkylation or protonation of cyclotri- or tetraphosphines has proven to be an efficient, high yielding synthetic route towards monocationic three-phosphorus and four-phosphorus[55] frameworks, respectively. The cyclotetraphosphines from which cationic frameworks are derived, however, has greater stability when alkylated compared to cyclotriphosphines, as examples of dicationic four-phosphorus frameworks have been isolated by sequential oxidation with MeOTf[56] or $PhICl_2$/TMSOTf.[57] Positive charges for dicationic frameworks have been isolated as 1,3- as well as 1,2-dications (Figure 1.20), although 1,2 dications are proposed to be formed by an alternate mechanistic pathway.[48]

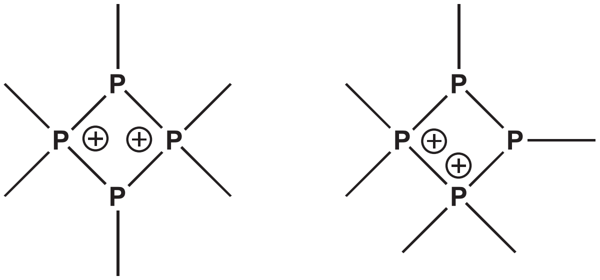


Figure 1.20 – 2,4-cyclodiphosphino-1,3-diphosphonium (left), 3,4-cyclodiphosphino-1,2-diphosphonium (right)

As phosphenium centers have been shown to insert into P-P bonds of acyclic[38] and clustered polyphosphines[51], it is envisaged that similar reactivity holds true for cyclopolyphosphines. Indeed, phosphenium centers have been shown to insert into the P-P bonds of cyclotri- as well as tetraphosphines to generate the corresponding ring-expanded monocationic cyclophosphines.[58] However, the thermodynamic preference for cyclopolyphosphines to adopt five atom rings is illustrated by the retention of the cyclopentaphosphorus ring when attempts are made to insert a phosphenium center into the P-P bond of a five phosphorus ring.[59-60] Nevertheless, protonation, alkylation, phosphenium insertion or combinations of these reactions have shown to be effective, high yielding methods towards racemic mixtures of mono- and dicationic pentaphosphorus frameworks.[58] Furthermore, the precedence for the oxidation to occur at the 1,3 positions is consistent for cyclotriphosphinodiphosphonium cations.[48]

The limited number of cationic cyclohexaphosphines is surprising, given the apparent preference for five and six phosphorus rings in neutral polycyclicphosphines.[7] Moreover, isolobality between methylene (CR_2) and phosphonium (PR_2^+) suggests that cyclohexaphosphorus cations are a viable synthetic target, given their similarity to cyclohexane. Although a number of neutral cyclohexaphosphines have been reported,[61] it has only been recently that the first cationic cyclohexaphosphine has been isolated as a dication.[62] It was shown that the neat combination of 0.8 of an equivalent of $(PPh)_5$ with 2 of Ph_2PCl or Me_2PCl and 2 of $GaCl_3$ facilitated the generation of a racemic mixture containing only two of seven possible isomers. Solution studies established the instability of the octaphenyl analogue, as decompostion was noted to occur with a half-life of approximately 24 h.

1.6: Phosphenium Cations

Two-coordinate phosphorus centers with a lone pair, or phosphenium cations, were initially proposed as transient intermediates, however, they have since been isolated as cyclic, as well as acyclic diaminophosphenium ions. For such isolable compounds, it has been shown that the electron deficiency in the π system is stabilized by delocalization of the lone pair of electrons on adjacent nitrogen centers (Figure 1.21).

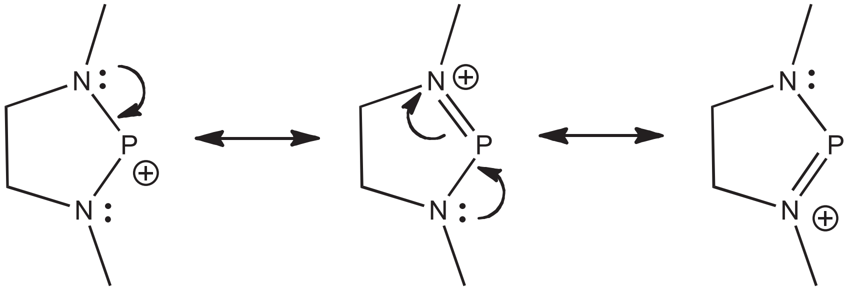


Figure 1.21 – Resonance delocalization of positive charge in diaminophosphenium cations

An interesting feature prominent in phosphenium ion chemistry is its electrophilic character induced by an unfilled valence shell, as well as nucleophilic character brought on by its lone pair of electrons. However, despite being isoelectronic and isolobal to the much more familiar carbene class of compounds, phosphenium cations have a greater tendency to act as Lewis acids, given an unfilled coordination sphere *and* electronic attraction brought on by the cationic formal charge.

The most widely employed method for preparing phosphenium ions is by the reaction of chlorophosphines with halide abstracting agents such as $GaCl_3$, $FeCl_3$, PCl_5, $AlCl_3$, or TMSOTf. Alternative methods to phosphenium cations include protonation of aminophosphines at the nitrogen center or protonation/alkylation of diphosphines.[63]

In the context of *catena*-phosphorus cations, a facile approach to generating P-P interactions has been shown to be by stabilization of phosphenium cations with neutral phosphines. Synthetic endeavours concentrated on generating phosphenium cations are typically done *in situ* by halide abstraction of chloro or dichlorophosphines. This generates highly unstable phosphenium ions that are stabilized intermolecularly by the lone pair of electrons of the chlorophosphine. This has been shown to be an effective system in solution studies, in addition to investigations that have shown molten mixtures of Ph_2PCl and $GaCl_3$ to be reactive sources of phosphenium cations.

1.7: Summary and outlook

The ability of $[PR_2^+]$ cations to act as Lewis acceptors has led to a number of novel cationic *catena*-phosphorus frameworks.[31] However, such reactivity has only been realized for phosphorus compounds containing simple hydrocarbon substituents. As such, there is great potential within the current sets of reactions for novel reactivity, given significant structural or electronic differences. To this end, expansion of cationic *catena*-phosphorus frameworks using current synthetic methods, in addition to combination of such methods to achieve novel phosphorus frameworks is the focus of this report. Specifically, the employment of perfluorinated organochlorophosphines, as well as sterically demanding phosphorus compounds will be examined in the context of current synthetic methods.

Chapter 2: Studies on 1,3-diphosphino-2-phosphonium cations

2.1: Introduction

A logical extension of the ligand exchange behaviour of phosphine-stabilized phosphenium cations replaces tertiary phosphines as the stabilizing ligand with diphosphines. With a phosphorus-phosphorus linkage already present, this methodology has been shown to be a convenient method for the preparation of 1,3-diphosphino-2-phosphonium cations $[R_2P\text{-}PR_2\text{-}PR_2]^+$.[39]

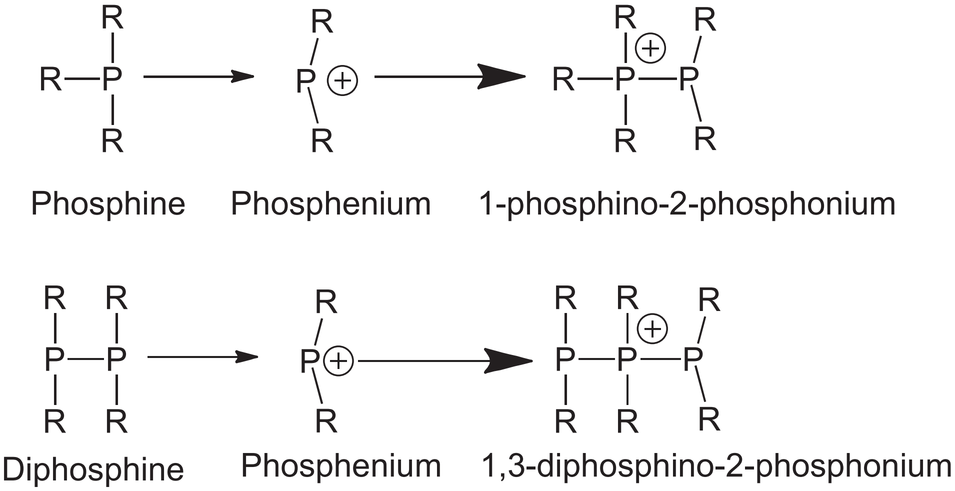


Figure 2.0 – Phosphenium cation stabilized by a tertiary phosphine (top) and diphosphine (bottom)

Studies have extrapolated on this reactivity by using differently substituted diphosphines that stabilize the phosphenium center by coordination of its lone pair. In these studies, it was determined that direct stabilization either occurs as a transient intermediate, or not at all. Consequently, the phosphenium cation appears to insert in to the phosphorus-phosphorus bond of the diphosphine, resulting in a symmetric, three phosphorus monocation that is indicated by an A_2B spin system in $^{31}P\{^1H\}$ NMR studies (Figure 2.1).[59]

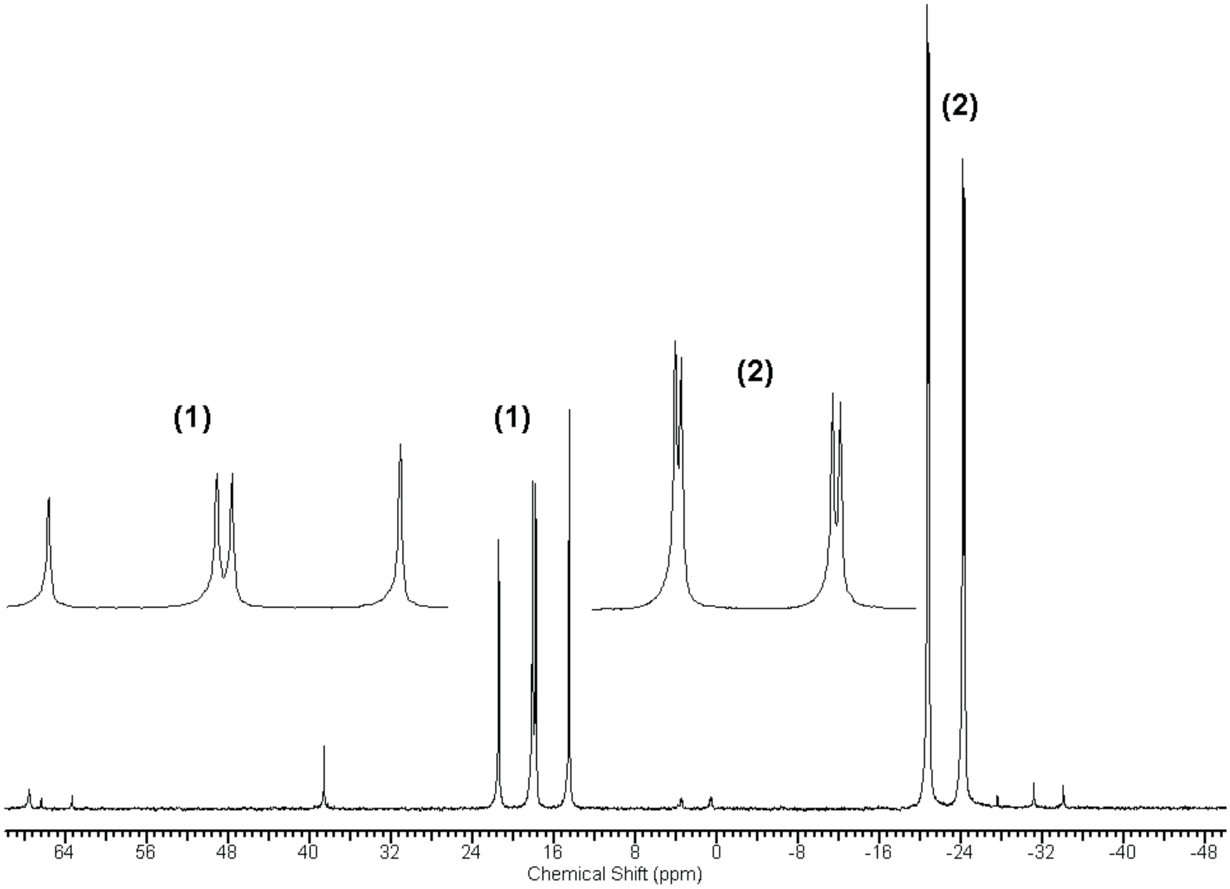
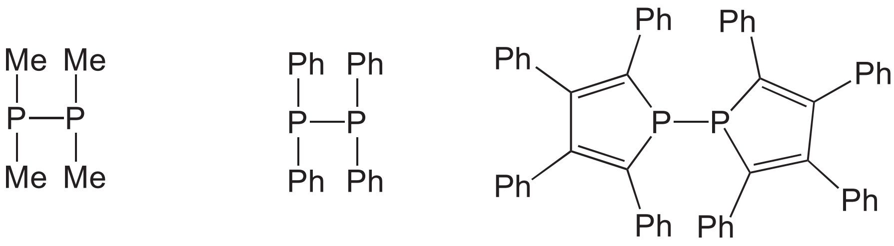


Figure 2.1 –A_2B spin system of [Me_2P-PMe_2-PMe_2][OTf] ($^{31}P\{^1H\}$ NMR)[59]

Phosphenium insertion of this type has been observed in a number of different systems.[31] However, experimental data to define the reaction pathway is not yet available. As such, this reaction mechanism was investigated so that further insight may be developed in to the diverse reactivity of phosphorus cations and may be applied towards the stepwise development of larger cationic *catena*-phosphorus frameworks.



1 2 3

Figure 2.2 - Diphosphines with substituents of varying steric bulk

2.2: Results and Discussion

Reactions of **1**, **2** and **3** with chlorophosphines (R'_2PCl; R = Me, Ph, Cy, iPr, tBu) in the presence of a halide abstracting agent (TMSOTf, AgOTf, $GaCl_3$, $AlCl_3$) were analyzed using ${}^{31}P\{{}^{1}H\}$ NMR. Solution ${}^{31}P\{{}^{1}H\}$ NMR studies have shown quantitative conversion of the three components to a phosphenium-inserted salt, evidenced by an A_2B spin system when small chlorophosphines (R'_2PCl; R′ = Me, Ph) were used.[59] This reactivity was seemingly independent of the steric bulk imposed by the substituents on the diphosphine, as **3** displayed the same reactivity as **1**. When steric bulk of the chlorophosphine R'_2PCl exceeded that of a phenyl group (i.e. R′ = Cy, ^{i}Pr, ^{t}Bu), a distribution of products was observed in the ${}^{31}P\{{}^{1}H\}$ NMR spectrum, in which many peaks could not be assigned to known ${}^{31}P\{{}^{1}H\}$ NMR chemical shifts. Numerous attempts to crystallize cationic derivatives from the mixtures were unsuccessful.

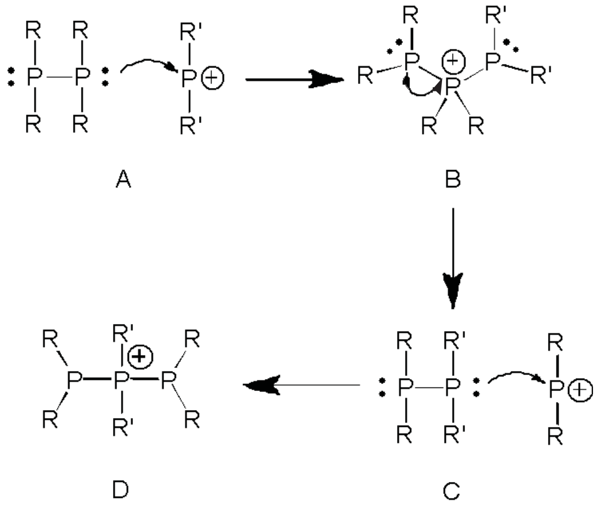


Figure 2.3 –Proposed mechanism for the insertion of phosphenium cations into diphosphines

Figure 2.3 shows a possible reaction pathway that provides an explanation for the observed phosphenium insertion. It is speculated that upon halide abstraction, the diphosphine stabilizes the phosphenium cation through coordination of its lone pair (Figure 2.3; A). This results in a non-symmetric, three phosphorus monocation (figure 2.3; B) that undergoes a four electron rearrangement (Figure 2.3; B) that results in a symmetric, three phosphorus monocation. In order to provide evidence for this proposal, low temperature $\{^1H\}^{31}P$ NMR studies were carried out. The reduced kinetics would increase the lifetime of the transient intermediates, and subsequently allow for their characterization by solution NMR spectroscopy. The proposed experiment is highlighted in Figure 2.4 and the individual components were selected based on their availability and favourable degree of product conversion.

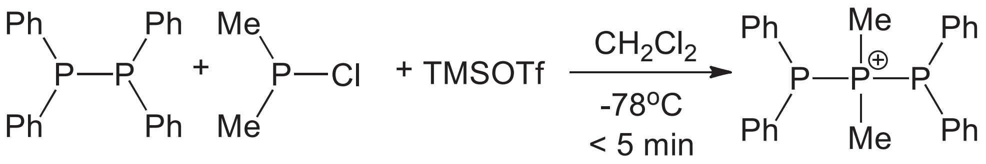


Figure 2.4 – Reaction scheme describing low temperature experiments targeted at elucidating phosphenium cation insertion into diphosphines

The three component reaction mixtures were analyzed at -78°C within five minutes of reaction initiation. However, the $^{31}P\{^1H\}$ NMR studies conducted on a number of various samples displayed an A_2B spin system, indicating a symmetric, phosphenium-inserted product. This demonstrates that the reaction pathway has a sufficiently low kinetic barrier, making it difficult to probe the mechanistic pathway using available NMR techniques.

2.3: Summary, Outlook and Conclusions

In summary, it was determined that the insertion of phosphenium cations into the P-P bonds of diphosphines occurs very rapidly. Moreover, there is a sufficiently small kinetic barrier that NMR studies conducted at 200 K were not sufficient in reducing the reaction rates that would allow for the observation of any transient intermediates. Future studies directed at elucidating this reaction pathway may include other spectroscopic methods, such as infrared or Raman spectroscopy. These methods have spectroscopic timescales that are shorter than NMR spectroscopy, and may be on the order of the reaction rates for this observed result.

Chapter 3: Derivatization of Cyclotriphosphinophosphonium Ions

3.1: Introduction

Cationic phosphorus rings are potentially valuable synthons in the systematic and rational development of *catena*-phosphorus cations. Moreover, they represent important synthetic targets in this pursuit.

Previously, it has been shown that cationic phosphorus rings can be generated by combining solutions containing a neutral phosphorus ring $(RP)_n$ (R = ^{t}Bu, Cy, ^{i}Pr, Ph, Me; n = 3-5) with MeI,[52-54] MeOTf[56] or the chloronium ion that is formulated in the solutions of binary mixtures: $GaCl_3/PCl_5$ or $TMSOTf/PhICl_2$.[57] Alternatively, phosphenium cations have been demonstrated to insert into the P-P bonds of neutral phosphorus rings, generating a cationic, ring expanded phosphorus ring.[59]

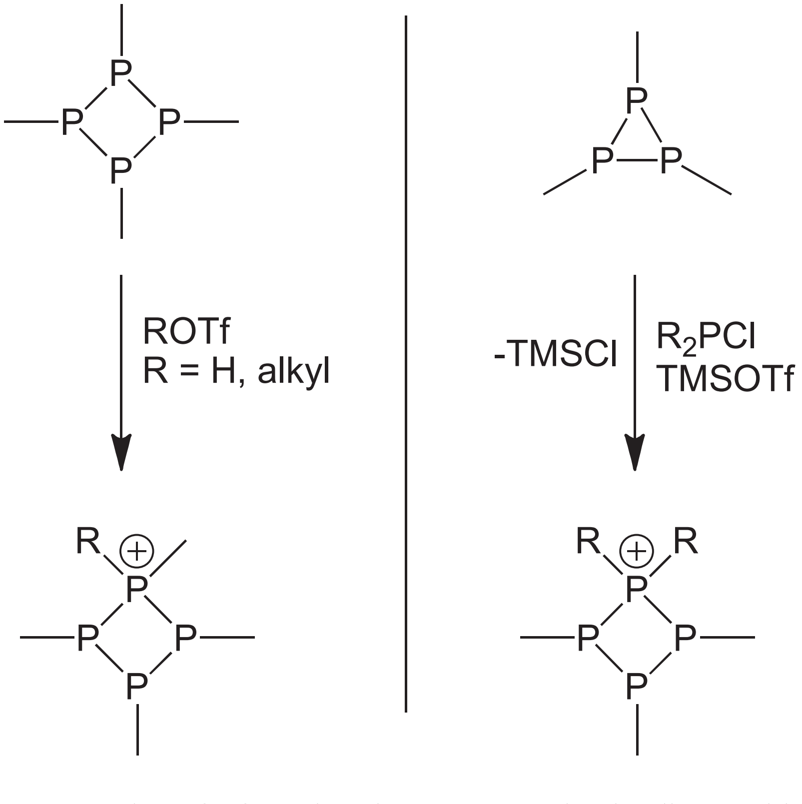


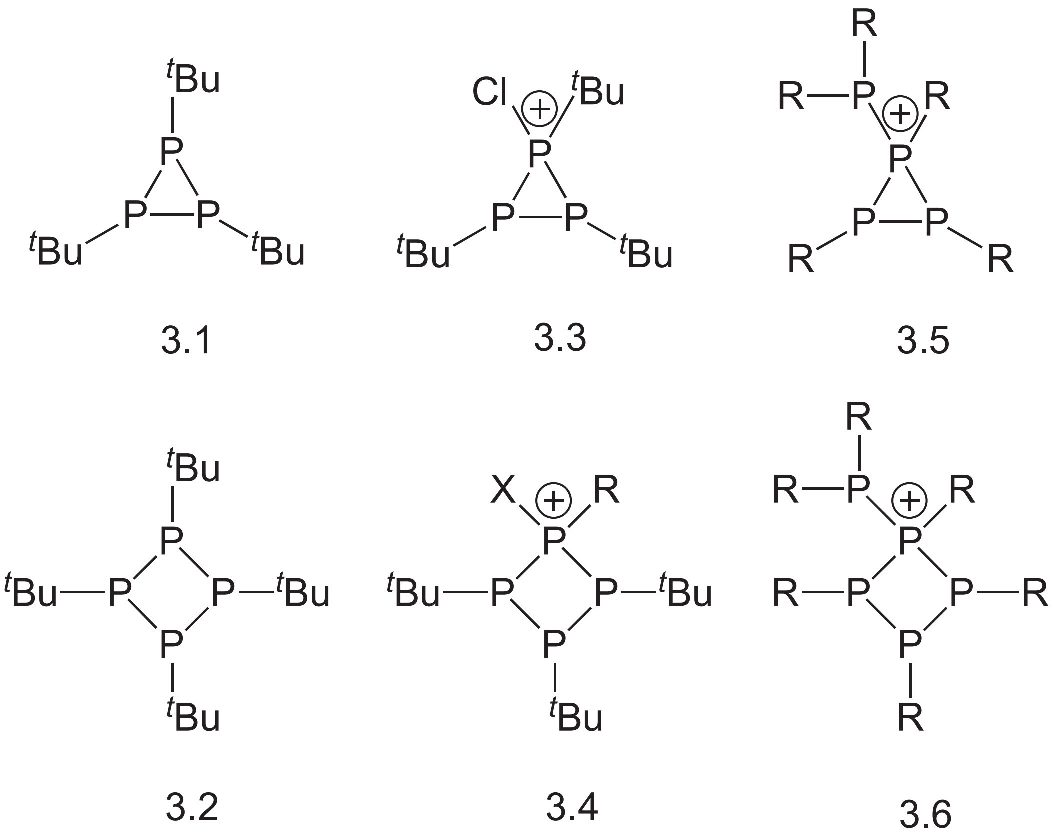
Figure 3.0 –Generation of a four phosphorus monocation by direct oxidation (left) and by phosphenium insertion (right). Unlabelled vertices are phosphorus. Unlabelled termini are alkyl/aryl substituents.

However, there are fewer reported examples of cationic rings that are produced from the insertion of phosphenium cations. Moreover, the reactivity of phosphenium cations may possibly be tuned by altering steric and/or electronic functionalities. This is similar to the carbene class of compounds that have demonstrated, by modifying its substituents, the ability to perform a wide array of chemical transformations.[64] This presents insight into the reactivity and possible applications of phosphenium cation chemistry. However, despite its presence in literature pertaining to *catena*-phosphorus cations, and its relationship to the carbene class of compounds, the insertion of phosphenium ions into P-P bonds is poorly understood. As steric and electronic properties have shown, in preliminary studies, to be important factors for novel reactivity[48] that produces new cationic phosphorus frameworks, a number of new *cyclo*-phosphorus cations were synthesized by the insertion of various phosphenium ions.

Phosphenium cations are generated by introducing a primary or secondary chlorophosphine to a halide abstracting agent. With the exception of $(C_6F_5)_2PCl$, the abstraction of a chloride ion produces a phosphino-chlorophosphonium cation $[R_2(Cl)P\text{-}PR_2]^+$, that is resulting from a free phosphenium cation stabilized intermolecularly by the lone pair of an unreacted chlorophosphine. By introducing a stronger donor, such as a tertiary phosphine, one can displace the chlorophosphine ligand, generating a phosphino-phosphonium cation $[R_3P\text{-}PR_2]^+$. Owing to the lability of a chlorophosphine ligand, the combination of a chlorophosphine with a halide abstracting agent may be considered an *in-situ* source of phosphenium cations.

Extending this reactivity to phosphorus rings or chains affords different results. Instead, the phosphenium cation inserts into the phosphorus-phosphorus bond of the ring or chain. One might have anticipated that the phosphenium cation would be stabilized through the lone pair of a phosphorus atom on the chain or ring, similar to the reactivity observed for tertiary phosphines. This, however, is not the case, as the branched cationic phosphorus frameworks **3.5-3.6** have yet to be reported.

Previous efforts towards generating cationic phosphorus rings employed phosphenium insertion.[60] In this case, phosphenium insertion was only examined as one of many available synthetic methods. As such, its potential reactivity was examined superficially, and consequently overlooked as a method to produce new cationic phosphorus frameworks. Ring expansion has been demonstrated for organocyclophosphines $(RP)_n$ of varying ring sizes (n = 3-5).[58,60,62] However, solution studies have determined that the reaction of a phosphenium cation with a five phosphorus ring (c.f. $(PhP)_5$) retains the cyclic five-phosphorus framework, resulting in a *cyclo*-tetraphosphinophosphonium framework. This type of reactivity differs from that observed for the three and four phosphorus rings, and so it will be omitted from the current study. Instead, focus is on synthesizing cationic phosphorus rings from neutral three- and four phosphorus rings as a part of the development of cationic *catena*-phosphorus frameworks. This will be achieved by phosphenium insertion, where the main focus will be on altering steric and/or electronic properties of phosphenium cations in order to develop better insight into phosphenium insertion of phosphorus-phosphorus bonds of neutral rings. However, oxidation of the same neutral rings with $[Cl]^+$ will be discussed in order to provide a comparison.


3.1

3.3

3.5

3.2

3.4

3.6

Figure 3.1 – Cationic and neutral *cyclo*-phosphorus compounds

3.2: Results and Discussion

Solutions containing **3.1**, a chlorophosphine (R'_2PCl; R' = Me, Ph, Cy, ^{i}Pr, ^{t}Bu) and a halide abstraction reagent such as $GaCl_3$ or Me_3SiOTf were analyzed using $^{31}P\{^1H\}$ NMR. In the case of the Lewis acid $GaCl_3$ and Ph_2PCl, the spectrum indicates quantitative formation of the corresponding *cyclo*-triphosphinophosphonium cation **[3.4(Ph$_2$)]**[$GaCl_4$] (Figure 3.2). The observed AM_2X spin pattern with relative intensities of 1:2:1 is consistent with three chemically inequivalent phosphorus atoms. The insertion of the *in-situ* formed phosphenium cation $[Ph_2P]^+$ occurs between the two phosphorus atoms where the *t*Bu-groups of **3.1** are arranged in a *cis* configuration to each other. This is in accordance with the already described insertion of $[Me_2P]^+$.[60]

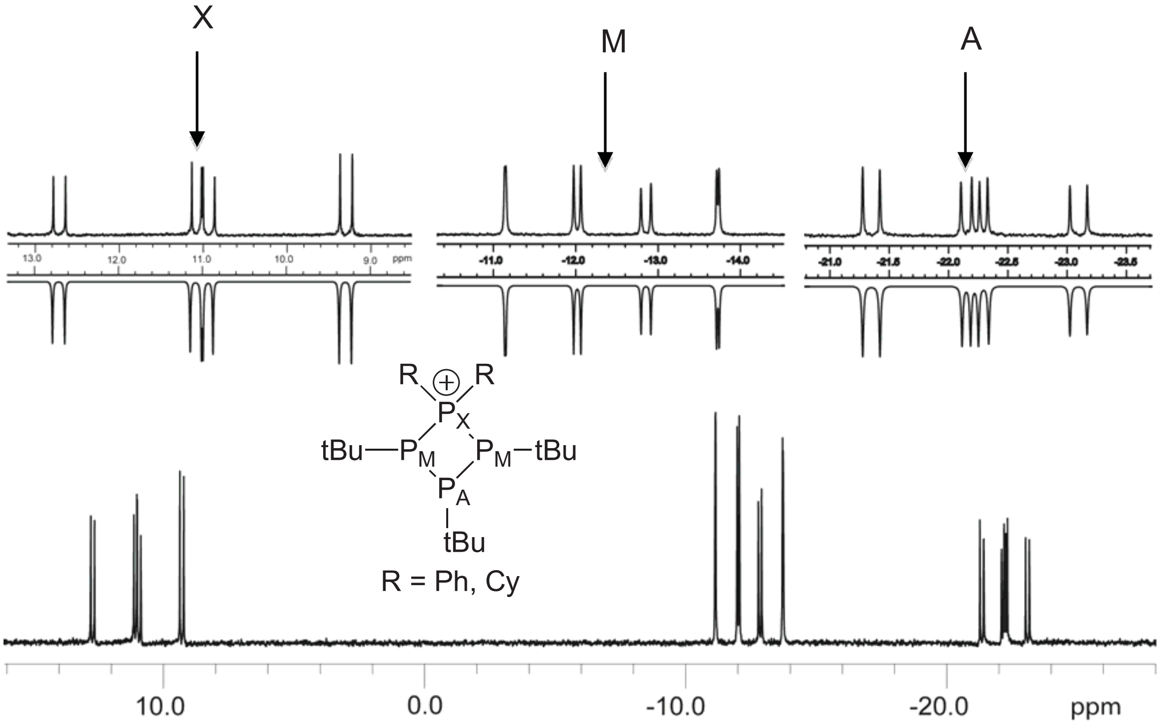


Figure 3.2 – $^{31}P\{^{1}H\}$ NMR spectrum of [**3.4(Ph$_2$)**][$GaCl_4$] with experimental (top) and iterative simulated spectrum (inverse)

The solid state structure of [**3.4(Ph$_2$)**][$GaCl_4$] is shown in figure 3.3 and confirms the product that is predicted by $^{31}P\{^{1}H\}$ NMR. The molecule displays a C_2 symmetric, puckered phosphorus ring, with the phenyl substituted phosphorus atom adopting a tetrahedral four coordinate bonding environment (C1–P1–C7: 108.43(7)°). The remaining phosphorus atoms in the ring adopt a *pseudo*-trigonal pyramidal (c.f. P2–P3–P4: 85.80(2)°), three coordinate bonding motif, which is consistent with non-hybridized, neutral phosphorus atoms. With p-orbitals in the x, y, and z planes, it is expected that the bonding angles are closer to 90°, rather than the 109.5° expected for an sp^3 hybridized phosphorus atom. The interactions between P1 and P2 or P4 (P1-P2: 2.1998(5) Å; P1-P4: 2.1951(5) Å) is noted to be slightly shorter than that of P3 and the same two atoms (P3-

P2: 2.2350(5) Å; P3–P4: 2.2352(5) Å). This is owing to the reduced covalent radius imparted by a cationic center and may be observed for the phosphorus-carbon interactions, as well (P1–C1: 1.801(2) Å vs. P3–C17: 1.885(2) Å). All neutral interactions are within the sum of their respective covalent radii and ionic interactions are within their respective van der waals radii.

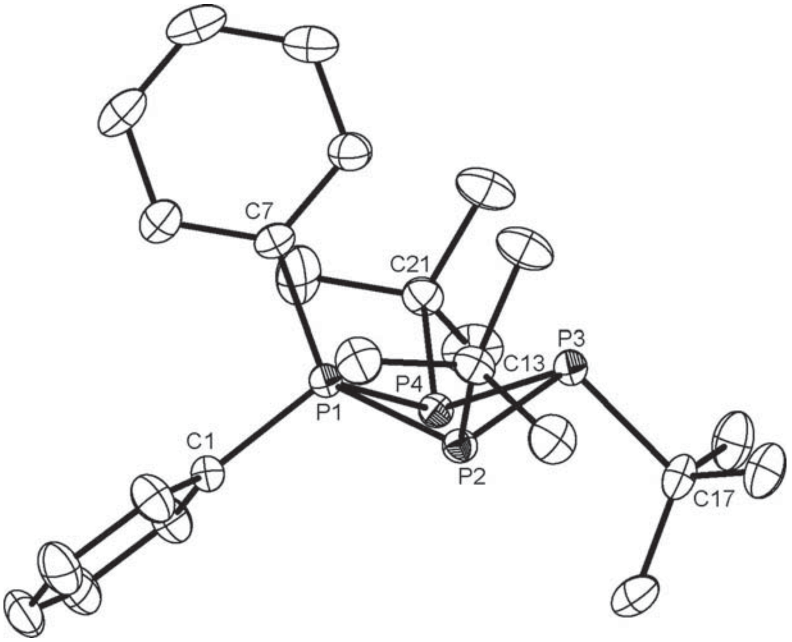


Figure 3.3 ORTEP plot of the molecular structure of the cation [**3.4**(**Ph$_2$**)]$^+$ in [**3.4**(**Ph$_2$**)][GaCl$_4$]. Thermal ellipsoids with 50% probability (hydrogen atoms and counteranions are omitted for clarity). Selected bond length (Å) and angles (°): P1–P2 2.1998(5), P2–P3 2.2350(5), P3–P4 2.2352(5), P4–P1 2.1951(5), P1–C1 1.801(2), P1–C7 1.806(2), P2–C13 1.899(2), P3–C17 1.885(2), P4–C21 1.899(2); P1–P2–P3 83.17(2), P2–P3–P4 85.80(2), P3–P4–P1 83.27(2), P2–P1–C1 111.00(5), P2–P1–C7 119.13(5), P1–P2–C13 112.49(5), P2–P3–C17 104.08(6), P3–P4–C21 110.20(5), C1–P1–C7 108.43(7).

Conversely, the reaction of **3.1** with Ph$_2$PCl and Me$_3$SiOTf afforded cation [**3.4**(**Ph$_2$**)][OTf] in less than 35% yield and **3.2** as the main product of this reaction, as shown by ^{31}P{^{1}H} NMR.

Other secondary chlorophosphines R'$_2$PCl (R' = Cy, ^{i}Pr, ^{t}Bu) were employed as phosphenium cation synthons, although only one additional derivative was prepared by the reaction of **3.1** with Cy$_2$PCl and GaCl$_3$. The solid state structural features of [**3.4(Cy$_2$)**][GaCl$_4$] are similar to those observed for [**3.4(Ph$_2$)**][GaCl$_4$], as the phosphonium center displays slightly shortened P$^+$-P (P$^+$-P$_{average}$ = 2.2201 Å) and P$^+$-C (P$^+$-C$_{average}$ = 1.845 Å) interactions when compared to analogous P-P (P-P$_{average}$ = 2.2259 Å) and P-C (P-C$_{average}$ = 1.901 Å) bond lengths. Solution ^{31}P{^{1}H} NMR studies on [**3.4(Cy$_2$)**][GaCl$_4$] display broadened resonances and so chemical shift, as well as coupling constants were not obtained.

However, when more spatially occupying organochlorophosphines were employed, a variety of unidentifiable resonances were observed in the ^{31}P{^{1}H} NMR. It is proposed that the steric bulk of both the *cyclo*-triphosphine and the secondary chlorophosphine preclude intramolecular collisons. When the steric bulk on the phosphenium cation exceeds that of a cyclohexyl substituent, the Lewis acidic phosphenium and Lewis basic phosphine atoms are shielded from one another by the steric bulk of their respective organic substituents, hence, products for competitive reaction pathways are observed in NMR spectra for these reaction mixtures.

Further investigations of phosphenium insertion explored the possibility of inserting a chlorine containing phosphenium cation [R(Cl)P]$^+$ into a phosphorus ring by reacting [tBuPCl][GaCl$_4$] with **3.3**. The resulting phosphonium center bearing a chlorine atom has the added benefit of being further functionalized through reductive coupling[4] or halide abstraction and subsequent coordination.[65]

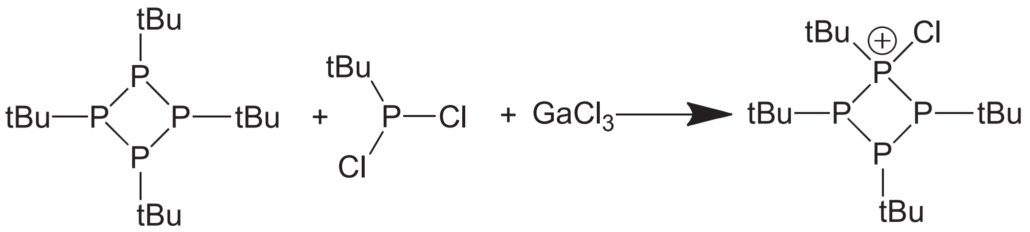


Figure 3.4 - reaction of [^{t}BuPCl]$^{+}$ with (^{t}BuP)$_4$ to produce [**3.4(*^{t}*Bu(Cl))**][GaCl$_4$]

Figure 3.4 illustrates the reaction of [^{t}BuPCl]$^{+}$ with (^{t}BuP)$_4$ to produce [**3.4(*^{t}*Bu(Cl))**][GaCl$_4$]. It is suprising, however, that the four phosphorus ring size is conserved, despite phosphenium insertion, as evidenced by an AM$_2$X spin system in the ^{31}P{^{1}H} NMR spectrum (Figure 3.5). It is hypothesized that a four phosphorus skeleton is favoured rather than a five phosphorus one due to the steric bulk of the tertiary butyl groups. This is consistent with larger organic substituents favouring smaller rings such as **3.1** and smaller organic substituents favouring larger phosphorus rings such as (MeP)$_5$.

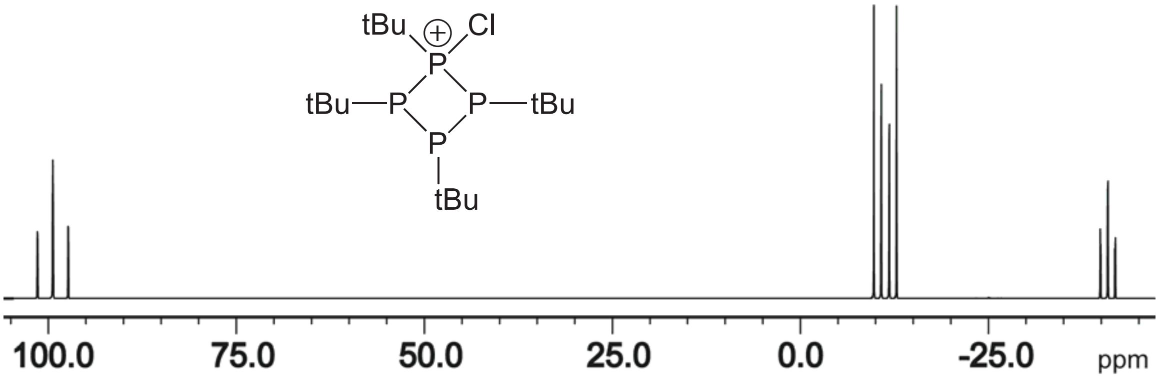


Figure 3.5 - ^{31}P{^{1}H} NMR spectrum of [**3.4(*^{t}*Bu(Cl))**][GaCl$_4$]

Cations [**3.4(*^{t}*Bu(Cl))**]$^{+}$ and [**3.4(Ph$_2$)**]$^{+}$ show similar features in their respective ^{31}P{^{1}H} NMR spectra. However, it is noted that the resonance that corresponds to the phosphonium center is shifted significantly (~ 90 ppm) downfield for [**3.4(*^{t}*Bu(Cl))**]$^{+}$. This is consistent with an enhanced electron deficiency at the phosphonium center due to the inductive withdrawal by the chlorine atom.

The synthesis of [**3.4(*t*Bu(Cl)**)]$^+$ may alternatively be achieved by oxidation of **3.2** with the chloronium ([Cl]$^+$) cation that is formulated from a mixture of PCl_5/$GaCl_3$ or $PhICl_2$/TMSOTf. Solution {^{1}H}^{31}P NMR indicates quantitative formation of [**3.4(*t*Bu(Cl)**)]$^+$ from equimolar reaction mixtures of **3.2**, PCl_5 and $GaCl_3$. Moreover, analytically pure crystalline material may be isolated in greater than 90% yield. However, due to poor quality data, definitive statements regarding the solid state structure of [**3.4(*t*Bu(Cl)**)][$GaCl_4$] can not be made.

The ^{31}P{^{1}H} NMR spectrum of the reaction mixture containing **3.2**, $PhICl_2$ and TMSOTf displays an AM_2X spin system, along with two other major resonances at δ = 192 ppm (s) and -59 ppm (s). The observed AM_2X spin system indicates the formation of [**3.4(*t*Bu(Cl)**)]$^+$, while the other resonances match literature values for ^{t}BuPCl$_2$ (δ = -192 ppm) and **3.2** (δ = -59 ppm). The interpretation of this result is highlighted in figure 3.6 and is based on results observed for a similar system involving $(CyP)_4$ in place of **3.2**.[57] Initially, the neutral ring is oxidized by addition of a chloronium ion to produce [**3.4(*t*Bu(Cl)**)][OTf]. A slight excess of $PhICl_2$/TMSOTf, however, results in a second oxidation to produce a dicationic ring. The dication is then reduced by chloride ions present in solution, thereby eliminating ^{t}BuPCl$_2$ and generating [^{t}Bu(Cl)P(^{t}BuP)$_2$]$^+$. This is, once again, reduced by a chloride ion, owing to its higher ring strain and reactivity, which eliminates ^{t}BuPCl$_2$ and produces a tertiarybutyl substituted diphosphene. The kinetic instability[66] of the diphosphene, however, causes it to dimerize and reproduce **3.2**.

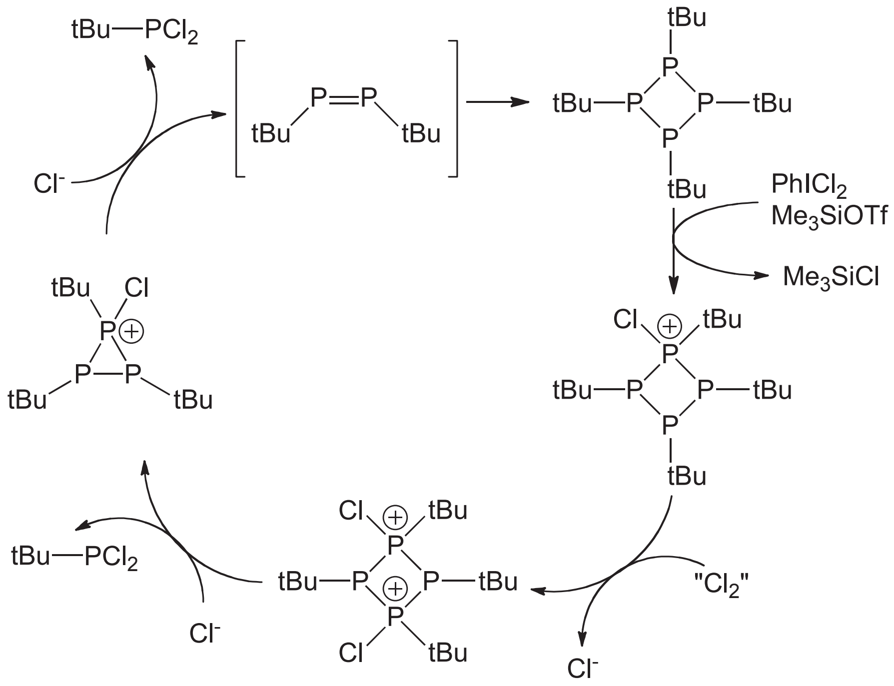


Figure 3.6 – Proposed mechanism rationalizing empirical results

Interestingly, attempts to produce [**3.4(^{t}Bu(Cl))**]$^+$ by the insertion of [tBuPCl]$^+$ into the P-P bond of **3.1** resulted in broad, featureless peaks in the ^{31}P{^{1}H} NMR spectrum. This is surprising, given that [**3.4(^{t}Bu(Cl))**]$^+$ may be obtained from the reaction of **3.2** with [^{t}BuPCl]$^+$. Additionally, **3.1** has a high degree of ring strain, and given that phosphenium cations have the propensity to activate P-P bonds, it is expected that this would be a facile route to generate [**3.4(^{t}Bu(Cl))**]$^+$ by phosphenium insertion. The broad features observed in the NMR spectrum suggests that there are dynamic processes occurring and so future studies directed at resolving the peaks may consider using low temperature NMR spectroscopy.

	[**3.4(Ph_2)**][$GaCl_4$]	[3.4(Ph_2)][OTf]	[3.4(^{t}Bu(Cl)][$GaCl_4$]
Spin system[a,b]	AM_2X	AM_2X	AM_2X
δ_A[c]	-22.2	-23.0	-42.6
δ_M	-12.4	-13.0	-11.1
δ_X	10.9	10.5	98.4
^1JAM[d]	-141.9	-141.7	-158.0
^1JMX	-277.3	-276.0	-329.5
^2JAX	-22.3	-22.4	7.0

[a] Furthest downfield resonance is denoted by the latest letter in the alphabet, and furthest upfield by the earliest letter. By convention the letter in the spin system is determined by the ratio $\Delta\delta(P_iP_{ii})/JP_iP_{ii} > 10$ (resonance considered to be pseudo-first order and the assigned letters that are separated)

Table 3.0 - $^{31}P\{^1H\}$ NMR Parameters for [**3.4(Ph_2)**][$GaCl_4$], [**3.4(Ph_2)**][OTf], and [**3.4(^{t}Bu(Cl)**][$GaCl_4$]

3.3: Controlled Isomerization of (^{t}BuP)$_3$ to (^{t}BuP)$_4$:

A major challenge in developing cyclic *catena*-phosphorus cations is the unavailablity of neutral phosphorus rings with substituents of varying steric or electronic properties. Novel reactivity can be directly related to varying these properties and, as such, having access to a larger array of neutral phosphorus rings may afford reactivity that would otherwise be inaccessible. It is for this reason that studies of (^{t}BuP)$_4$ as a neutral phosphine are of great interest, as it has been employed as a starting point with much less frequency when compared to the cyclohexyl substituted derivative. A major challenge in synthesizing (^{t}BuP)$_4$, however, is that it is collected as a minor fraction in the reduction of tBuPCl$_2$ with magnesium metal. The bulk of the tertiary butyl groups act as kinetic stabilizers, and so ring size distribution is favoured towards a three phosphorus ring. This makes it exceedingly challenging to exclusively synthesize (^{t}BuP)$_4$, without generating large amounts of (^{t}BuP)$_3$. As a means to preclude this wasteful technique, and having observed the preferential reduction of [tBu(Cl)P(tBuP)$_2$]$^+$ by chloride ions to produce (^{t}BuP)$_4$, efforts were focused on the conversion of (^{t}BuP)$_3$ to (^{t}BuP)$_4$.

Reaction mixtures containing **3.1**, PhICl$_2$ and TMSOTf displayed only one resonance in the ^{31}P{^{1}H} NMR spectrum at δ = - 56 ppm. This indicates complete conversion of (^{t}BuP)$_3$ (A$_2$B spin system; δ_A = -110 ppm, δ_B = -70 ppm) to (^{t}BuP)$_4$ (A$_4$ spin system; δ_A = - 56 ppm). While there is no evidence to suggest a particular mechanistic pathway, it is proposed that (^{t}BuP)$_3$ is oxidized by the chloronium ion that is formulated *in-situ*. The resulting [tBu(Cl)P(tBuP)$_2$]$^+$ cation eliminates ^{t}BuPCl$_2$ upon reduction by chloride ion, thereby producing ^{t}BuP=P^{t}Bu which dimerizes, owing to its kinetic instability (Figure 3.7).

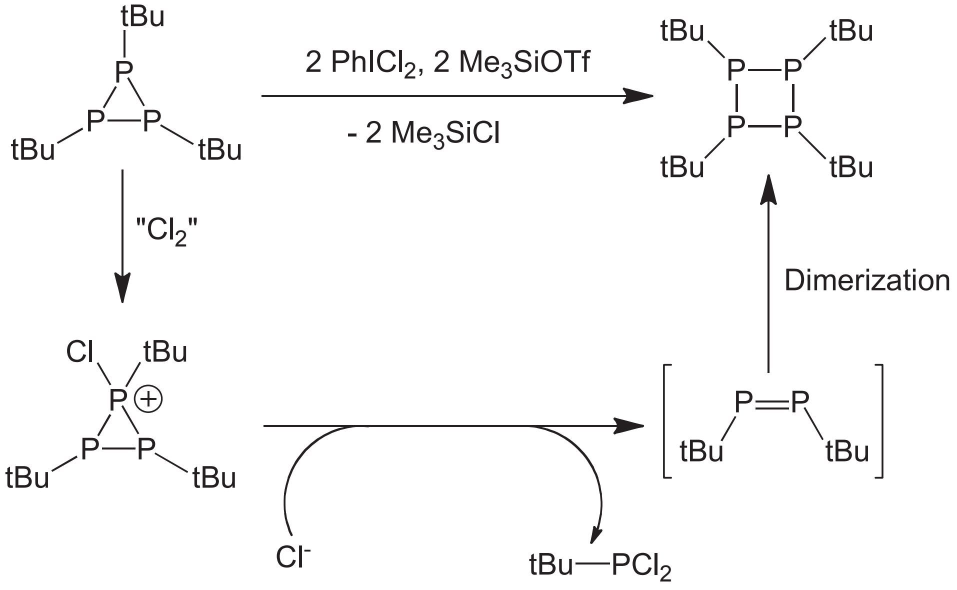


Figure 3.7 – Proposed intermediates in the isomerisation of (^{t}BuP)$_3$ to (^{t}BuP)$_4$

3.4: Summary, Outlook and Conclusions

In summary, four new *cyclo*-triphosphinophosphonium cations were synthesized and characterized using $^{31}P\{^1H\}$ NMR. Three of these derivatives were further characterized using X-ray crystallography.

It was determined that cation **3.4(*^{t}*Bu(Cl))** can be generated by three different methodologies. However, in the case where [**3.4(*^{t}*Bu(Cl))**]$^+$ is produced by oxidation of **3.2** with [Cl]$^+$ formed in the binary mixture of $PhICl_2$/TMSOTf, low conversions were recorded. This is consistent with previous studies and is rationalized by [Cl]$^-$ ions reducing *catena*-phosphorus cations that are present in solution. Extension of this reactivity by substituting **3.1** for **3.2** allows for full conversion of **3.1** to **3.2**, which presents a significant advantage in the bulk preparation of neutral *cyclo*-polyphosphines. Finally, the inverse relationship between steric bulk of substituents and phosphorus ring size was reconfirmed, as ring expansion from phosphenium insertion was not observed for **3.2**, which is in stark contrast to analogous reactions of $(CyP)_4$ with phosphenium cations that report ring expansion to five phosphorus frameworks.

Future studies may be directed at determining the reactivity of these cations with phosphorus-based Lewis bases, such as PMe_3 or Me_2P-PMe_2.

Chapter 4: 2-Phosphino-1,3-diphosphonium Ion Derivatives

In collaboration with Ryan Tilley and Yuen-ying Carpenter

4.1: Introduction

Acyclic cationic triphosphorus frameworks were originally reported by Schmidpeter and co-workers in 1982. The three phosphorus, triphosphenium framework, displayed a two-coordinate phosphorus center flanked by two four-coordinate phosphonium centers (Figure 4.0). Studies on the solid state structure revealed P-P$_{\text{average}}$ bond lengths of 2.125 Å, which is shorter than neutral P-P bonds of 2.20-2.24 Å. This was rationalized by the delocalization of a lone pair of electrons, resulting in a three center, two electron bond.[67] Subsequent studies in 1985 by Schmidpeter examined the oxidation of these compounds by protonation or alkylation (Figure 4.1; top), which resulted in the first 2-phosphino-1,3-diphosphonium derivatives.[68]

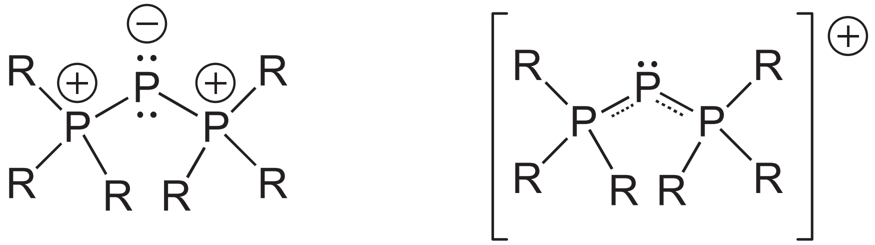


Figure 4.0 – Lewis (left) and delocalized (right) models for the triphosphenium framework reported by Schmidpeter and co-workers in 1982.

It was also determined in the 1985 report that 2-phosphino-1,3-diphosphonium cations could alternatively be obtained by combining an organodichlorophosphine with two equivalents of a Lewis acid and two equivalents of tertiary phosphine (Figure 4.1; bottom).

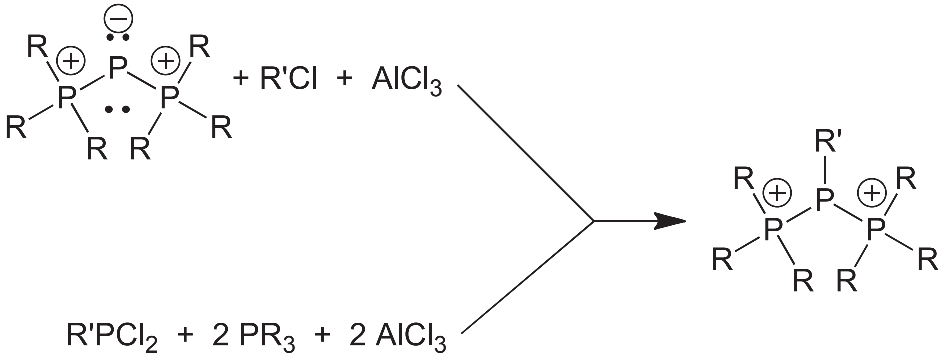
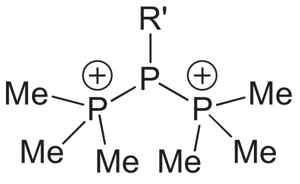
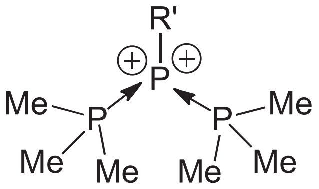


Figure 4.1 – Synthesis of a 2-phosphino-1,3-diphosphonium cation by alkylation (top) and by direct synthesis (bottom)

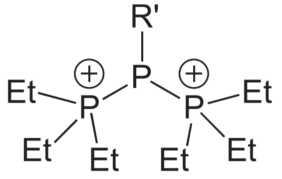
While both methods readily produce 2-phosphino-1,3-diphosphonium cations, the latter is the preferred method, owing to the greater versatility offered by a one-pot synthesis that avoids preparation of the triphosphenium cation.



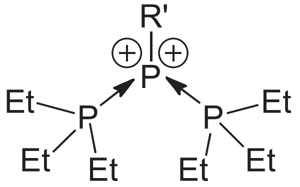
4.1



4.1



4.2



4.2

Figure 4.2 – Lewis (left column) and dative (right column) representations of **4.1** and **4.2**, respectively.

4.2: Results and Discussion

Reaction of two equivalents of a trialkylphosphine (PR_3; R = Me, Et; **4.1**, **4.2**) with an array of dichlorophosphines ($R'PCl_2$; R' = Me, ^{i}Pr, Cy, ^{t}Bu, Ph, N^iPr_2) and Me_3SiOTf in CH_2Cl_2 afforded opaque solutions, from which a solid precipitate was obtained by filtration. The solid was identified, in most cases, as the corresponding 2-phosphino-1,3-diphosphonium triflate salt. It was found that the same reactions carried out in MeCN did not produce a precipitate, which allowed reaction progress to be monitored by $^{31}P\{^{1}H\}$ NMR, as determined by consumption of starting materials. Full conversion was observed for **4.1(*ⁱ*Pr)**, **4.1(Cy)**, **4.1(*ᵗ*Bu)**, **4.1(N*ⁱ*Pr$_2$)**, and **4.2(*ⁱ*Pr)**, while the remaining reaction mixtures displayed a number of unidentified resonances, in addition to the 2-phosphino-1,3-diphosphonium cation of interest.

Derivatives of **4.1** exhibit a number of different spin systems, similar to other triphosphorus cations, with a broad range of $^{31}P\{^{1}H\}$ NMR chemical shifts for the central phosphine center (δ_{PR} = -63 to 31 ppm) when compared to that of the terminal phosphonium centers (δ_{PR3}= 19 to 43 ppm).

A comparison of the most extreme case of the chemical shifts reported for the central PR group gives insight into substituent effects on chemical shift. The chemical shift for the central phosphorus for derivative **4.1(NⁱPr$_2$)** (δ_{PR} = 31) is the most downfield resonance, and is approximately 39 ppm further downfield from the next closest example of **4.1** **(4.1(*ᵗ*Bu)**; δ_{PR} = -10 ppm **)**. Similarly, the resonance corresponding to the central phosphorus unit for **4.2(NⁱPr$_2$))** (δ_{PR} = 22) is the most downfield shifted resonance for derivatives of **4.2** with the next closest **(4.2(*ⁱ*Pr)**; δ_{PR} = -43 ppm **)** being approximately 65 ppm upfield. This can be rationalized by examining the electronic effects that amido-substitution has on phosphorus cations, as both these derivatives are amido substituted. While it may be expected that π-electron donation would result in an upfield shift due to an increased amount of shielding imparted by π-electron donation from the nitrogen atom, the amido-substituent is also expected to be strongly σ-electron withdrawing, owing to a greater electronegativity ($\chi_N = 3.0$; $\chi_P = 2.2$). The effect that σ-withdrawl has on the central phosphorus center must, therefore, be greater than that of π-electron donation from the lone pair of the nitrogen atom, as it is observed that amido substituted phosphorus cations are, overall, deshielded relative to organo-substituted derivatives.

The chemical shifts collected for phosphonium sites of derivatives **4.1** and **4.2** suggests that the chemical shift is largely independent of the substituent at the phosphonium sites, as there is a narrow window of chemical shifts and wide array of substitutions. However, chemical shifts for the terminal phosphonium center can be rationalized in terms of the relative Lewis acidity of the central phosphinidinium cation. A stronger Lewis acid withdraws more electron density from the stabilizing ligand, resulting in a deshielding of the ligand. Derivatives **4.1((N^{i}Pr$_2$)** and **4.2(N^{i}Pr$_2$)** have the most upfield chemical shifts for the phosphonium moieties. It is rationalized that this is due to the formal 2+ charge of the central phosphorus, delocalized between the phosphorus atom and the adjacent nitrogen. Resonance contributions average the formal charges on phosphorus for amido-substituted derivatives at 3/2, instead of a full 2+ charge for alkyl-substituted derivatives. This reduced formal positive charge gives evidence for a reduced Lewis acidity and thus, greater shielding of the stabilizing PMe_3 ligands, as there is less demand for electron density from the central phosphorus site. The greater shielding translates into an upfield chemical shift.

#	Compound [R$_3$P-PR′-PR$_3$][A]$_2$			Chemical Shift (ppm)		$^{1}J_{PP}$ (Hz)	Spin system
	R	R′	A	δ_{PR3}	δ_{PR}		
4.1	Me	Me	OTf	25.0	-62.6	-285 -295	AXX′
		^{i}Pr		23.0	-27.3	-305 -325	AXX′
		Cy		22.7	-30.8	-307 -326	AXX′
		^{t}Bu		22.3	-9.5	-333	AB$_2$
		Ph		24.7	-46.3	-286 -298	AXX′
		N^{i}Pr$_2$		19.3	31.2	-350	A$_2$B
4.2	Et	Me	OTf	41.7	-74.4	-300 -308	AXX′
		^{i}Pr		42.5	-42.9	-324 -337	AXX′
		Cy		42.4	-47.1	-326 -338	AXX′
		Ph		42	-60	---[a]	AXX′
		N^{i}Pr$_2$		39.6	22.0	-364	AB$_2$
4.3(1)	Ph	H	AlCl$_4$	23	-120	-286[b]	AX$_2$
		Me		23	-48	-330[b]	
		^{i}Pr		21	-23	-354[b]	

[a] $^{1}J_{PP}$ could not be assessed due to overlap with the ^{31}P chemical shifts of the diphosphinodiphosphonium product [b] $^{1}J_{PP}$ values were reported as positive by Schmidpeter(1) and coworkers. Negative values are reported here solely in accordance with the convention(2) used in this thesis as most values in the literature have not been definitively assigned.

Table 4.0 - ^{31}P{^{1}H} NMR parameters at 101.3 MHz for derivatives of the 2-phosphino-1,3-diphosphonium framework adapted from thesis by Y. Carpenter.[82] Coupling constants are derived by iterative fitting of the spectra at 298K and 101.3 MHz.

The downfield shift of the central phosphine center, combined with the upfield shift of the phosphonium sites, results in a reversal of the relative peak positions of the two phosphorus environments

Prior to the present study, the only crystallographically characterized derivative of a 2-phosphino-1,3-diphosphonium framework is $[Ph_3P\text{-}PH\text{-}PPh_3][AlCl_4]_2$ (**4.3(H)**) reported by Schmidpeter and coworkers.[68] Other comparative frameworks include the cyclic 2-phosphino-1,3-diphosphonium frameworks published by Dillon and coworkers in 2008,[69] who employed chelating phosphine ligands in place of discrete tertiary phosphines for phosphinidinium stabilization. However, in these examples, the geometric parameters of the P-P-P chain are largely dependent on the bite angle imposed by the carbon backbone. As such, a comparison of these examples to those examined in the present context is not instructive. The analysis of single crystals of **4.1**, thus, presents an opportunity to assess the effect of steric bulk on solid-state geometric parameters of these types of frameworks.

Four derivatives of **4.1** have been further characterized using single-crystal X-ray diffraction methods, and their relevant bond lengths and angles are summarized in table 4.1. Cations **4.1(Me)[OTf]$_2$, 4.1(Cy)[OTf]$_2$, 4.1(^{t}Bu)[OTf]$_2$** and **4.1(N^{i}Pr$_2$)[OTf]$_2$** feature distinctly longer P-P bonds ($P\text{-}P_{average}$: 2.2211 Å) in the solid state when compared to the only structurally characterized triphosphenium cation $[Ph_3P\text{-}P\text{-}PPh_3][AlCl_4]$ ($P\text{-}P_{average}$: 2.1311 Å). This supports single bond character of the P-P bonds found in the dication and partial double bond character of the monocation.

The monocationic triphosphorus frameworks $[Me_2P\text{-}PMe_2\text{-}PMe_2][OTf]$ features P-P bond distances of 2.2160(6) Å and 2.1883(6) Å ($\Delta = 0.0277$ Å; $3\sigma = 0.00025$; $\Delta > 3\sigma$). Using a dative model, it is expected that the shorter of the two occurs between the phosphorus atom from a diphosphine (R_2P-PR_2) and the phosphorus atom of a phosphenium cation (R_2P^+), as cationic centers have a reduced covalent radius. With this in mind, it is expected that a phosphine stabilized phosphinidinium dication (RP^{2+}) should posess two P-P^+ interactions on the same order as the shortest one observed for [Me_2P-PMe_2-PMe_2][OTf] (2.1883(6) Å). However, average P-P^+ bond distances for **4.1** and **4.3** ($P_{average}$ = 2.2197 Å) are longer than the aforementioned shorter bond in [Me_2P-PMe_2-PMe_2][OTf]. This provides evidence to suggest that other factors, such as steric hindrance, must be considered when examining the P-P interactions of *catena*-phosphorus cations and that cationic charge, alone, is not sufficient in predicting the Lewis acid/base bond length.

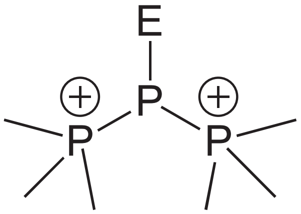


Figure 4.3 – Lewis model, highlighting the P-E interaction (E = C, N, H)

P-E (E = C, N, H) interactions for the central phosphorus atom (Figure 4.3) range from 1.13(2) Å for **4.3(H)** to 1.925(3) Å for **4.1(^{t}Bu)**. Although **4.3(H)** has the shortest P-E bond, this is likely due to the small covalent radius from the hydrogen atom. A comparison of P-E bonds for the remaining derivatives reveals a slightly shortened P-E bond for **4.1(N^{i}Pr$_2$)** when compared to the P-C bonds of the other derivatives. This provides further evidence for the idea that the lone pair of nitrogen is involved with π-electron donation to the phosphinidinium center, resulting in a resonance contributor with increased bond order. Cations **2.1(^{t}Bu)** and **2.1(N^{i}Pr$_2$)** possess weak cation-anion contacts in the solid state between the oxygen or fluorine atoms of the triflate counterion and one or more methyl hydrogens of the phosphonium moieties, but these distances approach the limiting sum of the van der Waals radii (Σr_{vdw}: OH 2.60 Å; HF 2.55 Å) and should not be considered significant.

	$[Me_3P\text{-}PR\text{-}PMe_3][OTf]_2$, 4.1(R)				**$[Ph_3P\text{-}PH\text{-}PPh_3][AlCl_4]_2$ 4.3(H)(1)**
	4.1(Me)	**4.1(Cy)**	**4.1(^{t}Bu)**	**4.1(N^{i}Pr$_2$)**	
P-P (Å)	2.2262(5) 2.2273(5)	2.1979(5) 2.1976(6)	2.2391(15) 2.2354(16)	2.2181(9) *to* 2.2271(9) *[σ = 0.004]*	2.205(1) 2.224(1)
P-P-P (°)	109.49(2)	103.11(2)	100.97(5)	105.06(7)	106.39(4)
P2-E (Å) E = H, C, N	1.8423(14)	1.8589(16)	1.925(3)	1.655(2) *to* 1.660(2) *[σ = 0.003]*	*1.13(2)*
P1/3-C_{avg}	1.7935(15)	1.7891(17)	1.810(3)	1.782(3) *to* 1.799(2) *[σ = 0.005]*	---
Σ_{angles} (at P2)	310°	318°	317°	318° *to* 319° *[σ = 0.7]*	287°

Table 4.1 - Selected relevant bond lengths and angles in the solid state structures of the dications in characterized acyclic 2-phosphino-1,3-phosphonium triflates **4.1**$[OTf]_2$. Table adapted from thesis by Y. Carpenter.[82]

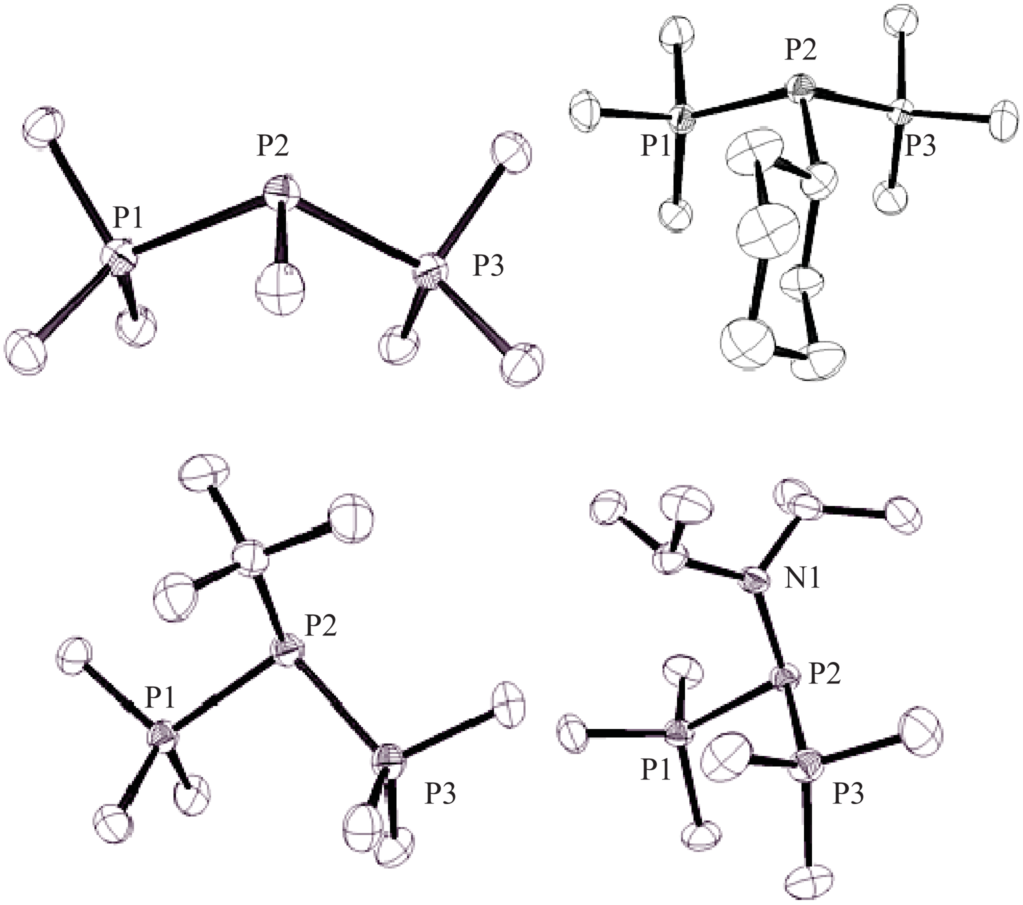


Figure 4.4 – ORTEP representations of the solid state structure of the cation in (left to right; top to bottom): **4.1(Me)[OTf]$_2$**, **4.1(Cy)[OTf]$_2$**, **4.1(^{t}Bu)[OTf]$_2$** and **4.1(N^{i}Pr$_2$)[OTf]$_2$**. Hydrogen atoms and counterions omitted for clarity. Thermal ellipsoids shown at the 50% probability level. Unlabelled atoms are carbon atoms. Relevant parameters are listed in Table 4.1.

It is proposed that the preparation of 2-phosphino-1,3-diphosphonium cations is achieved in two mechanistic steps. Initially, a chloride ion abstraction results in a chlorophosphenium cation that is stabilized by a phosphine ligand. This may alternatively be viewed as a chlorophosphino-phosphonium cation $[R_3P\text{-}PR(Cl)]^+$ that undergoes a second halide abstraction to produce a phosphenio-phosphonium dication $[R_3P\text{-}PR]^{2+}$ that is stabilized by another phosphine ligand. The resulting structure may be described as a

2-phosphino-1,3-diphosphonium cation using a Lewis model, or alternatively as a phosphine-stabilized phosphinidium cation (Figure 4.2).

4.3: Summary, Outlook and Conclusions

In summary, eleven derivatives of the 2-phosphino-1,3-diphosphonium framework were synthesized and characterized using $^{31}P\{^{1}H\}$ NMR spectroscopy. Four of these derivatives were further characterized using single crystal X-ray crystallography. Analysis of solid state geometric parameters revealed a range of P-P bond lengths (2.1976(6) Å - 2.2391(15) Å) and P-P-P bonding angles (100.97(5)° - 109.49(2)°). The only other derivative of this type to be crystallographically characterized ($[Ph_3P\text{-}PH\text{-}PPh_3][AlCl_4]_2$) has values within the respective range.

Chapter 5: Summary, Proposed Future Directions and Preliminary Results

5.1: Summary:

Despite many efforts, insight for the insertion of phosphenium cations into the P-P bond of varying *catena*-phosphines remains limited. This is largely due to fast rates of reaction that cannot be sufficiently reduced by low temperature NMR studies.

However, eight new derivatives of existing *catena*-phosphosphorus cationic frameworks have been synthesized, which provide comparative data for a broader understanding in this field. Moreover, these compounds provide a new basis for which larger, novel frameworks may be generated by new synthetic methods and help to demonstrate their versatility in the rational and systematic development of *catena*-phosphorus chemistry.

5.2: In series *catena*-phosphorus coordination complexes and subsequent derivitization:

It has been previously shown that a phosphenium cation can act as both a Lewis acid and a Lewis base within the same molecule.[75] Coordination of chlorophosphine-stabilized dimethylphosphenium to gallium trichloride results from a 1:1 stoichiometric reaction of dimethylchlorophosphine and gallium trichloride. The resulting complex can be described as an ‘in-series’ coordination complex, and is representative of an interesting type of reactivity for phosphorus (Figure 5.0).

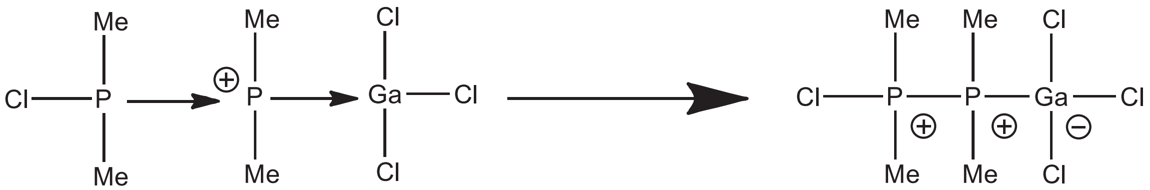


Figure 5.0 – ‘In-Series’ coordination of dimethylphosphenium to gallium trichloride

In light of this, it is suggested that reaction of dimethylchlorophosphino dimethylphosphonium ($[Me_2PCl \rightarrow PMe_2^+]$) or trimethylphosphino dimethylphosphonium ($[Me_3P \rightarrow Me_2P]$) with phosphenium ($[PR_2^+]$) centres possessing heightened Lewis acidity ($R = C_6F_5, CF_3$) would generate the novel 1-phosphino-2,3-diphosphonium framework (Figure 5.1).

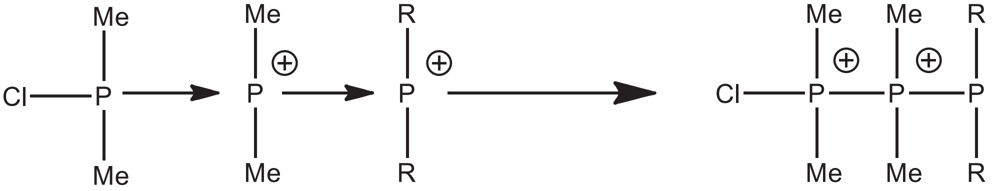


Figure 5.1 – Dative (left) and covalent (right) models for 1-phosphino-2,3-diphosphonium framework ($R = C_6F_5, CF_3$)

Generation of this novel framework could lead to other unprecedented frameworks, such as a 1,4-diphosphino-2,3-diphosphonium chain. This would be accomplished by the reaction of $[Me_2(Cl)P\text{-}PMe_2\text{-}PR_2]$ with tris(TMS)phosphine, as the thermodynamically favourable elimination of TMSCl allows for phosphorus-phosphorus bond formation with substitution of chlorine with a TMS_2P moiety, as shown in Figure 5.2.

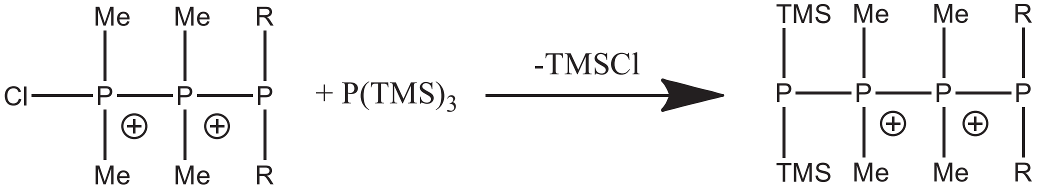


Figure 5.2 – Generation of a 1,4-diphosphino-2-3-diphosphonium framework by TMSCl elimination

5.3: Hypervalent phosphorus compounds:

Previous studies have shown that the addition of $(CF_3)_2P\text{-}P(CF_3)_2$ to $(CH_3)_2P\text{-}P(CH_3)_2$ yields the asymmetric diphosphine $(CF_3)_2P\text{-}PMe_2$.[72] Reaction of $(CF_3)_2P\text{-}PMe_2$ with MeOTf results in the phosphinophosphonium salt $[(CF_3)_2P\text{-}PMe_3][OTf]$, which can also be envisaged as trifluoromethylphosphenium cation stabilized by trimethylphosphine (Figure 5.3).

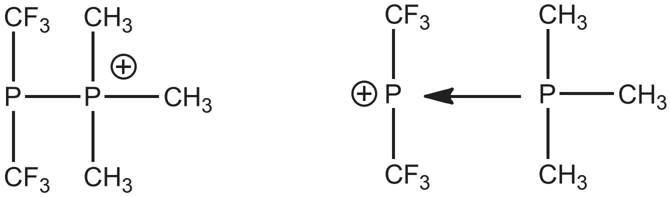


Figure 5.3 – $[(CF_3)_2P\text{-}PMe_3][OTf]$ (**3a)** as Lewis (left) and Coordination (right) models

The presence of six fluorine atoms provide significant inductive withdrawal of electron density from phosphorus. With this in mind, it may be possible that bis(trifluoromethyl)phosphenium is sufficiently electron deficient so as to accommodate an additional ligand when compared to traditional phosphenium centers, which would give rise to novel hypervalent phosphorus frameworks.

$[(CF_3)_2P\text{-}PMe_3][OTf]$ would not likely be susceptible to ligand displacement due to trimethylphosphine being a strong donor. However, it may be possible to react $[(CF_3)_2P\text{-}PMe_3][OTf]$ with an electron-rich phosphine at the three-coodinate phosphorus site, so as to generate a phosphinide-diphosphonium interaction (Figure 5.4).

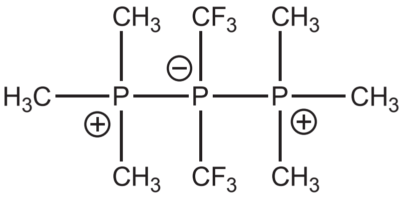


Figure 5.4 – 2-phosphinide-1,3-diphosphonium as proposed product of $[(CF_3)_2P\text{-}PMe_3][OTf]$ with PMe_3

This would give rise to an unprecedented framework, analogous to PBr_4^-.[75] Further studies could examine the reactivity of $[(CF_3)_2P\text{-}PMe_3][OTf]$ with a bidentate ligand. Bis(dimethylphosphino)ethane (dmpe) or Bis(dimethylphosphino)methane (dmpm) are likely candidates for this reaction, as they possess phosphine moieties with similar Lewis basicity to that of trimethylphosphine. Additionally, chelation to a phosphenium center would provide kinetic stability in the generation of complexes of the structure seen in figure 5.5.

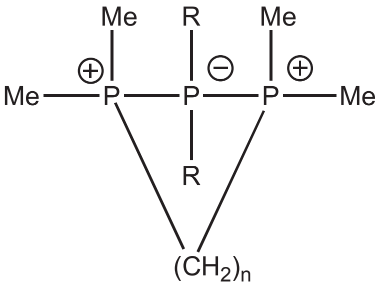


Figure. 5.5 – Proposed product of $[(CF_3)_2P\text{-}PMe_3][OTf]$ with a bidentate phosphine

Halide abstraction from a di-alkyl or aryl phosphine halides has been shown to be an effective method to access di-alkyl or aryl phosphenium cations. The reaction of R_2PX with MX_3 (M = Al, Ga; X = Cl, Br, I) generates halophosphine-stabilized phosphenium ions that can readily undergo ligand displacement, provided a more basic phosphine is introduced. Until recently, the most electrophilic phosphenium centers were those containing aryl or halo substituents, as they either possess a number of electron withdrawing sp^2 hybridized carbon atoms or halogen atoms. The alteration of phosphenium electronic properties may result in the generation of unprecedented phosphorus frameworks, as the implications of modifying this property have not been fully realized. Specifically, studying the reactivity of bis(pentafluorophenyl)chlorophosphine with simple donors such as PMe_3, $HPMe_2$ or Me_2PCl would be an interesting endeavour, as it may lead to neutral coordination complexes, similar to those shown by Sisler and co-workers.[76] Subsequent studies could exemplify the amphoteric nature of these complexes by reacting them with Lewis acids ($AlCl_3$, $GaCl_3$) or bases (NEt_3) to generate phosphino-phosphonium or phosphino-phosphido complexes, respectively (Figure 5.6).

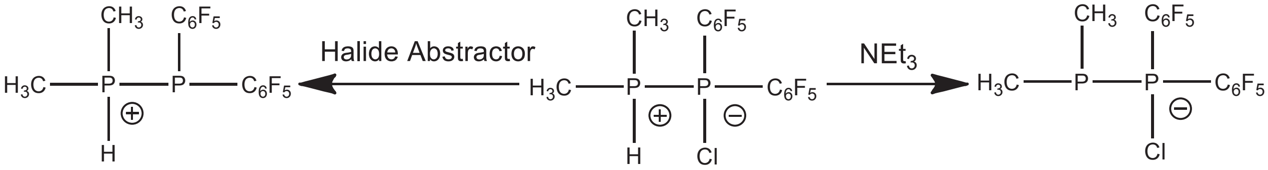


Figure 5.6 – Amphoteric reactivity of neutral coordination complexes

Additionally, bis(pentafluorophenyl)chlorophosphine may be a convenient source of $(C_6F_5)_2P^+$, which could possess novel reactivity in the context of hypervalent *catena*-phosphorus cationic frameworks.

5.4: Diphosphenes as alternate precursors to phosphinophosphonium compounds:

It has been previously shown that diphosphines readily react with electrophilic alkyl halides, as they were among the first investigations towards phosphinophosphonium complexes.[79] Furthermore, diphosphenes have been observed to have the same reactivity towards alkylating agents as diphosphines.[66] However, when diphosphines are reacted with Lewis acidic phosphenium centers, the P-P bonds are readily cleaved, as a phosphenium-inserted product is observed as the major product.[38] While it is unlikely that the P=P double bond will act as an insertion site, an interesting study would examine the interaction that Mes*P=PMes* would have with various phosphenium centers. Possible products include a phosphene-stabilized phosphenium, or a three-phosphorus monocationic framework, resulting from cleavage of a π bond (Figure 5.7). Although both these frameworks have been previously reported, this would represent a novel synthetic path to such frameworks. This supports the idea that these methods are versatile approaches to generate *catena*-phosphorus frameworks.

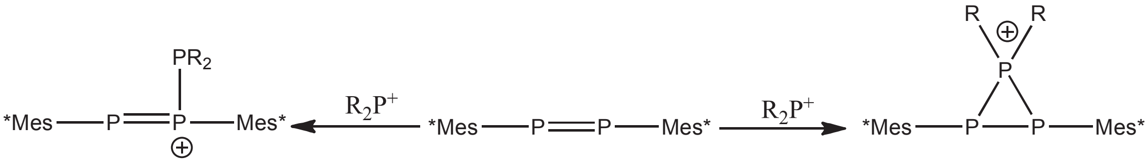


Figure 5.7 – Representation of potential reactivity of diphosphenes with respect to phosphenium cations

5.5: Melt reactions towards new cyclophosphorus cations:

It has been previously shown that molten mixtures of R_2PCl, $GaCl_3$ and neutral phosphorus compounds result in phosphenium insertion into a P-P bond in the neutral fragment, as the molten $R_2PCl/GaCl_3$ mixture is a reactive source of phosphenium ions. These previous efforts, however, only focused on the insertion of a phosphenium center into a five-membered phosphorus ring[62], or a P_4 tetrahedron.[50] In the latter case, it was noted that phosphenium ions could be inserted sequentially up to three times. However, the formed product was noted to be extremely unstable in solution, or in basic conditions. The propensity for the $P_7R_6^{3+}$ cation to undergo rapid decomposition under these conditions is likely due to the absence of stabilizing alkyl or aryl groups. The availability of other phosphorus rings $(RP)_n$ (R = Me, ^{t}Bu, Cy; n = 3, 4, 5, 6), along with the likelihood of the polyphosphenium inserted $(RP)_n$ products being more stable due to the presence of alkyl or aryl groups, suggests that molten mixtures of various chlorophosphines, gallium trichloride and $(RP)_n$ rings may be a viable synthetic strategy to obtain new polycyclic cationic phosphorus frameworks. Specifically, the reaction of $(^tBuP)_3$ has the potential for three phosphenium inserted products, assuming alternating cationic and neutral phosphorus centers. Thus the reaction of $(^tBuP)_3$ with up to three equivalents of R_2PCl and $GaCl_3$ is a likely method to generate a six phosphorus, tricationic complex, as it has significantly greater ring strain than the five phosphorus ring previously employed to generate a six phosphorus cationic ring.

Furthermore, by carrying out melt reactions with an excess of phosphenium centres relative to the neutral ring, we may consider all P-P bonds of the neutral ring to be activated and so we can tune how many "RP" and "R_2P^+" units there are available in the system. For example, by reacting 0.75 equivalents of $(CyP)_4$ with 3 equivalents of $R_2PCl/GaCl_3$ creates an environment with, effectively, 3"CyP" units and 3 "R_2P^+" units, which is analagous to the stoichiometry of a three phosphorus ring (three (CyP) units) with three phosphenium ions. It is suggested that the product of this reaction would be a six-phosphorus, tricationic ring. However, by adjusting the stoichiometry in this manner, the amount of P-P activating phosphenium cations increases, relative to the neutral ring and so creates a system with effectively free CyP and PR_2 moieties in a 1:1 ratio, which would facilitate the generation of the most thermodynamically stable molecule. This methodology could be extrapolated throughout several other ring systems and stoichiometries to generate a number of cationic phosphorus rings.

5.6: Non-symmetric diphosphines and diphospholes as mediators of novel *catena*-phosphorus chemistry:

In light of the fact that the reactivity is restricted in developing 1,3-diphosphino-2-phosphonium cations using a variety of phosphenium sources and limited number of diphosphines, further studies would target such cations by employing diphosphines that exhibit novel steric or electronic characteristics. Specifically, the employment of a non-symmetric diphosphine, such as $(CH_3)_2P\text{-}P(CF_3)_2$, or $(CH_3)_2P\text{-}P(C_6F_5)_2$ may induce novel reactivity, given the fact that the fluorine groups provide slight steric hindrance when compared to hydrogen. Furthermore, inductive withdrawal provided by the fluorine groups reduces the nucleophilicity on the nearest phosphorus site, thereby creating a variation in the ability of each phosphorus center to stabilize a phosphenium center. The combination of steric and electronic properties induced by the perfluoroorganic groups may prove to be an efficient method to generate an asymmetric triphosphine monocation.

Additional efforts in this context may include using a molecule with a phosphorus-phosphorus linkage that exhibits more steric bulk than other diphosphines. It has been previously studied that the lone pair on phosphorus of pentaphenylphosphole reacts readily with $Fe_3(CO)_{12}$ through either the 4π electrons of conjugated double bonds or by interaction with the lone pair of phosphorus.[78] In a similar example, tetraphenylphosphole (Figure 5.8) stabilizes $W(CO)_5$ through the lone pair on phosphorus.[79] These examples help to demonstrate the lack of participation of the electron pair on phosphorus in an aromatic sextet, which is in stark contrast to other heterocycles such as the pyrrole class of compounds that contain the same electronic configuration. This gives evidence for the probable reactivity of phospholes with Lewis acidic phosphenium centers. Tetraphenyldiphosphole has a phosphorus center flanked by phenyl-substituted carbon atoms in a five-membered unsaturated ring. Given the steric hindrance provided by the phenyl groups, a phosphenium linkage may provide thermodynamic stability and provide a route towards derivatization of 1,3-diphosphino-2-phosphonium cations.

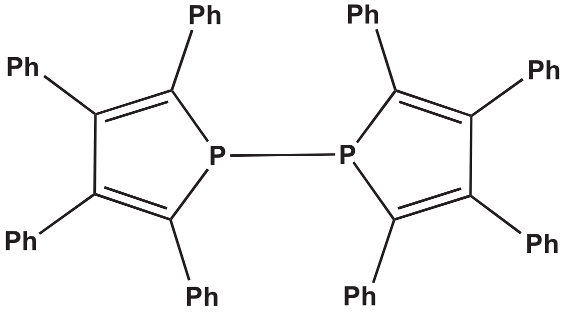


Figure 5.8 – Lewis structure of octaphenyldiphosphole

Preliminary studies involving octaphenyldiphosphole found that both diphenylphosphenium and dimethylphosphenium cations readily insert into the P-P bond of the parent diphosphole, as $^{31}P\{^1H\}$ NMR spectra reveal an A_2B spin system at room temperature. This is in contrast to all but one analogue of the type $[R_2P\text{-}PR`_2\text{-}PR_2][OTf]$ that display dynamic exchange at room tempreratureand suggests that a 1,3-diphosphino-2-phosphonium cations involving this diphosphole are more stable at room temperature than most of those attained using simpler organodiphosphines. This greater stability gives rise to the potential derivatization of cationic phosphorus frameworks of this type.

5.7: Perfluorinated phosphorus compounds as precursors for novel cationic phosphorus frameworks

A major challenge in expanding the series of known cationic *catena*-phosphorus frameworks has been to develop a synthetic method that facilitates the generation of a branched cationic ring of the types in figure 5.9.

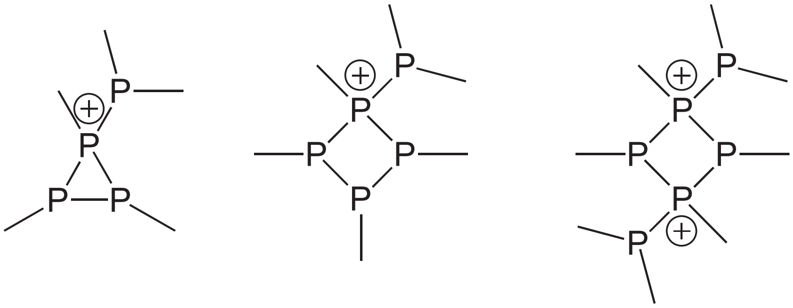


Figure 5.9 – Lewis model of various branched *catena*-phosphorus cations

To date, there have been no reports of such cations in the literature. Their isolation has remained elusive, presumably due to the strong preference for a phosphenium cation to insert into the P-P bond of the neutral ring, as opposed to remain as a coordination compound between the neutral phosphine donor and phosphenium cation acceptor. It is suspected that the phosphenium insertion occurs via an initial coordination by the lone pair of the phosphorus atom in the ring. Following this is an S_N2 type intermolecular rearrangement that gives rise to the observed product (Figure 5.10).

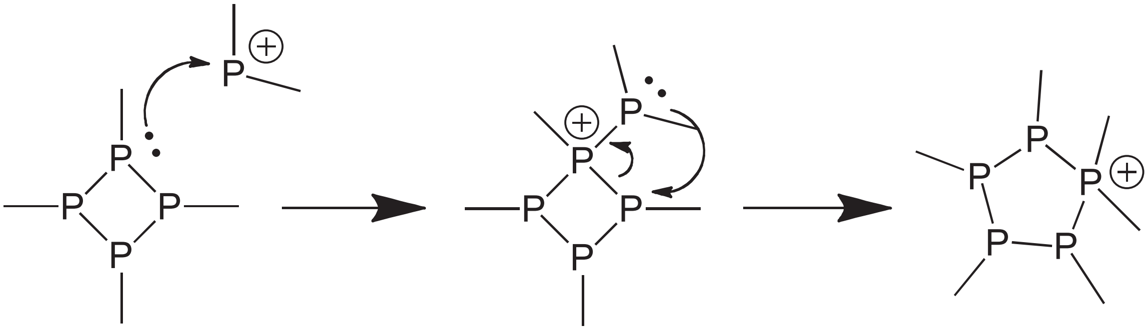


Figure 5.10 – Proposed S_N2 mechanism for the insertion of phosphenium cations into phosphorus rings

It is proposed that this rearrangement may be precluded by reducing the nucleophilicity of the branched phosphorus atom. Substituting the hydrogen atoms of the parent chlorophosphine with fluorine atoms may provide an electronic deficiency at the phosphorus center, such that its nucleophilicity is reduced and, thus, rearrangement is prevented. In considering possible perfluorinated chlorophosphines, perfluoromethyl ($-CF_3$) and perfluorophenyl ($-C_6F_5$) are good candidates. However, the synthesis, isolation and purification of perfluorinated alkyl phosphines is a challenging and dangerous task, whereas the perfluorophenyl analogue is prepared in safer conditions.

Preliminary investigations involving $(C_6F_5)_2PCl$ were to determine its reactivity towards a variety of halide abstractors. Typically, intermolecular stabilization of phosphenium cations occurs by coordination of a chlorophosphine. However, in this case, it was unclear as to whether or not $(C_6F_5)_2PCl$ would be sufficiently basic to stabilize a perfluoro-substituted phosphenium cation. Indeed, $^{31}P\{^1H\}$ NMR of reaction mixtures containing $(C_6F_5)_2PCl$ and $AlCl_3$, $GaCl_3$ or TMSOTf showed no reaction, which is in stark contrast to studies involving Ph_2PCl, or other dialkylchlorophosphines that display two doublets, assigned to a chlorophosphine stabilized phosphenium complex. However, upon addition of a Lewis base such as PMe_3, two resonances became present in the $^{31}P\{^1H\}$ NMR spectrum, which is consistent for a phosphinophosphonium cation. The $^1J_{PP}$ coupling constant is 304 Hz, and is consistent with a P-P interaction seen for phosphinophosphonium compounds of this type ($[Ph_3PPPh_2][GaCl_4]$, 340 Hz).[81] Secondary splitting (J_{PF} = 30 Hz) for the resonance at δ = -61.4 ppm is described as a quintet and is rationalized that the phosphorus center bearing the perfluorophenyl substituents is coupling to either the ortho, or meta-fluorine atoms of the phenyl groups. Phosphinophosphonium compounds of this type can be observed as triflate or aluminate salts.

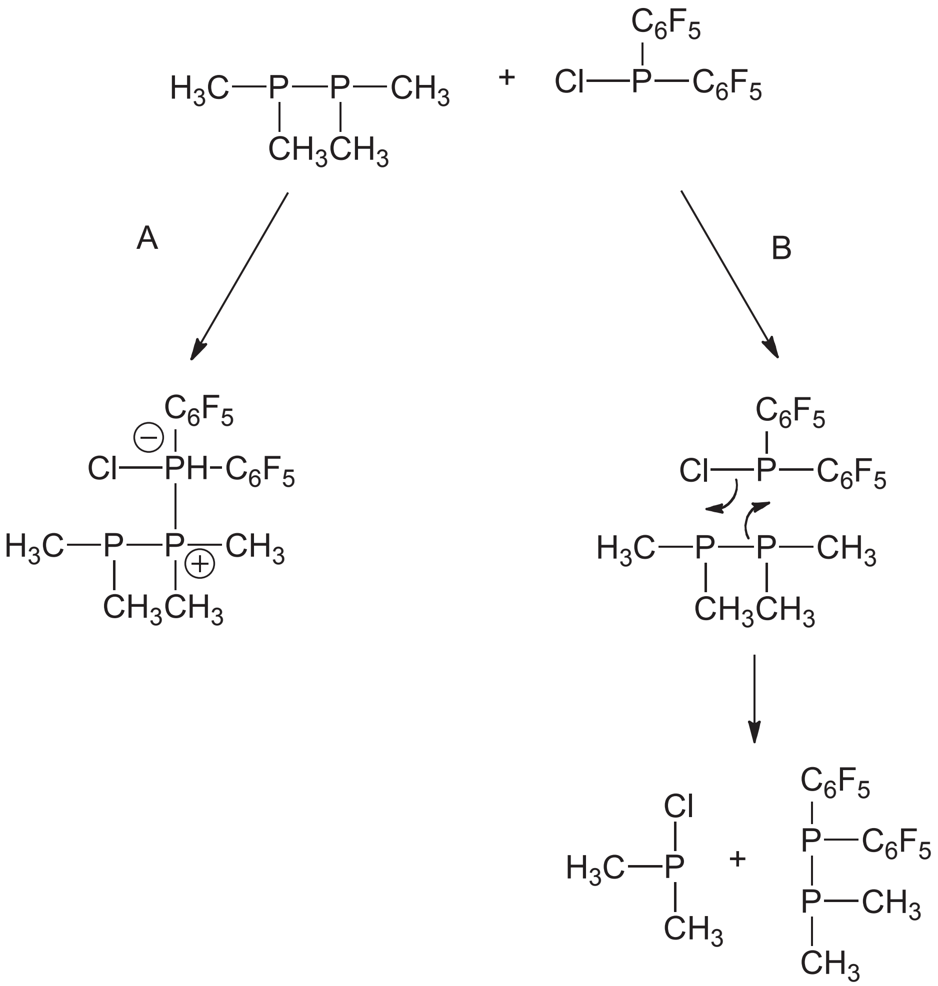


Figure 5.11 – Proposed neutral coordination complex (A) and metathesized products (B)

Further studies involving $(C_6F_5)_2PCl$ were focused on making neutral coordination complexes with Lewis bases. Specifically, $(C_6F_5)_2PCl$ was reacted with $Me_2P\text{-}PMe_2$ with the goal of generating an interaction between the diphosphine and chlorophosphine (Figure 5.11, path A). Interestingly, this results in metathesis of the two substrates, generating Me_2PCl ($^{31}P\{^1H\}$ $\delta = 89.6$ ppm) and $Me_2P\text{-}P(C_6F_5)_2$. This is evident by $^{31}P\{^1H\}$ NMR studies that show a multiplet at $\delta = -49.1$ ppm. Initially, it would appear as if the multiplet is a quartet of quintets. However, upon closer inspection, it is clear that there are two sets of peaks with the same $^1J_{PP}$ coupling, but different secondary splitting to the fluorine atoms (Figure 5.12).

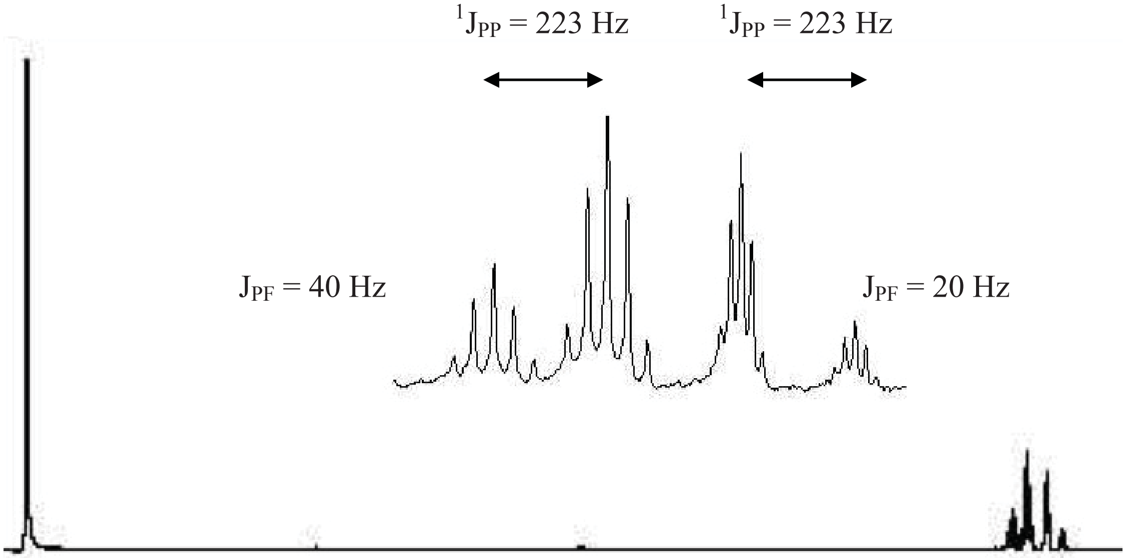


Figure 5.12 – ^{31}P NMR spectrum of a reaction mixture containing Me_2PCl and $Me_2P\text{-}P(C_6F_5)_2$

This result is rationalized by the proposed pathway described in figure 5.11, path B. Although reactivity of this type has been previously reported,[72] this provides a synthetically more convienent route to non-symmetric perfluorinated diphosphines, as reduction using mercury is not necessary to generate starting materials.[71]

5.8: Ligand Stabilization of Phosphorus(V) cations

An alternative approach to preclude phosphenium insertion and thus allowing for the preparation of branched cationic *catena*-phosphorus rings is highlighted in figure 5.9. It is proposed that phosphorus (V) cations in place of phosphorus (III) cations would facilitate this. In the proposed mechanism for the insertion of phosphenium cations in to phosphorus rings, there is a proposed S_N2 intermolecular rearrangement that may be considered a formal oxidation (from P(III) to P(V)) of the branched phosphorus unit. In line with this, it may be possible to prevent rearrangement by introducing a phosphorus unit that is already in the fifth oxidation state, thereby preventing further oxidation. A number of potential P(V), chlorine containing compounds are readily available from commercial chemical providers which gives rise to a wide range of possible reactivities. Moreover, compounds such as $POCl_3$ or $PSCl_3$ offer possibilities for further functionalization through the chlorine atoms.

Chapter 6: Experimental

6.1: General Procedures:

Reactions were carried out in a glove box under an inert N_2 atmosphere, with any glassware being heated to 350°C prior to use . Solvents, with the exception of diethylether and tetrahydrofuran, were dried on an MBraun solvent purification system and stored over molecular sieves prior to use. Diethyl ether and tetrahydrofuran were dried with sodium and benzophenone and distilled prior to use. Me_2PPMe_2,[70] $(CF_3)_2PP(CF_3)_2$, [71] $Me_2PP(CF_3)_2$, [72] $(C_6F_5)_2PCl$[73] and octaphenyldiphosphole[74] were prepared according to literature methods. Me_2PCl and PMe_3 (99%) were purchased from Strem, while MeOTf was purchased from Aldrich. All were used as received. Ph_2PCl and TMSOTf were purchased from Aldrich and were purified by vacuum distillation prior to use. Solution $^{31}P\{^1H\}$ NMR spectra for compounds were collected at room temperature on a Bruker AC-250 NMR spectrometer. Chemical shifts are reported in ppm relative to an external reference [100% $SiMe_4$ (^1H, ^{13}C), and 85% H_3PO_4 (^{31}P)]. NMR spectra of reaction mixtures were obtained by transferring an aliquot of the bulk solution to a 5 mm NMR tube. These tubes were capped and sealed with Parafilm. Experimental $^{31}P\{^1H\}$ NMR second order spin systems were fitted to data obtained from interative simulations by gNMR.

6.2: Preparation and Characterization of Compounds:

Numbering scheme: The first number is a reference to the chapter detailing the preparation and/or objectives in preparing the compound of interest (i.e. a compound labelled as **4.6** is from chapter 4). The second number differentiates between a number of similar compounds found within a particular chapter. Compounds discussed first have a lower number than those discussed later in the chapter (i.e. compound **4.6** is a different compound than **4.7**, however, both are detailed in chapter 4 and are prepared with the same objective). Any abbreviations in brackets that follow a number is meant to specify the substituents that are being modified in a given study.

Reaction of *t*Bu$_3$P$_3$ with PhICl$_2$ in the presence of Me$_3$SiOTf: To a solution of (^{t}BuP)$_3$ (264.3 mg, 1.0 mmol) and (CH$_3$)$_3$SiOTf (18.1 µL, 1.0 mmol) in C$_6$H$_5$F (2 mL) was added dropwise a solution of PhICl$_2$ (274.9 mg, 1.0 mmol) in C$_6$H$_5$F (2 mL) at ambient temperature. The reaction was monitored by means of ^{31}P{^{1}H} NMR spectroscopy.

Reaction of *t*Bu$_3$P$_3$ with [PCl$_4$][GaCl$_4$] To a solution of (^{t}BuP)$_3$ (264.3 mg, 1.0 mmol) in C$_6$H$_5$F (2 mL) was added a suspension of [PCl$_4$][GaCl$_4$] (1 mmol) at ambient temperature. The reaction mixture turned immediately orange and small amounts of orange precipitate were formed. After 60 min. a ^{31}P{^{1}H} NMR spectrum of the reaction mixture was recorded.

Isomerisation of *t*Bu$_3$P$_3$ in the presence of Me$_3$SiOTf To a solution of (^{t}BuP)$_3$ (264.3 mg, 1.0 mmol) in C$_6$H$_5$F (2 mL) was added (CH$_3$)$_3$SiOTf (18.1 µL, 1.0 mmol). The reaction mixture was stirred at room temperature and the reaction progress was monitored by ^{31}P{^{1}H} NMR experiments after 1 h, 12 h, 36 h and 72 h. *t*Bu$_4$P$_4$ can be received quantitatively by removing (CH$_3$)$_3$SiOTf and C$_6$H$_5$F *in vacuo*.

[3.4(Ph$_2$)][GaCl$_4$]: To a solution of (^{t}BuP)$_3$ (793.2 mg, 3.0 mmol) in C$_6$H$_5$F (5 mL) was slowly added Ph$_2$PCl (55.4 µL, 3.0 mmol) and GaCl$_3$ (528.2 mg, 3.0 mmol) dissolved in C$_6$H$_5$F (7 mL) at ambient temperature. After 30 min. a ^{31}P{^{1}H} NMR spectrum was recorded of the yellow coloured reaction mixture that indicated complete reaction. The addition of hexanes (5 mL) leads to the separation of orange oil that solidified after removing the supernatant and adding a second time hexane (5 mL). The obtained solid was washed with *n*-hexane (3 x 5 mL) and dried *in vacuo* to yield analytically pure, moisture and air-sensitive [3.4(Ph$_2$)][GaCl$_4$]; 1.3 g (2.0 mmol, 66%); m.p. 160 - 163°C;

Raman (200 mW, 300 K, cm^{-1}): 3060 (57), 2958 (33), 2896 (69), 1583 (75), 1459 (21), 1440 (12), 1168 (33), 1089 (28), 1027 (32), 999 (100), 617 (15), 575 (35), 550 (18), 498 (22), 345 (82), 227 (19), 187 (38), 162 (21), 150 (27); IR (ATR, 300 K, cm^{-1}): 3058 (vw), 2951 (s), 2858 (vw), 1734 (vw), 1716 (vw), 1698 (vw), 1684 (vw), 1653 (vw), 1558 (vw), 1541 (w), 1507 (vw), 1457 (m), 1438 (s), 1393 (w), 1364 (m),.1310 (w), 1156 (vs), 1097 (vw), 997 (m), 937 (w), 801 (m), 739 (s), 686 (m), 619 (vw), 593 (w), 548 (m), 502 (w), 471 (s); ^{1}H NMR (CD_2Cl_2, 300 K, [ppm]): δ = ^{1}H NMR (CD_2Cl_2, 300 K, [ppm]): δ = 1.30 (9H, d, $P_MC(CH_3)_3$, $^{3}J_{PH}$ = 8.4 Hz), 1.32 (9H, d, $P_MC(CH_3)_3$, $^{3}J_{PH}$ = 8.4 Hz), 1.38 (9H, d, $P_AC(CH_3)_3$, $^{3}J_{PH}$ = 14.3 Hz), 7.66 – 7.96 (10H, m, $P_X(C_6H_6)_2$); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 300 K, [ppm]): δ = 29.4 (3C, dt, $P_XC(CH_3)_3$, $^{2}J_{PC}$ = 15.9 Hz, $^{3}J_{PC}$ = 5.0 Hz), 31.3 (6C, m, $P_MC(CH_3)_3$), 31.9 (1C, m, $P_XC(CH_3)_3$), 37.6 (2C, m, $P_MC(CH_3)_3$), 117.6 (1C, m, *i*-Ph), 124.3 (1C, m, *i*-Ph), 131.1 (1C, d, *m*-Ph, $^{3}J_{PC}$ = 2.2 Hz), 131.2 (1C, d, *m*-Ph, $^{3}J_{PC}$ = 2.3 Hz), 133.5 (1C, dt, *o*-Ph, $^{2}J_{PC}$ = 9.9 Hz, $^{3}J_{PC}$ = 4.8 Hz), 135.0 (1C, d, *p*-Ph, $^{4}J_{PC}$ = 3.5 Hz), 135.6 (1C, dt, *o*-Ph, $^{2}J_{PC}$ = 10.1 Hz, $^{3}J_{PC}$ = 4.7 Hz), 136.1 (1C, d, *p*-Ph, $^{4}J_{PC}$ = 4.2 Hz); $^{71}Ga\{^{1}H\}$-NMR (CD_2Cl_2, 300 K, [ppm]): δ = 250.3 (s, $\Delta\nu_{1/2}$ = 55 Hz); $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2, 300 K, [ppm]): AM_2X spin system δ = -22.2 (P, $\mathbf{P}_A$), -12.4 (2P, $\mathbf{P}_M$), 10.9 (P, $\mathbf{P}_X$; $^{1}J_{AM}$ = -142 Hz, $^{1}J_{MX}$ = -277 Hz ,$^{2}J_{AX}$ = -22.3 Hz);. elemental analysis for $C_{24}H_{37}Cl_4GaP_4$ (660.98): calcd C 43.6, H 5.7; found: C 42.9, H 5.3. Recrystallization of **[3.4(Ph$_2$)]**[GaCl$_4$] from C_6H_5F/*n*-hexane at -32 °C yielded X-ray quality crystals.

[3.4(Ph$_2$)][OTf]: To a solution of (^{t}BuP)$_3$ (264.3 mg, 1.0 mmol) in C_6H_5F (1 mL) was slowly added Ph_2PCl (18.5 µL, 1.0 mmol) and $(CH_3)_3SiOTf$ (18.1 µL, 1.0 mmol) dissolved in C_6H_5F (1 mL) at ambient temperature. After 60 min. a $^{31}P\{^{1}H\}$ NMR spectrum was recorded of the reaction mixture. The addition of *n*-hexane (5 mL) to the reaction mixture leads to the formation of a yellow microcrystalline material. The obtained solid was washed with *n*-hexane (3 x 3 mL) and dried *in vacuo* to yield analytically pure, moisture and air-sensitive **[3.4(Ph$_2$)]**[OTf]; Yield: 197.0 mg (0.3 mmol, 33%); m.p. 144 - 147 °C; Raman (200 mW, 300 K, cm^{-1}): 3061 (29), 2896 (36), 2185 (14), 2061 (17), 1584 (35), 1168 (17), 1089 (18), 1027 (18), 999 (33), 345 (100), 227 (33), 187 (19); IR (ATR, 300 K, cm^{-1}): 2950 (s), 1979 (vw), 1570 (vw), 1457 (m), 1438 (s), 1392 (w), 1364 (s), 1311 (w), 1165 (vs), 1098 (s), 997 (m), 936 (vw), 801 (m), 749 (vw), 738 (m), 687 (s), 619 (w), 593 (w), 548 (s), 501 (w), 471 (m); ^{1}H NMR (CD_2Cl_2, 300 K, [ppm]): δ = 1.30 (9H, d, $P_MC(CH_3)_3$, $^{3}J_{PH}$ = 8.4 Hz), 1.32 (9H, d, $P_MC(CH_3)_3$, $^{3}J_{PH}$ = 8.4 Hz), 1.38 (9H, d, $P_AC(CH_3)_3$, $^{3}J_{PH}$ = 14.3 Hz), 7.66 – 7.96 (10H, m, $P_X(C_6H_6)_2$); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 300 K, [ppm]): δ = 29.3 (3C, dt, $P_AC(CH_3)_3$, $^{2}J_{PH}$ = 15.5 Hz, $^{3}J_{PH}$ = 4.8 Hz) 31.1 – 31.3 (6C, m, $P_MC(CH_3)_3$), 31.5 – 32.2 (1C, m, $P_AC(CH_3)_3$), 37.3 – 37.8 (2C, m, $P_MC(CH_3)_3$), $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 300 K, [ppm]): δ = 29.3 (3C, dt, $P_XC(CH_3)_3$, $^{2}J_{PC}$ = 15.6 Hz, $^{3}J_{PC}$ = 1.2 Hz), 31.2 (6C, m, $P_MC(CH_3)_3$), 31.9 (1C, m, $P_XC(CH_3)_3$), 37.6 (2C, m, $P_MC(CH_3)_3$), 117.6 (1C, m, *i*-Ph), 124.3 (1C, m, *i*-Ph), 131.1 (1C, d, *m*-Ph, $^{3}J_{PC}$ = 1.3 Hz), 131.2 (1C, d, *m*-Ph, $^{3}J_{PC}$ = 1.5 Hz), 133.5 (1C, dt, *o*-Ph, $^{2}J_{PC}$ = 11.1 Hz, $^{3}J_{PC}$ = 7.1 Hz), 135.0 (1C, d, *p*-Ph, $^{4}J_{PC}$ = 3.5 Hz), 135.6 (1C, dt, *o*-Ph, $^{2}J_{PC}$ = 10.0 Hz, $^{3}J_{PC}$ = 4.7 Hz), 136.1 (1C, d, *p*-Ph, $^{4}J_{PC}$ = 4.0 Hz); ^{19}F NMR (CD_2Cl_2, 300 K, [ppm]): δ = -78.8 (s, CF_3); $^{31}P\{^{1}H\}$ NMR (C_6D_6, 300 K, [ppm]): AM_2X spin system δ = -23.1 (P, P_A), -13.0 (1P, P_M), 10.5 (1P, P_X); $^{1}J_{AM}$ = -141, $^{1}J_{MX}$ = -275, $^{2}J_{AX}$ = -22 Hz). Elemental analysis for $C_{25}H_{37}F_3O_3P_4S$ (598.51): calcd C 50.2, H 6.2; found: C 49.7, H 5.6. Recrystallization of **[3.4(Ph$_2$)]**[OTf] from CH_2Cl_2/*n*-hexane at -30°C yielded X-ray quality crystals.

[3.4(Cy$_2$)][GaCl$_4$]: To a solution of (^{t}BuP)$_3$ (528.8 mg, 2.0 mmol) in C_6H_5F (5 mL) was slowly added Cy_2PCl (42.6 μL, 2.0 mmol) and $GaCl_3$ (652.1 mg, 2.0 mmol) dissolved in C_6H_5F (7 mL) at ambient temperature. The reaction mixture changed from a clear colourless solution to a clear and pale yellow solution over the course of 60 minutes. After 90 min, a $^{31}P\{^{1}H\}$ NMR spectrum was recorded of the yellow coloured reaction mixture that displayed broad resonances. The addition of hexanes (5 mL) lead to the separation of orange oil that solidified after removing the supernatant and adding a hexanes (5 mL). The obtained solid was washed with *n*-hexane (3 x 5 mL) and dried *in vacuo* to yield moisture and air-sensitive [3.4(Cy$_2$)][GaCl$_4$]; 0.353g (0.64 mmol, 32%); m.p. 160 - 163°C. Crystals suitable for X-ray diffraction were grown by dissolving [3.4(Cy$_2$)][GaCl$_4$] in CH_2Cl_2 and adding an equal volume of *n*-hexane to the solution and allowing the mixture to sit overnight.

[3.4(^{t}Bu(Cl))][GaCl$_4$]: A suspension of [PCl_4][$GaCl_4$] (4.0 mmol) in CH_2Cl_2 (20 mL) was added over the course of 30 min. to (tBuP)$_4$ (1409.6 mg, 4.0 mmol) in CH_2Cl_2

(15 mL) at -78°C. The reaction mixture was then allowed to warm to room temperature. The addition of *n*-hexane (40 mL) caused the precipitation of a pale yellow microcrystalline material. The obtained solid was washed with *n*-hexane (2 x 10 mL) and dried *in vacuo* to yield analytically pure, moisture and air-sensitive **[3.4(^{t}Bu(Cl))]**[$GaCl_4$]; 1.6 g (2.7 mmol, 67%) m.p. 160 - 161°C; Raman (200 mW, 300 K, cm^{-1}): 2963 (15), 2934 (11), 2897 (58), 1462 (21), 1441 (7), 1160 (15), 938 (8), 794 (19), 562 (26), 475 (7), 438 (19), 346 (38), 204 (9), 189 (20), 169 (7), 154 (100); IR (ATR, 300 K, cm^{-1}): 2950 (s), 2860 (vw), 2341 (vw), 2361 (m), 1716 (w), 1698 (vw), 1558 (vw), 1541 (w), 1507 (w), 1463 (s), 1394 (w), 1366 (m), 1245 (w), 1155 (vs), 1007 (m), 937 (w), 791 (m); ^{1}H NMR (CD_2Cl_2, 300 K, [ppm]): δ = 1.49 (9H, d, $P_XC(CH_3)_3$, $^3J_{PH}$ = 24.0 Hz), 1.51 (9H, d, $P_AC(CH_3)_3$, $^3J_{PH}$ = 15.1 Hz), 1.52 (18H, d, $P_MC(CH_3)_3$, $^3J_{PH}$ = 17.5 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 300 K, [ppm]): δ = 23.2 (3C, td, $P_XC(CH_3)_3$, $^3J_{PC}$ = 3.2 Hz, $^2J_{PC}$ = 2.5 Hz), 28.8 (3C, dt, $P_AC(CH_3)_3$, $^2J_{PC}$ = 15.7 Hz, $^3J_{PC}$ = 5.0 Hz), 30.0 (6C, ddd, $P_MC(CH_3)_3$, $^2J_{PC}$ = 15.6 Hz, $^3J_{PC}$ = 6.4 Hz, $^3J_{PC}$ = 4.4 Hz), 32.4 (1C, ddt, $P_AC(CH_3)_3$, J_{PC} = 29.5 Hz, J_{PC} = 17.7 Hz, J_{PC} = 13.4 Hz), 40.1 – 40.7 (2C, m, $P_MC(CH_3)_3$), 45.4 – 45.8 (1C, m, $P_XC(CH_3)_3$); $^{71}Ga\{^1H\}$-NMR (CD_2Cl_2, 300 K, [ppm]): δ = 250.1 (s, $\Delta\nu_{1/2}$ = 52 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 300 K, [ppm]): AM_2X spin system δ = -42.7 (1P, P_A), -11.1 (2P, P_M), 98.5 (1P, P_X); $^1J_{AM}$ = -157, $^1J_{MX}$ = -330 ,$^2J_{AX}$ = 8); elemental analysis for $C_{16}H_{36}Cl_5GaP_4$ (599.34): calcd C 32.1, H 6.1; found: C 31.6, H 5.8. Recrystallization of **[3.4(^{t}Bu(Cl))]**[$GaCl_4$] from CH_2Cl_2/*n*-hexane at -30°C yielded X-ray quality crystals.

Experimental details that describe the synthesis and characterization for derivatives **4.1** and **4.2** have previously been detailed.[82] Experimental data were collected by Ryan Tilley.

5.1: Preparation of Me_2P-$P(C_6F_5)_2$: Me_2P-PMe_2 (0.0144mL, 0.1mmol) was added to $(C_6F_5)_2PCl$ (0.0250 mL, 0.1 mmol) in C_6H_5F (1 mL). The solution turned opaque momentarily, then clear and colourless. The solution was stirred for 30 minutes. $^{31}P\{^1H\}$ NMR (C_6H_5F, 300 K, [ppm]): AB spin system δA = -51.5, δB = -46.7, $^1J_{AB}$ = 223 Hz, J_{AF} = 20 Hz, J_{BF} = 40 Hz.

5.2: Preparation of [Me_3P-$P(CF_3)_2$][OTf]: MeOTf (0.2263 mL 2.0 mmol) was added directly to $Me_2PP(CF_3)_2$ (prepared in situ, 0.2 mmol), which immediately generated a white solid. The solid was pumped to dryness and washed with pentane (2 x 1 mL). $^{31}P\{^1H\}$ NMR (CH_3CN, 300 K, [ppm]): -12.4 (ds), 28.7 (d), $^1J_{PP}$ = 253 Hz, $^2J_{PF}$ = 73 Hz.

5.3:[Me_3P-$P(C_6F_5)_2$][OTf]: $(C_6F_5)_2PCl$ (0.0500 mL, 0.2 mmol) and PMe_3 (0.0206 mL, 0.2 mmol) were combined in CH_3CN (2 mL). Upon addition, the solution went slightly opaque, precipitating small amounts of a white powder. TMSOTf (0.0398 mL, 0.22 mmol) was then added to the above solution, which immediately dissolved the white powder and gave a clear colourless solution. This solution was stirred for 30 minutes. $^{31}P\{^1H\}$ NMR (CH_3CN, 300 K, [ppm]): -64.4 (dq), 28.4 (d), $^1J_{PP}$ = 304 Hz, J_{PF} = 30 Hz.

5.4:[Me_3P-$P(C_6F_5)_2$][$AlCl_4$]: $(C_6F_5)_2PCl$ (0.025 mL, 0.1 mmol) and $AlCl_3$ (0.0147 g, 0.11 mmol) were combined in CH_2Cl_2 (1 mL) which gave an opaque yellow solution. Upon addition of PMe_3 (0.0103 mL, 0.1 mmol), the solution turned clear and colourless. $^{31}P\{^1H\}$ NMR (CH_3CN, 300 K, [ppm]): -63.8 (dq), 26.1 (d), $^1J_{PP}$ = 314 Hz, J_{PF} = 30 Hz.

5.5: [$(PhC)_4P$-$P(CPh)_4(Me)$][OTf]: MeOTf (0.0113 mL, 0.1 mmol) was added to a solution of $(PhC)_4P$-$P(CPh)_4$ (0.0775 g, 0.1 mmol) in CH_2Cl_2 (2 mL). The reaction turned a dark red-brown colour within 5 minutes. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 300 K, [ppm]): -29.2 (d), 30.2 (d), $^1J_{PP}$ = 335 Hz.

5.6: [$(PhC)_4P$-$P(Me)_2$-$P(CPh)_4$][OTf]: Me_2PCl (0.008 mL, 0.1 mmol) was added to a CH_2Cl_2 solution (1 mL) containing TMSOTf (0.0199 mL, 0.11 mmol). This solution was then added dropwise to a stirring solution of $(PhC)_4P$-$P(CPh)_4$ (0.0775 g, 0.1 mmol) in CH_2Cl_2 (1 mL). The solution turned a dark red-brown colour within 5 minutes. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 300 K, [ppm]): A_2B spin system; δA = -33.0, δB = 13.3, $^1J_{AB}$ = -326 Hz.

5.7:[$(PhC)_4P$-$P(Ph)_2$-$P(CPh)_4$][OTf]: Ph_2PCl (0.018 mL, 0.1 mmol) was added to a solution of TMSOTf (0.0199 mL, 0.11 mmol) in CH_2Cl_2 (1 mL). This solution was then added dropwise to a stirring solution of $(PhC)_4P$-$P(CPh)_4$ (0.0775 g, 0.1 mmol) in CH_2Cl_2

(1 mL). The solution turned a dark red-brown colour within 5 minutes. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 300 K, [ppm]): A_2B spin system; δA = -28.0, δB = 38.8, $^1J_{AB}$ = -337 Hz.

5.8:[(PhC)$_4$P-P(Ph)$_2$-P(CPh)$_4$][AlCl$_4$]: Ph_2PCl (0.018 mL, 0.1 mmol) was added to a solution (1 mL, CH_2Cl_2) containing $AlCl_3$ (0.133 g, 0.1 mmol), which generated a partially soluble white solid. The suspension was then added dropwise to a stirring solution containing $(PhC)_4P$-$P(CPh)_4$ (0.0775 g, 0.1 mmol) in CH_2Cl_2 (1 mL). The solution turned a dark red colour within 5 minutes. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 300 K, [ppm]): A_2B spin system; δA = -25.0, δB = 41.7, $^1J_{AB}$ = -343 Hz.

5.9:[(PhC)$_4$P-P(Ph)$_2$-P(CPh)$_4$][GaCl$_4$]: Ph_2PCl (0.0775 g, 0.1 mmol) was added to a solution (1 mL, CH_2Cl_2) containing $GaCl_3$ (0.0133 g, 0.1 mmol). The resulting pale yellow solution was then added dropwise to a stirring solution containing $(PhC)_4P$-$P(CPh)_4$ (0.0775 g, 0.1 mmol) in dichloromethane (1mL). The solution turned a dark red colour within 5 minutes. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 300 K, [ppm]): A_2B spin system; δA = -33.0, δB = 13.3, $^1J_{AB}$ = -326 Hz.

Appendix A:

Safe and Convenient Synthesis, Purification and Disposal of Tetramethyldiphosphine

Caution: Tetramethyldiphosphine is very volatile. Moreover, it is extremely pyrophoric. Any glassware that has come in contact with this material will produce smoke when exposed to atmospheric gases. Larger amounts (any visible amount of liquid) of the material will spontaneously ignite and produce a stench upon exposure to atmospheric gases. Follow these procedures for the safe preparation, purification and disposal of this material.

Preparation: Two dominant methods to reduce tetramethyldiphosphinebisulfide to tetramethyldiphosphine exist. The first method uses elemental iron as a reducing agent, whereas a more recent method uses tri(n-butyl)phosphine. Both methods are successful in reducing tetramethyldiphosphinebisulfide, however, the latter is preferred, owing to its higher yield and ease of handling. In this case, the neat combination of tetramethyldiphosphinebisulfide and tri(n-butyl)phosphine are heated according to literature. Neither starting materials need to be dried prior to use, although doing so may result in higher yields, owing to less material lost to oxidation. Taking a two or three-neck round bottomed flask, attach a long condenser to the middle opening, separated by an adaptor that has been specially made for this. The adaptor has a male and female joint, separated by a valve and allows for the removal of the condenser without exposing the roundbottom containing tetramethyldiphosphine to air. This make it easier to bring the flask in to the glovebox. Having a long condenser ensures that a minimum amount of the volatile product is lost to evaporation. In addition to greasing the joints well, ensure that the outside of all joints are taped with Teflon tape and clamped with metal clamps. Care should be taken to ensure that not too much grease is used, as tetramethyldiphosphine is corrosive towards most greases and so an excess will drip in to the reaction mixture and reduce yield. Having a Y-joint with two valves attached to the top of the condenser allows for better control of the system pressure, which is desired in this reaction, owing to the high vapour pressure of the product. Heating over approximately one hour is usually sufficient in allowing the product to completely react. Literature describes the reaction as “vigorous”, however, all that was observed was some low frequency bubbling, which seemed to be more as a result the refluxing solvent (tri(^{n}Bu)phosphine). After the reaction is completed, allow the vessel to cool to room temperature. Remove the condenser and bring the round bottom containing the crude reaction mixture in to the glovebox.

Purification:

Transfer the mixture into one of the flasks of a two-flask high vacuum apparatus. This will act as a closed system that may be opened to vacuum. Freeze the reaction mixture on one bulb with liquid nitrogen, then once frozen, expose the rest of the system to vacuum. After it has been allowed to pump for 20-30 minutes, close all valves, including the one linked to the vacuum. Allow the frozen reaction mixture to thaw. Place the empty flask into a dewar of liquid nitrogen. This, along with some gentle heating from a hairdryer should be enough to distill the product. Initially, no material appears to collect in the bridge, however this is because the material is sufficiently volatile and it simply does not condense in the bridge. Instead, it is collected frozen in the receiving flask. Collected yields have been noted to be 60-70%. Other attempts at vacuum distillation are possible, albeit much more difficult, as tetramethaldiphosphine has the propensity to evaporate in to the schlenk line. This is problematic for several reasons (pyrophoric, corrosive towards grease, reactive).

Disposal:

Trace amounts of tetramethyldiphosphine may be neutralized by exposure to air. This should be done in a fumehood and is best accomplished by having a sealed vessel closed to atmospheric gases, until it is in a proper working space. Slowly open any valves. This may produce some smoke. After exposure to atmospheric gases, full quenching may be completed by adding some diluted bleach.

Larger amounts of this material can be neutralized by first freezing a sealed vessel containing the product in liquid nitrogen. Remove from liquid nitrogen. While frozen, the vessel can be opened to atmospheric gases, then small amounts of bleach can be added to the frozen product. Allowing the solid to thaw slowly affords a slow neutralization process that is much safer than a fast quench. Nonetheless, ensure that the flask is in a secure location with sufficient ventilation and that anybody working in that space is aware of the dangers associated with this material.

Appendix B:

Crystallographic Tables

Data for derivatives of **3.4** were collected and refined at the University of Münster in Münster, Germany.

	[3.4(Ph$_2$)][GaCl$_4$]	[3.4(Ph$_2$)][OTf]	[3.4(Cy$_2$)][GaCl$_4$]	[3.4(^{t}Bu(Cl))][GaCl$_4$]
formula	$C_{24}H_{37}Cl_4GaP_4$	$C_{25}H_{37}F_3O_3P_4S$	$C_{24}H_{49}Cl_4GaP_4$	$C_{16}H_{36}Cl_5GaP_4$
M_r [g mol^{-1}]	657.99	598.49	564.86	595.95
dimension [mm^3]	0.12x0.10x0.08	0.15x0.12x0.05	0.18x0.08x0.01	0.09x0.05x0.04
color, habit	colorless block	colorless block	yellow block	yellow irregular
crystal system	triclinic	monoclinic	triclinic	tetragonal
Space group	*P*-1	*P*2$_1$/*n*	*P*-1	*I*-4
a [Å]	9.6669(7)	12.3446(5)	10.3303(6)	12.9276(2)
b [Å]	12.0355(9)	18.2397(8)	11.1726(7)	12.9276(2)
c [Å]	14.402(1)	13.7307(6)	14.6909(9)	8.2956(2)
α [°]	81.777(1)	90	90.2910(10)	90
β [°]	71.486(1)	104.233(1)	100.4260(10)	90
γ [°]	86.940(1)	90	96.3670(10)	90
V [Å^3]	1572.5(2)	2996.7(2)	1656.74(17)	1386.38(5)
Z	2	4	2	2
T [K]	153(1)	153(2)	153(1)	153(2)
ρ_c [g cm^{-3}]	1.396	1.327	1.349	1.436
F(000)	680	1256	704	616
λ, Å	0.71073 (MoK$_\alpha$)	0.71073 (MoK$_\alpha$)	0.71073 (MoK$_\alpha$)	1.54178 (CuK$_\alpha$)
μ [mm^{-1}]	1.431	0.365	1.359	7.988
absorption correction	SADABS	SADABS	SADABS	SADABS
reflections collected	17567	30143	16950	3854
reflections unique	8428	7130	7885	1231
R_{int}	0.0201	0.0189	0.0170	0.0377
reflection obs. [F>3σ(F)]	7277	6366	6667	1209
residual density [e Å^{-3}]	0.651, -0.437	0.588, -0.432	2.521, -1.153	0.266, -0.279
parameters	307	398	307	69
GOOF	1.042	1.037	1.051	1.055
R_1 [I>3σ(I)]	0.0293	0.0336	0.0566	0.0288
wR_2 (all data)	0.0787	0.0937	0.1604	0.0727

Data for derivatives of **4.1** were collected and refined at the University of Alberta.

	4.1(Me)[OTf]$_2$	**4.1(Cy)**[OTf]$_2$	**4.1(^{t}Bu)**[OTf]$_2$	**4.1(N^{i}Pr$_2$)**[OTf]$_2$
Formula	$C_9H_{21}F_6O_6P_3S_2$	$C_{14}H_{29}F_6O_6P_3S_2$	$C_{12}H_{27}F_6O_6P_3S_2$	$C_{14}H_{32}F_6NO_6P_3S_2$
molecular weight (g/mol)	496.29	564.40	538.37	581.44
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/n$	$Pba2$	$P2_1/c$	$P2_1$
Colour, habit	colourless	colourless, blocks	colourless, needles	colourless, blocks
a /Å	13.2969 (19)	16.7757 (19)	6.581 (4)	11.9037 (6)
b /Å	11.4350 (17)	22.426 (3)	21.895 (12)	13.9854 (7)
c /Å	13.956 (2)	6.3922 (7)	16.904 (9)	24.2752 (11)
α /°	90	90	90	90
β /°	108.8691 (16)	90	91.650 (8)	104.1515 (5)
γ /°	90	90	90	90
V / Å^3	2008.0 (5)	2404.8 (5)	2435 (2)	3918.6 (3)
T /K	193	193	193	193
Z	4	4	4	6
crystal size / mm^3	0.45 x 0.37 x 0.28	0.60 x 0.57 x 0.27	0.78 x 0.31 x 0.08	0.39 x 0.36 x 0.22
μ / mm^{-1}	0.581	0.495	0.485	0.459
$2\theta_{max}$ /°	55.18	54.98	53.20	55.02
reflections collected	17498	47736	18399	35259
independent reflections	4636	5523	5045	17964
R_{int}	0.0150	0.0235	0.0779	0.0151
parameters	235	286	262	884
R_1[a] $[F_o^2 \geq 2\sigma(F_o^2)]$	0.0253	0.0234	0.0524	0.0312
wR_2[b] (all data)	0.0699	0.0619	0.1061	0.0837
GoF[c]	1.049	1.047	1.093	1.012
$\Delta\rho$ max and min /e Å^{-3}	0.417, -0.309	0.362, -0.198	0.471, -0.424	1.439, -0.414

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$

[c] GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied)

References

(1) Smith, M. B.; March, J. *Advanced Organic Chemistry*. Wiley: New York, 2001.

(2) Emsley, J. *The Elements.* Oxford University Press: Oxford, 1998.

(3) Dyker, C. A.; Burford, N.; Lumsden, M. D.; Decken, A. *J. Am. Chem. Soc.* **2006**, *128*, 9632.

(4) Carpenter, Y.; Dyker, C. A.; Burford, N.; Lumsden, M. D.; Decken, A. *J. Am. Chem. Soc.* **2008**, *130*, 15732.

(5) Housecroft, C. E.; Sharpe, A. G.; *Inorganic Chemistry*, 2nd Ed. Pearson Education, **2005**.

(6) Winchester, R. A. L.; Whitby, M.; Shaffer, M. S. P. *Angew. Chem. Int. Ed.* **2009**, *48*, 3616.

(7) Baudler, M.; Glinka, K. *Chem. Rev.* **1993**, *93*, 1623.

(8) Baudler, M.; Glinka, K. *Chem. Rev.* **1994**, *94*, 1273.

(9) Kosolapoff, G. M.; Maier, L.; *Organic Phosphorus Compounds*; Wiley-Interscience: 1972.

(10) Fritz, G.; Matern, E.; Krautscheid, H.; Ahlrichs R.; Olkowska, J. W.; Pikies, J. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1604.

(11) Kohler, H.; Michaelis, A. *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 807.

(12) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

(13) Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 3357.

(14) Smith, R. C.; Ren, T.; Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2002**, 2779.

(15) Burford, N.; Clyburne, J. A. C.; Chan, M. S. W. *Inorg. Chem.* **1997**, *36*, 3204.

(16) Baudler. M. *Angew. Chem. Int. Ed.* **1987**, *26*, 419.

(17) Baudler, M. Exner, O.; *Chem. Ber.* **1983**, *116*, 1268.

(18) Baudler, M. Duster, D.; *Naturforsch.* **1987**, *B42*, 335.

(19) Fritz, G.; Harer, J.; Stoll, K.; Vaahs, T. *Phosphorus Sulfur* **1983**, *18*, 65.

(20) Schisler, A.; Lönnecke, P.; Huniar, U.; Ahlrichs, R.; Hey-Hawkins, E. *Angew. Chem. Int. Ed.* **2001**, *40*, 4217.

(21) Kraus, F.; Korber, N. *Chem. Eur. J.* **2005**, *11*, 5945.

(22) Geier, J.; Ruegger, H.; Worle, M.; Grutzmacher, H. *Angew. Chem. Int. Ed.* **2003**, *42*, 3951.

(23) Wolf, R.; Schisler, A.; Lonnecke, P.; Jones, C.; Hey-Hawkins, E. *Eur. J. Inorg. Chem.* **2004**, 3277.

(24) Lerner, H.-W.; Bolte, M.; Karaghiosoff, K.; Wagner, M. *Organomet.* **2004**, *23*, 6073.

(25) Kopp, R. W.; Bond. A. C.; Parry, R. W. *Inorg. Chem.,* **1976**, *15*, 3042.

(26) Schultz, C. W.; Parry, R. W. *Inorg. Chem.,* **1976**, *15*, 3046.

(27) Hoffmann, H.; Grunewald, R. *Chem. Ber.*, **1961**, *94*, 186.

(28) Burford, N.; Cameron, T. S.; Ragogna, P. J.; Ocando-Mavarez, E.; Gee, M.; McDonald, R.; Wasylishen, R. E. *J. Am. Chem. Soc.*, **2001**, *123*, 7947.

(29) Conrad, E.; Burford, N.; McDonald, R.; Ferguson, R. J. *J. Am. Chem. Soc.* **2009**, *131*, 17000.

(30) Loss, S.; Widauer, C.; Grutzmacher, H. *Angew. Chem. Int. Ed.***, 1999**, *38*, 3329.

(31) Dyker, C. A.; Burford, N. *Chem. Asian J.* **2008**, *3*, 28.

(32) Makovetskii, Y. P.; Feshchenko, N. G.; Malovik, V. V.; Semenii, V. Y.; Boldeskul, I. E.; Bondar, V. A.; Chernukho, N. P. *J. Gen. Chem.* **1980**, *50*, 1967.

(33) Schomburg, D.; Bettermann, G.; Ernst, L.; Schmutzler, R. *Angew. Chem. Int. Ed.* **1985**, *24*, 975.

(34) Alder, R. W.; Ganter, C.; Harris, C. J.; Orpen, A. G. *J. Am. Chem. Soc. Chem. Commun.*, **1992**, 1170.

(35) Kilian, P.; Slawin, A. M. Z.; Woollins, J. D. *Dalton Trans.*, **2006**, 2175.

(36) Weigand, J. J.; Riegel, S. D.; Burford, N.; Decken, A. *J. Am. Chem. Soc.* **2007**, *129*, 7969.

(37) Nikitin, E. V.; Romakhin, A. S.; Zagumennov, V. A.; Babkin, Y. A. *Electrochim. Acta.* **1997**, *42*, 2217.

(38) Burford, N.; Dyker, C. A. *Angew. Chem. Int. Ed.* **2005**, *44*, 2364.

(39) Krossing, I. *Dalton Trans.* **2002**, 500.

(40) Burford, N.; Ragonga, P. J.; McDonald, R.; Ferguson, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 14404.

(41) Lynam, J. M.; Copsey, M. C.; Green, M.; Jeffery, J. C.; McGrady J. E.; Russell, C. A.; Slattery, J. M.; Swain, A. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 2778.

(42) Romanenko, V. D.; Rudzevich, V. L.; Rusanov, E. B.; Chernega, A. N.; Senio, A.; Sotiropoulos, J. M.; Pfister-Guillouzo, G.; Sanchez, M. *J. Am. Chem. Soc.* **1995**, *117*, 1383.

(43) Schmidpeter, A.; Lochschmidt, S.; Wheldrick, W. S. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 226.

(44) Ellis, B. D.; Carlesimo, M.; Macdonald, C. L. B. *Chem. Comm.*, **2003**, *15*, 1946.

(45) Schmidpeter, A.; Lochschmidt, S.; Karaghiosoff, K.; Sheldrick, W. S. *J. Chem. Soc. Chem. Comm.* **1985**, *20*, 1447.

(46) Lochschmidt, S.; Muller, G.; Huber, B.; Schmidpeter, A.; *Z. Naturforsch B* **1986**, *41*, 444.

(47) Boyall, A. J.; Dillon, K. B.; Howard, J. A. K.; Monks, P. K.; Thompson, A. L. *Dalton Trans.* **2007**, *14*, 1374.

(48) Dyker, C. A. PhD Thesis "*catena*-Phosphorus Cations", Dalhousie Univeristy, **2006**.

(49) Krossing, I.; Raabe, I. *Angew. Chem. Int. Ed.* **2001**, *40*, 4406.

(50) Weigand, J. J.; Holthausen, M.; Frohlich, R. *Angew. Chem. Int. Ed.*, **2009**, *48*, 295.

(51) Weigand, J. J.; Holthausen, M. *J. Am. Chem. Soc.* **2009**, *131*, 14210.

(52) Issleib, K.; Hoffmann, M. *Chem. Ber.* **1966**, *99*, 1320.

(53) Appel, R.; Milker, R.; *Z. Anorg. Allg. Chem.* **1975**, *417*, 161.

(54) Issleib, K.; Rockstroh, C.; Duchek, I.; Fluck, E. *Z. Anorg. Allg. Chem.* **1968**, *360*, 77.

(55) Dyker, C. A.; Burford, N.; Menard, G.; Lumsden, M. D.; Decken, A. *Inorg. Chem.* **2007**, *46*, 4277.

(56) Weigand, J. J.; Riegel, S. D.; Burford, N.; Decken, A. *J. Am Chem. Soc.* **2007**, *129*, 7969.

(57) Weigand, J. J.; Burford, N.; Davidson, R. J.; Cameron, T. S.; Seelheim, P. *J. Am. Chem. Soc.* **2009**, *131*, 17943.

(58) Riegel, S. D.; Burford, N.; Lumsden, M. D.; Decken, A. *Chem. Comm.* **2007**, *44*, 4668.

(59) Burford, N.; Dyker, C. A.; Decken, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 2364.

(60) Burford, N.; Dyker, C. A.; Lumsden, M. D.; Decken, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 6196.

(61) Daley, J. J. *J. Chem. Soc.* **1965**, 4789.

(62) Weigand, J. J.; Burford, N.; Lumsden, M. D.; Decken, A. *Angew. Chem. Int. Ed.* **2006**, *45*, 6733.

(63) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.

(64) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

(65) Weigand, J. J.; Burford, N.; Mahnke, D.; Decken, A. *Inorg. Chem.* **2007**, *46*, 7689.

(66) Yoshifuju, M.; Shima, I.; Inamoto, N. *J. Am. Chem Soc.* **1981**, *103,* 4587.

(67) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem.*, *Int. Ed. Engl.* **1982**, *21*, 63.

(68) Schmidpeter, A.; Lochschmidt, S.; Karaghiosoff, K.; Sheldrick, W. *Chem. Comm.* **1985**, *20*, 1447.

(69) Dillon, K. B.; Goeta, A. E.; Howard, J. A. K.; Monks, P. K.; Shepherd, H. J.; Thompson, A. L. *Dalton Trans.* **2008**, *9*, 1144.

(70) Pindzola, B. A.; Jin, J.; Gin, D. L. *J. Am. Chem. Soc.* **2003**, *125*, 2940.

(71) Bennett, F. W.; Emeleus, H. J.; Haszeldine, R. N. *J. Chem. Soc.* **1953**, 1565.

(72) Avens, L. R.; Cribbs, L. V.; Mills, J. L. *Inorg. Chem.* **1989**, *28*, 211.

(73) Magnelli, D. D.; Tesi, G.; Lowe, J. U.; McQuistion, W. E. *Inorg. Chem.*, **1966**, *5*, 457.

(74) Charrier, C.; Bonnard, H.; Lauzon, G.; Mathey, F. *J. Am. Chem. Soc.* **1983**, *105*, 6871.

(75) Sheldrick, W. S.; Schmidpeter, A.; Zwaschka, F; Dillon, K. B.; Platt, A. W. G.; Waddington, T. C. *J. Chem. Soc. Dalton. Trans,* **1981**, *2*, 413.

(76) Summers, J. C.; Sisler, H. H. *Inorg. Chem.* **1970**, *9*, 862.

(77) Korber, N.; Daniels, J.; von Schnering, H. *Angew. Chem. Int. Ed.* **1996**, 35, 1107.

(78) Braye, E. H.; Hubel, W.; Caplier, I. *J. Am. Chem. Soc.* **1961**, *83*, 4406.

(79) Charrier, C.; Bonnard, H.; Lauzon, G.; Mathey, F.; *J. Am. Chem. Soc.* **1983,** *105*, 6871.

(80) Mancino, G.; Ferguson, A. J.; Beeby, A.; Long, N. J.; Jones, T. S. *J. Am. Chem. Soc.* **2005**, *127*, 524.

(81) Burford, N.; Cameron, T. S.; Ragogna, P. J.; Ocando-Mavarez, E.; Gee, M.; McDonald, R.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2001**, *123*, 7947.

(82) Carpenter, Y. S.; PhD Thesis “Investigations into the Reactivity and Structure of Phosphinophosphonium Cations and Related Species”, Dalhousie University, **2010**.