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Utilizing Phosphorus(I) Methods Towards Phosphorus(III) Heterocycles and Phosphorus(I) Macromolecules

Gregory Farrar

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Utilizing Phosphorus(I) Methods Towards Phosphorus(III) Heterocycles and Phosphorus(I) Macromolecules

By
Gregory Farrar

A Dissertation
Submitted to the Faculty of Graduate Studies Through Chemistry and Biochemistry in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at the University of Windsor

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Utilizing Phosphorus(I) Methods Towards Phosphorus(III) Heterocycles and Phosphorus(I) Macromolecules

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Declaration of Co-Authorship/Previous Publication

I. Co-Authorship Declaration

Some of the material contained within this document has been previously published in peer-reviewed journals. I acknowledge my supervisor Dr. Charles L. B. Macdonald as a co-author in all work and he has made significant contributions in all aspects of my research. Jonathon Dube and Stephanie Kosnik assisted in collection of raw data for Chapters 2 and 3 respectively. Dr. Benjamin Cooper performed all of the X-ray crystallography studies and was responsible for the refinement of the structures.

II. Declaration of Previous Publication

This thesis includes one original paper that has been previously submitted for publication in a peer reviewed journal, as follows:

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Abstract

The oxidation state of an atom provides details into the number of electrons associated with it, as well as the chemistry of the atom. Phosphorus can exhibit a range of oxidation states such as; +1, +3, and +5. One of the main focuses of my research is to utilize phosphorus in the electron-rich +1 oxidation state to produce neutral P(I)-containing complexes that are analogous to polyphosphazenes. We have extended the class of P(I)-containing complexes from small molecules to the production of oligomers. Our work is novel in that we have found a general method that allows us to partially or completely substitute the nitrogen sites to form oligomers that are isoelectronic to that of the polyphosphazene and that will have different properties than the parent polymers. Our method is the first, and to date only, method that can produce such materials and the ease and generality of the approach suggests excellent developments in the near and distant future.

Over the last two decades, N-heterocyclic phosphines have been an important class of compounds that has helped shape the development of modern main group chemistry. There have been numerous synthetic attempts to generate these species but usually involve harsh reaction conditions, long reaction times, multiple byproducts, or contain RedOX active anions. Herein, we have demonstrated the clean and spontaneous approach to generate N-heterocyclic phosphines in a high yielding, one-pot fashion. We have also established that the resulting bromophosphines have shown to be useful reagents for the generation of the corresponding N-heterocyclic phosphonium salts by several common methods of anion abstraction or metathesis reactions. We have also undertaken the task of generating new phosphorus containing heterocycles using
alternative ligands that include oxygen and sulfur elements.
family: any group of persons closely related by blood, as parents, children..etc.

This thesis is dedicated to my family,

their support has made my goal achievable.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Non-descript anion</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>Abs. coef</td>
<td>absorption coefficient</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>Ar-BIAN</td>
<td>bis(arylimino)acenaphthene</td>
</tr>
<tr>
<td>BIPY</td>
<td>2,2’-bpyridine</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>CAS</td>
<td>Chemical Abstracts System</td>
</tr>
<tr>
<td>CSD</td>
<td>Cambridge Structural Database</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl, C₅H₅⁻</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift (NMR)</td>
</tr>
<tr>
<td>d</td>
<td>doublet (NMR)</td>
</tr>
<tr>
<td>DAB</td>
<td>diazabutadiene</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
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<tr>
<td>Dipp</td>
<td>2,6-diisopropylphenyl</td>
</tr>
<tr>
<td>DippDAB</td>
<td>N,N’-bis(2,6-diisopropylphenyl)butadiene</td>
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<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>Do</td>
<td>donor</td>
</tr>
<tr>
<td>dppe</td>
<td>diphenylphosphinoethane</td>
</tr>
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<td>dppm</td>
<td>diphenylphosphinomethane</td>
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<tr>
<td>E</td>
<td>element</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HRMS</td>
<td>high-resolution mass spectrometry</td>
</tr>
<tr>
<td>IMPY</td>
<td>imino-pyridine</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>iPr</td>
<td>iso-propyl</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>J&lt;sub&gt;XY&lt;/sub&gt;</td>
<td>coupling constant between nuclei x and y</td>
</tr>
<tr>
<td>L</td>
<td>ligand</td>
</tr>
<tr>
<td>Lp</td>
<td>lone pair</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>m</td>
<td>multiplet (NMR)</td>
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<td>Me</td>
<td>methyl</td>
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<tr>
<td>Mes</td>
<td>mesytil, 2,4,6-trimethylphenyl</td>
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</tr>
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<td>mmol</td>
<td>millimole</td>
</tr>
<tr>
<td>mp</td>
<td>melting point</td>
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<tr>
<td>NBO</td>
<td>natural bond order</td>
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<tr>
<td>NHC</td>
<td>N-heterocyclic carbene</td>
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<tr>
<td>NHP</td>
<td>N-heterocyclic phosphine</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>OTf</td>
<td>triflate, trifluoromethanesulfonate</td>
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<tr>
<td>PDI</td>
<td>polydispersity index</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>Pn</td>
<td>pnictogen</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>q</td>
<td>quartet (NMR)</td>
</tr>
<tr>
<td>R</td>
<td>organic substituent</td>
</tr>
<tr>
<td>RedOx</td>
<td>reduction-oxidation</td>
</tr>
<tr>
<td>RNA</td>
<td>Ribonucleic acid</td>
</tr>
<tr>
<td>ROP</td>
<td>ring-opening polymerization</td>
</tr>
<tr>
<td>s</td>
<td>singlet (NMR)</td>
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<tr>
<td>t</td>
<td>triplet (NMR)</td>
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<td>---------</td>
<td>----------------</td>
</tr>
<tr>
<td>THF</td>
<td>tetrohydrofuran</td>
</tr>
<tr>
<td>TMEDA</td>
<td>tetramethylethylenediamine</td>
</tr>
<tr>
<td>WBI</td>
<td>Wiberg bond index</td>
</tr>
<tr>
<td>X</td>
<td>halogen</td>
</tr>
<tr>
<td>xs</td>
<td>excess</td>
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Chapter 1 – Introduction

1.1 Pnictogens

In the old Chemical Abstracts System (CAS) and International Union of Pure and Applied Chemistry (IUPAC) systems, the elements of what are now known as group 15 where known as the group VA and group VB elements, respectively.\(^1\) This resulted in much confusion as to which elements an author was actually discussing within a given publication. It was not until the late 1980’s until the modern IUPAC recommended the chemical community band together and adopt a single nomenclature for the use within the periodic table. The elements from group 15 (nitrogen, phosphorus, arsenic, antimony, and bismuth) are commonly referred to as the pnictogens (Pn).\(^2\) Pnictogen is derived from the Greek work \textit{pniktos} meaning “strangled” and will be used throughout this thesis to refer to the group 15 elements. All of these elements have five valence electrons in their outermost shell, two of which are in the s subshell and the remaining three are unpaired in the p subshell. For this reason, the group 15 elements are also known as the “pentels”.\(^3\)

With the exception of nitrogen, all of the pnictogens are solids at room temperature and vary greatly in their nature. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids, and bismuth is the only metal in the group.\(^4\) Nitrogen exists in nature as a diatomic element and can be represented by a Lewis structure that contains a nitrogen-nitrogen triple bond. An immense amount of energy is required to break these bonds (942 kJ/mol) and this remains the reason why nitrogen molecules are generally inert.\(^5\) Nitrogen and phosphorus are among some of the most important elements on earth. Naturally occurring nitrogen is almost exclusively found in
the atmosphere, where it represents nearly 80% of its composition. Plant and animal life depend on nitrogen as a source of nutrients to maintain growth and development. In addition, nitrogen containing amino acids help maintain cellular mechanisms vital for living organisms.

Phosphorus could be considered equally important as nitrogen, as it is one of the main components of DNA and RNA, which is found in every living organism known to mankind. A German alchemist named Hennig Brand accidentally discovered phosphorus in the late 1660’s. During this time, it was commonly believed that anything that was gold colored actually contained gold, thus urine was a popular target for extracting this “gold.” On his quest, Brand fermented urine, distilled the product and produced a white wax-like solid that is now known as white phosphorus. Elemental phosphorus has several allotropes of which include red, black, violet, and the aforementioned white. The two main allotropes are white and red phosphorus. They contain different bonding arrangements that cause each allotrope to have unique physical and chemical properties. White phosphorus, also known as yellow phosphorus because of its color change when exposed to light, is a tetrahedral arrangement of phosphorus atoms (Figure 1.1A) with the overall formula P₄. The inherent ring strain caused due to the arrangement of atoms makes white phosphorus an incredibly instable material that is extremely pyrophoric and for this reason it must be stored under water. The name phosphorus was derived from the pyrophoric nature of P₄, when white phosphorus is exposed to air in the absence of light, a chemiluminescence glow is observed. White phosphorus has been used in munitions since World War I. Red phosphorus on the other hand, is a relatively air stable polymeric form of phosphorus that is thought to contain a repeat structure whereby one of
the phosphorus-phosphorus bonds in $P_4$ is broken and forms a new bond with a adjoining tetrahedron (Figure 1.1B). More recently, red phosphorus is thought to be a tube-like structure that contains a $P_2(P_{10})$ fragment (Figure 1.1C), though the exact chemical formula is still unknown due to its polymeric nature, but is most likely a combination of many structures.\cite{9,10} Red phosphorus can most commonly be found in safety matches.

![Figure 1.1](image)

**Figure 1.1** A. Molecular structure of white phosphorus, $P_4$. B. Initially proposed repeat unit if red phosphorus. C. More recently proposed repeat unit of red phosphorus $P_2(P_{10})$.

The pnictogens are a versatile group because they exist in a variety of oxidation states but are most commonly found in the +3 and +5 states. The goal of this thesis is to examine phosphorus in its lower oxidation states; this will range from small phosphenium complexes in the +3 state and the lesser known +1 state, as well as larger low oxidation state phosphorus macromolecules. The study of low oxidation state phosphorus
compounds needs to be explored to offer a new class of alternative materials for further development.

1.2 Lewis Structures

Gilbert Newton Lewis, an American scientist, was the first to use diagrams to represent bonding between two or more atoms within a molecule.\[11\] He used dots as a way to identify valence electrons within an atom and lines to represent bonds between two atoms. These Lewis structures (also known as Lewis dot diagrams, or electron dot diagrams) were first introduced in 1916 in an article entitled “The Atom and the Molecule” as a way of visualizing valence electrons in an atom.\[11\] Unshared electrons were found in pairs while the shared electrons formed the bonds. He found that there were particular stable configurations of 2, 8, 18 and 32 electrons for specific elements. His most famous rule, the octet rule, was used for the majority of elements whereby elements were to react in a way where they would share, lose, or gain electrons in order to achieve a full valence shell configuration of 8 electrons, hence having a full “octet”.\[12\] There are exceptions to the octet rule however; the duet rule for example was used for hydrogen, when hydrogen had obtained two electrons, it had then achieved a stable valence shell electron configuration to that of helium. Similarly, the rule of 18 electrons was used from atoms for periods 4 and 5, and from period 6, the 32 electrons rule was employed. The problem with this assumption was that Lewis never provided how or why electrons were shared amongst atoms, and this remained unanswered until quantum theory was later developed.

Lewis theory is best described as being numerology; it identifies patterns and organizes these patterns in terms of electron accounting and special rules. Lewis
structures do not provide insight about the nature of a chemical structure or bonding environment but nonetheless, they are still used as the main tool to teach these ideas.\textsuperscript{13} An example where the Lewis method falls short is for the case of O\textsubscript{2}.\textsuperscript{4} Oxygen is diatomic and based on Lewis rules, its structure would be drawn as illustrated in Figure 1.2 (I). Oxygen has six valence electrons, two of which are unpaired and therefore would form a double bond. Experimentally, we know that this is not the case; O\textsubscript{2} is paramagnetic with each oxygen atom having an unpaired electron. In addition, the measured bond length of O\textsubscript{2} supports the presence of a double bond, which when drawn as paramagnetic (II) still is not exhibited.

![Lewis depictions of O\textsubscript{2}.](image)

\textbf{Figure 1.2.} Lewis depictions of O\textsubscript{2}.

While Lewis theory is best utilized in Valence Shell Electron Pair Repulsion (VSEPR) theory to help predict the shape of molecules based on the number of bonded atoms and nonbonding electrons, it has been quantum theory that has led to the development of atomic orbitals, molecular orbital (MO) theory, and valence bond (VB) theory. These quantum mechanical techniques help to explain why chemistry works the way it does and provide key evidence about chemical reactivity and structural insight.\textsuperscript{13} MO theory best describes the chemical nature of O\textsubscript{2} as eight electrons from each oxygen atom combine to fill the molecular orbitals in Figure 1.3 illustrating the paramagnetic nature of O\textsubscript{2} and giving an overall bond order of two.\textsuperscript{4} Overall, Lewis structures are a useful tool to explain reaction mechanisms, geometries, and other basic ideas but they should be used with caution as a tool to interpret chemical properties.
1.3 Valence States, Oxidation States and our Model

Two fundamental ideas used to describe structural features, bonding, and reactivity of a given atom is that of valence states and oxidation states.\textsuperscript{[15, 16]} Commonly, these terms are used interchangeably and often lead to a misinterpretation of their definition. The valence state of an atom has several varying definitions but is most simply understood by the number of electrons that an atom uses in bonding. Oxidation states are a measure of the number of electrons affiliated with a particular atom and represent the degree of oxidation. Oxidation states are assigned by simple rules whereby simple atoms have an oxidation number that is equal to their ionic charge. For example, hydrogen is “always” +1 and fluorine is “always” -1. Thus, the valence and oxidation states of a given
atom have different meanings and may give the same answer only as a matter of coincidence. For example, nitrogen in NH\(_3\) has a valence state of +3 because it uses three electrons in bonding and an oxidation number of -3 because of simple counting rules. By comparison, the central carbon atom in CH\(_2\)Cl\(_2\) has a valence of +4 because all electrons are involved in bonding, but its oxidation state is 0 because the +2 charge from the hydrogen atoms are equaled by the -2 charges from the chlorine atoms. Using these “accepted” counting rules, the pnictogens have been found in formal oxidation states ranging from -3 to +5.\(^{17-19}\)

This conventional model of assigning formal oxidation states can be useful for balancing reduction-oxidation (RedOX) reactions but can sometimes fail to provide an accurate depiction of the bonding and reactivity within a given complex. Thus, this concept should be used more as an aid in describing fundamental concepts rather than describing chemical systems as a whole. This ambiguity can be easily illustrated for the group 15 elements.\(^{20}\) One can compare three very different chemical systems; a phosphide (Li\(_3\)P), phosphine (PH\(_3\)), and a phosphonium ion (PH\(_4^+\)). All of these examples are in the -3 oxidation state based on the conventional definition of oxidation states, even though these complexes have very different chemical properties. In addition, when comparing similar group 15 compounds there is also a discrepancy. In PnH\(_3\) for example, when Pn is nitrogen the formal oxidation state is -3 and when Pn is the heavy pnictogens (arsenic, antimony, bismuth) the oxidation state is +3, which is misleading because this series of compounds exhibit a similar chemical, electronic, and structural behavior.\(^{20}\)

In the Macdonald group we use an alternative model to identify oxidation states that is based solely on the number of non-bonding electrons that are associated with the
atom in question (Figure 1.4). This methodology corresponds more closely with the definition of valence previously discussed. This model provides a more accurate depiction of the electronic and structural features and to an extent, the chemical behavior of compounds that are of the same oxidation state. The underlying assumption of this model is that we assume that all atoms bonded to Pn are more electronegative.\[20\]

![Diagram of oxidation states](image)

**Figure 1.4.** Oxidation states of pnictogen.

Most commonly, pnictogens are found in the +3 and +5 states. Pnictogens in even oxidation states are obviously paramagnetic and are considerably rare. The remaining negative oxidation states are also very uncommon and not readily observed. In our group, we have simplified the definition of oxidation states of pnictogen compounds to the number of “lone pairs” they possess (Figure 1.5). Pnictogens in the +5 oxidation state (Pn(V)) have no lone pairs of electrons associated with the Pn center. Therefore, all valence electrons are involved in bonding for Pn(V). A Pn(III) center contains one “lone pair” with the remaining valence electrons involved in bonding. And finally, the less common +1 oxidation state (Pn(I)) is a pnictogen center containing two “lone pairs” of electrons.
Figure 1.5. Bonding environments for Pn(V), Pn(III), and Pn(I).

1.4 Low Oxidation State Phosphorus Compounds

As stated above, in our group we define phosphorus in the +1 oxidation state as having two lone pairs of electrons. As in Figure 1.6, phosphorus(I) compounds have several different structural types and can be cationic, anionic, and neutral species.

Figure 1.6. General structural drawings for phosphorus(I) containing compounds.

Phosphinidenes (R-P) are elusive six electron species that are phosphorus analogues of carbenes.\textsuperscript{[21, 22]} To date, no stable phosphinidenes have been experimentally isolated, they exist only as highly reactive intermediates, which are prone to oligomerization to give either double bonded diphosphenes or more commonly, oligocyclophosphanes.\textsuperscript{[20]} As in the case for carbenes, phosphinidenes can exist in the singlet or, more commonly, triplet electronic states. The parent compound, PH, has a triplet ground state and has an experimentally determined triplet-singlet separation of 22 kcal/mol\textsuperscript{[22]}, which is significantly higher than the methylene carbene analogue. Based on the diagonal relationship of carbon and phosphorus, it can be presumed that it is possible to stabilize phosphinidenes using $\pi$-donor substituents, which may favor the singlet
ground state. It has been shown computationally that compounds such as \((\text{alkyl}_3\text{Si})_2\text{C}=\text{N}-\text{P}\) contain a singlet ground state and are stable against dimerization, and prove to be ideal synthetic targets to produce these species.\(^{[23]}\)

Recently, there has been increased interest in the investigation of phosphorus compounds in the +1 oxidation state. The synthesis of these species has become an attractive area of research due to the fact that they often led to alternative reactivities that may potentially offer new utilities of phosphorus. In the 1980’s, Schmidpeter began working with diphosphine ligands in the attempt to produce P(I) containing compounds.\(^{[24]}\) What he found was that by adding PCl\(_3\) with a chelating phosphine in the presence of a reducing agent, the P(I) cation \([(\text{dppe})\text{P}]^+ \; (1.1)\) could be generated.\(^{[25]}\) The general term given for these types of compounds is that of a “triphosphenium.”

\[
\begin{align*}
2 \text{PCl}_3 + 2 \text{SnCl}_2 + 2 \text{dppe} & \rightarrow [(\text{dppe})\text{P}]^+ + \left[\text{SnCl}_6\right]^{2-} + \text{SnCl}_4 \\

\text{Figure 1.7.} \text{ Schmidpeter’s first triphosphenium salt.}
\end{align*}
\]

This triphosphenium was characterized in a variety of ways including X-ray crystallography (Figure 1.8) and perhaps more importantly, by \(^{31}\)P NMR. Ideally, every triphosphenium could be characterized by X-ray crystallography but this is just not the case, and thus makes \(^{31}\)P NMR such an important tool for studying these systems. In solution, both phosphorus sites in a given triphosphenium are easily identifiable and give characteristic peaks of an AX\(_2\) spin system in the \(^{31}\)P NMR spectrum. In general, triphosphenium salts give rise to a high-frequency doublet and a low frequency triplet.
For Schmidpeter’s first triphosphenium ion [(dppe)P⁺], a doublet is seen at 63.8 ppm for the two P atoms and a triplet is observed at -231.6 ppm for the central P atom. There are large P-P coupling constants of 448.9 Hz, which confirms the equivalence of two phosphorus atoms from the bis(phosphine) ligand.

![Figure 1.8](image)

**Figure 1.8.** Ball and stick representation of the molecular structure of [(dppe)P⁺] cation. Hydrogen atoms have been omitted for clarity.

The molecular structure exhibits similar P-P bond distances of 2.122(1) and 2.128(2) Å, which are intermediate in length and fall between typical P-P single (2.20-2.25 Å)[26-30] and double bond (2.00-2.04 Å)[31-35] distances. Schmidpeter et al. subsequently prepared the tetrachloroaluminate salt and found it was in close agreement to the hexachlorostannate(IV) 1.1.[36] Schmidbaur and coworkers then employed the methods developed by Schmidpeter and prepared a six-membered cyclic triphosphenium ion and its arsenic equivalent 1.2.[37]
There are three possible Lewis-type drawings that could be used for cations of the formula \((\text{R}_3\text{P})_2\text{P}^+\) (Figure 1.10). These drawings should not be over-interpreted, but such models could potentially offer insight to structural features and reactivities of a given triphosphonium complex. The drawing for the P(V) center shows a linear geometry with no “lone pairs” of electrons and to date, there are no examples of linear triphosphonium complexes in the literature. In addition to this, the typical P-P bond length found in a triphosphonium cation is less than that of a P-P double bond. From this, it can be concluded that the P(V) Lewis structure is not a reasonable depiction for these cations. Most triphosphonium salts are in fact drawn using either the P(III) or P(I) model. In the P(III) model, the phosphorus center has one “lone pair” of electrons and contains delocalized \(\pi\)-bonding between the P-P-P bonds. This delocalized bonding could account for the intermediate bond length observed for these cations. The alternative structure that is used to depict these cations is that of a P(I) center, here the phosphorus center has two “lone pairs” of electrons and the coulombic attraction between the charged phosphorus atoms could explain the shorter than normal P-P bonds that are observed. The only difference between the P(III) and P(I) models is the number of lone pairs associated with each phosphorus center. It is therefore best to understand the real electronic structure to
assess which type of Lewis depiction best represents the structural properties and reactivities of these cations.

![Figure 1.10. Possible Lewis-type structures of triphospheniums of the form (R₃P)₂P⁺.](image)

The Macdonald research group performed density functional theory (DFT) calculations on simple model phosphinium compounds to examine the frontier orbitals of a variety of diimine and diphosphane ligands to provide the necessary insight that was clearly needed for triphosphinium cations. What they found was that the two highest occupied molecular orbitals, HOMO and HOMO-1, were very similar in appearance. Macdonald found the HOMO-1 orbital was consistent with a “lone pair” orbital on the central phosphorus atom. It was concluded that the HOMO’s were almost identical to water and that the P(I) depiction best represents the electronic structure of cations of the type (R₃P)₂P⁺. The P(I) depiction may also explain the high shielding of the central phosphorus atom observed in $^{31}$P NMR. It was also revealed that the energy of the HOMOs for diphosphane ligands were significantly lower than the analogous diimine ligand, allowing for an increase of the HUMO-LUMO gap and an explanation for the stability of triphosphinium complexes. This decrease in energy and increase in stability can be explained through the phosphine ligands. The phosphine ligands act as back-bonding acceptors because they contain empty anti-bonding orbitals that are of the correct symmetry and energy to accept electron density from the p-type orbital on the P(I) center (Figure 1.11).
The main drawback of using Schmidpeter’s approach to produce triphosphenium salts is the fact that an external reducing agent is needed, which causes the formation of inconvenient tin or aluminum containing anions. Tin anions can often lead to undesired reactivity and provide a formidable challenge to remove. In addition, aluminum anions may be susceptible to degradation by nucleophiles and salts containing these anions may be air and moisture sensitive. Although anion exchange reactions can be utilized to remove the SnCl$_6^{2-}$ anion, these reactions are never 100% efficient and in turn, some of the tin anion remains and often complicates further chemistry. In an attempt to improve the synthesis of triphosphenium salts, Dillon et al. found that diphosphanes could themselves act as reducing agents and consequently an external source was not required.$^{[39]}$ They found that by adding excess diphosphane, the subsequent triphosphenium could be isolated but additional by-products were observed. Dillon successfully extended these methods from five-membered ring cyclic triphosphenium salts to six- and seven-membered systems.$^{[40]}$ These salts had more convenient anions but the additional by-products made purification difficult, if not impossible. Several years later, Dillion was able to unequivocally establish the mechanism of formation for these triphosphenium species (Scheme 1.1).$^{[41]}$
Scheme 1.1. The mechanism of formation of cyclic triphosphenium ions prepared by Dillon and coworkers.

Looking for a more facile route to producing funtionalizable triphosphenium compounds, Macdonald *et al.* discovered a convenient synthesis for stable P(I) and As(I) iodide reagents.\[42\] By adding an equimolar amount of PI$_3$ or AsI$_3$ with bis(diphenylphosphino)ethane (dppe) in CH$_2$Cl$_2$ at room temperature, the product 1.3 in Figure 1.12 was obtained after just a few hours and was then subsequently washed to remove I$_2$.

\[
Pb_2P_2PPb_2 + PI_3 \rightarrow \text{1.3} \quad Pb_2P_2PPb_2 I^- + I_2
\]

Figure 1.12. A convenient “one-pot” approach to generating cyclic triphosphenium-iodide salts.
Unlike the mechanism proposed by Dillon, an additional source of dppe ligand is not required to act as the reducing agent. In solution, PI\textsubscript{3} is in equilibrium with P\textsubscript{2}I\textsubscript{4} and I\textsubscript{2} and it was postulated by Macdonald that there is further disproportionation to oligomeric (PI)\textsubscript{n} that is providing PI fragments for the chelating dppe ligand. The solid-state structure of the iodide anion was elucidated (Figure 1.13) and the metrical parameters fell within acceptable ranges of other reported triphosphenium cations. The closest P-I contacts are 4.702 Å, which lie out of the range of a typical P-I single bond of 2.50 Å.\textsuperscript{[43]} In solution, the reaction of PI\textsubscript{3} with dppe appears to be quantitative but ensuing removal of molecular iodine causes a significant loss of yield and remains as the only drawback of this newer synthetic approach. Anion exchange studies showed that the iodide anion could easily be exchanged without any further difficulty (Figure 1.13).

![Figure 1.13](image)

**Figure 1.13.** Ball and stick representation of the solid-state structure of [dppeP\textsuperscript{+}][I\textsuperscript{−}]. Hydrogen atoms have been removed for clarity.

The Macdonald research group sought a synthetic approach that would provide triphosphenium salts from PBr\textsubscript{3} and PCl\textsubscript{3} that would result in more conveniently
They decided that cyclohexene would be a suitable halide-scavenging agent as it has been demonstrated to remove bromine in organic syntheses. From the previous studies of Dillon, it is known that Br$_2$ and Cl$_2$ both oxidize the diphosphane ligand. Macdonald found that by adding equimolar amounts of PBr$_3$ and cyclohexene to an equimolar amount of dppe in dichloromethane, that the amount of oxidized dppe was significantly reduced. Subsequent studies were performed with additional amounts of cyclohexene to see if the removal of the unwanted by-product could be achieved. It was then found that when three equivalents of cyclohexene were used, that the oxidized product was prevented and the resultant by-product, 1,2-dibromocyclohexane, could be removed in vacuo. The solid-sate structure was obtained through single crystal X-ray diffraction studies, which yielded Figure 1.14, an isostructural variant of the corresponding iodide salt in Figure 1.13. The metrical parameters are all in good agreement with similar triphosphenium salts and do not warrant any additional comments.
Macdonald also discovered that the benefits of using a halide-scavenging agent for PBr$_3$ could not be translated into the PCl$_3$ system. It was found that using cyclohexene with PCl$_3$ produced a variety of side products that proved difficult to remove and significantly lowered the isolated yield of 1.5 [(dppe)P]$^+$][Cl$^-$] (Figure 1.15). In spite of this, the cleanest and simplest method of developing cyclic triphosphenium cations is to treat PBr$_3$ with a chelating diphosphine in the presence of excess cyclohexene.

**Figure 1.14.** Ball and stick solid-state structure of [dppeP]$^+$][Br$^-$. Hydrogen atoms have been removed for clarity.
1.5 The N-Heterocyclic Carbene

Carbenes are compounds that contain a divalent carbon that is connected by two groups through covalent bonds. They are usually found as short-lived reactive species and have the general formula of RR’C with the simplest form of a carbene is that of methylene, H₂C. The carbene compound has two nonbonding electrons that can have either parallel or antiparallel spins. The antiparallel spins produce a singlet state, whereby the electrons are paired together in the same orbital. The parallel spins produce a triplet state carbene with the two electrons occupying different orbitals (Figure 1.16).[45]
Figure 1.16 A,B. The general formulation of a carbene. C. A carbene in the singlet state D. Excited singlet state carbene. E,F. Triplet state carbenes.

The favored state of the carbene depends on the substituents that are attached to the central carbon atom and the relative energies of the singlet and triplet electronic states. If both orbitals on carbon are degenerate, the electrons are filled according to Hund’s rule, thus occupying different orbitals. If this is not the case, the electrons spin pair and a singlet state is observed. Because of this, the triplet state is more favorable but experimentally it is the singlet state produces the more stable compounds. This can be explained by looking at the relative energies of both states, whereby computational calculations of the triplet-singlet splittings has provided significant insight into why the singlet state is more stable.[46] For the parent carbene H₂C, a ground state triplet, the triplet-singlet splitting is 13.7 kcal/mol.[46] This leads to the instability of H₂C and helps explain why most triplet species are just short-lived intermediates and not actually an isolatable species. In fact, the most stable triplet carbenes have a half-life of only mere minutes.[47] To increase the stability of the singlet state carbenes, electron donors can be utilized to provide increased electron density to the valence shell of the electron deficient carbon atom, which ultimately promotes the formation of a singlet state carbene over the triplet state compound. The most popular and pre-dominant of these use nitrogen groups to produce N-heterocyclic carbenes (NHCs).[48]
The first isolated “bottleable” carbene was synthesized in 1991 by Arduengo (Figure 1.17).[49] This led to the development of the p-block analogues, which are known as the “main group carbenoids”. These main group N-heterocyclic carbene analogues have been successfully synthesized for groups 13,[50-54] 14,[55-57] 15,[58-61] and 16 (Figure 1.18).[62-64]

![Figure 1.17. The Arduengo carbene.](image)

![Figure 1.18. Known N-heterocyclic carbene analogues.](image)

N-Heterocyclic carbenoids have a dicoordinate main-group center, which has a lone pair of electrons and a formal anionic (group 13), neutral (group 14), cationic (group 15), or dicationic (group 16) charge (Figure 1.18). The general mechanism for the formation of these compounds involves a two-electron intramolecular charge transfer, whereby the C-N bonds become elongated and the backbone C-C bond becomes shortened. Gudat and coworkers were the first to synthesize and study the tin version of the N-heterocyclic carbene.[57] What they found was that the tin analogue produced a chemical reactivity atypical for the carbenoid species and is best described as a dicoordinate group 14 element with the oxidation state of zero. Similarly, Ragogna et al.
completed a comprehensive computational study on the \(N\)-heterocyclic carbenes and found that the chalcogen dications, as well as the stibenum cation, all give electronic structures that are different to the other main group carbenoids.\(^{[65]}\) It was found that the C-N bonds and C-C backbone had not changed significantly from the parent free ligand and that the C-N bonds were shorter than the other \(p\)-block analogues while the C-C backbone bond was elongated. Ragogna et al. were able to experimentally confirm this when they synthesized the first selenium dicationic \(N\)-heterocyclic carbene.\(^{[63]}\) They found that the C-N bonds were shortened (1.293(7) Å) and the C-C bond was elongated (1.415(10) Å) in good agreement with the computational results. These complexes are best described as being a sequestered cation (Sb) or dication (chalcogens) stabilized by a chelating diimine ligand II (Figure 1.19) rather than the typical carbenoid I. The structure II was further supported by the topical analysis of the electron localization function, which exhibited that the selenium center carries two lone pairs of electrons instead of the anticipated one.

\[ E = \text{Al}^+, \text{Ga}^-, \text{In}^-, \text{Sn}^+, \text{Sb}^{2+}, \text{Se}^{2+}, \text{Te}^{2+} \]

**Figure 1.19.** Lewis depictions of atypical \(N\)-heterocyclic carbene analogues.

### 1.6 Phosphenium Cations

A phosphenium cation is a cation that contains a dicoordinate phosphorus center bearing a total of six valence electrons and is the isovalent analogue of a carbene.\(^{[59, 66]}\) Numerous types of phosphenium cations have been prepared and studied, but the most
important class of these cations are the relatively stable species in which the dicoordinate phosphorus center is supported by two adjacent amido substituents. These \( N \)-heterocyclic phosphonium (NHP) compounds in Figure 1.20 predate Arduengo’s carbene by nineteen years and have been an important class of compounds that have helped the development of modern main group chemistry.\[^{67, 68}\]

![Image of NHP compounds](image)

**Figure 1.20.** The first examples of the \( N \)-heterocyclic phosphonium cations.

The stability of phosphenium cations depends on charge delocalization by incorporating a phosphorus atom into a conjugated \( \pi \)-electron system. The cations can be divided into two categories that differ in charge distribution within the \( \pi \)-electron system. The first type of cation is that of a phosphenium whereby the positive charge is localized on the substituents only (Figure 1.21A). The positive charge can be localized on either substituent giving the central phosphorus atom a neutral charge, or on both substituents giving the central phosphorus a negative \( \pi \)-charge. The phosphorus center in this case is mainly nucleophilic because it contains either a neutral or anionic charge.\[^{69}\] An example of this type of cation is that of a triphosphenium.\[^{25, 42, 44}\] In the second type, the phosphorus center either bears a neutral charge with the positive charge located on the substituents or a positive \( \pi \)-charge and can thus be classified as having both nucleophilic and electrophilic character (Figure 1.21B). This is best represented as a NHP cation.\[^{70}\]
Figure 1.21. The two main types of phosphenium cations. A. Triphosphonium. B. \(N\)-heterocyclic phosphenium.

One of the main reasons that NHPs predate the first isolatable carbenes is because the enhanced stability of NHPs can be easily explained through the conjugated \(\pi\)-system that delocalizes the positive charge. This is possible because phospheniums are more stable in the singlet electronic state and thus the p-orbitals are available for \(\pi\)-donation from ligands such as diimines (Figure 1.22).[^69]

Figure 1.22. The molecular orbital illustration of the ligand stabilized singlet electronic state.

A significant amount of focus has been placed on discovering an improved synthesis in producing NHP cations that contain a variety of anionic substituents. Early investigations by Litvinov and co-workers, Denk and co-workers, and Gudat and co-workers showed that reacting \(\text{PCl}_3\) with a diimine ligand could produce these phosphenium cations, albeit with complicating features in each of their synthetic
approaches. For the case of Litvinov, they proposed the synthesis for the unsaturated analogues of the first reported NHPs discussed above in Figure 1.20. What they found was that by adding PCl$_3$ and a base, the diimine ligand undergoes a chlorine halogenation reaction and produces the unexpected product 1.7 in Scheme 1.2.[71] Denk et. al synthesized the chlorophosphane by first reducing the diimine ligand 1.8, followed by a reaction with SiCl$_4$ 1.9, and then subsequently refluxing for five days with PCl$_3$ to yield 1.10.[72] In an attempt to improve this synthesis, Denk added PCl$_3$ to the doubly reduced DAB ligand and found that reaction resulted in an insoluble orange product that is thought to be a polymer of the formula [PCl]$_n$.[72] Improving upon this procedure, Gudat et al. reported a synthesis that had fewer steps but was a more time consuming process overall. Here, the DAB ligand was added with chlorosilane to produce the sila-heterocycle 1.9 which was refluxed over seven days with PCl$_3$.[73] Overall, these mulit-step reactions produce poor yields, inconvenient by-products and long reaction conditions and are not ideal as synthetic procedures for easily producing phosphenium cations.
Scheme 1.2. Synthetic approaches for producing NHP’s from starting with a diimine ligand. (a) PCl$_3$/NEt$_3$, (b) 2Li, (c) SiCl$_4$/2LiCl, (d) HSiCl$_3$/diazabicyclooctane, (e) PCl$_3$/reflux 5-7 days, (f) Me$_3$SiOTf.

More recently, Cowley et al. were interested in exploring the possibility of trapping pnictogen(I)-chloride molecules with ligands other than diphosphines and carbenes, which are predominant ligands found in the literature. It has been known for close to thirty years that when the reducing agent stannous chloride is added to PCl$_3$ in the presence of a chelating bis(phosphine), the formation of a cyclic triphosphilenium ion results.\cite{25} Similarly, triphosphilenium salts can be synthesized from the reaction of phosphorus triiodide and bis(phosphine) ligands to produce the analogous cation with an I$_3^-$ anion.\cite{42} Cowley first attempted to trap these P-Cl fragments by employing the SnCl$_2$ methodology where they then proceeded to attempt to capture these fragments using 1,2-bis(arylimino)acenaphthene (Aryl-BIAN) ligands.\cite{74} What they found was that the
ligand underwent an intramolecular charge transfer and the phosphorus atom adopted the +3 oxidation state. This was confirmed by X-ray diffraction studies where the C-C backbone bond distance decreased considerably from 1.527 Å in the free ligand to 1.395(5) Å in the phosphениum complex and is more indicative of a C-C double bond. The C-N bonds become longer in the complex (1.385(5) Å) than in the free ligand (1.272 Å) and are more similar to that of a C-N single bond.\[75] The resulting [SnCl$_5$•THF]$^-$ anion is essentially octahedral and the closest P-Cl contacts are 3.374(5) Å and 3.328(5) Å, which are considerably longer than typical P-Cl contacts (2.2 – 2.6 Å).\[76, 77] The reason that the diimine ligand undergoes an intramolecular charge transfer and the corresponding bis(phosphine) does not, can be attributed to the low lying LUMO in the $\alpha$-diimine ligand and the aromaticity the doubly reduced ligand now contains (Figure 1.23). Cowley found that using PI$_3$ in the absence of a reducing agent, the ligand again underwent the intramolecular charge transfer and the same phosphениum cation was generated with an I$_3^-$ anion. It is postulated that the reaction initially involves the formation of a donor-acceptor complex [(aryl-BIAN)PI] and I$_2$, whereby the I$^-$ is then abstracted by I$_2$. In summation, Cowley and coworkers were able to produce phosphениum cations in a much simpler way than Litinov, Denk, and Gudat. These reactions exhibit an easy way to produce phosphениum cations in a one-step approach. The only drawback to Cowley’s synthesis is that these counteranions may limit the use of these materials for further reactions due to the increased redox activity of I$_3^-$ and SnCl$_5^-$.\[74] These methods have been extended to other $\alpha$-diimine ligand complexes and further studies have been shown that the phosphениums can undergo facile anion exchange reactions.\[78]
Figure 1.23. Cowley’s aryl-BIAN phosphonium and the molecular orbital depictions that help describe the increased stability.

In the pursuit to find a more simplistic way to produce chlorophosphanes, Gudat et al. revisited their study on these systems.\cite{177} Their goal was to avoid the previously discussed synthetic procedures, because of the limitations of the reactions (i.e. low yields, side reactions, harsh conditions, and redox activity of anions), and to produce high yielding, one pot, phosphonium complexes that could be simply prepared. They reacted a variety of diimine ligands and generated a one-pot approach to producing the chlorophosphanes 1.12 in high yields in Figure 1.24. The main drawback to this synthesis
is the fact that unwanted by-products needed to be removed. It is obvious that a clean and spontaneous approach to synthesize chlorophosphanes would be highly desirable.

Figure 1.24. Gudat’s synthetic approach to NHP’s. (a) 2 Li, 2 HNEt3Cl, -78°C; (b) PCl3, -78°C; (c) Me3SiOTf, -78°C, -ClSiMe3 or GaCl3, Y = OTf⁻ or GaCl4⁻.

NHP’s have been studied extensively in the literature [59, 79] and some recent highlights are included in Scheme 1.3 and include: reversible cycloaddition chemistry [80, 81] azide chemistry [82] hydride chemistry [83, 84] and precursors for hydride transfer reagents [84] substituent displacement reactions [85] P-X bond hydrolysis [79] the use of NHP fragments for P-P bond activation to produce highly polarized diphosphines [84, 86-88] and the use of NHPs as analogues of NHC ligands [89].
Scheme 1.3. Some examples recently reported activity for N-heterocyclic chlorophosphines and the corresponding NHP salts. Reagents: (a) LiAlH₄, -LiCl;[84] (b) NaNH₂, NH₃, -NaCl;[85] (c) H₂O, -HCl;[79] (d) (aryl)DABP-Cl, -HCl;[79] (e) NaN₃, -NaCl;[82] (f) LiPR₂, -LiCl;[86] (g) GaCl₃, Y = GaCl₄,[81] or Me₃SiOTf, -ClSiMe₃, or AgOTf, -AgCl, Y = OTf.[80]

1.7 Phosphorus Containing Polymers

Organic macromolecules are ubiquitous and play an important role in our everyday life. In spite of their utility, they exhibit deficiencies and limitations including thermal instability and chemical reactivity.[90] Polymers composed primarily of inorganic elements in the main chain may avoid some or all of these problems altogether. Inorganic polymers offer different properties that organic polymers may not possess: they can...
feature alternative reactivities, bonding interactions that are more robust for some applications (e.g. physiological), and desired physical properties.\textsuperscript{[90]} In the last decade, new approaches to several different classes of phosphorus-containing oligomers and polymers have been investigated by a number of different research groups (Figure 1.25).\textsuperscript{[91-95]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{phosphorus-containing-polymers-oligomers.png}
\caption{Some examples of phosphorus-containing polymers and oligomers.}
\end{figure}

For example, Lucht and co-workers synthesized poly($p$-phenylene phosphine) by the palladium catalyzed reaction of diiodobenzene with monoalkyl/m monoaryl phosphines.\textsuperscript{[91]} These compounds are analogous to polyanilines, which are known for their high electrical conductivity. In addition, Baumgartner \textit{et al.} has incorporated phospholes in highly conjugated polythiophene macromolecules, which have led to the development of various $\pi$-conjugated phosphole containing oligothiophenes for potential applications as chemical sensors and integration into electronic devices like organic light-emitting diodes (OLED’s).\textsuperscript{[96]} The polymerization techniques to produce phosphorus-containing polymers have primarily been focused on ring-opening polymerization as well as condensation polymerization methods. Recently, the Gates research group has been able to use the anionic addition polymerization across $P=C$ bonds
to produce the only alternating carbon-phosphorus polymer known to date (Figure 1.26).\textsuperscript{92, 97}

\textbf{Figure 1.26.} Living anionic polymerization of phosphaalkenes.

In spite of these developments, the most important non-biological phosphorus-containing polymers remain the polyphosphazenes, which have been intensely investigated and used industrially. Polyphosphazenes are used in applications including elastomers, biological instruments, batteries, and fuel-cell membranes. Although alternative approaches have been developed\textsuperscript{98-102} these materials are generally made from one of two methods; thermal ring-opening polymerization (ROP) or cationic chain-growth polymerization. The first method involves the thermal ring-opening polymerization of a cyclic chlorinated phosphazene trimer at 250°C, in which there is an ionization of a chloride atom from the phosphorus followed by an electrophilic attack to
give an alternating PNP structure (Scheme 1.4).\textsuperscript{103} Unfortunately, there are disadvantages to using the ROP approach, such as lack of control over polymer molecular weights, high degrees of polydispersity (measure of molecular weight distribution in a polymer), and less than ideal reaction conditions. It has been shown however, that using catalysts, such as AlCl\textsubscript{3} or BCl\textsubscript{3}, can increase the rate of reaction and allow for slightly lower reaction temperatures. Unfortunately, the addition of a catalyst had zero affect on the molecular weight or the polydispersity index (PDI) of the ensuing polymer. The substituents on phosphorus in poly(dichlorophosphazene) can easily be changed using chloride ion metathesis to link alkoxy, aryloxy, or amine groups to the phosphorus atoms of the phosphazene polymer.

\textbf{Scheme 1.4.} Ring-opening polymerization of the cyclic phosphazene trimer.

The post-polymerization exchange of substituents on the phosphorus atom allows the properties of the resultant polymers to be easily tuned although the possible substituents that may be introduced in this manner are typically restricted to alkoxy or amido groups (when R = alkyl, aryl the polymer is often degraded). Furthermore, Manners et. al. have successfully related polymers such as, poly(carbophosphazenes)
1.13, poly(thiophosphazenes) 1.14, and poly-(thionylphosphazenes) 1.15, in which one of the PR$_2$ fragments of the phosphazene has been formally replaced with an isolobal fragment. Again, the polymeric forms are produced by the thermal ring-opening polymerization of the corresponding cyclic phosphazene analogue however it should be noted that this approach is only applicable to monomers bearing chlorine substituents.\[104-106\]

\[ \begin{array}{c}
\text{R} \\
\text{C=N-P=N-P=N} \\
\text{R} \\
\end{array} \]

1.13

\[ \begin{array}{c}
\text{S} \\
\text{S=N-P=N-P=N} \\
\text{R} \\
\end{array} \]

1.14

\[ \begin{array}{c}
\text{O} \\
\text{S=N-P=N-P=N} \\
\text{R} \\
\end{array} \]

1.15

**Figure 1.27.** Related polymers produced by Manners and coworkers.

Alternatively, living cationic chain-growth polymerization can be utilized to produce the same target polymers in a more controllable manner. By reacting trace amounts of phosphorus pentachloride with trichloro(trimethylsilyl)-phosphoranimine (Cl$_3$P=NSiMe$_3$) over a twenty-four hour period at room temperature, poly(dichlorophosphazene) can be obtained.\[107\] By altering the ratio of PCl$_5$ to Cl$_3$P=NSiMe$_3$, polymers with controllable molecular weights and lower degrees of polydispersity (1.04 – 1.40) can be produced. Until recently, the mechanism as to the formation of poly(dichlorophosphazene) was not well understood. As illustrated in Figure 1.29, it is believed the initiation step involves the reaction of one molecule of monomer Cl$_3$P=NSiMe$_3$ (1.16) with two molecules of PCl$_5$ to produce [Cl$_3$P=N=PCl$_3$]$^+$[PCl$_6$]$^-$ (1.17). It was following proposed that the propagation step involved the reaction between the cation of the initiation step 1.17 with additional monomer, in which the reaction proceeded until all the monomer was consumed and ultimately yielded a living polymer.
$[\text{Cl}_3\text{P}=\text{N}=(\text{PCl}_2=\text{N})_n\text{PCl}_3]^+\text{[PCl}_6^-]$ 1.18 and a trimethylsilyl chloride by-product (Figure 1.28).[99]

**Initiation**

\[
\begin{align*}
\text{Cl}_3\text{P}=\text{NSiMe}_3 & \quad \xrightarrow{2\text{PCl}_3} \quad [\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]^{\oplus}[\text{PCl}_6]^{\ominus} \\
1.16 & \quad 1.17
\end{align*}
\]

**Propagation**

\[
[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3]^{\oplus}[\text{PCl}_6]^{\ominus} \xrightarrow{\text{Cl}_3\text{P}=\text{NSiMe}_3} \left[ \begin{array}{c}
\text{Cl} \\
\text{P} \\
\text{P} \\
\text{N} \\
\text{P} \\
\text{N} \\
\text{P} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{n} \\
\text{Cl} \\
\end{array} \right]^{\oplus} \quad \text{[PCl}_6]^{\ominus} \\
1.17 & \quad 1.18
\]

**Figure 1.28.** PCl$_5$-initiated cationic chain-growth polymerization.

It is possible however, that the cationic propagation site may in fact be capable of chain-growth at either chain end. It has been found by Manners that the molecular weights of polyphosphazenes prepared from Cl$_3$P=NSiMe$_3$ are usually double those predicted by the initiator:monomer ratio indicating bidirectional chain-growth.[108]

Manners also found that model reactions of the chloride salt 1.19 with a stoichiometric amount of monomer suggested only one chain end may be active.[109] In a more recent study, Manners utilized model compounds to explain these contradictory observations (Figure 1.29).[99] What they found was that these statements, although different, both hold true. Model reactions of 1.19 with N-silylphosporanimine (Ph$_3$P=NSiMe$_3$) showed that monodirectional chain-growth was favored but when the starting monomer was larger (1.21), bidirectional chain-growth was also observed. This can be explained through ion pair effects, whereby the shorter monomers have more steric hindrance at one end and less delocalization of the positive charge as compared to the larger monomers. The increased delocalization causes the binding to be weaker and allows the monomer to
undergo bidirectional chain-growth. Shorter monomers would have less delocalization and more steric hindrance at one end, thus favoring monodirectional chain-growth. In addition to this chain-growth study, it was also found that the PCl$_6^-$ counteranion is a reactive species and an active participant in the polymerization process. PCl$_6^-$ was found to react with N-silylphosphoranimine to produce undesired phosphazene oligomers. The reactivity of PCl$_6^-$ has important implications for molecular weight control and may provide an explanation for the higher polydispersities that can be seen for poly(dichlorophosphazene) synthesized by this method. It was also found that PCl$_3$ end groups are required for the reactions to proceed, as the monomer does not react with internal P-Cl bonds, resulting in essentially linear polyphosphazenes. The Manners group is currently working on end-capping the initiator to ensure monodirectional chain-growth and also using less reactive counteranions, which could potentially provide greater control of polymerization and even lower polydispersities. These more controlled synthetic approaches to polyphosphazenes are of considerable interest both industrially and academically.

**Figure 1.29.** Monodirectional versus bidirectional chain-growth polymerizations.
1.8 Dissertation Overview

In the light of the recent developments in main group phosphorus chemistry, the remainder of this dissertation will focus on recent developments of new phosphorus(III) heterocycles and phosphorus(I) containing oligomers. Such species can be synthesized using the low-oxidation state phosphorus methods previously developed in our lab.

The contents of this thesis focus on two distinct projects. Chapters 2 and 3 will focus on our development of N-heterocyclic phosphines and the progress made towards producing new phosphorus containing heterocycles with alternative ligands. Chapters 4 and 5 focus on the development of low-oxidation state phosphorus(I) oligomers and their potential use as target monomers for the development of a new class of polymeric materials. Lastly, Chapter 6 will provide a brief overview of our most significant developments and the potential they contain for future research.
1.9 References


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Chapter 2 – N-Heterocyclic Phosphines

2.1 Introduction

As previously discussed, phosphonium cations have generally been prepared from the addition of either a metathesis or chloride anion abstraction reagent to the chlorinated precursor. The groups of Litvinov, Denk, and Gudat have demonstrated that the reaction of unsaturated α-diimines with PCl₃ produces a variety of complicating reaction schemes and/or products. Litvinov found that by adding PCl₃ and base, the ligand undergoes an undesirable chlorine halogenation reaction.[1] Denk found that by first reducing the diimine ligand and subsequently adding PCl₃, an orange insoluble [PCl]ₙ polymer was formed.[2] And finally, in separate studies, both Denk and Gudat found that by refluxing the doubly reduced ligand in PCl₃ over a long period of time (5-7 days), the chlorinated phosphonium could be produced.[3] Overall, these multi-step reactions require undesirable reaction conditions and produce poor yields and inconvenient by-products. Therefore they are not ideal as viable synthetic approaches for easily producing phosphonium cations. It is surprising that convenient and high-yielding synthetic approaches to chlorinated precursors of NHP’s remained absent until relatively recently. Gudat was successfully able to produce the chlorinated precursor in a multi-step, one-pot method. The chlorinated NHP was produced in good yield but contained undesirable by-products that needed to be removed before a pure product was obtained.[4]

Building upon Schmidpeter’s early investigations into triphosphonium cations,[5, 6] our research group has recently developed methods for the generation of triphosphonium salts (I⁻, Br⁻) that contain a central P(I) synthon (Scheme 2.1).[7, 8] In addition to our work
in this field, our group and Cowley’s group have extended the methods developed to produce P(1) synthons to yield \( N \)-heterocyclic phosphonium cations as chlorostannate or triiodide salts.\(^9\) Unfortunately, these salts prove to be unfavorable for further development due to the reactive nature of the counteranions. Given their long history and potential utility, we thought it was imperative that a clean and simple approach be developed. In this light, we have extended our newest method for developing triphosphoniums to generate high-yielding \( N \)-heterocyclic bromophosphines in a one-step approach. These NHP’s have proved to be excellent precursors for the generation of phosphonium salts by either metathesis or bromide anion abstraction reactions. To date, this is the simplest way to synthesize NHP salts in good yields and provides a favorable route to generating new phosphonium reagents and ligands for further development.

Scheme 2.1. Synthetic routes to mononuclear P(I) containing salts.
2.2 Experimental

General Procedures

All manipulations were carried out using standard inert atmosphere techniques. Phosphorus(III) chloride was purchased from Strem Chemicals Inc., and all other chemicals and reagents were purchased from Aldrich. Phosphorus(III) was distilled before use, and all other reagents were used without further purification. All solvents were dried using a series of Grubbs’-type columns and were degassed prior to use. CD$_2$Cl$_2$, and CDCl$_3$ were dried over calcium hydride. The compounds 1,4-bis(t-butyl)-1,4-diazabutadiene ($^{t}$BuDAB),$^{[10]}$ 1,4-Bis(2,4,6-trimethylphenyl)-1,4-diazabutadiene ($^{\text{Mes}}$DAB-H),$^{[11]}$ 1,4-bis(2,4,6-trimethylphenyl)-2,3-dimethyl-1,4-diazabutadiene ($^{\text{Mes}}$DAB-CH$_3$),$^{[12]}$ 1,4-Bis(2,6-diisopropylphenyl)-1,4-diazabutadiene ($^{\text{Dipp}}$DAB-H),$^{[13]}$ 1,4-bis(2,6-diisopropylphenyl)-2,3-dimethyl-1,4-diazabutadiene ($^{\text{Dipp}}$DAB-CH$_3$),$^{[12]}$ 1,2-bis(2,4,6-trimethylphenylimino)-acenaphthene ($^{\text{Mes}}$BIAN),$^{[12]}$ and 1,2-bis(2,6-diisopropylphenylimino)-acenaphthene ($^{\text{Dipp}}$BIAN)$^{[12]}$ were synthesized according to literature procedures.

NMR spectra were recorded at room temperature in CDCl$_3$ solutions on a Bruker Advance 300-MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards (SiMe$_4$ for $^1$H and $^{13}$C, and 85% H$_3$PO$_4$ for $^{31}$P). Coupling constant magnitudes, |J|, are given in Hz. The high-resolution mass spectra (HRMS) were obtained using electro-spray ionization of acetonitrile solutions of species either by The McMaster Regional Centre for Mass Spectrometry, Hamilton, Canada or in house; calculated and reported mass:charge ratios are reported for the most intense signal of the isotopic pattern. Elemental analysis was performed by Atlantic Microlabs, Norcross, Georgia, USA.
Specific Procedures

General Synthetic Route to Diaminobromophosphines

A solution of the given \( \alpha \)-diimine (0.74 mmol) in \( \text{CH}_2\text{Cl}_2 \) (ca. 20 mL) was added to a solution of \( \text{PBr}_3 \) (0.74 mmol) and cyclohexene (2.22 mmol) in \( \text{CH}_2\text{Cl}_2 \) (ca. 20 mL). Upon addition, each solution undergoes a color change specific to the diimine employed and the resulting reaction mixture was stirred for 36 hours. The volatile components were removed under reduced pressure to afford very dark colored foam-like solids, which were covered with pentane and sonicated for 1 h. The remaining solids were filtered and washed with pentane and then any remaining volatile components were removed in under reduced pressure to afford solid powders of the diaminobromophosphines. The reactions are almost quantitative as assessed by \(^{31}\text{P}\) NMR but the purification procedure reduces the isolated yield; the specific observations and characterization data for the materials are detailed below.

Synthesis of \(^{\text{Mes}}\text{DAB}\)-H\( \text{P} \)-Br, (2.1)

Reagents: \( \text{PBr}_3 \) (1.490 mg, 5.50 mmol); cyclohexene (1.357 g, 16.50 mmol); \(^{\text{Mes}}\text{DAB}\)-H (1.610 g, 5.50 mmol). Reaction mixture color changes: initially bright red and gradually became dark green. Product: light green solid powder. 72% (2.050 g, 5.06 mmol). \(^{31}\text{P}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2\): } \delta 174.9; \(^1\text{H} \text{NMR (CD}_2\text{Cl}_2\): } \delta 7.02 \text{ (s, 4 H, m-}\text{H}_{\text{Mes}}\text{), 6.70 \text{ (s, 2H, H-DAB), 2.37 \text{ (s, 12H, o-CH}_3\text{), 2.28 \text{ (s, 6H, p-CH}_3\text{); } ^{13}\text{C}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2\): } \delta 139.1 \text{ (N-C), 135.9 \text{ (i-C}_{\text{Mes}}\text{), 133.4 \text{ (o-C}_{\text{Mes}}\text{), 130.3 \text{ (m-C}_{\text{Mes}}\text{), 123.7 \text{ (p-C}_{\text{mes}}\text{), 21.0 \text{ (o-CH}_3\text{), 19.3 \text{ (p-CH}_3\text{).}}


Synthesis of ($^{\text{Mes}}$DAB-CH$_3$)P-Br, (2.2)

Reagents: PBr$_3$ (200 mg, 0.74 mmol); cyclohexene (180 mg, 2.22 mmol); $^{\text{Mes}}$DAB-CH$_3$ (236 mg, 0.74 mmol). Reaction mixture color changes: initially bright red and gradually became dark green. Product: brown solid powder characterized as 5-¾CH$_2$Cl$_2$. 72% (310 mg, 0.53 mmol). $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ 188.8; $^1$H NMR (CDCl$_3$): $\delta$ 7.03 (s, 4H, $m$-H$_{\text{Mes}}$), 2.27 (s, 6H, CH$_3$), 2.11 (s, 12H, $o$-CH$_3$), 2.06 (s, 6H, $p$-CH$_3$); $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 142.4 (N-C), 141.0 ($i$-C$_{\text{Mes}}$), 136.2 ($o$-C$_{\text{Mes}}$), 131.1 ($m$-C$_{\text{Mes}}$), 129.7 ($p$-C$_{\text{Mes}}$), 21.1 (CH$_3$) 19.2 ($o$-CH$_3$), 12.8 ($p$-CH$_3$). HRMS: Calcd for C$_{22}$H$_{28}$N$_2$P$^+$ 351.1990, found 351.2005 (+4.2 ppm). Elemental Anal.: Calcd for C$_{22}$H$_{28}$N$_2$PBr·¾CH$_2$Cl$_2$: C, 55.19; H, 6.01; N, 5.66. Found: C, 55.08; H, 6.63; N, 5.51%.

Synthesis of ($^{\text{Dipp}}$DAB-H)P-Br, (2.3)

Reagents: PBr$_3$ (1.330 g, 4.91 mmol); cyclohexene (1.211 g, 14.7 mmol); $^{\text{Dipp}}$DAB-H (1.850 g, 4.91 mmol). Reaction mixture color changes: initially bright red and gradually became green. Product: light yellow solid powder. 69% (1.662 g, 3.38 mmol). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 168.6; $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.44 (t, 2H, $^3$J$_{HH}$ = 7.5, $p$-C$_{\text{dipp}}$), 7.32 (d, 4H, $^3$J$_{HH}$ = 7.5, $m$-C$_{\text{dipp}}$), 6.22 (s, 2H, H-DAB), 3.34 (m, 4H, $^i$Pr-H), 1.34 (d, 12H, $^i$Pr-CH$_3$), 1.21 (d, 12H, $^i$Pr-CH$_3$); $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 147.6 (N-C), 133.2 ($ipso$-C$_{\text{dipp}}$), 129.9 ($o$-C$_{\text{dipp}}$), 125.0 ($m$-C$_{\text{dipp}}$), 124.0 ($p$-C$_{\text{dipp}}$), 29.3 ($^i$Pr-CH), 25.5 ($^i$Pr-CH$_3$), 24.7 ($^i$Pr-CH$_3$).

Synthesis of ($^{\text{Dipp}}$DAB-CH$_3$)P-Br, (2.4)

Reagents: PBr$_3$ (200 mg, 0.74 mmol); cyclohexene (180 mg, 2.22 mmol); $^{\text{Dipp}}$DAB-CH$_3$ (300 mg, 0.74 mmol). Reaction mixture color changes: initially bright red
and gradually became dark purple. Product: light green solid powder characterized as 
\(6\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2\). 69% (356 mg, 0.51 mmol). \(^{31}\text{P}\{^1\text{H}\}\text{ NMR (CDCl}_3\): } \delta 191.7; \(^1\text{H}\text{ NMR (CDCl}_3\): } \delta 7.42 (t, 2H, \(J_{\text{HH}} = 7.8\), \(p\text{-C}_{\text{dipp}}\)), 7.25 (d, 4H, \(J_{\text{HH}} = 7.8\), \(m\text{-C}_{\text{dipp}}\)), 2.66 (m, 4H, \(i\text{-Pr}_2\)), 2.13 (s, 6H, \(\text{CH}_3\)), 1.15 (m, 24H, \(i\text{-Pr}_2\)), \(^{13}\text{C}\{^1\text{H}\}\text{ NMR (CDCl}_3\): } \delta 146.8 (N-C), 131.1 (o-C_{\text{dipp}}), 125.1 (m-C_{\text{dipp}}), 124.2 (p-C_{\text{dipp}}), 29.2 (Pr-CH), 28.8 (Pr-CH), 26.1 (Pr-CH), 24.0 (CH3), 23.7 (Pr-CH). HRMS: Calcd for \(\text{C}_{28}\text{H}_{40}\text{N}_2\text{P}^+ 435.2929\), found 435.2928 (+0.3 ppm). Elemental Anal.: Calcd for \(\text{C}_{28}\text{H}_{40}\text{N}_2\text{PBr}\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2\): C, 61.35; H, 7.41; N, 5.02. Found: C, 61.67; H, 7.69; N, 5.02%.

\((\text{MesBIAN})\text{P-Br}, (2.5)\)

Reagents: PBr\(_3\) (200 mg, 0.74 mmol); cyclohexene (180 mg, 2.22 mmol); MesBIAN (207 mg, 0.74 mmol). Reaction mixture color changes: gradually darkens from orange to dark red. Product: purple solid powder characterized as \(7\cdot1.5\text{CH}_2\text{Cl}_2\). 65% (334 mg, 0.481 mmol). \(^{31}\text{P}\{^1\text{H}\}\text{ NMR (CDCl}_3\): } \delta 202.0; \(^1\text{H}\text{ NMR (CDCl}_3\): } \delta 7.67 (d, 2H, \(J_{\text{HH}} = 8.4\)), 7.33 (t, 2H, \(J_{\text{HH}} = 8.1\)), 7.09 (s, 4H), 6.82 (d, 2H, \(J_{\text{HH}} = 6.9\)), 2.52 (s, 12H, o-CH\(_3\)), 2.41 (s, 6H, p-CH\(_3\)); \(^{13}\text{C}\{^1\text{H}\}\text{ NMR (CDCl}_3\): } \delta 139.6 (N-C), 136.5, 130.7, 130.4, 128.1, 127.9, 127.2, 120.9, 119.9, 21.6 (p-CH\(_3\)), 19.8 (o-CH\(_3\)). HRMS: Calcd for \(\text{C}_{30}\text{H}_{28}\text{N}_2\text{P}^+ 447.1990\), found 447.2003 (+2.9 ppm). Elemental Anal.: Calcd for \(\text{C}_{30}\text{H}_{28}\text{N}_2\text{PBr}\cdot1.5\text{CH}_2\text{Cl}_2\): C, 57.78; H, 4.77; N, 4.28. Found: C, 57.84; H, 5.15; N, 4.06%.

Crystals of 7 suitable for analysis by single-crystal X-ray diffraction experiments were obtained by the slow evaporation of a solution of the compound in acetonitrile.
(DippBIAN)P-Br, (2.6)

Reagents: PBr$_3$ (200 mg, 0.74 mmol); cyclohexene (180 mg, 2.22 mmol); DippBIAN (373 mg, 0.74 mmol). Reaction mixture color changes: gradually changes from orange to dark red. Product: light brown solid 8·½CH$_2$Cl$_2$. 83% (375 mg, 0.62 mmol).

$^{31}$P{$_1^1$H} NMR (CDCl$_3$): $\delta$ 202.1; $^1$H NMR (CDCl$_3$): $\delta$ 7.88 (d, 2H, $^3$J$_{HH} = 6.0$), 7.56 (m, 2H), 7.3-7.1 (m, 6H), 6.64 (d, 2H, $^3$J$_{HH} = 6.3$), 3.03 (m, 4H), 1.24 (d, 12H, $^3$J$_{HH} = 6.3$), 0.97 (d, 12H, $^3$J$_{HH} = 6.7$); $^{13}$C NMR (CDCl$_3$): $\delta$ 161.0, 147.9, 135.6, 129.0, 128.0, 127.3, 125.1, 123.5, 120.8, 29.0, 28.7, 25.6, 25.0, 23.4, 23.2. HRMS: Calcd for C$_{36}$H$_{40}$N$_2$P$^+$ 531.2929, found 531.2946 (+3.2 ppm). Elemental Anal.: Calcd for C$_{28}$H$_{40}$N$_2$PBr·½CH$_2$Cl$_2$: C, 61.35; H, 7.41; N, 5.02. Found: C, 61.67; H, 7.69; N, 5.02%.

Synthesis of (t-BuDAB-H)P-Br, (2.7)

A solution of PBr$_3$ (5.94 mmol) and cyclohexene (17.83 mmol) in CH$_2$Cl$_2$ (ca. 10 mL) was added to a -78 °C solution of t-BuDAB-H (5.94 mmol) in CH$_2$Cl$_2$ (ca. 40 mL). Upon addition, the solution changed from colourless to orange and the resulting reaction mixture was stirred for 24 hours. The volatile components were removed under reduced pressure to afford an orange foam-like solid, which was covered with pentane and sonicated for 1 h. The remaining solid was filtered and washed with pentane and then any remaining volatile components were removed in under reduced pressure to afford a solid orange powder. The reaction is almost quantitative as assessed by $^{31}$P NMR but the purification procedure reduces the isolated yield. (t-BuDAB)P-Br. 85.3% (1.450 g, 5.07 mmol). $^{31}$P{$_1^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 185.8; $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.29 (s, 1H, H-DAB),
1.73 (d, 9H, CH₃); ¹³C{¹H} NMR (CD₂Cl₂): δ 124.3 (s, N-C), δ 59.1 (d, C(CH₃)₃), δ 29.8 (d, CH₃).

**Synthesis of [(⁺⁻BuDAB-H)P][OTf], 2.8[OTf]**

Trimethylsilyltrifluoromethanesulfonate (TMS-OTf) (0.42 ml, 0.50 mmol, 1.228 g/mL) was added by syringe to a flask containing a solution of [(⁺⁻BuDAB-H)P][Br] (650 mg, 2.33 mmol) in CH₂Cl₂ (40 mL). The reaction mixture was stirred overnight. The volatile components were removed under reduced pressure to give a crude product, which was sonicated for 1 h in pentane. The remaining solid was filtered and washed with pentane and then any remaining volatile components were removed in under reduced pressure to afford a solid off-white powder [(⁺⁻BuDAB)P][OTf]. 88.8% (720 mg, 2.07 mmol). ³¹P{¹H} NMR (CD₂Cl₂): δ 202.7; ¹H NMR (CD₂Cl₂): δ 8.26 (s, 1H, H-DAB), 1.82 (d, 9H, CH₃); ¹³C{¹H} NMR (CD₂Cl₂): δ 132.8 (s, N-C), δ 62.8 (d, C(CH₃)₃), δ 31.1 (d, CH₃).

**Synthesis of [(MesDAB-CH₃)P][SnCl₅], 2.9[SnCl₅]**

A solution of PCl₃ (100 mg, 0.74 mmol) and MesDAB-CH₃ (237 mg, 0.74 mmol) in dichloromethane (40 mL) was added to a flask containing SnCl₂ (139 mg, 0.74 mmol). Upon addition the solution turns from green to dark red. The resulting reaction mixture was stirred overnight before the volatiles were removed under reduced pressure to produce the dark red solid [(MesDAB)P][SnCl₅]. Crude yield: 78% (375 mg, 0.58 mmol). Elemental Anal.: Calcd for C₂₂H₂₈N₂PSnCl₅: C, 40.81; H, 4.36; N, 4.33. Found: C, 41.60; H, 4.57; N, 4.21%. ³¹P{¹H} NMR (CDCl₃): δ 199.9, 198.1 (please see Results and Discussion); HRMS: Calcd for C₂₂H₂₈N₂P⁺ 351.1990, found 351.1989 (-0.3 ppm), calcd
for SnCl$_3^-$ 224.8088, found 224.7971 (-52.0 ppm), calcd for SnCl$_5^-$ 294.7465, found 294.7616 (+51.2 ppm).

**Synthesis of [($^{^{\text{Mes}}}$DAB-CH$_3$)P][I$_3$], 2.9[I$_3$]**

To a flask containing PI$_3$ (200 mg, 0.485 mmol) was added a solution of $^{^{\text{Mes}}}$DAB-CH$_3$ (155 mg, 0.485 mmol) in dichloromethane (40 mL). Upon addition the solution turns from red to dark red. The resulting reaction mixture was stirred overnight before the volatiles were removed under reduced pressure to produce the dark red solid [($^{^{\text{Mes}}}$DAB-CH$_3$)P][I$_3$]. Recrystallization by slow evaporation in acetonitrile yielded red crystals suitable for analysis by single-crystal X-ray diffraction. Crude yield: 76.0% (270 mg, 0.369 mmol). $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ 201.78; $^1$H NMR (CDCl$_3$): $\delta$ 7.18 (s, 4 H, $m$-H$_{\text{mes}}$), 2.43 (s, 6H, CH$_3$), 2.31 (s, 6H, $p$-CH$_3$), 2.18 (s, 12H, $o$-CH$_3$); $^{13}$C NMR (CDCl$_3$): $\delta$ 142.80 (s, N-C), 141.99 (s, $i$-C$_{\text{mes}}$), 134.33 (s, $o$-C$_{\text{mes}}$), 130.81 (s, $m$-C$_{\text{mes}}$), 129.40 (s, $p$-C$_{\text{mes}}$), 21.49 (s, CH$_3$), 18.71 (s, $o$-CH$_3$), 13.62 (s, $p$-CH$_3$). HRMS: Calcd for C$_{22}$H$_{28}$N$_2$P$^+$ 351.1990, found 351.1973 (-4.9 ppm), calcd for I$_3^-$ 380.7134, found 380.7133 (-0.3 ppm). Elemental Anal.: Calcd for C$_{22}$H$_{28}$N$_2$PI$_3$: C, 36.09; H, 3.85; N, 3.83. Found: C, 38.32; H, 4.12; N, 3.91%.

**Synthesis of [($^{^{\text{Mes}}}$DAB-CH$_3$)P][PF$_6$], 2.9[PF$_6$]**

To a flask containing KPF$_6$ (115 mg, 0.50 mmol) was added a solution of [($^{^{\text{Mes}}}$DABP-CH$_3$)P][Br ](215 mg, 0.50 mmol) in CH$_3$CN (40 mL). The reaction mixture was stirred overnight before the resulting KBr was removed by filtration. The volatile components were removed from the filtrate under reduced pressure to give a crude product, which was washed in pentane and sonicated for 1h. The product was extracted
with acetonitrile and removal of the volatile components provided the dark red solid 
\([\text{MesDAB}]\text{P}[\text{PF}_6] \). 84.7\% (210 mg, 0.423 mmol). $^{31}\text{P}\{\text{^1H}\}$ NMR (CDCl$_3$): $\delta$ -143.9 (sept, $^1\text{J}_{\text{P-F}}$=712), 199.8; $^1\text{H}$ NMR (CDCl$_3$): $\delta$ 7.14 (s, 4H, $m$-H$_{\text{mes}}$), 2.40 (s, 6H, CH$_3$), 2.24 (s, 6H, $p$-CH$_3$), 2.11 (s, 12H, $o$-CH$_3$); $^{13}\text{C}$ NMR (CDCl$_3$): $\delta$ 144.93 (s, N-C), 142.14 (s, $i$-C$_{\text{mes}}$), 134.96 (s, $o$-C$_{\text{mes}}$), 130.84 (s, $m$-C$_{\text{mes}}$), 129.78 (s, $p$-C$_{\text{mes}}$), 21.64 (s, CH$_3$), 18.10 (s, $o$-CH$_3$), 13.01 (s, $p$-CH$_3$); $^{19}\text{F}\{\text{^1H}\}$ NMR (CDCl$_3$): $\delta$ -72.26 (d, $^3\text{J}_{\text{F-F}}$=712). HRMS: Calcd for C$_{22}$H$_{28}$N$_2$P$_+^+$ 351.1990, found 351.1984 (-1.7 ppm), calcd for PF$_6^-$ 144.9642, found 144.9780 (+95 ppm).

**Synthesis of \([\text{MesDAB-CH$_3$}]\text{P}[\text{B(C$_6$F$_5$)$_4$}]\), 2.9[B(C$_6$F$_5$)$_4$]**

To a flask containing LiB(C$_6$F$_5$)$_4$·OEt$_2$ (380 mg, 0.50 mmol), was added a solution of \([\text{MesDAB-CH$_3$}]\text{P}[\text{Br}]\) (215 mg, 0.50 mmol) in CH$_3$CN (40 mL). The reaction mixture was stirred overnight before filtration to remove LiBr. The filtrate was concentrated under reduced pressure to give a crude product, which was washed in pentane and sonicated for 1h. Any remaining volatile components were removed under reduced pressure to afford the light brown solid \([\text{MesDAB}]\text{P}[\text{B(C$_6$F$_5$)$_4$}]\). 92.4\% (476 mg, 0.463 mmol). $^{31}\text{P}\{\text{^1H}\}$ NMR (CDCl$_3$): $\delta$ 200.8; $^1\text{H}$ NMR (CDCl$_3$): $\delta$ 7.18 (s, 4H, $m$-H$_{\text{mes}}$), 2.42 (s, 6H, CH$_3$), 2.18 (s, 6H, $p$-CH$_3$), 2.06 (s, 12H, $o$-CH$_3$); $^{13}\text{C}$ NMR (CDCl$_3$): $\delta$ 148.2 (d(m), $^JC_{\text{C-F}}$: 234, C$_6$F$_5$ $m$-C) 143.4 (N-C), 142.6 ($i$-C$_{\text{mes}}$), 133.7 ($o$-C$_{\text{mes}}$), 130.7 ($m$-C$_{\text{mes}}$), 21.1 (CH$_3$), 17.3 ($o$-CH$_3$), 12.2 ($p$-CH$_3$); $^{11}\text{B}\{\text{^1H}\}$ NMR (CDCl$_3$): $\delta$ -12.27; $^{19}\text{F}\{\text{^1H}\}$ NMR (CDCl$_3$): $\delta$ -166.22 (t, 8F, $^3\text{J}_{\text{F-F}}$=17.8, $m$-F), -162.42 (t, 4F, $^3\text{J}_{\text{F-F}}$=20.9, $o$-F), -132 (d, 8F, $^3\text{J}_{\text{F-F}}$=24.0, $o$-F). HRMS: Calcd for C$_{22}$H$_{28}$N$_2$P$_+^+$ 351.1990, found 351.1987 (-0.9 ppm), calcd for BC$_{24}$F$_{20}^-$ 679.0358, found 678.9781 (-1.1 ppm).
Synthesis of [(MesDAB-CH₃)P][OTf], 2.9[OTf]

To a flask containing trimethylsilyltrifluoromethanesulfonate (TMS-OTf) (111 mg, 0.50 mmol) was added a solution of [(MesDAB-CH₃)P][Br] (215 mg, 0.50 mmol) in CH₂Cl₂ (40 mL). The reaction mixture was stirred overnight. The volatile components were removed under reduced pressure to give a crude product, which was washed by in pentane and sonicated for 1h. The product was extracted with acetonitrile and removal of the volatile components provided the dark brown solid [(MesDAB)P][OTf]. 89.6% (224 mg, 0.448 mmol). ³¹P{¹H} NMR (CDCl₃): δ 199.6; ¹H NMR (CDCl₃): δ 7.14 (s, 4H, m-Hmes), 2.40 (s, 6H, CH₃), 2.28 (s, 12H, o-CH₃), 2.12 (s, 6H, p-CH₃); ¹³C NMR (CDCl₃): δ 144.90 (s, N-C), 142.15 (s, i-Cmes), 134.89 (s, o-Cmes), 130.84 (s, m-Cmes), 129.78 (s, p-Cmes), 21.62 (s, CH₃), 18.17 (s, o-CH₃), 13.23 (s, p-CH₃); ¹⁹F{¹H} NMR (CDCl₃): δ -78.62. HRMS: Calcd for C₂₂H₂₈N₂P⁺ 351.1990, 351.1996 found (+1.7 ppm), calcd for SO₂CF₃, 148.9520, found 148.9662 (+96 ppm).

Synthesis of [(MesDAB-CH₃)P][AlBr₄], 2.9[AlBr₄]

To a flask containing AlBr₃ (95 mg, 0.357 mmol), was added a solution of [(MesDAB-CH₃)P][Br] (153.5 mg, 0.357 mmol) in toluene (40 mL). The volatile components were removed from the filtrate under reduced pressure to give a crude product, which was washed in pentane and sonicated for 1h. The product was extracted with acetonitrile and removal of the volatile components provided the dark purple solid [(MesDAB)P][AlBr₄]. Crude yield: 72.4% (180 mg, 0.258 mmol). ³¹P{¹H} NMR (CDCl₃): δ 197.89; ¹H NMR (CDCl₃): δ 7.16 (s, 4H, m-Hmes), 2.41 (s, 6H, CH₃), 2.28 (s, 6H, p-CH₃), 2.12 (s, 12H, o-CH₃); ¹³C NMR (CDCl₃): δ 143.8 (N-C), 142.0 (i-Cmes), 134.2 (s, o-Cmes), 130.6 (s, m-Cmes), 129.1 (s, p-Cmes), 21.2 (s, CH₃), 18.1 (s, o-CH₃), 13.3 (s,
$^{27}$Al{\textsuperscript{1}H} NMR (CDCl$_3$): $\delta$ 80.4. HRMS: Calcd for C$_{22}$H$_{28}$N$_2$P$^+$ 351.1990, found 351.2005 (+$4.2$ ppm), calcd for AlBr$_4$ 342.6549, found 342.6568 (+$5.5$ ppm).

**Synthesis of [(MesDAB-H)P][OTf], 2.10[OTf]**

To a flask containing trimethylsilyl trifluoromethanesulfonate (TMS-OTf) (529 mg, 2.38 mmol) was added a solution of [(MesDAB-H)P][Br] (960 mg, 2.38 mmol) in CH$_2$Cl$_2$ (40 mL) at -30°C. The reaction mixture was stirred overnight. The volatile components were removed under reduced pressure to give a crude product, which was washed by in pentane and sonicated for 1h, whereby the solid was then collected by filtration. The subsequent solid was washed with pentane and then any remaining volatile components were removed in under reduced pressure to afford the green powder [(MesDAB-H)P][OTf], 93.4% (1.050 g, 2.22 mmol). $^{31}$P{\textsuperscript{1}H} NMR (CD$_2$Cl$_2$): $\delta$ 205.4; $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 8.17 (s, 2H, H-DAB), 7.16 (s, 4 H, m-H$_{\text{Mes}}$), 2.40 (s, 12H, o-CH$_3$), 2.20 (s, 6H, p-CH$_3$); $^{13}$C{\textsuperscript{1}H} NMR (CD$_2$Cl$_2$): $\delta$ 142.2 (N-C), 138.6 (i-C$_{\text{Mes}}$), 134.2 (o-C$_{\text{Mes}}$), 131.6 (m-C$_{\text{Mes}}$), 130.6 (p-C$_{\text{mes}}$), 21.3 (o-CH$_3$), 17.7 (p-CH$_3$).

**Synthesis of [(DippDAB-H)P][OTf], 2.11[OTf]**

To a flask containing trimethylsilyl trifluoromethanesulfonate (TMS-OTf) (369 mg, 1.66 mmol) was added a solution of [(DippDAB-H)P][Br] (810 mg, 1.66 mmol) in CH$_2$Cl$_2$ (40 mL) at -30°C. The reaction mixture was stirred overnight. The volatile components were removed under reduced pressure to give a crude product, which was washed by in pentane and sonicated for 1h, whereby the solid was then collected by filtration. The subsequent solid was washed with pentane and then any remaining volatile
components were removed in under reduced pressure to afford the light yellow powder [(Mes-DAB-H)P][OTf]. 91.9% (850 mg, 1.53 mmol). $^{31}$P{$^{1}$H} NMR (CD$_2$Cl$_2$): δ 205.8; $^{1}$H NMR (CD$_2$Cl$_2$): δ 8.39 (s, 2H, H-DAB), 7.65 (t, 2H, $^3$J$_{HH}$ = 7.8, p-C$_{dipp}$), 7.45 (d, 4H, $^3$J$_{HH}$ = 7.8, m-C$_{dipp}$), 2.45 (m, 4H, $^i$Pr-H), 1.31 (d, 12H, $^i$Pr-CH$_3$), 1.26 (d, 12H, $^i$Pr-CH$_3$); $^{13}$C{$^{1}$H} NMR (CD$_2$Cl$_2$): δ 145.2 (N-C), 140.0 (ipso-C$_{dipp}$), 132.6 (o-C$_{dipp}$), 130.2 (m-C$_{dipp}$), 125.4 (p-C$_{dipp}$), 29.6 ($^i$Pr-CH), 25.5 ($^i$Pr-CH$_3$), 24.0 ($^i$Pr-CH$_3$).

**X-Ray Crystallography**

Each crystal was covered in Nujol and placed rapidly into a cold N$_2$ stream of the Kryo-Flex low temperature device. The data were collected using the SMART$^{[14]}$ software package on a Bruker APEX CCD diffractometer employing a graphite monochromated Mo Kα radiation ($λ = 0.71073$ Å) source. Hemispheres of data were collected using counting times of 10-30 seconds per frame at -100 °C. The details of crystal data, data collection, and structure refinement are listed in Tables 1 and 2. Data reductions were performed using the SAINT$^{[15]}$ software package and the data were corrected for absorption using SADABS.$^{[16]}$ The structures were solved by direct methods using SIR97$^{[17]}$ and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the non-H atoms using SHELXL-97$^{[18]}$ and the WinGX$^{[19]}$ software package and thermal ellipsoid plots were produced using SHELXTL.$^{[18]}$
Table 2.1. Summary of X-ray crystallographic data for $^{(\text{Mes\text{BIAN})P-Br}}$, 2.5, and $^{[(\text{Mes\text{DAB})P][I_3]}$, 2.9[I$_3$].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{(\text{Mes\text{BIAN})P-Br}}$</th>
<th>$^{[(\text{Mes\text{DAB})P][I_3]}$</th>
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<tbody>
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<td>Empirical formula</td>
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<td>174(2)</td>
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<td>0.71073</td>
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</tr>
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<td>Orthorhombic</td>
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<td>$\gamma$ (°)</td>
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<td></td>
<td>-22 &lt; k &lt; 22,</td>
<td>-19 &lt; k &lt; 20,</td>
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<td></td>
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Independent reflections  17321  11915

$R_{int}$  0.3695  0.0550

Absorption correction  SADABS  SADABS

Refinement method  Full-matrix least-squares on $F^2$

Data / restraints / parameters  17321 / 0 / 919  11915 / 0 / 506

Goodness-of-fit on $F^2$  0.975  1.029

Final $R$ indices$^{a}$  
$I>2\sigma(I)$
$R1$: 0.1038,
$wR2$: 0.1603 $R1$: 0.0464,
$wR2$: 0.0900

$R$ indices (all data)  
$R1$: 0.3088,
$wR2$: 0.2386 $R1$: 0.0772,
$wR2$: 0.1068

Largest difference map peak and hole (e Å$^{-3}$) 1.544 and -0.511 1.950 and -0.534

$^{a}R1(F): \Sigma |F_o| - |F_c|)/\Sigma|F_o| \}$ for reflections with $F_o > 4(\sigma(F_o))$. $wR2(F^2): \{ \Sigma w(|F_o|^2 - \Sigma w(|F_c|^2) \}^{1/2}$ where w is the weight given each reflection.

Table 2.2. Summary of X-ray crystallographic data for ($^\text{Mes}$DAB-CH$_3$)SnCl$_4$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>($^\text{Mes}$DAB-CH$_3$)SnCl$_4$</th>
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<tbody>
<tr>
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<td>Formula weight</td>
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<td>Temperature (K)</td>
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<td>Wavelength (Å)</td>
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</tr>
<tr>
<td>Habit, Color</td>
<td>Plate, Orange</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
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<td>Unit cell dimensions:</td>
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<tr>
<td>$a$ (Å)</td>
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<tr>
<td>$b$ (Å)</td>
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<tr>
<td>Parameter</td>
<td>Value</td>
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<td>-----------</td>
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<tr>
<td>(c) (Å)</td>
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<td>(R_{int})</td>
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<td>Absorption correction</td>
<td>SADABS</td>
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<td>Refinement Method</td>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on (F^2)</td>
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<td>Final (R) indices(^a)</td>
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<td>([I&gt;2\sigma(I)])</td>
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<td>(R) indices (all data)</td>
<td>(R1: 0.0438, wR2: 0.0718)</td>
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<tr>
<td>Largest difference map peak and hole (e Å(^{-3}))</td>
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\(^a\)\(R1(F): \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\) for reflections with \(F_o > 4(\sigma(F_o))\). \(wR2(F^2): \{\Sigma w(|F_o|^2 - |F_c|^2)^2)/\Sigma w(|F_o|^2)^2\}^{1/2}\) where \(w\) is the weight given each reflection.
2.3 Results and Discussion

In light of our recent developments of P(I) bromide salts,[8] we reasoned that a similar approach might be suitable for the synthesis of N-heterocyclic bromophosphines. The room temperature reaction of a dichloromethane solution of a given α-diimine with a solution containing one equivalent of PBr₃ and excess cyclohexene results in the corresponding N-heterocyclic bromophosphines, as illustrated in Scheme 2.2. In the absence of cyclohexene, the reaction proceeds much slower and presents a variety of phosphorus containing products including the desired bromophosphine in modest yield. In addition, by changing the reaction solvent to donors such as THF, multiple products were obtained even when using a large excess of cyclohexene.

![Scheme 2.2. Preparation of N-heterocyclic bromophosphines by redox cycloaddition.](image)

The formation of the cyclic diaminobromophosphines is consistent with the formal generation of the “P(I)-Br” synthon with the simultaneous elimination of 1,2-dibromocyclohexane. The “P(I)-Br” synthon undergoes a formal 4 + 2 electron cycloaddition with the α-diimine ligand. This cycloaddition process results in the formal transfer of two electrons from the putative P(I) center to the diimine ligand and thus produces the observed P(III) center ligated by the corresponding diamido dianion. It should be highlighted that Dillon and Monks have performed an excellent ³¹P NMR study that has provided mechanistic insight into related phosphorus(I) systems with non-reducible ligands such as diphosphines (Scheme 2.3).[20] Dillon found that such
reactions most likely occur in a step-wise manner and the redox process occurs after the phosphorus atom is chelated by the ligand. It was also discovered that the rate-determining step was the formal elimination of $X_2$, which in the absence of a halide-scavenging agent, quickly oxidizes the diphosphine ligand to generate undesirable products. It is probable that the reactions described above occur in a similar manner, but the addition of cyclohexene allows for the elimination of $X_2$ in a clean and effective fashion (Scheme 2.4). [8] As $X_2$ approaches the $\pi$-bond of cyclohexene, the $X_2$ molecule becomes polarized. The X-X bond is then heterolytically cleaved and the partially positively charged halide acts as an electrophile, reacting with the C=C double bond. The cyclic species is attacked from the back-side by the additional halide ion to produce 1,2-dihalocyclohexane.

Scheme 2.3. Dillon and Monks mechanism of triphosphonium cation formation where $X = $ Cl or Br.
Scheme 2.4. Removal of $X_2$ using cyclohexene, $X = \text{Cl}$ or Br.

Cowley and co-workers have recently demonstrated that related redox cycloaddition reactions can occur with the extended aromatic $\alpha$-diimines of the BIAN family.\[^9\] Interested in trapping putative “P(I)-Cl” molecules with ligands other than diphosphines, Cowley \textit{et al.} added equimolar amounts of PCl$_3$ and SnCl$_2$ to DippBIAN at room temperature, which ultimately yielded $[(\text{DippBIAN})P]^+[\text{SnCl}_5\cdot\text{THF}]$. It was found that the C-C bond distance was significantly shorter than that of the uncoordinated ligand thus indicating double bond character.\[^{21}\] The [SnCl$_5$•THF]$^-$ counteranion is octahedral with the closest P$^-$•••Cl contacts at 3.374(5) and 3.328(5) Å. The initial formation of the “P-Cl” molecule functions as a two electron reductant towards the DippBIAN ligand and as a result, the phosphorus cation adopts the +3 oxidation state and not the +1 oxidation state as found by Schmidpeter \textit{et al.} when using diphosphine ligands.

Figure 2.1. Postulated reaction mechanism for the formation of $[\text{ArylBIANP}]^+[\text{SnCl}_5]^-$. Similarly, Cowley and co-workers also investigated the reaction of DippBIAN with PI$_3$ in the absence of a reducing agent, which resulted in the complex $[(\text{DippBIAN})P][\text{I}_3]$. It has been postulated that the mechanism of formation of $[(\text{DippBIAN})P]^+$ is similar to that
of the PCl₃ reaction whereby a putative “P-I” molecule is trapped by the BIAN ligand to give [(DippBIAN)PI], from which I⁻ is then abstracted by I₂ followed by an intramolecular charge transfer of two electrons from phosphorus to the ligand, ultimately affording the product [(DippBIAN)P][I₃] (Figure 2.2B).

Figure 2.2. Ball and stick representation of [(DippBIAN)P][SnCl₅•THF] (left) and [(DippBIAN)P][I₃] (right).[9]

Comparably, we wanted to investigate the reactivity of the "P(I)-Br" synthon with aryl-BIAN ligands. By adding a solution of PBr₃ and excess cyclohexene to a solution of arylBIAN, we able to successfully produce bromophosphines 2.5-2.6 in quantitative yield according to ³¹P NMR spectroscopy. These complexes also contain very identifiable ³¹P chemical shifts of 202 ppm, which falls in the region observed for phosphonium cations of this type.[3, 4, 22]
Figure 2.3. Synthetic route to aryli^B^A^N^ bromophosphines.

In the case of the mesitylene-substituted BIAN ligand, we were able to obtain a solid from the recrystallization of 2.5 in acetonitrile that was suitable for examination by single-crystal X-ray diffraction studies. Although the data from even the best of the crystals that we examined was of low-quality, the solution and refinement of the structure confirms the identity and connectivity of the compound.

The bromophosphine 2.5 crystallizes in the space group P2_1/c with three crystallographically-independent, yet similar molecules present in the asymmetric unit, as illustrated in Figure 2.4. In each molecule, the metrical parameters are identical and are consistent with the BIAN ligand having undergone a two-electron reduction during the formation of the product. The heterocyclic C-N bonds range from 1.380(10) to 1.402(10) Å in comparison to the distance of 1.266(2) Å reported for the free Mes^BIAN^ ligand and are thus indicative of C-N σ-bonds. Consequently, the endocyclic C-C distances for the five-membered ring range from 1.348(11) to 1.362(10) Å in comparison to the distance of 1.528(2) Å in the free ligand and are in accordance with a C-C π-bond. Additionally, the C-N and C-C bond distances in 2.5 are very similar to those observed in the related cations in the salts [(Dipp^BIAN^)P][SnCl_5•THF] and [(Dipp^BIAN^)P][I_3]^9 and can be found in Table 2.3.
Figure 2.4. Asymmetric unit for 2.5 showing the three crystallographically-independent molecules (right) and a ball and stick illustration of [(MesBIAN)P][Br] (left). In each instance, hydrogen atoms are omitted for clarity.

Table 2.3. Selected metrical parameters for MesBIAN, [(DippBIAN)P][SnCl$_5$•THF], and [(DippBIAN)P][I$_3$] for comparison to bromophosphine 2.5. Distances are reported in Ångströms and angles in degrees (X = Cl, I, or Br).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MesBIAN</th>
<th>[(DippBIAN)P][SnCl$_5$•THF]$^9$</th>
<th>[(DippBIAN)P][I$_3$]$^9$</th>
<th>[(MesBIAN)P][Br] (2.5)</th>
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<tr>
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<tr>
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<td>mol 1. 2.432(3)</td>
<td>mol 2. 2.452(3)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>mol 3. 2.506(3)</td>
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<td>Distance 2</td>
<td>Distance 3</td>
<td>Distance 4</td>
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<td>------------</td>
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<tr>
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</table>

There are unexpectedly few compounds that contain the N₂P(III)-Br moiety reported in the Cambridge Structural Database (CSD)\(^{23}\) for comparison and the P-Br distances in 2.5 (2.432(3) – 2.506(3) Å) are very long in relation to the P-Br distances in those diamidobromophosphines in Figure 2.5A (range: 2.2815(10) – 2.334(1) Å\(^{24-26}\) but are shorter than similar NHP-Br complexes (2.6181(10) – 2.947(1) Å\(^{22, 27}\) in Figure 2.5B, which can be explained by the increased π-delocalization in the acenapthene backbone of BIAN ligand. The long bonds in the bromophosphine are consistent with the long phosphorus element bonds observed for NHP-H, NHP-Cl and other compounds containing the unsaturated NHP core.
Figure 2.5. Phosphorus bromide bond lengths in reported complexes from the CSD, values reported in Ångströms (Å).

The first chlorophosphene, [(tBuDAB-H)P][Cl], was originally characterized as an ionic phosphenium chloride because of the elongated P-Cl bond length. It was later discovered that this was the incorrect interpretation and that this compound represents an extreme case whereby the unusual length of these bonds can be attributed to the bond weakening induced by the hyperconjugation of the π-system on the NHP core with the anti-bonding σ*-orbital of the phosphorus-chlorine element bond. This unique chemical reactivity increases the occurrence of heterolysis and thus the relative weight of the "no-bond" canonical structure in the accepted "bond – no-bond resonance" scheme illustrated in Scheme 2.6. Upon closer examination of the factors controlling the bonding heterolysis in the P-X bonds of halogenated NHPs, it can be attributed to a balance between factors for and against the formation of an ionic species. The resulting 6π-aromatic phosphenium cation provides a strong driving force for the dissociation of the cation and anion, but Gudat et al. found that the destabilizing effect of charge separation and the loss of P-X bond energy is the main deterring factor against
spontaneous heterolysis.\textsuperscript{[22]} The P-X bond energies decrease with increasing size of X (X = F(496), Cl(328), Br(264), I(184 kJ/mol)), as does the Coulombic attraction between ions of opposite charge. Thus, iodophosphines should provide the best chance to observing the classical “no-bond” structure. This phenomenon is also reflected in the $^{31}$P NMR signals of P-halogenated NHPs, whereby the iodophosphines ($\delta^{31}$P 195 ppm)\textsuperscript{[22]} are more deshielded than bromophosphines ($\delta^{31}$P 185 ppm)$^{[3]}$ and chlorophosphines ($\delta^{31}$P 168 ppm)$^{[2, 29]}$ and are very similar to that of fully ionic salts that contain anions such as triflate, triiodide, tetraphenylborate, gallium tetrachloride, or stannic pentachloride ($\delta^{31}$P ~201-210 ppm).\textsuperscript{[3, 4, 9]}

\begin{center}
\includegraphics[width=0.5\textwidth]{scheme26.png}
\end{center}

**Scheme 2.6.** Suggested "Bond – No-bond resonance" for some substituted NHP derivatives (X = H, Cl, Br, I, PR$_2$, etc.)

We decided to examine the reactions of [($^{\text{Mes}}$DAB-CH$_3$)P][Br] with a series of anion metathesis or halide abstracting agents to confirm the applicability of the $N$-heterocyclic bromophosphines obtained using the method outlined for the preparation of NHP salts. The treatment of a solution of 2.2 in either methylene chloride or acetonitrile with a solution containing an equimolar quantity of K[PF$_6$/Li[B(C$_6$F$_5$)$_4$/TMSOTf/or AlBr$_3$ results in the rapid and quantitative formation of the corresponding NHP salt [($^{\text{Mes}}$DAB-CH$_3$)P][X], as indicated by multinuclear NMR experiments and HRMS studies. The corresponding $^{31}$P NMR resonance shifts from 189 ppm for the bromophosphine to $\delta$ 198 ppm for the aluminum tetrabromide containing salt. Similarly, anion metathesis reactions with K[PF$_6$] or Li[B(C$_6$F$_5$)$_4$] result in the complete
loss of the initial bromophosphine $^{31}\text{P}$ NMR resonance for 2.2 and the appearance of a new signal at $\delta$ 200 ppm for the uncoordinated phosphenium cation 2.9. Finally, the treatment of 2.2 with TMS-OTf produced 2.9[OTf], as indicated by the $^{31}\text{P}$ resonance at $\delta$ 200 ppm. All of these $^{31}\text{P}$ NMR peaks are within the accepted range of ionic NHP salts.

Scheme 2.7. Bromide abstraction reactions of 2.2 that produce NHP salts of 2.9.

We were unable to obtain crystalline samples of the NHP salts of 2.9 derived from the brominated precursor 2.2. Even though the spectroscopic data confirmed the formation of the desired products, we still wanted to structurally characterize the cation. To do so, we decided to employ the less desirable direct NHP redox syntheses previously reported by Cowley. Thus, the $\alpha$-diimine ($^{\text{Mes}}\text{DAB-CH}_3$) was treated with PCl$_3$ and the
reducing agent SnCl₂ in CH₂Cl₂ in an attempt to produce the analogous cation with a SnCl₅⁻ anion. Upon obtaining the ³¹P solution NMR spectrum, we were surprised to observe two distinct singlet signals at δ 200 ppm and δ 198 ppm, with both peaks being consistent with the cation. We hypothesized that the close interaction of two different anions with the cation might explain the observation of two distinct signals. The negative ion mode ESI mass spectra of solutions of "2.9[SnCl₅]" contained signal manifolds that confirmed the presence of both [SnCl₃]⁻ and [SnCl₅]⁻ anions and are consistent with the our hypothesis and the observations seen in the ³¹P NMR spectrum. Fortunately, we were able to isolate crystalline material suitable for single crystal diffraction experiments; unfortunately the product was not what we desired. Solvent evaporation of 9 from THF yielded a MesDAB-CH₃ structure that had sequestered a “SnCl₄” molecule (Figure 2.7). Although undesirable, this structure did not come as a surprise as Cowley et al. has recently established that α-diimines prove to be excellent ligands for heavy p-block elements.[³⁰] The metrical parameters for the MesDAB-CH₃ fragment are very similar to that of the uncomplexed ligand, the C-C bonds are 1.520(6) Å for the trapped “SnCl₄” structure compared to 1.500(2) Å of the free ligand and are both indicative of a single bond.[¹²] The C-N bond lengths are also similar, 1.278(5)-1.289(5) Å for the complex and 1.278(2) Å for the free ligand, thus indicating C=N bonds. The Sn-N bond distances are (2.278(3) and 2.282(3) Å) typical of N-Sn(IV) donor-acceptor bonds in the related [DippBIAN][SnCl₄] structure (2.293(5)-2.300(5) Å). To date, “SnCl₄” trapped moieties have not been reported with diimine ligands that do not contain the BIAN framework and this example represents the first sequestered “SnCl₄” with a diimine other than arylBIAN’s.
Figure 2.7. Thermal ellipsoid plot (30% probability surface) illustrating the asymmetric unit for \[^{\text{Mes}}\text{DAB-CH}_3][\text{SnCl}_4\]. Hydrogen atoms are omitted for clarity.

Due to the inability to obtain structural information of the cation using the PCl\(_3\)/SnCl\(_2\) approach, we decided to employ the other redox method involving the disproportionation of phosphorus triiodide in the presence of an \(\alpha\)-diimine ligand. By adding a CH\(_2\)Cl\(_2\) solution of PI\(_3\) to a solution containing \(^{\text{Mes}}\text{DAB-CH}_3\), the corresponding phosphenium triiodide salt \([^{\text{Mes}}\text{DAB-CH}_3]P[I_3]\) was obtained quantitatively by \(^{31}\text{P}\) NMR. Luckily, a concentrated solution of the salt in acetonitrile produced crystals suitable for X-ray crystallography.

The salt 2.9[I\(_3\)] crystallizes in the \(P2_12_12_1\) space group with two pairs of crystallographically-independent cations and anions in the asymmetric unit, as illustrated in Figure 2.8. The metrical parameters (Table 2.4) in the cation are completely consistent with those reported for related unsaturated NHP cations, whereby the “P-Br” fragment undergoes a formal 4 + 2 electron cycloaddition with the \(\alpha\)-diimine. For comparison, the P-N distances, which range from 1.655(5) to 1.680(6) Å, are indistinguishable from the P-N distances of 1.665(3) reported for the related \(^{\text{Mes}}\text{DAB-H}\) triiodide salt.\(^{31}\) The metrical parameters of the triiodide anions are consistent with those anticipated for salts in which there is not extensive interaction between the cations and the anions.
Table 2.4. Selected metrical parameters for $^{\text{Mes}}$DAB-CH$_3$ and $[(^{\text{Mes}}\text{DAB-}H)\text{P}][\text{I}_3]$ for comparison to salt 2.9[I$_3$]. Distances are reported in ångströms and angles in degrees.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$^{\text{Mes}}$DAB-CH$_3$</th>
<th>$(^{\text{Mes}}\text{DAB-H})\text{P}][\text{I}_3]^{[31]}$</th>
<th>$[(^{\text{Mes}}\text{DAB-CH}_3)\text{P}][\text{I}_3]$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Distances</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(x)-N(x1)</td>
<td>1.665(3) mol 1. 1.665(5) mol.2 1.658(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(x)-N(x2)</td>
<td>1.665(3)</td>
<td>1.667(6) 1.680(6)</td>
<td></td>
</tr>
<tr>
<td>C(x1)-N(x1)</td>
<td>1.278(2) 1.371(6)</td>
<td>1.376(8) 1.380(8)</td>
<td></td>
</tr>
<tr>
<td>C(x2)-N(x2)</td>
<td>1.278(2) 1.371(6)</td>
<td>1.371(8) 1.370(8)</td>
<td></td>
</tr>
<tr>
<td>C(x1)-C(x2)</td>
<td>1.500(2) 1.342(9)</td>
<td>1.356(8) 1.359(9)</td>
<td></td>
</tr>
<tr>
<td>I(x1)-I(x2)</td>
<td>2.9214(12)</td>
<td>2.9814(9) 2.8821(8)</td>
<td></td>
</tr>
<tr>
<td>I(x2)-I(x3)</td>
<td>2.9214(12)</td>
<td>2.8632(9) 2.9762(8)</td>
<td></td>
</tr>
<tr>
<td><strong>Angles</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(x1)-P(x)-N(x2)</td>
<td>89.4(2)</td>
<td>89.0(3)</td>
<td></td>
</tr>
<tr>
<td>I(x1)-I(x2)-I(x3)</td>
<td>180.000</td>
<td>179.10(2)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.8. Depiction of the asymmetric unit for \([\text{MesNHP}]\text{I}_3\) showing the two crystallographically-independent ion pairs (left) and a ball and stick illustration indicating the numbering scheme employed for each molecule (right). In each instance, hydrogen atoms are omitted for clarity.

The structure of salt 2.9[I₃] clearly contains the cation postulated to exist in the products of the halide-abstraction reactions described above. Most importantly, the spectroscopic data for the cation in 2.9[I₃] is indistinguishable to those observed for the salts generated from the bromophosphine reagent 2.2 obtained using our new PBr₃/cyclohexene synthetic approach. Alternatively, we were able to validate our synthetic approach by comparing the cation \([(\text{tBuDAB-H})\text{P}]^+\) (2.8) to similar salts previously recorded by Gudat et al.\[^{[3]}\] We were able to synthesize \([(\text{tBuDAB-H})\text{P}][\text{OTf}]\) (2.8[OTf]) by first using our PBr₃ and cyclohexene approach to produce \([(\text{tBuDAB-H})\text{P}][\text{Br}],\) followed by subsequent anion metathesis with trimethylsilyl trifluoromethanesulfonate. The resulting spectroscopic data was in agreement with Gudat’s crystallographically characterized 2.8[X] (X = BF₄, GeCl₃, SnCl₃). Both 2.8[BF₄] and 2.8[OTf] products have a $^{31}\text{P}$ NMR shift of 202 ppm and subsequent $^1\text{H}$ NMR studies exhibited peaks that are indistinguishable from one another. In addition, it has been
previously suggested that the backbone proton in $^{t\text{Bu}}$DAB-H reveals an identifiable shift based on nature of the resulting heterocycle,\textsuperscript{[32]} therefore the concurrence of the $^1$H NMR shifts also provides good evidence of the cation [($^{t\text{Bu}}$DAB-H)P]\textsuperscript{+}. The backbone proton shifts from 7.29 ppm for the more covalent species [($^{t\text{Bu}}$DAB-H)P][Br] to greater than 8.08 ppm for a wide variety of truly ionic cations [($^{t\text{Bu}}$DAB-H)P]\textsuperscript{+} (Table 2.5). It appears the nature of the anion in the ionic species provides little change to the shift of the backbone hydrogen atom. Overall, it is obvious the crystallographic results of 2.8[BF$_4$] and 2.9[I$_3$] confirm the spectroscopic identification of the cation and illustrate the viability of our new synthetic approach.

![Figure 2.9. Synthetic route to [($^{t\text{Bu}}$DAB-H)P][OTf], 2.8[OTf].](image)

**Table 2.5 Selected NMR frequencies of 8[X].**

<table>
<thead>
<tr>
<th>Compound</th>
<th>NMR Solvent</th>
<th>$^{31}$P NMR frequency (ppm)</th>
<th>$^1$H NMR C-H frequency (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8[Br]</td>
<td>CD$_2$Cl$_2$</td>
<td>185.8</td>
<td>7.29</td>
</tr>
<tr>
<td>8[I]$^{[22]}$</td>
<td>CD$_2$Cl$_2$</td>
<td>195.7</td>
<td>7.47</td>
</tr>
<tr>
<td>8[PF$_6$]$^{[33]}$</td>
<td>CD$_2$Cl$_2$</td>
<td>202.3</td>
<td>8.08</td>
</tr>
<tr>
<td>8[GeCl$_3$]$^{[34]}$</td>
<td>CDCl$_3$</td>
<td>202.6</td>
<td>8.24</td>
</tr>
<tr>
<td>8[SnCl$_3$]$^{[34]}$</td>
<td>CDCl$_3$</td>
<td>205.0</td>
<td>8.18</td>
</tr>
<tr>
<td>8[BF$_4$]$^{[3]}$</td>
<td>CD$_2$Cl$_2$</td>
<td>202.0</td>
<td>8.17</td>
</tr>
<tr>
<td>8[OTf]</td>
<td>CD$_2$Cl$_2$</td>
<td>202.7</td>
<td>8.26</td>
</tr>
</tbody>
</table>
2.4 Conclusions

In summary, the PBr$_3$ and cyclohexene method outlined above indicates that the redox-cycloaddition methodology can be employed for the convenient synthesis of unsaturated diaminobromophosphine precursors to NHP cations in good yields. In every case, the results are consistent with electron transfer between a given $\alpha$-diimine with a putative "P(I)-Br" fragment with a formal 4+2 cycloaddition. It has been shown that salt metathesis does not work well for the preparation of unsaturated NHP precursors, and thus makes our mild and simple redox approach described above a simple and effective synthetic route to this increasingly-important class of reagents. We have demonstrated the resulting diaminobromophosphines have shown to be useful reagents for the generation of the corresponding $N$-heterocyclic phosphonium salts by several common methods of anion abstraction or metathesis reactions. More generally, our approach provides synthetic alternatives to metathesis chemistry for the preparation of inorganic heterocyclic ligands.
2.5 References


Chapter 3 – Alternative Ligands to Phosphorus Containing Heterocycles

3.1 Introduction

Although phosphorus is most frequently found in the +3 or +5 oxidation state, the +1 state remains the most common of the lower oxidation states. These phosphorus(I) species contain four non-bonding electrons and can be depicted by several structural drawings that range from mono-coordinate and neutral to di-coordinate and either neutral or charged (Figure 3.1).[1]

![Figure 3.1](image)

Figure 3.1. Depictions of compounds containing phosphorus(I) centers.

Phosphinidenes are neutral mono-coordinate P(I) compounds of the form R-P and are phosphorus analogues of carbenes.[2] To date, no stable “free” phosphinidene has been reported and P(I) compounds have only been synthesized as di-coordinate complexes. However, phosphinidenes have been reported as short-lived intermediates in several reaction mechanisms and have only been detected at low temperatures as ground state triplets (Figure 3.2).[3-5]

![Figure 3.2](image)

Figure 3.2. Triplet phosphinidene studied by Gaspar et al.

Based on the well-known diagonal relationship between phosphorus and carbon,[6] it has been reasoned by Benkö et al. that it should be possible to synthesize and isolate phosphinidenes.[7] Phosphinidene PH exists in the triplet ground state, with the singlet state being less stable by 22 kcal/mol. Comparatively, the energy difference between the singlet and triplet states for the CH₂ carbene is 14 kcal/mol, which indicates the relative
instability of phosphinidenes. Although these calculations suggest that “naked” phosphinidines would be difficult to synthesize, it has been shown computationally by Nguyen et al. that N-P- and S-substituted phosphinidenes exist in the singlet ground state and would be an ideal synthetic target.\[^8\] More recently, Benkö et al. found computationally that H\(_2\)C=N-P has a singlet ground state and the lone pair of electrons on nitrogen acts as a donor, while the \(\pi^*\)-orbital on H\(_2\)C=N acts as an acceptor towards backbonding of a lone pair from the phosphinidene (Figure 3.3).\[^7\]

**Figure 3.3.** Stabilizing effect of \(\pi\)-donation and backdonation for the phosphinidene H\(_2\)C=N-P.

Benkö also found that \(\sigma\)-electron donors and \(\pi\)-electron withdrawing groups attached to the carbon atom increase the singlet-triplet gap and thus increase the stabilization of the phosphinidene. Perhaps the most likely synthetic target to these species is (Me\(_3\)Si)\(_2\)C=N-P but to date, no facile synthetic route has been established to produce these potentially important class of compounds.

In spite of the fact that no stable free phosphinidenes have been reported thus far, there are many examples of complexed phosphinidines with d-, f-, and p-block elements.\[^9\] The first of these types was reported by Mathey in the early 80’s, whereby the pyrolysis of phosphanorbornadiene produced terminal phosphinidene complexes (Figure 3.4).\[^10, 11\]
Figure 3.4. Terminal phosphinidene complex from the decomposition of phosphanorbornadiene.

More recently, Arduengo and co-workers exhibited that \(N\)-heterocyclic carbenes are adequately nucleophilic to deoligomerize \((\text{PPh})_5\) and \((\text{PCF}_3)_4\) and produce carbene-PR phosphinidenes (Figure 3.5).\(^{[2, 12]}\) Two canonical forms can be written for these compounds, structure I is that of a terminal phosphinidene with a phosphorus-carbon dative bond and structure II is that of phosphaalkene with a phosphorus-carbon double bond. In discussing the bonding in these systems it is perhaps best to draw similarities from metal-carbene complexes where phosphorus is playing the role of metal in this case. Thus, structure I is akin to Fischer-type carbenes and structure II resembles Schrock-type carbenes. There are obvious differences between structures I and II such as bond orders and oxidation states, but the biggest difference remains the number of lone pairs associated with phosphorus. In order to determine the appropriate canonical structure, the Lewis basicity of the resultant species was determined by adding two equivalents of borane and resulted in the formation of the bis(borane) adduct thus verifying that phosphinidene adduct I is the best representation of this complex.\(^{[13]}\)

Figure 3.5. Carbene-phosphorus analogue of metal-carbene complexes. I; Fischer-type phosphinidene and II; Schrock-type phosphaalkene.
As mentioned in Chapter 2, the bonding between N-heterocyclic phosphonium ions can be attributed to the increased π-delocalization, which provides increased stabilization of the cation. The interaction of the lone pair on nitrogen with the σ*-anti-bonding orbitals of phosphorus in N-heterocyclic phosphines is responsible for the ability of P-X to participate in bond activation reactions. It has been found that certain P-substituted N-heterocyclic phosphines have the ability to modify these effects.\[^{14}\] For instance, P-amino substituted NHP’s strengthen the exocyclic phosphorus-nitrogen bond and thus weakens the endocyclic phosphorus-nitrogen bonds. Recently, Gudat and coworkers have been computationally investigating potential complexes for the dissociation of free phosphinidenes.\[^{2, 15}\] It was found that NHPs made from bipyridine derivatives can be described as phosphinidene complexes with N-donor ligands and as such, they may dissociate to form free phosphinidines (Figure 3.6). One of the most important features of these types of reactions is the formation of aromatic stabilization of the N-donor ligand upon fragmentation of the phosphinidene species, thus making conventional diazabutadiene containing NHPs less than desirable starting points.

**Figure 3.6.** Postulated generation of free phosphinidenes from the decomposition of bipyridine containing N-heterocyclic phosphines.\[^{2, 15}\]

Obviously, to test this hypothesis, Benkő and Gudat had to experimentally synthesize new N-heterocyclic phosphines by carefully selecting ligands that could promote generation of free phosphinidenes.\[^{16}\] The α-monoiminopyridine (IMPY) ligand was chosen for use as a viable starting point. In addition to the above reasons, pyrido
derivatives of $N$-heterocyclic phosphoniums would also be potentially interesting in order to study the physical and chemical properties of the resulting unknown complexes. Benkő and Gudat modeled their synthesis after the reactions reported by Cowley et al. whereby the addition of $\text{PI}_3$ to a diimine ligand produced the phosphonium cation with a triiodide anion. Thus, by adding equimolar amounts of 2,6-diisopropyl-$N$-((pyridine-2-yl)methylene)benzenamine and $\text{PI}_3$ in ether, produced the corresponding triiodide phosphonium salt (Scheme 3.1). Subsequent anion exchange reactions with trimethylsilyl triflate (TMSOTf) were used to produce a more inert anion for the formation of $N$-heterocyclic aminophosphines.

**Scheme 3.1.** New phosphonium complexes using the $\alpha$-monoiminopyridine ligand.

The $^{31}$P NMR chemical shifts are similar to those of other $N$-heterocyclic phosphonium anions at ~200 ppm. X-ray diffraction studies were performed on single crystals to better understand the nature of bonding in this complex. It was found that the bond lengths were in accordance with the ligand undergoing a two-electron charge transfer upon complexation to phosphorus and are similar to those previously discussed in Chapter 2 with the exception of the N-C bond from the pyridine fragment, which is slightly longer due to steric reasons. Overall, these new phosphonium cations contain extended conjugated $\pi$-electron systems that have a similar degree of aromaticity found for previously recorded phosphoniums. To date, these new targeted compounds have failed to lead to free phosphinidene species and more investigations are needed.
In light of our previous developments in generating facile routes to $N$-heterocyclic phosphonium cations, and the recent finding of Gudat, we wished to extend the development of small heterocycles to further grow the area of phosphonium chemistry. We are actively interested in a variety of combinations of imine, pyridine, carbonyl, and thioketone containing ligands (Figure 3.7), with the goal of producing new phosphonium complexes that may contain fascinating properties. We are interested in producing these complexes using the low oxidation state phosphorus methods previously reported by our group. A comprehensive computational study into the resulting oxidation state of the phosphorus atom in these new complexes is needed.

![Figure 3.7. Potential ligands towards new phosphorus containing heterocycles.](image)

3.2 Experimental

**General Procedures**

All manipulations were carried out using standard inert atmosphere techniques. Phosphorus(III) chloride was purchased from Strem Chemicals Inc., and all other chemicals and reagents were purchased from Aldrich. Phosphorus(III) was distilled before use, and all other reagents were used without further purification. All solvents
were dried using a series of Grubbs’-type columns and were degassed prior to use. CD$_2$Cl$_2$, and CDCl$_3$ were dried over calcium hydride. All starting ligands were synthesized according to literature procedures and recrystallized a minimum of three times to ensure their purity.

NMR spectra were recorded at room temperature in CDCl$_3$ solutions on a Bruker Advance 300-MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards (SiMe$_4$ for $^1$H and $^{13}$C, and 85% H$_3$PO$_4$ for $^{31}$P). Coupling constant magnitudes, |J|, are given in Hz.

**Theoretical Methods**

Calculations were carried out with the Gaussian 09 program package using density functional theory (DFT).\textsuperscript{[17]} All structures were calculated with the B3PW91/6-31+G(d) basis set.\textsuperscript{[18,19]} The geometries were restricted to the highest possible symmetry and for each of the optimized structures, vibrational analysis was performed to check whether the stationary point was located at a minimum. The electronic energies of the molecules have been corrected by the zero-point vibrational energy and are reported in atomic units (au). Single Point Energies of the electron density were calculated for complexed molecules using the B3PW91/6-311+G(3df,2p) basis set and in the case of the [(BIPY)P]$^+$ B3PW91/6-311+G(2df,2p) was used. The Natural Bond Order (NBO) method was used to conduct population analysis studies to determine the maximum occupancy in each orbital.\textsuperscript{[20]} The calculations of the Laplacians were done using Molden.\textsuperscript{[21]} Depictions of the optimized structures of the model compounds were made using Shelx, while representations of the Laplacians and molecular orbitals were made using Molden.
Specific Procedures

General Synthetic Route to P-Heterocycles Using PX₃.

PCl₃: PCl₃ was added to a dichloromethane solution of the respective ligand of choice. After a period of 10 minutes, the subsequent solution was transferred to a schlenk flask containing a solution of SnCl₂ and was allowed to stir overnight.

PI₃: A diethyl ether solution of a given ligand was transferred to a solution of PI₃ at -78°C. The reaction was vigorously stirred overnight.

PBr₃: A dichloromethane solution of PBr₃ and excess cyclohexene was added to a solution of the given ligand and was left to stir overnight.

Reaction of C₁₈H₂₂N₂ with PI₃, 1[I₃]⁺

2,6-Bis(1-methylethyl)-N-(2-pyridinylmethylene) benzenamine (500 mg, 1.87 mmol) was added to PI₃ (772 mg, 1.87 mol) in a solution of diethyl ether (~40 mL) and left to stir overnight. The red mixture was filtered through a frit and volatiles were removed from the collected solution. $^{31}$P{$^{1}$H} NMR: 203.1, 181.7.

Reaction of C₁₈H₂₂N₂ with PCl₃ and SnCl₂

PCl₃ (0.183 mL, 2.10 mmol) and 2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene) benzenamine (562 mg, 2.10 mmol) was added to SnCl₂ (400 mg, 2.10 mmol) in a solution of dichloromethane (50 mL) and left to stir overnight. The resulting reaction mixture was orange with a small amount of yellow-orange precipitate present. The mixture was separated and the volatiles were removed from the solution. The resulting orange solid
was re-dissolved in dichloromethane and recrystallization by slow evaporation yielded orange-yellow crystals. $^{31}$P$\{^1$H$\}$ NMR: 201.3, 149.5.

**Reaction of C$_{18}$H$_{22}$N$_2$ with PBr$_3$ and excess cyclohexene**

PBr$_3$ (0.27 mL, 2.89 mmol) and three equivalents of cyclohexene (0.88 mL, 8.67 mmol) were added to a dichloromethane solution of 2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene) benzenamine (770 mg, 2.89 mmol) and was allowed to stir for 48 hours. The resulting solution was dark red-brown and was dried *in vacuo*. $^{31}$P$\{^1$H$\}$ NMR: 228.82, 201.8, 188.9, 172.9, -5.4.

**Reaction of C$_{18}$H$_{22}$N$_2$ with PCl$_3$ and cobaltocene**

A yellow solution of 2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene) benzenamine (250 mg, 0.89 mmol) and PCl$_3$ (0.19 mL, 0.89 mmol) in dichloromethane (50 mL) was transferred to a schlenk containing cobaltocene (330 mg, 1.78 mmol). The dark brown solution was left to stir for 48 hours and was subsequently dried *in vacuo*. $^{31}$P$\{^1$H$\}$ NMR: 219.67, 185.93, 8.20, -30.62.

**Reaction of C$_{19}$H$_{24}$N$_2$ with PCl$_3$ and SnCl$_2$**

Upon the addition of 2,6-bis(1-methylethyl)-N-[1-(2-pyridinyl)ethylidene] benzenamine (250 mg, 0.89 mmol) and PCl$_3$ (0.077 mL, 0.89 mmol) to SnCl$_2$ (168 mg, 0.89 mmol) in dichloromethane, the solution turned from pale yellow to bright orange. The solution was left to stir overnight and the resulting mixture was orange with an orange precipitate. The solution was filtered and the solvent was removed under reduced pressure. $^{31}$P$\{^1$H$\}$ NMR: 201.1, 268 (d).
**Reaction of C\textsubscript{19}H\textsubscript{24}N\textsubscript{2} with PI\textsubscript{3}**

To a red solution of PI\textsubscript{3} (250 mg, 0.89 mmol) in diethyl ether (50 mL) was added a solution of 2,6-bis(1-methylethyl)-N-[1-(2-pyridinyl)ethylidene] benzenamine (367 mg, 0.89 mmol). The cold reaction mixture was left to stir for 36 hours prior to separation of the dark red precipitate from the solution. \textsuperscript{31}P\{\textsuperscript{1}H\} NMR: \textbf{165.2}, 98.00.

**Reaction of C\textsubscript{19}H\textsubscript{24}N\textsubscript{2} with PBr\textsubscript{3} and excess cyclohexene**

The pale yellow solution of 2,6-bis(1-methylethyl)-N-[1-(2-pyridinyl)ethylidene] benzenamine (280 mg, 0.998 mmol) in dichloromethane (40 mL) turned orange-red upon the addition of PBr\textsubscript{3} (0.094 mL, 0.998 mmol) and cyclohexene (0.303 mL, 2.99 mmol). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR: \textbf{228.9}, 201.8, 190.4,156.2, 6.2.

**Reaction of C\textsubscript{20}H\textsubscript{15}NO with PCl\textsubscript{3} and SnCl\textsubscript{2}**

A yellow solution of 1,2-diphenyl-1-(phenylimino) ethanone (500 mg, 1.75 mmol) and PCl\textsubscript{3} (0.152 mL, 1.75 mmol) in dichloromethane (50 mL) was added to a schlenk containing 330 mg of SnCl\textsubscript{2}. The resulting yellow solution was filtered and volatiles were removed under reduced pressure. \textsuperscript{31}P\{\textsuperscript{1}H\} NMR: \textbf{219.9}, 177.5.

**Reaction of C\textsubscript{20}H\textsubscript{15}NO with PBr\textsubscript{3} and Na**

1,2-Diphenyl-1-(phenylimino) ethanone (94 mg, 0.329 mmol) and Na\textsuperscript{o} (15 mg, 0.658 mmol) were added together in THF (40 mL). To the resulting blue solution was added PBr\textsubscript{3} (0.033mL, 0.35 mmol) and cyclohexene (0.035 mL, 0.35 mmol) in THF. The
resultant yellow solution was evaporated to dryness in vacuo. $^{31}$P{$^1$H} NMR: 201.1, 185.1, 8.1, 6.2.

**Reaction of C$_{21}$H$_{17}$NO**

To a vial containing 2-[(4-methylphenyl)imino]-1,2-diphenyl-ethanone was added PBr$_3$ and excess cyclohexene, and was left to stir for 48 hours. The resulting golden yellow solution was evaporated to dryness. $^{31}$P{$^1$H} NMR: 228.8, 175.8.

**Reaction of C$_{21}$H$_{17}$NO$_2$ with PBr$_3$ and excess cyclohexene**

PBr$_3$ and excess cyclohexene were added to a small vial containing 2-[(4-methoxyphenyl)imino]-1,2-diphenyl ethanone. The mixture was left to stir overnight and the resultant golden yellow was evaporated to dryness. $^{31}$P{$^1$H} NMR: 228.8, 176.3.

**Reaction of C$_{21}$H$_{17}$NO$_2$ with PCl$_3$ and SnCl$_2$**

A yellow solution of 2-[(4-methoxyphenyl)imino]-1,2-diphenyl ethanone (500 mg, 1.58 mmol) and PCl$_3$ (0.138 mL, 1.58 mmol) in dichloromethane (50 mL) was added to a schlenk containing SnCl$_2$ (299 mg, 1.58 mmol). The resulting yellow solution was evaporated to dryness. $^{31}$P{$^1$H} NMR: 219.9, 177.6, 4.8.

**Reaction of C$_{21}$H$_{17}$NO$_2$ with PI$_3$**

To a schlenk containing PI$_3$ (650 mg, 1.58 mmol) in diethyl ether (40 mL) was added 2-[(4-methoxyphenyl)imino]-1,2-diphenyl ethanone (500 mg, 1.58 mmol). The resulting red mixture stirred overnight and the resultant precipitate was filtered and volatiles were removed. $^{31}$P{$^1$H} NMR: 173.71, 102.4.
Reaction of C$_{20}$H$_{14}$ClNO and PI$_3$

2-[(4-Chlorophenyl)imino]-1,2-diphenylethanone (440 mg, 1.37 mmol) was added to a solution of PI$_3$ (565 mg, 1.37 mmol) in diethyl ether (40 mL). The resulting dark red solution was evaporated to dryness. $^{31}$P{$^1$H} NMR: 165.5, 10.9, -3.1, -27.3.

X-Ray Crystallography

Each crystal was covered in Nujol and placed rapidly into a cold N$_2$ stream of the Kryo-Flex low temperature device. The data were collected using the SMART$^{[22]}$ software package on a Bruker APEX CCD diffractometer employing a graphite monochromated Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) source. Hemispheres of data were collected using counting times of 10-30 seconds per frame at -100 °C. The details of crystal data, data collection, and structure refinement are listed in Tables 1 and 2. Data reductions were performed using the SAINT$^{[23]}$ software package and the data were corrected for absorption using SADABS.$^{[24]}$ The structures were solved by direct methods using SIR97$^{[25]}$ and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the non-H atoms using SHELXL-97$^{[26]}$ and the WinGX software package and thermal ellipsoid plots were produced using SHELXTL.$^{[26]}$
Table 3.1. Summary of X-ray crystallographic data for C\textsubscript{26}H\textsubscript{27}NO, C\textsubscript{13}H\textsubscript{12}N\textsubscript{2}, and C\textsubscript{21}H\textsubscript{17}NO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C\textsubscript{26}H\textsubscript{27}NO</th>
<th>C\textsubscript{13}H\textsubscript{12}N\textsubscript{2}</th>
<th>C\textsubscript{21}H\textsubscript{17}NO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C\textsubscript{26}H\textsubscript{27}NO</td>
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<td>C\textsubscript{21}H\textsubscript{17}NO\textsubscript{2}</td>
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<td>173(2)</td>
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<td>Block, Yellow</td>
<td>Block, Colourless</td>
<td>Prism, Yellow</td>
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<td>Monoclinic</td>
<td>Triclinic</td>
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<td>Pn</td>
<td>P2(1)/c</td>
<td>P-1</td>
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<td>9.1410(11)</td>
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<td>$b$ (Å)</td>
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<tr>
<td>$c$ (Å)</td>
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<tr>
<td>$\gamma$ (°)</td>
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<td>90</td>
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<td>1.270</td>
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<td>332</td>
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<td>1.11 to 27.50</td>
<td>2.11 to 27.50</td>
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<td>-24 &lt; h &lt; 24,</td>
<td>-11 &lt; h &lt; 12,</td>
</tr>
<tr>
<td></td>
<td>-10 &lt; k &lt; 10,</td>
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<td>-12 &lt; k &lt; 12,</td>
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Reflections collected 11025 10330 9611
Independent reflections 2373 2329 3716
$R_{int}$ 0.0691 0.0429 0.0444
Absorption correction SADABS SADABS SADABS
Refinement method Full-matrix least-squares on $F^2$
Data / restraints / parameters 2373 / 2 / 253 2329 / 0 / 136 3716 / 0 / 217
Goodness-of-fit on $F^2$ 1.295 1.326 1.042
Final $R$ indices\(^a\) $R1$: 0.0923, $wR2$: 0.2173 $R1$: 0.0897, $wR2$: 0.2262 $R1$: 0.0582, $wR2$: 0.1249
$[I>2\sigma(I)]$ $R1$: 0.1071, $wR2$: 0.2282 $R1$: 0.1022, $wR2$: 0.2427 $R1$: 0.0949, $wR2$: 0.1546
$R$ indices (all data) $R1$: 0.1071, $wR2$: 0.2282 $R1$: 0.1022, $wR2$: 0.2427 $R1$: 0.0949, $wR2$: 0.1546
Largest difference map peak and hole (e Å\(^{-3}\)) 0.354 and -0.365 0.495 and -0.377 0.275 and -0.203

\(^a\) $R1(F)$: $\Sigma|F_o| - |F_c|)/\Sigma|F_o|$ for reflections with $F_o > 4(\sigma(F_o))$. $wR2(F^2)$: $\{\Sigma w(|F_o|^2 - |F_c|^2)^2)/\Sigma w(|F_o|^2)^2\}^{1/2}$ where $w$ is the weight given each reflection.

Table 3.2. Summary of X-ray crystallographic data for C\(_{20}\)H\(_{14}\)ClNO, and C\(_{18}\)H\(_{22}\)Cl\(_4\)N\(_2\)Sn.
<table>
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<th>Value 2</th>
</tr>
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<tr>
<td>(b) (Å)</td>
<td>8.2480(8)</td>
<td>9.9360(12)</td>
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<tr>
<td>(c) (Å)</td>
<td>19.4547(19)</td>
<td>15.1940(19)</td>
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<tr>
<td>(\alpha) (°)</td>
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<td>90</td>
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<tr>
<td>(\beta) (°)</td>
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<tr>
<td>(\gamma) (°)</td>
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<td>90</td>
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<tr>
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<td>8</td>
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<td>(F(000))</td>
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<td>2096</td>
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<td>1.45 to 27.50</td>
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<td>Absorption correction</td>
<td>SADABS</td>
<td>SADABS</td>
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<tr>
<td>Refinement method</td>
<td></td>
<td></td>
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<tr>
<td>Data / restraints / parameters</td>
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<td>4663 / 0 / 226</td>
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<tr>
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<td>(R1): 0.0272, (wR2): 0.0713</td>
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<td>([I &gt; 2\sigma(I)])</td>
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<tr>
<td>(R) indices (all data)</td>
<td>(R1): 0.0844, (wR2): 0.1577</td>
<td>(R1): 0.0307, (wR2): 0.0822</td>
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<td>Largest difference map peak and hole (e Å(^{-3}))</td>
<td>0.339 and -0.217</td>
<td>0.842 and -0.438</td>
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\[^a\]R1(\(F\)): \(\sum(F_o - |F_c|)/\sum|F_o|\) for reflections with \(F_o > 4(\sigma(F_o))\). \(wR2(\(F^2\))\) = \(\{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2\}^{1/2}\) where \(w\) is the weight given each reflection.
3.3 Results and Discussion

3.3.1 Computational Investigations

The oxidation state of an atom in a molecule provides insight into its bonding, structural features, and potential reactivity.\(^{[27, 28]}\) Pnictogens in the +1 state are of particular interest due to the fact that they possess properties not seen in higher oxidation states.\(^{[29]}\) As previously discussed, extensive investigations have been performed on bis(phosphine) chelating ligands that form cyclic triphosphenium ions containing phosphorus in the +1 state. In addition to our group, Cowley has shown that N,N'-diimino chelating type ligands can capture phosphorus(I) moieties, whereby the ligand undergoes a two electron charge transfer and the phosphorus atom adopts an overall +3 oxidation state.\(^{[30, 31]}\) Recently, Cowley has extended the generation of phosphonium cations by using β-diketiminate ligands.\(^{[32, 33]}\) N,N'-chelated β-diketiminate complexes are particularly interesting as they exhibit unusual oxidation states and present novel bonding arrangements. Cowley found that the use of a β-diketiminate ligand followed by the addition of \(n\)-BuLi, PCl\(_3\), and finally TMSOTf, resulted in a new class of N,N'- and N,C-chelated phosphonium complexes (Figure 3.8).

![Figure 3.8](image)

**Figure 3.8.** N,N’- and N,C-chelated phosphonium complexes.

In an attempt to better understand both the chelating behavior of the ligand and the oxidation state of phosphorus in the potential phosphonium complexes, we performed a variety of DFT calculations and NBO analysis on a series of model compounds (Figure
We are looking at three main types of ligands. The first of which are a series of small ligands that are analogues to the extensively characterized diazabutadiene (DAB) type ligands (Type I). The second type contains a benzannulated backbone (Type II) and the third type includes potentially exciting di-nitrogen containing ligands (Type III). All substituents in the model compounds have been replaced with hydrogen atoms and models of the free ligands and their doubly-reduced analogues were also calculated for bond length comparison purposes. In all cases, the highest point symmetry was enforced; $C_{2v}$ for the symmetric models and $C_s$ was used for the asymmetric ligands. Important computational energies are reported in Table 3.3.

![Figure 3.9. Model ligands used for comparison purposes.](image)
Table 3.3. Selected computational energies for reduced, free, and complexed systems.

<table>
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<tr>
<th>Model</th>
<th>Sym</th>
<th>Corrected Energy, $E_{\text{total}}$ (au)$^b$</th>
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<th>LUMO (eV)</th>
<th>HOMO-LUMO Gap (eV)</th>
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<td>-2.89</td>
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<tr>
<td>[BIPY]²⁻</td>
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<td>-10.53</td>
<td>-6.81</td>
</tr>
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</table>

*a* Point group symmetry. *b* E_{total} = E_{calculated} + ZPVE.
The optimized geometries of the free ligands and their corresponding phosphorus containing complexes are depicted in Figures 3.10-3.12 and include important metrical parameters. The metrical parameters are in good agreement with previous experimentally characterized structures for the free ligands, as well as for the phosphorus complex of the DAB type ligands. The computational methods employed are similar to those already reported by Gudat et al. and give results that are in good agreement to with these ligands and model complexes.\[2, 15, 34\]

![Figure 3.10](image)

**Figure 3.10.** Optimized structures of complexes using Type I ligands for \([\text{C}_2\text{H}_3\text{NO}]\text{P}^+\), \([\text{C}_2\text{H}_3\text{NS}]\text{P}^+\), \([\text{C}_2\text{H}_2\text{O}_2]\text{P}^+\), \([\text{C}_2\text{H}_2\text{OS}]\text{P}^+\), \([\text{C}_2\text{H}_2\text{S}_2]\text{P}^+\), and the corresponding free ligands. Selected bond distances (Å) and angles (°) are indicated.
Figure 3.1. Optimized structures of complexes using Type II ligands [(C₆H₅NO)⁺], [(C₆H₅NS)⁺], [(C₆H₄O₂)⁺], [(C₆H₄OS)⁺], [(C₆H₄S₂)⁺], and the corresponding free ligands. Selected bond distances (Å) and angles (°) are indicated.
Figure 3.12. Optimized structures of complexes using Type III ligands for [(DAB)P]+, [(IMPy)P]+, [(BIPY)P]+, and the corresponding free ligands. Selected bond distances (Å) and angles (°) are indicated.

The bond distances in the above compounds provide significant information on the nature of the bonding between the elements. The bonding angles are within expected ranges and do not warrant any further comment. From a simple comparison of the phosphorus-element bonds in the complexes, it can be seen that the P-E bonds for nitrogen and oxygen in Figures 3.9 and 3.10 suggest the existence of partial multiple-bonding. The P-N bond lengths range from 1.67 – 1.68 Å and are significantly shorter than common P-N σ-bonds (1.80 Å). Similarly, the P-O bond lengths range from 1.62 – 1.64 Å compared to 1.76 Å typically observed for P-O single bonds. The P-S bonds also exhibit some degree of multiple-bonding character and are slightly shorter (2.05 Å) than typical σ-bonds of the type (2.11 Å) in Figure 3.13 (far right). Overall, these bond distances are within good agreement with previously synthesized compounds that have been structurally characterized (Figure 3.13).
Figure 3.13. Selected P-E bond distances (Å) for structurally characterized compounds.\cite{35-38}

Perhaps the most interesting results are the differences between the P-N bond lengths in the diimine structures of [(DAB)P]$^+$, [(IMPY)P]$^+$, and [(BIPY)P]$^+$ which differ from 1.69 Å in the DAB complex to 1.70 – 1.73 Å for the [(IMPY)P]$^+$, while the BIPY containing cation is 1.74 Å and is more typical of a P-N σ-bond. The differences between the P-N bond lengths are attributed to the degree of multiple bonding between the phosphorus atom and the ligands.

It is also noteworthy to examine the structural changes that occur in the ligands upon coordination of phosphorus. We wish to highlight the occurrence of intramolecular charge transfer, or lack thereof, between the various models of phosphorus complexes. As electron density is transferred from phosphorus to the corresponding LUMO of the ligand, one would expect an elongation of the E-C (E = N, O, S) bond lengths and a shortening of the C-C backbone bond. In order to illustrate this rationale, we have calculated the optimized structures and metrical parameters for the doubly-reduced ligands for comparison purposes. It was found that for all cases, with the exception of IMPY and
BIPY, the N-C bond length stretched from ~1.27 Å in the free ligand to ~1.37 Å in the complexed model compounds and more closely resembles the bond distance seen in the reduced ligands (~1.38 Å). Similarly, all O-C and S-C bond lengths elongated from 1.22 and 1.65 Å to 1.37 and 1.73 Å respectively, and are again are in good agreement to the reduced ligands. For the C₂H₂ model compounds (Type I), the C-C bond shortened in the complexed systems to 1.36 Å and is slightly shorter than that seen in the doubly-reduced ligands. For the case of the benzannulated model structures (Type II), at first glance the C-C backbone does not seem to exhibit the same degree of double-bond character but further examination of the entire backbone structure demonstrates the delocalization of electron density into the π-system producing an overall aromatic backbone. We hope that this will be a significant driving force in producing new alternative phosphorus containing heterocycles. The [(IMPY)P]+ and [(BIPY)P]+ complexes provide metrical parameters that fall between that of the free ligand and the doubly-reduced form, where both complexes have parameters more closely resembling the latter. Overall, the examination of the metrical parameters revealed that the IMPY and BIPY ligands are not as easily reduced upon complexation to putative P(I) centers as compared to the various nitrogen, oxygen, and sulfur-containing combinations.

It is also noteworthy to discuss the Wiberg bond indices (WBI) for these compounds. A Natural Bond Orbital (NBO) analysis was used in order to quantify the degree of interaction between the various ligands and the corresponding phosphorus center (Figures 3.4 to 3.6). The NBO analysis provides chemical insight into things such as charges, Lewis structures, bonding types, bonding orders, and other useful information. As a whole, the WBI values of the complexed structures parallel the metrical parameters previously discussed and are very much similar to the doubly-reduced model compounds.
Therefore, the “ligand framework” of the phosphorus complexed models does not warrant any discussion in extensive detail.

Again, the [(IMPY)P]$^+$ and [(BIPY)P]$^+$ have values that lie between those observed for the free and doubly-reduced ligands with [(BIPY)P]$^+$ more closely resembling the free ligand. Complexes of the type [(DAB)P]$^+$ have been structurally isolated and characterized for a number of years. The previous computed P-N bond indices of this type exhibit values of approximately 1.0. It is likely to assume that diimines or imine-pyridine complexes with similar values would likely be viable synthetic targets. From an examination of the Wiberg bond indices in Table 3.4, the P-N bonds are all approximately 1.0 with the exception of [(BIPY)P]$^+$, which has the lowest value of all of the complexes at 0.856. This is most likely due to the aromaticity of the pyridine rings, which will likely impede the reduction of the ligand. In light of this, cations of the type [(IMPY)P]$^+$ and [(BIPY)P]$^+$ may still present as reasonable synthetic targets.

An examination of the P-O bond indices shows values ranging from 0.88 to 0.92. This can be attributed to the larger electronegativity difference between phosphorus and oxygen leading to a higher percentage of ionic character between the two. In contrast, the P-S WBI’s are significantly larger and vary from 1.30 – 1.38 and is due to the increased delocalization between sulfur and the heterocyclic framework. An examination of the S-C indices also supports the evidence of multiple bonding character as the values are all significantly greater than 1.
Table 3.4. Selected Wiberg bond indices for the free and reduced ligand systems.

<table>
<thead>
<tr>
<th>Model</th>
<th>N-C&lt;sub&gt;imine&lt;/sub&gt; WBI</th>
<th>O-C&lt;sub&gt;imine&lt;/sub&gt; WBI</th>
<th>S-C&lt;sub&gt;imine&lt;/sub&gt; WBI</th>
<th>C&lt;sub&gt;imine&lt;/sub&gt;-C&lt;sub&gt;α&lt;/sub&gt; WBI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Free Ligands:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;NO</td>
<td>1.9674</td>
<td>1.8828</td>
<td>N/A</td>
<td>0.9910</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;NS</td>
<td>1.3544</td>
<td>N/A</td>
<td>1.2494</td>
<td>0.9456</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;OS</td>
<td>N/A</td>
<td>1.8644</td>
<td>1.9557</td>
<td>1.0164</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>N/A</td>
<td>1.9099</td>
<td>N/A</td>
<td>0.9401</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>N/A</td>
<td>N/A</td>
<td>1.8735</td>
<td>1.1266</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;NO</td>
<td>1.8521</td>
<td>1.7326</td>
<td>N/A</td>
<td>0.9505</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;NS</td>
<td>1.8178</td>
<td>N/A</td>
<td>1.6851</td>
<td>0.9988</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;OS</td>
<td>N/A</td>
<td>1.7629</td>
<td>1.7476</td>
<td>0.9572</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>N/A</td>
<td>1.8001</td>
<td>N/A</td>
<td>0.9026</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>N/A</td>
<td>N/A</td>
<td>1.6766</td>
<td>1.0362</td>
</tr>
<tr>
<td>DAB</td>
<td>1.9505</td>
<td>N/A</td>
<td>N/A</td>
<td>1.0275</td>
</tr>
<tr>
<td>IMPY</td>
<td>1.3741(N&lt;sub&gt;pyridine&lt;/sub&gt;)</td>
<td>N/A</td>
<td>N/A</td>
<td>1.0418</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reduced Ligands:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;NO]&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>1.3257</td>
<td>1.2655</td>
<td>N/A</td>
<td>1.5516</td>
</tr>
<tr>
<td>[C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;NS]&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>1.4203</td>
<td>N/A</td>
<td>1.1169</td>
<td>1.5596</td>
</tr>
<tr>
<td>[C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;OS]&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>N/A</td>
<td>1.3426</td>
<td>1.1073</td>
<td>1.6200</td>
</tr>
<tr>
<td>[C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;]&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>N/A</td>
<td>1.2746</td>
<td>N/A</td>
<td>1.5817</td>
</tr>
<tr>
<td>[C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;]&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>N/A</td>
<td>N/A</td>
<td>1.1590</td>
<td>1.7194</td>
</tr>
<tr>
<td>Model</td>
<td>P-N WBI</td>
<td>P-O WBI</td>
<td>P-S WBI</td>
<td>N-C WBI</td>
</tr>
<tr>
<td>-------------------------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>[(C₆H₅NO)P⁺]</td>
<td>1.0899</td>
<td>0.8550</td>
<td>N/A</td>
<td>1.1909</td>
</tr>
<tr>
<td>[(C₆H₅NS)P⁺]</td>
<td>1.0646</td>
<td>N/A</td>
<td>1.3307</td>
<td>1.2185</td>
</tr>
<tr>
<td>[(C₆H₅OS)P⁺]</td>
<td>N/A</td>
<td>0.8854</td>
<td>1.3879</td>
<td>N/A</td>
</tr>
<tr>
<td>[(C₆H₅O₂)P⁺]</td>
<td>N/A</td>
<td>0.9231</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>[(C₆H₅S₂)P⁺]</td>
<td>N/A</td>
<td>N/A</td>
<td>1.3481</td>
<td>N/A</td>
</tr>
<tr>
<td>[(C₆H₅NO)P⁺]</td>
<td>1.0926</td>
<td>0.8793</td>
<td>N/A</td>
<td>1.1368</td>
</tr>
<tr>
<td>[(C₆H₅NS)P⁺]</td>
<td>1.0804</td>
<td>N/A</td>
<td>1.3070</td>
<td>1.1468</td>
</tr>
<tr>
<td>[(C₆H₅OS)P⁺]</td>
<td>N/A</td>
<td>0.8904</td>
<td>1.3712</td>
<td>N/A</td>
</tr>
<tr>
<td>[(C₆H₅O₂)P⁺]</td>
<td>N/A</td>
<td>0.9176</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>[(C₆H₅S₂)P⁺]</td>
<td>N/A</td>
<td>N/A</td>
<td>1.3442</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 3.5. Selected Wiberg bond indices for phosphorus containing systems.
\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{[(DAB)P]^+} & 1.0517 & \text{N/A} & \text{N/A} & 1.2293 & \text{N/A} & 1.5448 \\
\text{[(IMPY)P]^+} & 0.9043 & \text{N/A} & \text{N/A} & 1.1146 & \text{N/A} & 1.3568 \\
\text{[(BIPY)P]^+} & 0.8560 & \text{N/A} & \text{N/A} & 1.151 & \text{N/A} & 1.2074 \\
\hline
\end{array}
\]

NBO Wiberg bond indices for the specified bonds.

The stability of a phosphonium cation depends on the charge delocalization when a phosphorus atom is incorporated into a conjugated \( \pi \)-electron system. The cations can be potentially divided into two categories that differ in charge distribution within the \( \pi \)-electron system.

![Figure 3.14](image)

**Figure 3.14.** The two main types of phosphonium cations. **A.** Triphosphonium. **B.** \( N \)-heterocyclic phosphine.

The first type of cation is that of a phosphonium whereby the positive charge is localized on the substituents only (Figure 3.14A).\(^{39}\) An example of this type of cation is that of a triphosphonium. Here the phosphorus atom is best represented as a trapped P(I) center. The phosphine ligand acts as back-bonding acceptor because it contains empty anti-bonding orbitals that are of the correct symmetry and energy to accept electron density from the p-type orbital from the P(I) center (Figure 3.15).
Figure 3.15. Back-bonding interaction between empty anti-bonding orbitals on the phosphine ligand and filled 3p orbital on the P³ center (left). The molecular orbital illustration of a phosphonium in the +3 oxidation state (right).

In the second type, the phosphorus center either bears a neutral charge with the positive charge located on the substituents or a positive π-charge (Figure 3.14B). This is best represented as a NHP cation.[31] The stability of NHPs can be easily explained through the conjugated π-system that delocalizes the positive charge. This is possible because in phosphenumns the phosphorus p-orbitals are available for π-donation from ligands such as diimines (Figure 3.15).

In order to explore the stability of various nitrogen-, oxygen-, and sulfur-containing ligands, it is important that the nature of the phosphorus-ligand interaction be explored further. This will provide key support that intramolecular charge transfer to the ligand has occurred and will ultimately afford key evidence indicating the oxidation state of the central phosphorus atom. To illustrate this rationale we looked at two pieces of key information, the charge and occupancy of the p-type orbitals on phosphorus. In all cases, the phosphorus atoms have a significantly positive charge. This indicates that ligands of these types have a phosphorus center that is substantially electron deficient and thus again supports the idea that the ligands become reduced upon ligation
to phosphorus. From an examination of the charge values, it appears as though a trend does emerge. The di-nitrogen complexes have values close to that of 1.0, the incorporation of oxygen into the ligand causes the phosphorus atom to become even more electron deficient presumably due to the increased ionicity of the bond. In contrast, the introduction of sulfur affords phosphorus centers that are less electron deficient in comparison, probably due to the fact that sulfur itself is more electron rich.
### Table 3.6. Selected energies for phosphorus containing systems.

<table>
<thead>
<tr>
<th>Model</th>
<th>Q(P) (^a)</th>
<th>Occ P (p(\pi)) (^b)</th>
<th>LP Pop (^c)</th>
<th>E(_{LP}) (eV) (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(C(_2)H(_3)NO)P] (^+)</td>
<td>1.34930</td>
<td>0.80576</td>
<td>1.98408</td>
<td>-20.89</td>
</tr>
<tr>
<td>[(C(_2)H(_3)NS)P] (^+)</td>
<td>0.85477</td>
<td>0.91413</td>
<td>1.98345</td>
<td>-20.64</td>
</tr>
<tr>
<td>[(C(_2)H(_3)OS)P] (^+)</td>
<td>1.02922</td>
<td>0.83919</td>
<td>1.98609</td>
<td>-21.20</td>
</tr>
<tr>
<td>[(C(_2)H(_3)O(_2))P] (^+)</td>
<td>1.52929</td>
<td>0.69904</td>
<td>1.98393</td>
<td>-21.65</td>
</tr>
<tr>
<td>[(C(_2)H(_3)S(_2))P] (^+)</td>
<td>0.48670</td>
<td>0.95391</td>
<td>1.98110</td>
<td>-20.90</td>
</tr>
<tr>
<td>[(C(_6)H(_5)NO)P] (^+)</td>
<td>1.35312</td>
<td>0.79004</td>
<td>1.98514</td>
<td>-20.32</td>
</tr>
<tr>
<td>[(C(_6)H(_5)NS)P] (^+)</td>
<td>0.86998</td>
<td>0.88969</td>
<td>1.98408</td>
<td>-20.12</td>
</tr>
<tr>
<td>[(C(_6)H(_5)OS)P] (^+)</td>
<td>0.86998</td>
<td>0.83286</td>
<td>1.98660</td>
<td>-20.57</td>
</tr>
<tr>
<td>[(C(_6)H(_5)O(_2))P] (^+)</td>
<td>1.50879</td>
<td>0.70701</td>
<td>1.98497</td>
<td>-20.92</td>
</tr>
<tr>
<td>[(C(_6)H(_5)S(_2))P] (^+)</td>
<td>0.48997</td>
<td>0.94420</td>
<td>1.98059</td>
<td>-20.27</td>
</tr>
<tr>
<td>[(DAB)P] (^+)</td>
<td>1.17071</td>
<td>0.89287</td>
<td>1.98320</td>
<td>-20.21</td>
</tr>
<tr>
<td>[(IMPY)P] (^+)</td>
<td>1.01058</td>
<td>1.09420</td>
<td>1.98259</td>
<td>-19.37</td>
</tr>
<tr>
<td>[(BIPY)P] (^+)</td>
<td>0.86830</td>
<td>1.27819</td>
<td>1.98152</td>
<td>-18.67</td>
</tr>
</tbody>
</table>

\(^a\) NBO charge on P atom. \(^b\) NBO population of valence p orbital on P atom suitable for interaction with the pi-system of the ligand. \(^c\) NBO population of the lone pair on P. \(^d\) Energy of the lone pair orbital localized on the P.

Previous computational and experimental work on phosphoranes from our group and others, has demonstrated that diphosphine ligands are useful ligands to trap phosphorus(I) centers. The computed models have revealed that the electrons in the P p(\(\pi\)) orbitals have an occupancy of 2.0, thus suggesting that no electron density was
transferred into the \( \pi \)-system of the ligand. Because no electron density was transferred, the ligand did not undergo any reduction. It is thus important to look at these valence \( p \) orbitals of \( \pi \)-type symmetry in these new models to evaluate and confirm the potential of \( \pi \)-donation from phosphorus into the ligand. It is safe to assume that the ligands will generate the \( \sigma \)-bonding structure of the complex, and that the four valence electrons in the phosphorus cation will be occupied in two separate orbitals. One set of electrons will be occupied as a “lone pair,” while the other set will remain in the \( p(\pi) \) orbital. As in the case for triphosphoniums, a value of \(~2.0\) for these model compounds would also indicate that there was no transfer of electron density and that the product should yield a phosphonium with a putative \( P(I) \) fragment.

From the examination of the occupancy values for the phosphorus centers in Table 3.6, each model system exhibits a significant loss of electron density. Both the small five-membered ring systems as well as the benzannulated analogues, have values less than 1.0 and are again consistent with our previous findings that suggest there should be significant transfer of electron density from the phosphorus center to the ligand. The \([\text{BIPY}P]^+\) model complex has somewhat less transfer of electron density with an occupancy of 1.28 electrons in the \( p \) orbital.

The Laplacian is constructed from the second partial derivatives and shows where electron density is locally concentrated or depleted. This ultimately provides detailed information about the bonding and the number of lone pairs associated with a particular atom in question. By examining the Laplacian of the electron density, we can observe the number of lone pairs and thus, the oxidation state each of the phosphorus centers in our model complexes. The Laplacian provides a 2-deminsional plot with areas of charge concentrations and charge depletions. An area of charge concentration in the valence shell
behaves as a Lewis base or nucleophile. Conversely, the area of the charge depletion behaves as a Lewis acid or electrophile. According to Valence Shell Electron Pair Repulsion (VSEPR) theory, the electron pair domain is the area of increased probability of finding two electrons of opposite spins. When this increase of electron density transpires, a larger concentration of electron charge density is built up and can be observed in the contour plot of the Laplacian. Figure 3.16 shows the contour plot of the Laplacian for the NOP five-membered heterocycles. Here, the area of increased charge density is represented in yellow and the area of charge depletion is in red. We observe an area of charge concentration, which corresponds to a single lone pair of electrons on the phosphorus center.

![Figure 3.16](image)

**Figure 3.16.** Two-dimensional contour plot (left) and three-dimensional plot (middle) of the Laplacian of the electron density indicating one lone pair of electrons (right).

Thus far, from the analysis of the metrical parameters, Wiberg indices, charges, and occupancy of the p orbitals of \( \pi \)-type symmetry on phosphorus, we would expect a phosphorus center in the +3 oxidation state for the small heterocyclic systems as well as their benzannulated analogues. All of the previous computational information on these complexes has given rise to the assumption that the ligand becomes reduced and in the process, the phosphorus atom becomes oxidized and as one would expect, the Laplacian
of these two types of structures verifies this conclusion in Figure 3.17 with one lone pair of electrons associated with each phosphorus atom.

**Figure 3.17.** Three-dimensional representation of the Laplacian of the electron densities for the 5-membered heterocyclic compounds and their benzannelated analogues.

More intriguingly are the Laplacian pictures of the phosphorus containing IMPY and BIPY model complexes. These display the presence of two lone pairs of electrons on each of the respective phosphorus centers. Previous computational studies on these two complexes (performed by Dr. Macdonald) used electron localization functions (ELF) in order to quantify the number of electrons associated with each lone pair on phosphorus. It was found for the case of [(IMPY)P]+, each lone pair had an occupancy 1.62 electrons and in the case of [(BIPY)P]+, each lone pair contained 1.76 electrons. As previously discussed, the metrical parameters of the [(IMPY)P]+ model are more closely related to the doubly reduced ligand than to that of the free ligand, consequently this information in addition to the Laplacian, indicates that [(IMPY)P]+ is probably best represented as a P(I)-P(III) hybrid. As expected, the combination of both the metrical parameters, and the
Laplacian of the electron density, reveals a [(BIPY)P]$^+$ complex with a formally P(I) center.

**Figure 3.18.** Three-dimensional representation of the Laplacian of the electron densities for [(IMPY)P]$^+$ (left) and [(BIPY)P]$^+$ (right).

In addition to the Laplacian of the electron densities, it is necessary to examine the frontier orbitals to gain further understanding into the electronic structure of these models. The small five-membered ring systems all reveal that the highest occupied molecular orbitals (HOMO) are consistent with previously studied DAB type analogues, and display the $\pi$-system (Figures 3.19 – 3.23).\textsuperscript{29, 34, 40, 41} In addition, each set of frontier orbitals contains a depiction that represents a $\sigma$-type lone pair of electrons on the phosphorus center and can be seen in the HOMO-1 orbital for the NOP, OOP, and OSP Type I models. The remaining NSP and SSP models contain the lone pair in the HOMO-2 orbital with additional $\pi$-system interactions viewed in the HOMO-1 and are completely consistent with the [(DAB)As]$^+$ cation previously computed by our group.\textsuperscript{29} The HOMO-2 for the OOP complex displays a $\sigma$-type lone pair on each of the oxygen atoms. Overall, these results again support the identity of a P(III) cation in these systems.
Figure 3.19. Selected frontier orbitals for “NOP” [C\textsubscript{2}H\textsubscript{3}NOP]\textsuperscript{+}.

Figure 3.20. Selected frontier orbitals for “NSP” [C\textsubscript{2}H\textsubscript{3}NSP]\textsuperscript{+}.

Figure 3.21. Selected frontier orbitals for “OOP” [C\textsubscript{2}H\textsubscript{2}O\textsubscript{2}P]\textsuperscript{+}.
The benzannulated (B-) Type II versions of the phosphorus containing model compounds reveal some contrasting behavior (Figures 3.24 – 3.28). The BNOP and BOOP models exhibit bonding between the phosphorus-element bonds, whereas the remaining HOMO’s for BNSP, BOSP, and BSSP clearly indicate no interaction between any of the P-E bonds. The HOMO-1 orbitals of these complexes are more consistent to that of the HOMO’s of BNOP and BOOP. The sulfur containing systems all exhibit a $\sigma$-type lone pair in the HOMO-3, while the models without sulfur contain the lone pair in the HOMO-5 and can be attributed to the larger difference in electronegativities. Each complex displays an extended $\pi$-system that appears delocalized over the now aromatic benzene backbone. Not surprisingly, the BNSP and BOSP complexes reveal an extended delocalized system that encompasses the sulfur substituents. As observed in the metrical
parameters and the WBI’s, the S-C bonds depict the presence of some multiple bonding character. Again the results obtained mirror the trends previously discussed suggesting these systems are best represented as having a P(III) cation.

![Selected frontier orbitals for “BNOP” [C₆H₅NOP]⁺.](image)

**Figure 3.24.** Selected frontier orbitals for “BNOP” [C₆H₅NOP]⁺.

![Selected frontier orbitals for “BNSP” [C₆H₅NSP]⁺.](image)

**Figure 3.25.** Selected frontier orbitals for “BNSP” [C₆H₅NSP]⁺.
Figure 3.26. Selected frontier orbitals for “BOOP” \([\text{C}_6\text{H}_4\text{O}_2\text{P}]^+\).

Figure 3.27. Selected frontier orbitals for “BOSP” \([\text{C}_6\text{H}_4\text{OSP}]^+\).
Figure 3.28. Selected frontier orbitals for “BSSP” \([\text{C}_2\text{H}_4\text{S}_2\text{P}]^+\).

Probably the most interesting orbital depictions are that of the \([(\text{IMPY})\text{P}]^+\) and the \([(\text{BIPY})\text{P}]^+\) cations (Figures 3.29 – 3.30). For the case of \([(\text{IMPY})\text{P}]^+\) there appears to be two lone pairs of electrons. The \(\sigma\)-type lone pair can be clearly observed in the HOMO-3, whereas the \(\pi\)-type lone pair is somewhat less obvious. The metrical parameters showed some transfer of electron density and not surprisingly, the HOMO has some small degree of delocalization, but the majority of the electron density is associated on the phosphorus atom. Again, this is consistent with the findings of the Laplacian of the electron densities, which suggested the presence of two lone pairs. The presence of the \([(\text{BIPY})\text{P}]^+\ \sigma\)- and \(\pi\)-type lone pairs is significantly more obvious. The HOMO-5 visibly indicates the \(\sigma\)-type, while the HOMO is easily attributable to \(\pi\)-type lone pair. There is no evidence of delocalization and this complex is best represented as a trapped \(\text{P(I)}\) species.
From the examination of all the computed calculations, it can be concluded that the $4\pi$ and $8\pi$ containing ligands undergo a two-electron intramolecular charge transfer and yield a phosphorus center that is best represented as being oxidized from P(I) to P(III). The IMPY containing complex produces somewhat more ambiguous results. It is evident that the ligand exhibits a small degree of charge transfer from the phosphorus center and is supported by similar trends for the WBI's which indicate the presence of a possible
P(III) center. At first glance, the Laplacian and orbital depictions show the presence of a second lone pair on the phosphorus atom, but further investigation shows a small degree of delocalization and a lower than expected value for the number of electrons associated with each lone pair. Overall, [(IMPY)P]⁺ is best represented as a P(I)-P(III) hybrid structure. On the other hand, all of the computed data for the [(BIPY)P]⁺ complex clearly indicates that the most likely representation is that of a trapped P(I) cation.

The large HOMO-LUMO gaps observed for the 5-membered rings systems are vary similar to that observed for the [(DAB)P]⁺ complexes and thus are ideal synthetic targets for producing new phosphorus containing heterocycles.[29] In contrast, the benzannulated analogues exhibit smaller HOMO-LUMO gaps, which can be attributed to the increased π-character from the benzene backbone. Although the values are smaller, they should not be taken too literally as the orbital contribution from the phosphorus center is better represented in an orbital representation below that of the HOMO. Despite this, ligands of the type still present as desirable targets.

3.3.2 Experimental Insights

We first attempted to generate the P(I) trapped species using the 2,2’-bipyridine ligand with the reaction of PBr₃ and excess cyclohexene. We found that the resultant product was not that of a putative P(I) fragment, but was actually a sequestered PBr₂ cation (Scheme 3.2). We were able to confirm its identity from the single crystal X-ray diffraction data. Although the results were of poor quality, the connectivity clearly allowed us to confirm the structure of the resultant complex. The single crystal structure revealed a dimeric arrangement in the solid state (Figure 3.31).
Scheme 3.2. PBr₃ + BIPY and excess cyclohexene.

Figure 3.31. Chem-draw diagram illustrating the dimeric arrangement in the solid state.

We used DFT calculations to optimize the geometry of the [(BIPY)PBr₂]⁺ cation and compared the metrical parameters to that observed for the experimental solid state structure and the previously computed free ligand. The bond lengths found in the experimental solid state structure and its computed variant are in vary good agreement (Figure 3.32) and are both similar to that observed for the free ligand.

Figure 3.32. Ball and stick representation of single crystal structure of [(BIPY)PBr₂]⁺ (left) and its computed analogue (right). Selected interatomic distances are shown in Å.
Additionally, the Laplacian of the electron density is consistent with the superposition of a trapped P(III) center with one lone pair of electrons (Figure 3.33).

Figure 3.33. Three-dimensional representation of the Laplacian of the electron density for [(BIPY)PBr$_2$]$^+$. 

As previously mentioned, Gudat and coworkers were attempting to produce free phosphinidines and while attempting to do so, they employed the mono-pyridine type ligands that we are also interested in using.\textsuperscript{[16]} They found by adding equimolar amounts of 2,6-diisopropyl-N-((pyridine-2-yl)methylene)benzenamine and PI$_3$ in ether, produced the corresponding triiodide phosphonium salt (Scheme 3.1). The resultant phosphonium salt displays an extended conjugated $\pi$-electron system and produces $^{31}$P NMR frequencies in line with P(III) centers that are observed for NHPs. Although our computational studies hint at the possible formation of a P(I) center, it is not surprising that the resultant complex underwent an intramolecular charge transfer reaction. For example, the metrical parameters displayed some degree of electron transfer and the ELF calculations showed the two lone pairs associated with the phosphorus center contained significantly less than two electrons in each. Having this information we wanted to extend our PBr$_3$ and cyclohexene methodology to produce the corresponding bromide analogues (Figure 3.34).
Although we were successfully able to produce the anticipated five-membered heterocycles, we were unfortunately unable of converting all of the starting material into our desired product (Figure 3.35). The $^{31}$P NMR spectrum is consistent with the formation of the phosphonium bromide salt with unreacted PBr$_3$ still left in the reaction mixture. Ongoing studies are being performed to find the optimal reaction conditions to increase the conversion of product for the PBr$_3$ reactions. We have switched from using CH$_2$Cl$_2$ as a solvent to toluene, this allows us to reflux at higher temperatures but sadly we have had only limited success.

![Figure 3.34](image1.png)

**Figure 3.34.** Potential synthetic route to pyrido-annulated phosphorus heterocycles.

![Figure 3.35](image2.png)

**Figure 3.35.** $^{31}$P NMR spectrum of the reaction mixture of C$_{18}$H$_{22}$N$_2$ with PBr$_3$ and excess cyclohexene.
As Gudat et al. have demonstrated, the PI₃ reaction works cleanly and efficiently for these types of systems, we wished to extend this series of compounds to encompass the tin containing anions. Thus, we reacted the ligand with PCl₃ in the presence of the reducing agent SnCl₂. For the case when R = CH₃ we observe the expected product at 201 ppm with a small amount of impurity at 269 ppm. When R = H, we again observe the product peak at 201 ppm with a small impurity at 149 ppm, which can be attributed to P₂Cl₄.[42]

We were able to obtain a single crystal suitable for X-ray diffraction analysis, but again we obtained a similar trapped SnCl₄ structure (Figure 3.36) in analogy to what we observed for the MesDAB type ligands in Chapter 2. We are currently focused on the removal of impurities to produce clean product for further characterization.

![Figure 3.36.](image)

**Figure 3.36.** Thermal ellipsoid plot (30% probability surface) illustrating the asymmetric unit for [C₁₈H₂₂N₂][SnCl₄]. Hydrogen atoms are omitted for clarity.

To validate our computational investigations, we desired to study the potential utility of imine-ketone type ligands in order to generate new heterocyclic phosphinenium complexes. These types of ligands are typically attainable from the condensation reaction between a given aniline and quinone of choice. We targeted a series of benzil monoarylimines synthesized by Charrier and coworkers.[43] Here, they reacted benzyl and
acetic acid with a variety of aryl amines to afford a variety of ligands with different substitution patterns on the aromatic directly attached to the nitrogen atom. A common problem with these types of reactions is that the amino groups can sometimes elicit a double condensation reaction and replace both oxygen atoms. Fortunately, in addition to our $^1$H and $^{13}$C NMR spectroscopic data, we were able to obtain single crystals suitable for X-ray diffraction studies, which clearly supported the formation of benzil monoarylimine ligands (Figure 3.37).

**Figure 3.37.** Thermal ellipsoid plot (30% probability surface) illustrating the asymmetric units for $[\text{C}_{20}\text{H}_{17}\text{NO}]$ (left) and $[\text{C}_{19}\text{H}_{14}\text{NCl}]$ (right). Hydrogen atoms are omitted for clarity.

We again wanted to employ our PBr$_3$ and cyclohexene approach (Figure 3.38), as well as the PI$_3$ and PCl$_3$ methodologies, to produce new phosphonium heterocycles incorporating the N,O-containing ligands. We attempted a variety of reaction conditions to generate our desired phosphonium peaks but as of yet, we have been unsuccessful in producing the resultant products in a clean and efficient manner (Table 3.7).
Figure 3.38. Potential synthetic route to new phosphonium centers.

Table 3.7. A comprehensive study towards the synthesis of new N,O-containing phosphorus heterocycles.

<table>
<thead>
<tr>
<th>Ligand C$<em>{19}$H$</em>{14}$N-R</th>
<th>Method</th>
<th>$^{31}$P NMR Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = H</td>
<td>PCl$_3$/SnCl$_2$</td>
<td>219.9, 177.5</td>
</tr>
<tr>
<td>R = H</td>
<td>PI$_3$</td>
<td>173.8</td>
</tr>
<tr>
<td>R = H</td>
<td>PBr$_3$</td>
<td>201.1, 185.1, 8.1, 6.2</td>
</tr>
<tr>
<td>R = H</td>
<td>Na/PCl$_3$</td>
<td>218.8, 169.1, 155.2, -32.2, -37.1</td>
</tr>
<tr>
<td>R = H</td>
<td>Na/PBr$_3$</td>
<td>201, 185, 8.6</td>
</tr>
<tr>
<td>R = CH$_3$</td>
<td>PBr$_3$</td>
<td>228.8, 175.8</td>
</tr>
<tr>
<td>R = CH$_3$</td>
<td>Na/PCl$_3$</td>
<td>219.9</td>
</tr>
<tr>
<td>R = OCH$_3$</td>
<td>PCl$_3$/SnCl$_2$</td>
<td>219.9, 177.6, 4.8</td>
</tr>
<tr>
<td>R = OCH$_3$</td>
<td>PI$_3$</td>
<td>173.7, 102.4</td>
</tr>
<tr>
<td>R = OCH$_3$</td>
<td>PBr$_3$</td>
<td>228.8, 176.3</td>
</tr>
<tr>
<td>R = OCH$_3$</td>
<td>Na/PCl$_3$</td>
<td>218.8, 155.4</td>
</tr>
<tr>
<td>R = Cl</td>
<td>PCl$_3$/SnCl$_2$</td>
<td>219</td>
</tr>
<tr>
<td>R = Cl</td>
<td>PI$_3$</td>
<td>174.2, 15.7</td>
</tr>
<tr>
<td>R = Cl</td>
<td>PBr$_3$</td>
<td>228, 176.8</td>
</tr>
<tr>
<td>R = Cl</td>
<td>Na/PCl₃</td>
<td>219, 169</td>
</tr>
<tr>
<td>R = Cl</td>
<td>Na/PBr₃</td>
<td>201, 185, 8.1</td>
</tr>
</tbody>
</table>

Majority peak listed in bold.

Although our success has been limited in these studies, an examination of the $^{31}$P NMR frequencies from the PBr₃ reactions clearly demonstrates the applicability of this approach for the generation of novel phosphoniums as the observed $^{31}$P NMR peak in Figure 3.39 is similar to that of the diimine analogues. However, we found that the addition of PI₃ with a given ligand in most cases produced no phosphonium product as generally only unreacted PI₃ or the disproportionation of PI₃ to P₂I₄ was observed. Similarly, the PCl₃ and SnCl₂ method gave unreacted PCl₃ as the majority product but showed significant potential as the expected triphosphonium cation was present in each reaction. In addition to the common methodologies used to generate phosphonium species, we added sodium metal to induce the reduction of the ligand. We then added PCl₃ or PBr₃ to generate the formation of the desired cation. Fortunately, we were able to observe the expected peaks in greater intensity in the $^{31}$P NMR spectra and in some cases, the complete conversion of PX₃ was observed but the spectra contained multiple products that we have been unable to discern or separate from the reaction mixture.
Figure 3.39. $^{31}\text{P}$ NMR spectra of $\text{C}_{20}\text{H}_{17}\text{N}$ (top) and $\text{C}_{20}\text{H}_{17}\text{NO}$ (bottom) with PBr$_3$ and three equivalents of cyclohexene.

3.4 Conclusions

In conclusion, the computational investigation shows that results for ligands of the type I and II are consistent with significant electron transfer from the putative P(I) fragment to the given ligand, ultimately yielding a formal 4+2 cycloaddition reaction with an overall P(III) center. More interestingly, the [(IMPY)P]$^+$ cation was found to be best represented as a P(I)-P(III) hybrid structure with bond lengths showing some degree of electron transfer and the [(BIPY)P]$^+$ complex revealed that this species is best represented as a trapped P(I) cation.

The experimental results proved that the PBr$_3$ and cyclohexene method indicates that the redox-cycloaddion methodology can be employed for the synthesis of these new
phosphenium cations, but additional investigation is needed in order to produce sufficiently pure materials for further characterization and study purposes. Overall, the results are consistent with the computational observations, yielding cations that evidence suggests are best described as P(III) heterocycles.
3.5 References


Chapter 4 – An Alternative Approach to Phosphorus Containing Macromolecules

4.1 Introduction

As stated in Chapter 1, the most important non-biological phosphorus-containing polymers remain the polyphosphazenes, which have been intensely investigated and used industrially. Polyphosphazenes are used in applications including elastomers, biological instruments, batteries, and fuel-cell membranes.\textsuperscript{[1-5]} Although alternative approaches have been developed, these materials are generally made from the thermal ring-opening polymerization of the cyclic chlorinated phosphazene trimer, in which there is an ionization of a chloride from the phosphorus followed by an electrophilic attack to give an alternating PNP structure.\textsuperscript{[6]} The substituents on phosphorus can easily be changed using chloride ion metathesis to link alkoxy, aryloxy, or amine groups to the phosphorus atoms of the phosphazene polymer.

The post-polymerization exchange of substituents on the phosphorus atom allows the properties of the resultant polymers to be easily tuned although the possible substituents that may be introduced in this manner are typically restricted (when \( R = \text{alkyl, aryl} \) the polymer is often degraded). Furthermore, the Manners group has successfully synthesized related polymers such as, poly(carbophosphazenes), poly(thiophosphazenes), poly(thionylphosphazene) (Figure 4.1), in which one of the PR\textsubscript{2} fragments of the phosphazene has been formally replaced with an isolobal fragment. Again, the polymeric forms are produced by the thermal ring-opening polymerization of the corresponding cyclic phosphazene analogue, however it should be noted that this approach is only applicable to monomers bearing chlorine substituents.\textsuperscript{[7-9]}
In order to illustrate the rationale for the approach that we are pursuing for the preparation of phosphorus-containing macromolecules, we wish to highlight a more justifiable Lewis-type description of the electron distribution in a polyphosphazene (illustrated in Figure 4.2), which features a formally anionic di-coordinate nitrogen center flanked by two tetra-coordinate phosphonium ions. In this light, the di-coordinate nitrogen atom bearing two lone pairs of electrons is clearly isovalent with the univalent phosphorus centers in “triphosphenium” species. Given our experience in developing new synthetic approaches for the preparation of triphosphenium ions, and our interest in this functional group, we reasoned that synthetic protocols used to produce triphosphenium salts could provide a convenient route to make phosphorus containing oligomers and polymers. In particular, we postulated that the combination of suitable anionic diphosphine linkers with P(I) fragments should be able to produce analogues of phosphazenes whereby some or all of the nitrogen atoms have been substituted with other anionic linkers (Figure 4.2).

**Figure 4.1.** Related polymers produced by Manners and co-workers.

**Figure 4.2.** Examples of possible anionic linkers that could be potentially used to obtain the target compounds.
4.2 Experimental

General Procedures

All manipulations were carried out using standard inert atmosphere techniques. Phosphorus(III) bromide, sodium cyclopentadienide, and all other chemicals and reagents were purchased from Aldrich. Phosphorus(III) bromide was distilled before use, and all other reagents were used without further purification. All solvents were dried using a series of Grubbs-type columns and were degassed prior to use. THF-d₈ was dried over sodium and benzophenone.

NMR spectra were recorded at room temperature in THF-d₈ solutions on a Bruker Advance 300-MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards (SiMe₄ for ¹H and ¹³C, 85% H₃PO₄ for ³¹P). Coupling constant magnitudes, |J|, are given in Hz. The high-resolution mass spectra (HRMS) were obtained using electrospray ionization of acetonitrile solutions of species either by The McMaster Regional Centre for Mass Spectrometry, Hamilton, Canada or in house; calculated and reported mass:charge ratios are reported for the most intense signal of the isotopic pattern. Melting points were obtained on samples sealed in glass capillaries under dry nitrogen using an Electrothermal® Melting Point Apparatus. Elemental analysis was performed by Atlantic Microlabs, Norcross, Georgia, USA.

General Synthetic Route to potassium phosphinocyclopentadienides

A solution of the given chlorophosphine (10.2 mmol) in Et₂O (ca. 30 mL) was canulated to a solution containing 2 M NaCp in THF (10 mmol) and Et₂O (ca. 15 mL) at -30 °C. Upon addition, each solution undergoes a color change specific to the phosphine employed and the resulting reaction mixture was stirred for 2 hours. The reaction mixture was filtered through celite to remove any sodium chloride and was then subsequently
washed with Et₂O. The filtrate was evacuated under reduced pressure to remove the volatile components, which afforded various colored oils. Toluene was added to the oils, which were then cooled to -78 °C. KNTMS₂ (10.4 mmol) was dissolved in toluene and was slowly added to the cold solution containing the oils. The resultant solutions afforded a white precipitate and Et₂O was added after 1 hour of stirring and the solution was allowed to stir for an additional 3 hours. The resulting solids were filtered and washed with ether; any remaining volatile components were removed in under reduced pressure to afford white solid powders of the potassium phosphinocyclopentadienides. The reactions are quantitative as assessed by ³¹P NMR; the specific observations and characterization data for the materials are detailed below.

**Specific Procedure**

**Potassium (diphenylphosphino)cyclopentadienide, (4.1)**

Reagents: NaCp (5.0 ml, 10.0 mmol); ClPPh₂ (2.251 g, 10.2 mmol); KNTMS₂ (2.074 g, 10.4 mmol). Reaction mixture color changes: initially red and gradually became orange. A white precipitate appeared upon the addition of KNTMS₂. Product: white solid powder characterized as 1. 97% (2.800 g, 0.97 mmol). ³¹P{¹H} NMR (THF-d₈): δ -17.65; ¹H NMR (THF-d₈): δ 7.33-7.29 (m, 4H, Ph-ortho); 7.14-7.07 (m, 8H, Ph-meta/para); 5.97-5.87 (m, 4H, C₅H₄); ¹³C{¹H} NMR (THF-d₈): δ 147.26 (d, J_PC = 13.2 Hz, Ph-ipso); 133.72 (d, J_PC = 18.3 Hz, Ph-ortho); 127.98 (d, J_PC = 6.2 Hz, Ph-meta); 126.70 (s, Ph-para); 114.44 (d, J_PC = 22.7 Hz, C₂ in C₅H₄P); 109.1 (d, J_PC = 10.1 Hz, C₃ in C₅H₄P); 104.78 (d, J_PC = 4.2 Hz, C₁ in C₅H₄P). HRMS: calcd for C₁₇H₁₄P 249.0840, found 249.0833 (-2.8 ppm).
Potassium (diisopropylphosphino)cyclopentadienide, (4.2)

Reagents: NaCp (5.0 ml, 10.0 mmol); ClP(i-Pr)₂ (1.557 g, 10.2 mmol) ; KNTMS₂ (2.074 g, 10.4 mmol). Reaction mixture color changes: initially red and gradually became peach. A white precipitate appeared upon the addition of KNTMS₂. Product: white solid powder characterized as 2. 96% (2.106 g, 0.96 mmol). ³¹P{¹H} NMR (THF-d₈): δ 0.66; ¹H NMR (THF-d₈): δ 5.81-5.75 (m, 4H, C₅H₄); 1.83 (sept, 2H, J₃H=7.0 Hz, J₅H=1.2 Hz, CH); 0.99-0.88 (m, J₃H= 7.0 Hz, 12H, CH₃); ¹³C{¹H} NMR (THF-d₈): δ 113.62 (d, J₉C = 18.5 Hz, C₂ in C₅H₄P); 107.25 (d, J₉C = 8.0 Hz, C₃ in C₅H₄P); 104.19 (s, C₁ in C₅H₄P). 23.19 (s, CH); 21.31 (d, J₉C = 19.6 Hz, CH₃); 21.10 (d, J₉C = 9.1 Hz, CH₃). HRMS: calcd for C₁₁H₁₈P⁻ 181.1169, found 181.1146 (-12.7 ppm).

K(CpPPh₂)₂P, (4.3)

A solution containing two equivalents of KCpPPh₂ (0.110 g, 0.38 mmol) in THF (ca. 5 mL) was added to a flask containing one equivalent of dppePBr (0.097 g, 0.19 mmol) in THF (ca. 5 mL) at -30°C. The solution gradually became yellow and was allowed for 3 hours. The reaction mixture was filtered to remove any impurities and was then washed with pentane. The resultant yellow powder contained K(CpPPh₂)₂P and dppe. Any attempts to remove one of the two products have proven to be unsuccessful. ³¹P{¹H} NMR (THF): δ 20.01 (d, J₉P,P = 465 Hz); -162.14 (t, J₉P,P = 465 Hz); -11.98 (dppe). HRMS: calcd for C₃₄H₂₈P₃⁻² 529.1387, found 529.1404 (+3.2 ppm).

K(CpP-iPr)₂P, (4.4)

A solution containing two equivalents KCpP-iPr₂ (0.110 g, 0.50 mmol) in THF (ca.
5 mL) was added to a flask containing one equivalent of dppePBr (0.127 g, 0.25 mmol) in THF (ca. 5 mL) at -30°C. The solution gradually became light yellow and was allowed for 3 hours. The reaction mixture was filtered to remove any impurities and was then washed with pentane. The resultant pale yellow solid contained K(CpP-iPr₂)₂P and dppe. Any attempts to remove one of the two products have proven to be unsuccessful. ³¹P {¹H} NMR (THF): δ 39.39 (d, J_P-P = 511 Hz); -220.60 (t, J_P-P = 511 Hz); -11.98 (dppe). HRMS: calcd for C₂₂H₃₆P₃² 393.2026, found 393.2030 (+1.0 ppm).

**Potassium 1,3-bis(diphenylphosphino)cyclopentadienide, (4.5)**

A solution of chlorodiphenylphosphine (2.306 g, 10.05 mmol) in toluene (ca. 80 mL) was canulated to a solution containing the previously prepared KCpPPh₂ (2.955 g, 10.2 mmol) in toluene (ca. 20 mL) at -78 °C. Upon addition, the solution undergoes a color change to orange and gradually became yellow over time. The resulting solution was allowed to stir for 2 hours whereby it was then filtered through celite to remove the potassium chloride and was then subsequently washed with toluene (ca. 10 mL). The filtrate was cooled to -78°C, where KNTMS₃ (2.125 g, 10.7 mmol) was then dissolved in toluene (ca. 30 mL) and was slowly added to the cold filtrate. The resultant solution afforded a white precipitate and was refluxed for 3 hours. Et₂O (ca. 50 mL) was then added to the solution and was allowed to stir for an additional hour. The resulting solid was filtered and washed with ether (ca. 50 mL) and then any remaining volatile components were removed from the solid under reduced pressure to afford a white powder of the KCp(PPh₂)₂ characterized as 5. 99% (4.800 g, 10.2 mmol). ³¹P {¹H} NMR (THF-d₈): δ -18.25; ¹H NMR (THF-d₈): δ 7.36-7.30 (m, 4H, Ph-ortho); 7.17-7.10 (m, 8H,
Ph-meta/para); 7.36-7.30 (m, 1H, C₅H₃); 7.17-7.10 (m, 2H, C₅H₃); ¹³C{¹H} NMR (THF-d₈): δ 146.00 (d, J₂₃ = 13.1 Hz, Ph-ipo); 133.80 (d, J₂₃ = 19.2 Hz, Ph-ortho); 128.15 (d, J₂₃ = 5.7 Hz, Ph-meta); 127.13 (s, Ph-para); 124.00 (t, J₂₃ = 20.1 Hz, C in C₅H₃P₂); 117.32-116.97 (dd, J₂₃ = 18.2 Hz, C in C₅H₃P₂); 110.36 (d, J₂₃ = 9.0 Hz, C in C₅H₃P₂). HRMS: calcd for C₂₉H₂₃P₂-433.1283, found 433.1275 (-1.8 ppm).

[-C₅H₃-PPh₂-P-PPh₂]₂, (4.6)

To a flask containing dppePBr (1.500 g, 2.95 mmol) in THF (20 mL) was added a solution of KCp(PPh₂)₂ (1.391 g, 2.95 mmol) in THF (30 mL) at -78°C. The reaction mixture was stirred for 2 hours before the resulting KBr was removed by filtration. The volatile components were removed from the filtrate under reduced pressure to give a crude product, which was washed in ether and sonicated for 1h. The product crashed out of ether and was collected by filtration, removal of the volatile components provided a pale yellow solid. 95% (1.300 g, 1.4 mmol). Crystals suitable for X-ray diffraction were obtained by dissolving the powder in CH₂Cl₂ followed by vapor diffusion with Et₂O. ³¹P{¹H} NMR (THF-d₈): δ 19.71 (d, ¹J₃₁=P = 459 Hz), -148.40 (t, ¹J₃₁=P = 459 Hz); ¹H NMR (THF-d₈): δ 7.74-7.68 (m, 8H, Ph-ortho); 7.34-7.20 (m, 12H, Ph-meta/para); 6.21 (s, 1H, C₅H₃); 5.84 (s, 2H, C₅H₃); ¹³C{¹H} NMR (THF-d₈): δ 134.86 (d, J₂₃ = 16.3 Hz, Ph-ipso); 133.55 (d, J₂₃ = 3.5 Hz, Ph-ortho); 131.22 (s, Ph-meta); 128.63 (s, Ph-para); 119.20 (broad singlet, C in C₅H₃P₂); 97.65 (broad singlet, C in C₅H₃P₂); (C₁ in C₅H₃P₂ not visible). Mp. 164-168 °C.
To a flask containing NH(PPh$_2$)$_2$ (1.000 g, 2.59 mmol) in THF (50 mL) was added 1.3 equivalents of n-Buli (1.62 mL, 3.37 mmol) via syringe at -78°C. The reaction mixture was stirred for 2 hours and was then added to a -78°C solution of dppePBr (1.321 g, 2.59 mmol) in THF (20 mL). The reaction was allowed to stir overnight before the resulting solid was filtered and washed with hexane, which yielded a yellow solution containing dppe. The solvent was removed under reduced pressure and the subsequent paste was then sonicated for 1 hour in hexane and was filtered and washed with hot hexane (100 mL) to give the pale yellow oligomeric solid. 79% (0.850 g, 1.02 mmol).

$^{31}$P{$^1$H} NMR (THF-d$_8$): $\delta$ 35.52 (d, $\text{J}_{P-P} = 423$ Hz), -140.22 (t, $\text{J}_{P-P} = 422$ Hz); $^1$H NMR (THF-d$_8$): $\delta$ 7.66-7.59 (m, 2H, Ph-meta); 7.12-7.09 (m, 1H, Ph-para); 7.10-6.98 (m, 2H, Ph-ortho); $^{13}$C{$^1$H} NMR (THF-d$_8$): $\delta$ 134.86 (d, $\text{J}_{PC} = 16.3$ Hz, Ph-ipso); 133.55 (d, $\text{J}_{PC} = 3.5$ Hz, Ph-ortho); 131.22 (s, Ph-meta); 128.63 (s, Ph-para); 119.20 (broad singlet, C in C$_5$H$_3$P$_2$); 97.65 (broad singlet, C in C$_5$H$_3$P$_2$); (C$_1$ in C$_5$H$_3$P$_2$ not visible).

**X-Ray Crystallography**

Each crystal was covered in Nujol and placed rapidly into a cold N$_2$ stream of the Kryo-Flex low temperature device. The data were collected using the SMART$^{[12]}$ software package on a Bruker APEX CCD diffractometer employing a graphite monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) source. Hemispheres of data were collected using counting times of 10-30 seconds per frame at -100 °C. The details of crystal data, data collection, and structure refinement are listed in Table 1. Data reductions were performed using the SAINT$^{[13]}$ software package and the data were corrected for absorption using SADABS.$^{[14]}$ The structures were solved by direct methods.
using SIR97\textsuperscript{[15]} and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the non-H atoms using SHELXL-97\textsuperscript{[16]} and the WinGX software package and thermal ellipsoid plots were produced using SHELXTL.\textsuperscript{[16]}

**Table 4.1.** Summary of X-ray crystallographic data for [-N-PPh$_2$-P-PPh$_2$-]$_2$, 4.7, and [-P-PPh$_2$-P-PPh$_2$-], 4.6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>[-N-PPh$_2$-P-PPh$_2$-]$_2$</th>
<th>[-P-PPh$_2$-P-PPh$_2$-]$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$C_{48}H_{40}N_2P_6$</td>
<td>$C_{58}H_{46}P_6$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1830.46</td>
<td>928.77</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>173(2)</td>
<td>173(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Habit, Color</td>
<td>Prism, Colourless</td>
<td>Block, Yellow</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2/c</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>12.153(2)</td>
<td>8.8372(9)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>9.3574(16)</td>
<td>11.4766(11)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>23.480(3)</td>
<td>12.3849(12)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>90</td>
<td>74.9890(10)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>121.056(6)</td>
<td>72.7390(10)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>90</td>
<td>80.5240(10)</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>2287.4(6)</td>
<td>1153.3(2)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Density (calculated) (g cm$^{-3}$)</td>
<td>1.329</td>
<td>1.337</td>
</tr>
<tr>
<td>Absorption coefficient (mm$^{-1}$)</td>
<td>0.389</td>
<td>0.274</td>
</tr>
</tbody>
</table>
F(000) | 948 | 484
\(\theta\) range for data collection (\(^\circ\)) | 1.96 to 27.50 | 1.77 to 27.48
Limiting indices | \(-15 \leq h \leq 15,\) | \(-11 < h < 11,\)
| \(-12 \leq k \leq 12,\) | \(-14 < k < 14,\)
| \(-30 \leq l \leq 29\) | \(-15 < l < 15\)
Reflections collected | 24927 | 12634
Independent reflections | 5195 | 5068
\(R_{int}\) | 0.0265 | 0.0430
Absorption correction | SADABS | SADABS
Refinement method | Full-matrix least-squares on \(F^2\)
Data / restraints / parameters | 5195 / 0 / 271 | 5068 / 0 / 289
Goodness-of-fit on \(R^2\) | 1.149 | 1.196
Final \(R\) indices\(^8\) | \(R1 = 0.0400,\) | \(R1: 0.0676,\)
\([I > 2\sigma(I)]\) | \(wR2 = 0.1052\) | \(wR2: 0.1661\)
\(R\) indices (all data) | \(R1 = 0.0452\) | \(R1: 0.0823,\)
| \(wR2 = 0.1138\) | \(wR2: 0.1831\)
Largest difference map peak and hole (e Å\(^{-3}\)) | 0.556 and -0.302 | 0.432 and -0.466

\(^8\)R1(F): \(\Sigma(F_o - |F_c|)/\Sigma|F_o|\) for reflections with \(F_o > 4\sigma(F_o)\). wR2(F\(^2\)): \(\{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2\}^{1/2}\) where \(w\) is the weight given each reflection.

### 4.3 Results and Discussion

Our recent success in producing facile and quantitative routes to small phosphenium and triphosphenium systems has led us to develop an alternative approach to producing larger phosphorus-containing macromolecules. It should be noted that Schmidpeter \textit{et al.} were able to make one of the types of compounds we have targeted through the reaction of phosphinous amide with elemental phosphorus (Figure 4.3),\(^{[17]}\) however this reaction yielded multiple products and the use of white phosphorus is a less than desirable reaction condition.
We had hoped that the readily-prepared, air-stable P(I) precursor might provide a more convenient and general route to such species. Building upon Schmidpeter’s synthesis, we were successfully able to synthesize the same dimer using ligand substitution, a well-developed method for the exchange of the phosphine ligands supporting the P(I) centers, and it is this methodology we employ to produce various low oxidation state phosphorus oligomers. We first targeted this dimer by adding bis(diphenylphosphino)amine with [dppeP][Br] (i.e. P(I) salt) at -78 °C followed by dropwise addition of n-butyl lithium. It was found that after several hours the product precipitated out of solution and was isolated by filtration (Figure 4.4). The $^{31}$P NMR yielded a spectrum that contained the desired product as well as the impurity dppe. The solubility of dppe is very similar to that of most phosphorus-containing compounds we encounter, and thus presents a formidable challenge to remove.

Despite being able to make the dimer based on $^{31}$P NMR studies, we still desired to pursue a more clean and effective synthetic approach whereby the dppe impurity could be removed and the product could be isolated and characterized. Metalated phosphinous
amide is notoriously difficult to isolate and because of this it was used as an in situ reagent during our second attempt. Excess n-butyl lithium was added to the hydrogenated amide and allowed to stir for an hour, the resulting solution was added to a cold solution of P(I) salt. The resultant dimer precipitated from solution and was subsequently sonicated in hexane and filtered with hot hexane to remove the dppe, and pure dimer 4.7 was produced in good yield (Figure 4.5).

![Diagram](image)

**Figure 4.5.** Modified synthetic route to clean [-N-PPh₂-P-PPh₂⁻]₂.

While this product had been obtained previously, the $^{31}$P NMR spectrum of the compound we obtained (4.7) is surprisingly not consistent with the values reported by Schmidpeter and co-workers. They reported the oligomer as having an AA’A’’A’’’BB’’ spin system, however we see a spectrum for an AX₂ spin system, which corresponds to a doublet and triplet as one would expect (Figure 4.6A). Schmidpeter had reported a crystal structure of the oligomer from CH₂Cl₂ and, in order to confirm that we had indeed produced the same compound in light of the differences in the spectral data, we crystallized the compound produced using our method and determined the single-crystal X-ray structure as illustrated in Figure 4.6B. The structure is indistinguishable from that reported previously and, although it confirms the viability of our synthetic approach, the reason for the different $^{31}$P NMR spectra remains unanswered.
Figure 4.6. A. $^{31}$P NMR spectrum of 4.7 as obtained by our ligand exchange approach. B. Ball and stick illustration of the contents of the asymmetric unit 4.7. The hydrogen atoms and dichloromethane solvent of crystallization have been removed for clarity. Selected interatomic distances [Å]: P(1)-N(1) 1.5955(14), P(3)-N(1’) 1.6023(15), P(1)-P(2) 2.1390(6), P(3)-P(2) 2.1310(6). Selected bond angles [°]: P-P-P 95.44(3), P-N-P 130.94(9).

In order to prove the generality of our synthetic approach for the preparation of oligomers based on anionic linkers, we targeted the oligomers derived from the non-chelating 1,3-diphosphinocyclopentadienide ligand. The presence of a cyclopentadiene group acts as the anionic linker, which is essential in the production of the neutral target complexes. First, we consulted the literature for the synthesis of lithium (diphenylphosphino)cyclopentadienide. It was stated by Brasse and coworkers that [Li][Cp(PPh$_2$)] could be isolated by adding equimolar amounts of NaCp and ClPPh$_2$ in ether at -30 C, followed by filtration and the subsequent addition of one equivalent a $n$-BuLi (Figure 4.7).\textsuperscript{18} Unfortunately we were unable to reproducibly obtain substantially
pure material using this procedure, but nonetheless we used this material to synthesize our target ligand.

Figure 4.7. Initial synthesis used to produce [Li][Cp(PPh₂)] using the procedure from Brasse et al.

The second step in the ligand synthesis was adding a second phosphine group in order to produce a ligand that would be suitable for exchange with the P(I) salt. Again, we also consulted the literature procedure\textsuperscript{[19]} and upon synthesis there were again several products in the phosphorus NMR (Figure 4.8).

Figure 4.8. Initial synthesis used to produce [Li][Cp(PPh₂)₂] using the procedure from Broussier et al.

Although we were unable to initially obtain pure starting reagents, we decided to use the [Li][Cp(PPh₂)₂] mixture in a ligand substitution reaction with our previously synthesized P(I) salt. We had hoped that the resulting oligomer would exhibit an alternative solubility and that it may be easily separated from the initial impurities present
in the reaction mixture. It was found that by adding P(I) salt to the impure [Li][Cp(PPh₂)₂] in THF (Figure 4.9), we could obtain what appeared to be two oligomeric products and a variety of other peaks including dppe as seen in the ³¹P NMR spectrum in Figure 4.10.

![Figure 4.9. Initial synthetic route to Cp-containing macromolecules.](image)

**Figure 4.9.** Initial synthetic route to Cp-containing macromolecules.

![Figure 4.10. ³¹P NMR spectrum of the products from the reaction of LiCp(PPh₂)₂ with our P(I) salt, which indicates two separate sets of triphosphromium peaks.](image)

**Figure 4.10.** ³¹P NMR spectrum of the products from the reaction of LiCp(PPh₂)₂ with our P(I) salt, which indicates two separate sets of triphosphonium peaks.

In addition to ligand exchange reactions, we also desired to make the oligomer using our PBr₃ and cyclohexene approach that was discussed in detail in Chapter 2. This approach is potentially useful because the elimination 1,2-dibromocyclohexane is easily accomplished *in vacuo* whereas for the P(I) salt ligand exchange reactions, a method to
remove dppe must be investigated, which depending on product solubility, may be a tedious task. Thus, using the same reaction conditions as above, PBr$_3$ and cyclohexene were added to a solution of impure [Li][Cp(PPh$_2$)$_2$] and according to the $^{31}$P solution NMR spectrum (Figure 4.11), there was a set of peaks that corresponded to a single triphosphenium complex as well as a variety of other unidentifiable products. We tried various purification methods but were never successful in obtaining pure product. We postulated that this triphosphenium peak may be the trimer of the desired target complex, but we had no other forms of identification to aid in our hypothesis.

![Figure 4.11. $^{31}$P NMR spectrum of the products of the reaction of LiCp(PPh$_2$)$_2$ with PBr$_3$ and excess cyclohexene, indicating one set of triphosphenium peaks.](image)

Although there are two reported syntheses for the production of lithium (diphenylphosphino)cyclopentadienide, we were unable to produce sufficiently pure enough ligands viable for further use and thus we decided to undertake the development
of a superior approach to the preparation of such ligands. The synthesis described by Brasse et al. stated above produced the best results so we used this as a starting point and changed from metalating with $n$-BuLi in THF to a milder base KNTMS$_2$ in toluene. Our modified synthesis produced the potassium variant in quantitative yield with absolutely no by-products observed whatsoever and is supported by a variety of microanalytical tests.

To produce the bisphosphine ligand, we used the synthesis by Broussier and coworkers as a starting point and changed a few of the reaction conditions. Again, we used KNTMS$_2$ instead of $n$-BuLi as our metalating agent and used a solvent mixture of 1:1 toluene to diethylether instead of just toluene.

**Scheme 4.1.** Our improved synthetic routes to $[\text{K}][\text{Cp}(\text{PPh}_2)]$ (4.1) and $[\text{K}][\text{Cp}(\text{PPh}_2)_2]$ (4.5).

This protocol generates the desired compounds in essentially quantitative yield with no side products observed. The anionic diphosphine ligand was subsequently used in the ligand substitution reaction with our previously synthesized P(I) salt.

$^{31}\text{P}$ NMR spectroscopy reveals that when a THF solution of 1,3-bis(diphenylphosphino)cyclopentadienylpotassium is mixed with a THF solution of
dppePBr, the desired oligomer 4.6 is produced (Figure 4.12), as well as the contaminant by-product dppe. In order to remove the dppe, an extensive solubility study was performed with various solvents until a suitable combination was found that would separate the two products. We found that by sonicating the mixture in diethylether, the product macrocycle precipitates out of solution and may be collected as a pure product by filtration (Figure 4.13). It is worth noting however that the sonication of the mixture for an extensive period (more than a few hours) results in the precipitation of some dppe along with the desired product.

![Synthetic route to the Cp-containing macrocycle.](image1)

**Figure 4.12.** Synthetic route to the Cp-containing macrocycle.

![31P solution NMR spectrum of 4.6, our cyclopentadienide containing macrocycle.](image2)

**Figure 4.13.** $^{31}$P solution NMR spectrum of 4.6, our cyclopentadienide containing macrocycle.
The recrystallization of the product generated crystals suitable for examination by single-crystal X-ray diffraction. The details of the data collection and refinement can be found in Table 4.1. The macrocycle crystallizes in the space group \( P-1 \), with half of the molecule present in the asymmetric unit; the complete molecular structure is depicted in Figure 4.14. The metrical parameters of the oligomer fall within the ranges of P-P bond distances for previously reported cyclic triposphenium complexes\(^{[10, 20-24]} \) (2.113(2) - 2.184(2) Å) found in the CSD. In addition, the P-P-P bond angle lies in accordance with other reported triphosphenium complexes.\(^{[10, 21, 23, 25]} \) 5 and 6-membered cyclic triphospheniums range from 86.44(8)° - 88.37(7)°, and 93.76(5)° - 98.30(5)°, respectively, while the acyclic 1,1,1,3,3,3-hexaphenytriphosphenium tetrachloroaluminate is 102.16(5)°. Our dimer has a P-P-P angle of 100.83(5)°, which fits nicely between the cyclic and acyclic examples found in the literature. The distance between the two cyclopentadienyl rings (3.200 Å) is in a comparable range to ferrocene (3.317 Å) and cobaltocene (3.21 - 3.25 Å) and thus allows us to believe that this may potentially be an ideal ligand to coordinate various metal centres.\(^{[26]} \) The simulated powder XRD pattern of the dimer is in good agreement to that of the bulk sample and confirms that sample contains only a single crystalline product (Figure 4.15).
Figure 4.14. Thermal ellipsoid plot (30% probability plot) of the contents of the cyclopentadienide containing dimer (6), hydrogen atoms omitted for clarity. Selected interatomic distances [Å]: P101-P103 2.1583(13), P102-P103 2.1259(13). Selected bond angles [°]: P102-P103-P102 100.83(5). Ball and stick diagram showing the distance between the two Cp rings (3.200 Å).

Figure 4.15. Powder XRD pattern of 4.6, experimental pattern (left) and the simulated (right).

We undertook the task of analyzing the donor ability of the P(I) centers by adding the Lewis acids; borane and boron trifluoride. Although at first glance this presents as a simple study, the high molecular weight of the dimer 4.6 makes small to moderate sized reactions awkward due to the minuscule amount of Lewis acid that is needed. Despite this, we added two equivalents of BH$_3$ to one equivalent of the Cp-containing dimer (which
contains two P(I) centers). Suprisingly, there was no interaction between the two reactants and the $^{31}$P NMR showed unreacted starting material. More interestingly however, the analogous reaction with BF$_3$ produced a shifted doublet from 19 ppm in the dimer to ~62.5 ppm in the donor-acceptor complex and a triplet shifted from -148 ppm to -205 ppm as observed in $^{31}$P NMR spectrum in Figure 4.16. The coupling constant increases from 462 Hz to 503 Hz which may be explained by the increased steric crowding around the P(I) centers.$^{[27]}$ Unfortunately we were unable to isolate sufficiently pure material, but overall this spectrum shows the utility of P(I) centers as potential donors for Lewis acids. These types of studies would be more ideal with a dimer that has smaller R-groups, such as ethyl, on the phosphorus substituents as this would greatly reduce the molecular weight.

![Figure 4.16. $^{31}$P solution NMR spectrum of 6 + two equivalents of BF$_3$.](image)

Ultimately, our goal is to extend these small oligomeric materials into polymers that may offer new and unique properties that organic polymers may not possess. We started by first attempting thermal ring-opening polymerization (ROP) by heating our Cp dimer at 250 °C for 3 hours. We found that the product resulted in a black plastic like
substance that was insoluble in every solvent, however during the course of the reaction a pink volatile was given off and was collected by distillation. We were able to obtain a single crystal suitable for X-ray diffraction and found this product was actually pentaphenyl cyclopentaphosphine (Figure 4.17), which has been known for decades. The Burford group has recognized that the catenation of carbon is essentially responsible for the diversity of organic chemistry and that the similar electronegativities of phosphorus and carbon, as well as their “diagonal relationship” in the Periodic Table, has lead to the development of catena-phosphorus frameworks from pentaphenyl cyclopentaphosphine and similar derivatives (Figure 4.18).\textsuperscript{[28-33]} Also interesting, pentaphenyl cyclopentaphosphine has been recently employed as an additive in some polymerization materials as oligophosphenes show good flame retardance.\textsuperscript{[34, 35]}

\textbf{Figure 4.17.} Ball and stick representation of pentaphenyl cyclopentaphosphine, $P_5\text{Ph}_5$. Hydrogens have been omitted for clarity for the structure on the right.
Figure 4.18. Examples of common catena-phosphorus cations.

It should be noted that the lack of success in our thermal ROP studies does not come as a surprise as nearly all polyphosphazenes that are polymerized in this manner results from the ionization of halogen (usually chloride) followed by electrophilic attack. Thus, an ideal target oligomer to aid in polymerization would obviously be the chlorinated analogue of 6. One plausible synthesis for this complex would be to make the 1,3-bis[(bisdiethylamino)phosphino] cyclopentadienide ligand followed by the ligand exchange reaction with our P(I) salt. Subsequent exposure to HCl (g) should afford the desired chlorinated monomer (Figure 4.19).

Figure 4.19. Potential synthetic route to a more desirable monomer for thermal ROP.

In addition to thermal ROP studies, we have attempted anionic ROP using $n$-Buli and MeOTf but unfortunately all of our results seem to indicate that the dimer was completely broken apart and in every case, there was no less then a dozen peaks in the $^{31}$P NMR
spectrum of each reaction. To date, we have still been unable to polymerize our
cyclopentadienide-containing dimer.

We have endeavored to extend the methodology used to synthesize
1,3-bis(diphenylphosphino)cyclopentadienide (4.5) to produce a variety of other
phosphine-containing cyclopentadienyl ligands with alternative substituents on the
phosphorus atoms. Using the methodology described above, we attempted to synthesize
the related 1,3-bis(phosphino)cyclopentadienides using chlorodiisopropylphosphine and
bis(diethylamino)chlorophosphine. Both failed to give the desired
1,3-bis(phosphino)cyclopentadienide ligands but were successful in the production of the
mono-phosphine substituted cyclopentadienide. We decided to use the
mono-diisopropylphosphine substituted ligand with the methods above in order to
produce the corresponding anionic triphosphenium species. There are various compounds
that contain multiple phosphorus atoms bonded together and contain a negative charge,
such as the phosphinylidenephosphinates and phosphinoylphosphides (Figure 4.20), but
our new compounds represent the first examples of an anionic triphosphonium salts.

![Figure 4.20. Phosphinylidenephosphinates(left) and phosphinoylphosphides(right).](image)

We observed that the reaction of the potassium
(diisopropylphosphino)cyclopentadienide ligand with [(dppe)P][Br] took much longer
than that of the related phenyl version. We were thus fortunate enough to be able to
spectroscopically hypothesize the intermediates of the reaction mixture by continually
monitoring the $^{31}$P NMR spectrum. Luckily we were able to elucidate the mechanism of the formation of the anionic triphosphenium as illustrated in Scheme 4.2. It should be noted that Dillon et al. were able to follow the mechanism of formation for cyclic triphosphenium ions by $^{31}$P NMR only for alkylated phosphine ligands because of their relatively sluggish rates compared to those of aryl phosphine ligands.$^{[36]}$ Thus an NMR sample containing dppePBr in THF was frozen in liquid nitrogen. To this was added KCpP-$^i$Pr$_2$ in THF and was also frozen, the sample was then sealed and subsequent NMR spectra were acquired. As illustrated in Figure 4.21, even after 15 minutes the doublet (39.39 ppm, 511 Hz) and triplet (220.60 ppm, 511Hz) corresponding to the triphosphenium were present but only at very low intensity. The most informative set of peaks are that of free and complexed 1,2-bis(diphenylphosphino)ethane peaks near -12 ppm and the doublet of doublets at -194.77 ppm (505 Hz), which we believe corresponds to the unsymmetrical intermediate. As the reaction proceeds, it becomes evident the asymmetrical intermediate is consumed and the product is formed. There are slight impurities at around -2.0 ppm that remain unidentified and are difficult to completely wash out from an NMR scale reaction but are easily removed by washing with pentane when the reaction is done on a larger scale.
**Scheme 4.2.** Reagents, intermediate products and products observed by $^{31}$P NMR for substitution reaction.

**Figure 4.21.** Stackplot of $^{31}$P NMR spectra for the reaction of dppePBr + KCpP$^\text{iPr}_2$.

In addition to producing the nitrogen and cyclopentadienide containing dimers, we had wished to extend our class of anionic linkers to include a carbanion. We again
consulted the literature hoping to find a facile synthetic procedure for the preparation of metalated bis(diphenylphosphino)methane compounds. A simple search for bis(diphenylphosphino)methyllithium in SciFinder yielded twenty-one results from 1970 to 2010. We were initially pleased with this finding but upon further review, it became apparent that this might be a challenging complex to synthesis. We were unable to find extensive information on reaction conditions, as most of the references stated the product could be produced by adding $n$-BuLi to dppm. Products were only characterized by $^{31}$P NMR. Most of the references also used this complex as an in situ reagent and did not actually isolate any [Li][dppm] as starting materials. It emerged that every reference came back to one paper entitled “Reactions of bis(diphenylphosphine)methyllithium and bis(diphenylphosphinyl)methyllithium” by Issleib and Abicht. One specific author references this article and states “lithium bis(diphenylphosphanyl)methanide has been well-known for nearly forty years.” Based on the title by Issleib and Abicht, and the statement by Westerhausen et al., we were very encouraged to gain new insight into the synthesis of the desired starting material. Issleib and Abicht stated that [Li][dppm] could be made from the exothermic reaction of dppm and $n$-BuLi in ether. Again, after attempting to replicate this procedure well over ten times, we were never able to produce a product other than unreacted dppm in our $^{31}$P NMR spectrum. The paper has no mention of any spectroscopic data, such as NMR, and only an elemental analysis was carried out for lithium and phosphorus in the benzene adduct of [Li][dppm]. The expected percentage of lithium and phosphorus for the benzene adduct is 1.48% and 13.22% respectively, whereby the reaction was found to actually contain 1.42% and 13.30% of lithium and phosphorus. These values are also very close to that of a mixture of unreacted dppm and $n$-BuLi (1.55% Li and 13.81% P). Unfortunately, it appears this complex does not seem
to be as “well-known” as previously stated. Since the publication of the original paper, there have been various reports of crystal structures of the etherate, THF, and TMEDA adducts of \([\text{Li}][\text{dppm}]\), but the details of their synthesis and characterization remains vague. The identity of the single crystal does not conclude the bulk material was actually \([\text{Li}][\text{dppm}]\).

Thus, this led us to attempt to elucidate the best reaction conditions for the formation of \([\text{Li}][\text{dppm}]\) and an extensive study was performed (Table 4.2). We found that the addition of \(n\)-BuLi to dppm (as per Issleib and Abicht) in a variety of different solvents all produced no reactions as the \textit{in situ} \(^{31}\text{P}\) NMR revealed unreacted dppm on every occasion. We decided to proceed to use a stronger base, \(t\)-BuLi, but again there was no reaction. We did however have limited success using excess amounts of \(t\)-BuLi but the reaction mixture contained multiple products that we were unable to isolate, but promisingly the majority peak was \([\text{Li}][\text{dppm}]\). During this tedious study, we found that the only way to synthesize pure \([\text{Li}][\text{dppm}]\) was to use a two and a half fold excess of \(t\)-BuLi and with excess TMEDA to quantitatively afford \([\text{Li}][\text{dppm}][\text{TMEDA}]\).
Table 4.2. A comprehensive study of the synthesis of [Li][dppm].

<table>
<thead>
<tr>
<th>Reagents (dppm +)</th>
<th>Solvent</th>
<th>Additional Reaction Conditions</th>
<th>$^{31}$P NMR shifts (majority peak bolded)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-BuLi</td>
<td>THF/Ether</td>
<td>Refluxed o/n</td>
<td>-21(s) (dppm)</td>
</tr>
<tr>
<td>$n$-BuLi/TMEDA</td>
<td>THF</td>
<td>Stir o/n</td>
<td>-21(s)</td>
</tr>
<tr>
<td>$t$-BuLi</td>
<td>THF</td>
<td>Stir o/n</td>
<td>-21(s)</td>
</tr>
<tr>
<td>2 $t$-BuLi</td>
<td>THF</td>
<td>Stir o/n</td>
<td>1.88(s), -8.36, -21(s), -26.34(s)</td>
</tr>
<tr>
<td>$t$-BuLi/TMEDA</td>
<td>Toluene</td>
<td>Refluxed o/n</td>
<td>1.14(s), -21(s)</td>
</tr>
<tr>
<td>$t$-BuLi/TMEDA</td>
<td>THF</td>
<td>Stir o/n</td>
<td>1.54(s), -21(s)</td>
</tr>
<tr>
<td>1.1 $t$-BuLi + 2 TMEDA</td>
<td>THF</td>
<td>Stir o/n over Na$^0$</td>
<td>2.23(s), -21(s)</td>
</tr>
<tr>
<td>2 $t$-BuLi + xs TMEDA</td>
<td>THF</td>
<td>Stir o/n</td>
<td>1.55(s), -21(s)</td>
</tr>
<tr>
<td>2.5 $t$-BuLi + 1.5 TMEDA</td>
<td>THF</td>
<td>Stir o/n</td>
<td>1.50(s)</td>
</tr>
<tr>
<td>NaNH$_2$/Na$^0$</td>
<td>THF</td>
<td>Refluxed o/n</td>
<td>-21(s)</td>
</tr>
<tr>
<td>Na$^0$</td>
<td>THF</td>
<td>Refluxed o/n</td>
<td>-21(s)</td>
</tr>
<tr>
<td>Li$^0$</td>
<td>THF</td>
<td>Refluxed o/n</td>
<td>-21(s)</td>
</tr>
<tr>
<td>MeLi</td>
<td>THF</td>
<td>Stir o/n</td>
<td>1.939(s), -21(s)</td>
</tr>
<tr>
<td>MeLi</td>
<td>Toluene</td>
<td>Stir o/n</td>
<td>-21(s)</td>
</tr>
<tr>
<td>$t$-BuOK + $t$-BuLi</td>
<td>Ether</td>
<td>Stir o/n</td>
<td>-0.39(s), -21(s)</td>
</tr>
</tbody>
</table>

Once being able to produce sufficiently pure starting material, we focused on producing the desired macrocycle. We began ligand exchange reactions of the TMEDA
complex of [Li][dppm] with our P(I) salt as in accordance with the oligomer 6. Unfortunately, during the reaction an orange insoluble product precipitates from solution which is postulated to be a polymer(s) of the form [PBr]ₙ. This did not come as a surprise as it is well known in our group that when P(I) salts are exposed to TMEDA, an insoluble orange product results. The same result also occurs when we try to utilize the PBr₃ and cyclohexene approach. This led us to again consult the literature, whereby we found a complicated procedure to produce the potassium salt of dppm. Here, Liddle and Izod added n-BuLi to a cold concentrated solution of dppm and potassium t-butoxide in ether. The resulting precipitate was stirred overnight and subsequently isolated by filtration to produce [K][dppm] in good yield. Unfortunately, we were again unable to replicate the outcome so we contacted the authors and they suggested we run our N₂ gas through a drying column before exposing it to our reaction mixture. This gave limited success, however we observed a major improvement of the product to unreacted dppe ratio by switching from using n-BuLi to t-BuLi. We observed about 60% conversion to [K][dppm]. Although having impure starting reagent is less than desirable, we used this product for further ligand exchange studies. To our surprise, when we added impure [K][dppm] to a THF solution of P(I) salt, we observed only two peaks in our ³¹P NMR, We characterized these peaks to be uncomplexed dppe and unreacted dppm that was present from the initial impure starting material. The solution mixture turns bright red and crashes out a small amount of precipitate. The precipitate does not produce any observable peaks when dissolved in CH₂Cl₂, presumably because this was KBr. This left us puzzled as to where the P(I) fragment and [K][dppm] disappeared to. As already stated, the solution turned a bright red colour which is atypical for reactions of this kind. Both dppe and dppm are colourless in solution and thus led us to believe that possibly the
intense colour and lack of $^{31}$P NMR signals was due to the formation of a radical species in solution. Subsequent electron paramagnetic resonance (EPR) studies were performed on the product, but amazingly we did not see any peaks corresponding to a radical species. This result has left us perplexed and still remains unexplained.

As other research groups have demonstrated to have success with [Li][dppm] as an *in situ* reagent, we decided to pursue this chemistry further. Not surprisingly, by adding *n*-BuLi to dppm with subsequent addition to our P(I) salt, no reaction was obtained. Fortunately, we found that by using *t*-BuLi and dppm *in situ* followed by addition of PBr$_3$ and cyclohexene, we finally observed a doublet at $\delta$ 24.93 and a triplet at -205.44 ppm in the $^{31}$P NMR spectrum (Figure 4.22).

![Figure 4.22. Reaction mixture of *t*-BuLi + dppm + PBr$_3$ and xs cyclohexene.](image)

Obviously, these peaks could correspond to a number of potential products but are most likely attributed to either our desired oligomer species, or possibly a four-membered dppm-triphosphenium (Figure 4.23), although the inherent ring strain would probably be a deterring factor for the formation of the latter. While the doublet and triplet appear to be the majority product, there remains a significant amount of impurities in the NMR
spectrum. The major impurity appears at 72.81 ppm, which corresponds to bromodiphenylphosphine. We found that as we try to isolate pure product, the bromodiphenylphosphine impurity peak seemingly gets larger as the product peaks become smaller until they eventually disappear. This result leads us to believe that we are forming an instable four-membered triphosphenium salt that is decomposing in solution.

![Figure 4.23. Possible products from the reaction of [Li][dppm] and PBr₃/cyclohexene.](image)

In order to gain more insight into the nature of the resulting product, we revisited some chemistry involving only protonated dppm. Before we conducted our extensive metalated dppm study, we found that the reaction of PBr₃ and cyclohexane with dppm in dichloromethane produced the insoluble orange polymer. This was somewhat expected as we didn’t envision the 4-membered ring to be a favorable product. For obvious reasons we cannot make the *in situ* t-BuLi/dppm reagent in dichloromethane and thus we subsequently found that the reaction proceeded best when toluene was used as the solvent. We felt it was imperative to test the reaction of dppm with PBr₃ and cyclohexane in toluene in case this was possibly a potential reaction product. To our suprise, the reaction mixture provided the same results as we had seen earlier. The doublet and triplet appear at the same chemical shift and again, bromodiphenylphosphine was the majority impurity. Again, these shifts could potentially correspond to a four- or even an eight-membered ring but the inherent instability of the resultant material leads us to believe that the four-membered species may be the most reasonable hypothesis. Obviously, further
experiments and insight is required and obtaining mass spectrometry results would be very desirable.

4.4 Conclusions

In summary, we have demonstrated that ligand exchange using our stable P(I) reagents is a viable synthetic approach for the preparation of electron-rich phosphorus-rich cyclic oligomers. The use of this protocol for the generation of such macrocycles appears only to be constrained by the preparation of suitable diphosphine ligands. We are currently evaluating a variety of methods for the reliable production of larger oligomers and the related polymeric species. Furthermore, the macrocycles presented herein are also being studied to examine the chemical functionalities of the Cp ring with metals such as Fe, Co, and Mn.

4.5 References


5.1 Introduction

Ferrocenophanes are a result of ferrocene derivatives that have two cyclopentylidienyl rings linked by one or more bridging atoms. The first example of this was synthesized in the 1960 by Rinehart et al. whereby a ferrocene unit was linked by a two atom hydrocarbon to produce [2]ferrocenophane (Figure 5.1). It was initially believed that the two Cp rings could not be bridged by a single atom due to the inherent ring strain that would be generated but it was later proven by Osborne in 1975 that [1]ferrocenophanes could actually be generated using silicon bridges. It was reasoned that the larger atomic radii of silicon resulted in less tilted Cp rings and thus, a more stable complex overall. This family of bridged [1]ferrocenophanes has been expanded as bridged species incorporating elements such as germanium, phosphorus, sulfur and selenium, and others have been isolated.

Figure 5.1. Rinehart’s first [2]ferrocenophane and other common [1]ferrocenophanes.

Ferrocenophanes have desirable properties that are similar to ferrocene; the \(\pi\)-electrons of the Cp rings are delocalized through the d-electrons of iron, which can produce good conducting and optoelectronic materials. Unlike ferrocene, these compounds have restricted rotation of the Cp rings and the dihedral angle between the
two rings can be varied depending on the size, position, and structure of the bridge. These structural variations can affect properties such as the degree of ring strain, and therefore can lead to different reactivities for the resultant ferrocenophane.\cite{2}

The tilting of the two Cp rings is best measured as \( \alpha \) in Figure 5.2, with common angles between 16 – 31\(^\circ\) for [1]ferrocenophanes. This degree of tilt allows for ring-opening polymerizations (ROP) to easily occur and ultimately produce high molecular weight poly(ferrocenophanes).

![Diagram of tilt angle (\( \alpha \))](image)

**Figure 5.2.** The determination of tilt angle (\( \alpha \)) in [1]ferrocenophanes.

Phosphorus-bridged [1]ferrocenophanes have a tilt angle of 26.9\(^\circ\)\cite{3} and can be simply made from the reaction of 1,1\( ' \)-dilithioferrocene·TMEDA with dichloro(organo)phosphines and can be subsequently polymerized using thermal and anionic ROP techniques. Manners *et al.* accomplished thermal ROP by heating the phosphorus-bridged [1]ferrocenophane at 120\(^\circ\)C to produce high molecular weight poly(ferrocenophanes). These homopolymers do not elute from a gel permeation chromatograph (GPC) column while using THF as an elution solvent, but by functionalizing the polymer through a reaction with elemental sulfur, the resulting poly(ferrocenylphosphine sulfide) can be analysed by GPC (Scheme 5.1). It is therefore very common for most poly(ferrocenophosphines) to be sulfurized to better understand the size of the resultant polymers.\cite{4}
Anionic ROP of (1-1’-ferrocenediyl)phenylphosphine was first attempted by Seyferth and coworkers in the early 1980’s, but with limited success. What they found was that when the organolithium reagent PhLi was added to the phosphine, only oligomers ranging from dimers to pentamers could be obtained. Unfortunately, no polymeric material was produced from the reaction mixture and chromatography needed to be used to obtain pure oligomers. Notwithstanding, Seyferth was able to produce a wide range of poly(ferrocenophosphines) from low to high molecular weights through a condensation polymerization of 1,1’-dilithioferocene•TMEDA and Cl₂PPh in hexanes at room temperature. Manners et al. were able to show that anionic ROP of phosphorus-bridged [1]ferrocenophane could actually be accomplished and when they carefully controlled the reaction conditions, the polymerization was living (Scheme 5.2). This allowed Manners to produce polymers with controlled molecular weights as well as the first poly(ferrocenophosphine) containing block copolymers. By reacting various amounts of n-BuLi with (1-1’-ferrocenediyl)phenylphosphine for thirty minutes at ambient temperature, the living polymer poly(ferrocenophosphines) was formed. Subsequently quenching with water gave an assortment of polymers with varying chain lengths. As previously discussed, the polymers had to be reacted with elemental sulfur to produce the poly(ferrocenophosphate sulfides) in order to get detailed information about
molecular weights and polydispersities. The resultant molecular masses of the polymers could be controlled from $M_n = 2.4 \times 10^3$ to $3.6 \times 10^4$ with varying PDI values ranging between $1.08 - 1.25$ by simply varying the initiator to monomer ratio. By reacting the living polymer with poly(dimethylsiloxane) or poly(ferrocenylsilane) fragments, soluble block copolymers could be obtained and were easily analyzed by GPC without the need to undergo sulfurization reactions.$^{[11,12]}$

Our previous attempts to produce polymeric materials from our oligomers in Chapter 4 proved to be tiresome and unsuccessful. The long synthetic route to our Cp containing dimer makes these precursors less than desirable for extensive polymerization studies. In this light, we have again extended our newest method for generating triphospheniums to produce some of the first triphosphenium-bridged [3]ferrocenophanes
Figure 5.3) in the hope of potentially utilizing ROP techniques to produce phosphorus rich polymers.[13]

![Figure 5.3. Triphosphenium-bridged [3]ferrocenophanes.](image)

**5.2 Experimental**

**General Procedures**

All manipulations were carried out using standard inert atmosphere techniques. Phosphorus(III) bromide, ferrocene, and all other chemicals and reagents were purchased from Aldrich. Phosphorus(III) bromide and N,N,N',N'-tetramethylethylenediamine were distilled before use, and all other reagents were used without further purification. All solvents were dried using a series of Grubbs’-type columns and were degassed prior to use. THF-d₈ was dried over sodium and benzophenone.

NMR spectra were recorded at room temperature in CD₂Cl₂ solutions on a Bruker Advance 300-MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards (SiMe₄ for ¹H and ¹³C, 85% H₃PO₄ for ³¹P). Coupling constant magnitudes, |J|, are given in Hz.
Specific Procedures

Synthesis of 1,1’-dilithioferrocene•TMEDA, (5.1)
Following modified procedure by Butler,\cite{Butler} 1,1’-dilithioferrocene ferrocene was isolated from the reaction of a solution of 2.5 equivalents of \textit{n}-BuLi and 2.6 equivalents of TMEDA, with 1 equivalent of ferrocene in Et\textsubscript{2}O at -30°C. The deep red solution was left to and after 2 hours, whereby a dark red precipitate was formed. The precipitate was isolated by filtration and was washed with a small amount of Et\textsubscript{2}O.

Synthesis of Fe\{C\textsubscript{5}H\textsubscript{4}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}\}, (5.2)
Two equivalents of chlorodiphenylphosphine (0.86 mL, 4.6 mmol) were added to a red solution of 1,1’-dilithioferrocene•TMEDA (1.0 g, 2.3 mmol) in toluene. The resulting brown solution was stirred overnight and volatiles removed under reduced pressure. The thick brown paste was redissolved in toluene (50 mL) and concentrated with heat. Hexane was added and crystals were obtained by evaporation at 4°C. Recrystallization was performed to yield orange crystals of the product 1,1’-bis(diphenylphosphino)ferrocene (dppf). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR: δ - 16.1 (s). Yield: 1.94 g, 76%.

Synthesis of Fe\{C\textsubscript{5}H\textsubscript{4}P(C\textsubscript{5}H\textsubscript{9})\textsubscript{2}\}, (5.3)
Two equivalents of chlorodicyclopentylphosphine (0.89 mL, 4.6 mmol) were added to a red solution of dilithiated ferrocene (1.0 g, 2.3 mmol) in toluene (20 mL). This red solution was left to stir overnight, after which point the precipitate was filtered and volatiles removed under reduced pressure. The resulting powder was recrystallized in hexanes (20 mL) to afford the orange crystalline product 1,1’-bis(dicyclopentylphosphino)ferrocene (dcppf). Yield: 2.02 g, 84%. \textsuperscript{31}P\{\textsuperscript{1}H\} NMR
(CD<sub>2</sub>Cl<sub>2</sub>): δ -10.33 (s); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 4.19-4.28 (m, 4H, C<sub>5</sub>H<sub>4</sub>); 1.40-2.00 (m, 18H, C<sub>5</sub>H<sub>9</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 78.65 (d, J<sub>PC</sub> = 17.7 Hz, C<sub>3</sub> in C<sub>5</sub>H<sub>4</sub>P); 72.48 (d, J<sub>PC</sub> = 9.5 Hz, C<sub>2</sub> in C<sub>5</sub>H<sub>4</sub>P); 71.62 (s, C<sub>1</sub> in C<sub>5</sub>H<sub>4</sub>P); 36.30 (d, J<sub>PC</sub> = 11.0 Hz, C<sub>1</sub> in C<sub>5</sub>H<sub>9</sub>); 31.04 (d, J<sub>PC</sub> = 18.3 Hz, C<sub>2</sub> in C<sub>5</sub>H<sub>9</sub>); 26.50 (s, C<sub>2</sub> in C<sub>5</sub>H<sub>9</sub>).

**Synthesis of Fe[C<sub>5</sub>H<sub>4</sub>P(NEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub>, (5.4)**

Following the literature procedure,<sup>15</sup> two equivalents of chlorodiethylaminophosphine (0.98 mL, 4.6 mmol) were added to a cold, red-coloured slurry of dilithium ferrocene (1.0 g, 2.3 mmol) in hexane (20 mL). The resulting red/orange solution was stirred overnight and subsequently filtered through celite. Volatiles were removed under reduced pressure to produce the oily orange product 1,1'-bis(diethylaminophosphino)ferrocene (deapf). <sup>31</sup>P{<sup>1</sup>H} NMR: δ -16.2 (s).

**Reaction of dppf, SnCl<sub>2</sub> and PCl<sub>3</sub>, (5.5[SnCl<sub>3</sub>])**

To a flask containing an orange solution of dppf (250 mg, 0.45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) P<sub>1</sub><sub>3</sub> (0.04 mL, 0.45 mmol) was added via syringe. This solution was allowed to stir for 10 minutes before being added to a flask containing SnCl<sub>2</sub> (171 mg, 0.45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), which was then left to stir overnight. Volatiles were removed under reduced pressure from the orange cloudy solution to produce an orange product. <sup>31</sup>P{<sup>1</sup>H} NMR: δ 35.1 (d), -134.3 (t).

**Reaction of dppf and P<sub>1</sub>3, (5.5[I])**

To a schlenk flask containing a clear red solution of dppf (250 mg, 0.45 mmol) in Et<sub>2</sub>O (20 mL) a solution of P<sub>1</sub><sub>3</sub> (130 mg, 0.45 mmol) was added. The reaction was allowed to
stir overnight. Volatiles were removed under reduced pressure and the subsequent solid was filtered in pentane, filtered and the product was isolated as an orange solid. $^{31}$P{^1}H NMR: $\delta$ 45.2 (s), 34.5 (d), 30.5 (s), -138.8 (t).

**Reaction of dppf, PBr$_3$ and cyclohexene, (5.5[Br])**

PBr$_3$ (0.08 mL, 0.45 mmol) and three equivalents of cyclohexene (0.27 mL, 0.9 mmol) were added to a solution of dppf (250 mg, 0.45 mmol) in CH$_2$Cl$_2$ (15 mL). Volatiles were removed under reduced pressure from the resulting orange/red solution to yield a red solid. $^{31}$P{^1}H NMR: $\delta$ 34.9 (d), -136.9 (t).

**Reaction of dcppf, SnCl$_2$ and PCl$_3$, (5.6[SnCl$_5$])**

To a flask containing an orange solution of dcppf (250 mg, 0.48 mmol) in CH$_2$Cl$_2$ (15 mL) PCl$_3$ (0.04 mL, 0.45 mmol) was added via syringe. This solution was allowed to stir for 10 minutes before being added to a flask containing SnCl$_2$ (90 mg, 0.48 mmol) in CH$_2$Cl$_2$ (10 mL), which was then left to stir overnight. Volatiles were removed under reduced pressure from the orange cloudy solution to produce an orange product. $^{31}$P{^1}H NMR: $\delta$ 49.3 (d), 16.2 (s), -153.4 (t).

**Reaction of dcppf and PI$_3$, (5.6[I])**

To a schlenk flask containing a clear red solution of dcppf (40 mg, 0.076 mmol) in Et$_2$O (20 mL) was added a solution of PI$_3$ (130 mg, 0.45 mmol). The reaction was allowed to stir overnight. Volatiles were removed under reduced pressure and the subsequent solid was filtered in pentane, filtered and the product was isolated as a reddish-orange solid. $^{31}$P{^1}H NMR: $\delta$ 66.6 (s), 45.5 (d), 42.1 (s), 38.2 (s), -146.9 (t).
Reaction of dcppf, PBr$_3$ and cyclohexene, (5.6[Br])

PBr$_3$ (0.045 mL, 0.48 mmol) and three equivalents of cyclohexene (0.145 mL, 0.48 mmol) were added to a solution of dcppf (250 mg, 0.48 mmol) in CH$_2$Cl$_2$ (15 mL). Volatiles were removed under reduced pressure from the resulting orange/red solution to yield a red solid. $^{31}$P{$_1$H} 49.4 (d), -147.4 (t).

Reaction of deapf, SnCl$_2$ and PCl$_3$, (5.7[SnCl$_5$])

To a flask containing an orange solution of deapf (150 mg, 0.35 mmol) in CH$_2$Cl$_2$ (15 mL) PCl$_3$ (0.025 mL, 0.35 mmol) was added via syringe. This solution was allowed to stir for 10 minutes before being added to a flask containing SnCl$_2$ (50 mg, 0.35 mmol) in CH$_2$Cl$_2$ (10 mL), which was then left to stir overnight. Volatiles were removed under reduced pressure from the orange cloudy solution to produce a red product. $^{31}$P{$_1$H} NMR: $\delta$ 148.2 (s), 88.7 (d), 52.4 (s), -135.2 (t).

Reaction of deapf and PI$_3$, (5.7[I])

To a schlenk flask containing a clear red solution of deapf (250 mg, 0.58 mmol) in Et$_2$O (20 mL) was added a solution of PI$_3$ (240 mg, 0.58 mmol). The reaction was allowed to stir overnight. Volatiles were removed under reduced pressure and the subsequent solid was filtered in pentane, filtered and the product was isolated as a reddish-orange solid. $^{31}$P{$_1$H} NMR: $\delta$ 89.7 (d), 67.4 (s), 39.8 (s), 42.7 (s), -134.0 (t).
**Reaction of deapf and PBr₃, (5.7[Br])**

PBr₃ (0.03 mL, 0.28 mmol) was added to a solution of deapf (150 mg, 0.28 mmol) in cyclohexene (10 mL). The product was collected by filtration and the volatiles were removed under reduced pressure to yield a red solid. $^{31}\text{P}^\{\text{H}\}$ NMR: δ 89.1 (d), -134.1 (t).

**5.3 Results and Discussion**

Our interest in triphosphonium-bridged [3]ferrocenophanes arose for two main reasons; the first is due to our inability to introduce transition metal centers into our previously discussed cyclopentadienide-containing dimer, the second is our desire to synthesize potential polymerization precursors. We had hoped that the cavity size of the dimer ([-C₅H₃-PPh₂-P-PPh₂-]₂) would be large enough where the Cp rings could coordinate an iron atom, but after several failed attempts we decide to pursue this using other approaches. We used two different synthetic approaches as potential methods to produce complexes that incorporate iron into the phosphonium salt. In our first method, we decided to build the target ligands around iron and thus decided to use ferrocene as a starting point. Reacting ferrocene with 2.5 equivalents of $n$-BuLi and 2.6 equivalents of TMEDA in ether, produces 1,1’-dilithioferrocene•TMEDA as a red precipitate. Due to the extreme pyrophoric nature of this compound, it is almost exclusively used as an *in situ* reagent, however with careful handling, the product can be filtered and stored safely under an inert atmosphere. Subsequent reactions with two equivalents of a given chlorophosphine of choice produces the desired ligand, Fe(CpPR₂)₂. Alternatively, the reaction of iron(II) chloride with our previously synthesized potassium (diphosphino)cyclopentadienide ligands from Chapter 4 produces the analogous ligands. Overall, both approaches are suitable however we found that using the first method
proved to be the more cost efficient and the easier synthetic approach in producing the target ligands we desired.

Scheme 5.3. Synthesis of target ligands. Method 1: 2 ClPPh₂, -2 LiCl. Method 2: FeCl₂, -2 KCl.

By consulting the literature and utilizing the methods above, we were successfully able to produce the previously characterized 1,1’-bis(diphenylphosphino)ferrocene\(^{[14]}\) (dppf) and 1,1’-bis[bis(diethylamino)phosphino]ferrocene (deapf).\(^{[15]}\) We were also successful in producing a new ligand, 1,1’-bis(dicyclopentylphosphino)ferrocene (dcppf) as small yellow crystals but unfortunately they were not suitable for single crystal X-ray diffraction. Three methods for the preparation of triphosphenium complexes were discussed in previous chapters. Using these phosphinoferrocene ligands, all three of these methods would be employed for the generation of these new ferrocene containing triphosphenium complexes (Scheme 5.4). As it was the preferred method for the generation of small triphosphenium heterocycles, we first attempted to generate these species from the reaction of PBr₃ and excess cyclohexene. We found for the dppf and dcppf ligands that the reaction proceeded in a clean and efficient manner. As illustrated in Figure 5.4, the products revealed a doublet and triplet in the \(^{31}\)P NMR spectrum as expected (have both dppf and dcppf). Unfortunately, the reaction with the deapf ligand did not proceed in a similar manner and multiple products were observed in the \(^{31}\)P NMR.
It appears as though the subsequent release of bromide during the reduction of the phosphorus center complicated the chemistry by causing the ligand to undergo a variety of side reactions. By reacting PBr$_3$ with deapf and using cyclohexene as a solvent, we were successfully able to produce the analogous triphosphenium complex cleanly (Figure 5.5).

Scheme 5.4. Possible synthetic routes to triphosphenium bridged [3]ferrocenophanes.
Figure 5.4. $^{31}$P spectrum of 5.5[Br], the reaction of PBr$_3$/cyclohexene with 1,1’-bis(diphenylphosphino)ferrocene.

Figure 5.5. $^{31}$P spectrum of 5.7[Br], the reaction of PBr$_3$ with 1,1’-bis[bis(diethylamino)diphenylphosphino]ferrocene using cyclohexene as a solvent.

In addition to our PBr$_3$ method, we were also able to apply the previously reported PCl$_3$ and PI$_3$ methodologies to the dppf and dcppf ligand systems. Both produced a set of doublet of triplets that are in a similar range observed for their bromide counterparts but contained very minor unidentified impurities that have proven difficult to remove.
While attempts to clean up these reactions are ongoing, no additional comments regarding these systems are warranted. The deapf ligand proved to be the most challenging and although we were able to produce the corresponding triphosphenium peaks, there were significantly more impurities in the reaction mixture compared to those observed in the dppf and dcppf systems.

From the examination of the two Cp rings from our crystalline structure of the dimer in Chapter 4, it appears that the tilt angle between the two rings is 0° and are parallel to one another (Figure 5.6). It can most likely be assumed that the incorporation of iron between the Cp rings will likely result in a similar structure with relatively little physical strain. It is thus likely that thermal ring-opening attempts to polymerize these triphosphenium-bridged [3]ferrocenophanes would be ineffective. Although unfortunate, this did not come as a surprise as nearly all three atom-bridged ferrocenophanes have little to moderate ring strain.\(^{[16-23]}\) (Figure 5.7).

![Figure 5.6. Tilt angle for dimer.](image)

\[\text{mean: C1 C5 C4 C3 C2} \]
\[\text{mean: C1 C2 C3 C4 C5} \]
The deapf triphosphonium complex, 5.7[Br], presents an ideal target monomer for further polymerization investigations. Punji et al. has demonstrated that these deapf ligands easily undergo halogenation reactions when exposed to HCl, ultimately generating 1,1’-bis(dichlorophosphino)ferrocene.\textsuperscript{[15]} To date, there have not been any reported synthetic methods that produce triphosphoniums with phosphorus substituents that contain halogen R-groups. These types of ligands are poor donors and make ligand exchange type reactions with P(I) salts very unlikely and reactions with PX\textsubscript{3} improbable. To overcome this challenge, we propose that exposing HCl to 5.7[Br], may be an ideal synthesis toward producing triphosphoniums with Cl as substituents on the phosphorus atoms of the ligand framework (Scheme 5.5). Although these compounds probably have little to no ring strain, the chlorinated triphosphonium complex may polymerize in a similar manner to that observed for polyphosphazenes. We theorize that thermal ROP of the chlorinated triphosphonium may yield our target polymer that incorporates low oxidation state phosphorus centers. The chloride substituents would also allow for further metathesis-type reactions, which would allow the substituents on the tetra-coordinate phosphorus atoms be easily changed which should lead to different properties for the resultant polymeric material.
5.4 Conclusion

In conclusion, we have demonstrated the ability to cleanly produce low oxidation state phosphorus containing [3]ferrocenophanes using our PBr₃ and cyclohexene approach. We have also demonstrated the PCl₃ and to a lesser extent, PI₃, are both viable approaches to these complexes. The diethylamino species, 5.7[Br], is an interesting complex for the potential production of polymeric species.
5.5 References


Chapter 6 – Dissertation Summary and Future Outlook

6.1 Summary

In the Macdonald group, we define the oxidation state of phosphorus based solely on the number of non-bonding electrons that are associated with the atom in question. Phosphorus in the +5 oxidation state has no “lone pairs” of electrons, a P(III) center contains one “lone pair” and finally, phosphorus in the +1 state contains two “lone pairs” of electrons. Compared to more traditional methods this model provides a more accurate depiction of the electronic and structural features and to an extent, the chemical behavior of compounds that are of the same oxidation state.\(^1\)

Over the last two decades, \(N\)-heterocyclic phosphines have been an important class of compounds that have helped the development of modern main group chemistry.\(^2\)-\(^7\) There have been numerous synthetic attempts to generate these species in a facile manner that is both atom economic and employs mild reaction conditions. Cowley \textit{et al.} were the first to generate phosphenium cations in a one-pot approach. By extending the methodologies used to make P(I) containing heterocycles, they were able to synthesize phosphenium cations albeit with complicating features. The redox activity of the resulting \([\text{SnCl}_5]^-\) and \([\text{I}_3]^-\) anions made further chemistry challenging and it was evident that a more desirable approach needed to be developed.\(^8\) Gudat developed a one-pot approach to chloro-phosphines although the synthesis contained unwanted by-products that needed to be removed.\(^9\)

Herein, we have demonstrated that our PBr\(_3\) and cyclohexene approach indicates that redox-cycloaddition methodology can be employed for the convenient synthesis of
$N$-heterocyclic bromophosphines in good yields. Our one-pot mild approach to these species is a simple and effective way of generating this increasingly-important class of reagents. We have also established that the resulting bromophosphines are useful reagents for the generation of the corresponding $N$-heterocyclic phosphonium salts by several common methods of anion abstraction or metathesis reactions.

Our computational investigations into the applicability of using other $4\pi$ and $8\pi$-electron ligand systems to synthesize P(I) complexes are consistent with significant electron transfer from the putative P(I) fragment to the given ligand, ultimately undergoing a two electron intramolecular charge transfer and yielding a heterocyclic species with an overall P(III) center. The experimental results proved to be difficult in obtaining clean and pure products. In spite of this, the spectroscopic data clearly showed that the PBr$_3$ and cyclohexene methodology indicates that the redox-cycloaddition chemistry may be employed for the synthesis of these new phosphonium cations.

Organic polymers are ubiquitous and play an important role in our everyday life. In spite of their utility, they exhibit deficiencies and limitations including thermal instability and chemical reactivity. We believe polymers composed primarily of inorganic elements in the main chain may avoid some or all of these problems altogether. Inorganic polymers offer different properties that organic polymers may not possess: they can feature alternative reactivities, bonding interactions that are more robust, and desired physical properties.$^{[10]}$

We have demonstrated that ligand exchange reactions using our stable P(I) reagent is a viable synthetic approach for the preparation of electron-rich phosphorus-rich cyclic oligomers. The use of this protocol for the generation of such macrocycles appears only
to be constrained by the preparation of suitable diphosphine ligands. Although we have been unable to incorporate various metal centers within our oligomers, we have demonstrated the ability to cleanly produce low oxidation state phosphorus containing [3]ferrocenophanes. These complexes remain an attractive monomer for further polymerization studies.

6.2 Future Work

We are currently exploring various synthetic routes towards new heterocyclic phosphines using a clean and unobstructed method. We have demonstrated the ability to extend these systems from diimine containing complexes to species with ligands containing both oxygen and nitrogen. It is clear that there is still a significant amount of work needed into finding the ideal reaction conditions for the development of these new types of heterocycles. In addition to nitrogen containing ligands, we also desired exploring sulfur-containing systems. We propose that the addition of Lawesson's reagent to various oxygen-containing ligands should afford the sulfur variants, which we could then use to employ our PBr$_3$ and cyclohexene approach (Scheme 6.1).
Scheme 6.1. Potential synthetic route towards sulfur-containing phosphorus heterocycles.

Given our experience in developing new synthetic approaches for the preparation of triphosphenium ions,\cite{11} we reasoned that synthetic protocols used to produce triphosphenium salts could provide a convenient route to make phosphorus containing oligomers and polymers. We have demonstrated the ability to successfully incorporate low oxidation state phosphorus centers to oligomeric materials. We have been unsuccessful in our polymerization attempts of these materials but to overcome this challenge we propose that exposing HCl to our amino substituted triphosphenium bridged [3]ferrocenophane, may prove to be an ideal synthesis towards producing triphosphoeniums with Cl groups as substituents on the phosphorus atoms (Scheme 6.2). This chlorinated triphosphenium complex may polymerize in a similar manner to that observed for polyphosphazenes.\cite{10} We theorize that thermal ROP of the chlorinated triphosphenium may yield our target polymer that incorporates low oxidation state phosphorus centers into the repeating unit. These cyclic systems would represent a new and exciting area for inorganic polymer chemistry.
Scheme 6.2. Potential synthetic route to new triphosphenium containing polymers.
6.3 References


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